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Heterobimetallic Complexes Supported by Phosphinoamide Ligands

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of Philosophy

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The work described in this thesis was carried out at the University of Nottingham from October 2011 to December 2014, under the supervision of Prof. Stephen T. Liddle. All the work is my own, unless stated to the contrary and has not been previously submitted for any degree at this or any other university.

A. J. Ayres

September 2016

Abstract

Many major advances in our fundamental chemical knowledge have emerged from novel metal-metal chemistry. Such complexes which exhibit metal-metal interactions, have provided excellent tools for developing our understanding of chemical structure and bonding, catalysis, metal surface chemistry and bioinorganic chemistry. However, whilst metal-metal bonding is now well understood in the p- and d- blocks and to some extent the s-block of the Periodic Table very little is known, in comparison, about that for the f-block and especially the actinide elements. Traditionally the chemistry of molecular f-element compounds has been dominated by the use of carbon, nitrogen, oxygen and halogen based ligands with the implementation of metal-based fragments as ligands considerably less developed.

In recent years dinuclear species containing a metal-metal bond between two different transition metal centres bridged by a supporting ligand structure have rapidly been gaining interest, as they would be expected to exhibit different reactivity to those of monometallic or homobimetallic complexes. Early/late heterobimetallic complexes, featuring metal-metal interactions supported by a phosphinoamine ligand system, have received particular attention due to their two very different reaction sites, inherent bond polarity, and synergy between the two centres resulting in unique reactivity.

A range of novel phosphinoamines, including MesN(H)PPh₂, have been successfully synthesised to accompany the previously reported phosphinoamines DippN(H)PPh₂ and MesN(H)PⁱPr₂. All phosphinoamines were successfully deprotonated using ⁿBuLi to afford the corresponding lithium salts as ligand transfer reagents. Reaction of uranium tetrachloride or thorium tetrachloride with three molar equivalents of either [Li(MesNPPh₂)(Et₂O)₂] or [{LiNMes(PⁱPr₂)(Et₂O)}₂] resulted in the respective tris(phosphinoamide) actinide(IV) chloride complexes [AnCl(MesNPPh₂)₃] and [AnCl(MesNPⁱPr₂)₃] (An = U, Th). Treatment of the tris(phosphinoamide) actinide(IV) halide complexes with Me₃SiI afforded the corresponding tris(phosphinoamide) actinide(IV) iodide complexes.

The installation of cobalt iodide into the coordination sphere of the uranium was achieved in the presence of zinc powder to afford the two uranium-cobalt complexes $[\text{UCl}(\text{MesNPPH}_2)_3\text{CoI}]$ and $[(\text{MesNP}^i\text{Pr}_2)\text{U}(\mu\text{-X})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ ($\text{X} = 41\% \text{ I}, 59\% \text{ Cl}$). $[\text{UCl}(\text{MesNPPH}_2)_3\text{CoI}]$ adopts a paddle-wheel structure whereas $[(\text{MesNP}^i\text{Pr}_2)\text{U}(\mu\text{-X})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ exhibits a structure with at best C_{2v} symmetry and two bridging phosphinoamides and one bridging halide ligand. These structural differences confer very different magnetic behaviour. At low temperature $[\text{UCl}(\text{MesNPPH}_2)_3\text{CoI}]$ can be formulated as an $S = 1$ spin system resulting from a combination of a magnetic singlet uranium(IV) and triplet cobalt(I). However, in contrast $[(\text{MesNP}^i\text{Pr}_2)\text{U}(\mu\text{-X})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ is an $S = 0$ spin system at low temperature with antiferromagnetic exchange between uranium and cobalt proposed. Density functional theory calculations and topological bond analyses support the notion of formally dative $\text{Co} \rightarrow \text{U}$ bonds in both complexes. In an attempt to further support the claim of antiferromagnetic exchange between uranium and cobalt the thorium analogues were synthesised. To date, investigations into the respective electronic structures are still on going and conclusions about the exact nature of the cobalt centres cannot be drawn. There is however sufficient evidence which warrants further investigation that would be expected to be very detailed and that is thus unfortunately beyond the timeframe of this PhD.

Reaction of the same four tris(phosphinoamide) actinide(IV) chlorides, that resulted in the synthesis of the actinide-cobalt complexes, with $[\text{Mo}(\text{MeCN})_3(\text{CO})_3]$ in dichloromethane afforded the heterobimetallic uranium- and thorium-molybdenum complexes $[\text{AnCl}(\text{MesNPR}_2)_2(\text{MesNPR}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ ($\text{An} = \text{U}, \text{R} = ^i\text{Pr}$; $\text{An} = \text{Th}, \text{R} = ^i\text{Pr}$; $\text{An} = \text{U}, \text{R} = \text{Ph}$; $\text{An} = \text{Th}, \text{R} = \text{Ph}$). In contrast treatment of the tris(phosphinoamide) actinide(IV) iodides $[\text{IAn}(\text{MesNP}^i\text{Pr}_2)_3]$ ($\text{An} = \text{Th}, \text{U}$) with $[\text{Mo}(\text{MeCN})_3(\text{CO})_3]$ in toluene resulted in the formation of the complexes $[(\eta^2\text{-MesNP}^i\text{Pr}_2)\text{AnI}(\text{MesNP}^i\text{Pr}_2)(\{\mu\text{-NCMe}\}\text{MesNP}^i\text{Pr}_2)\text{Mo}(\text{CO})_3]$ ($\text{An} = \text{U}, \text{Th}$). These compounds show unprecedented acetonitrile insertion as a bridging ligand between the actinide metal and Mo with structural analysis suggests an activation of the nitrile group.

To synthesise the analogous actinide-molybdenum paddlewheel complexes to $[\text{UCl}(\text{MesNPPH}_2)_3\text{CoI}]$, the appropriate tris(phosphinoamide) actinide(IV) halides were treated with $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ to afford the heterobimetallic uranium- and

thorium-molybdenum complexes $[M(X)(\text{MesNPPH}_2)_3\text{Mo}(\text{CO})_3]$ ($M = \text{U}$, $X = \text{Cl}$; $M = \text{U}$, $X = \text{I}$; $M = \text{Th}$, $X = \text{Cl}$; $M = \text{Th}$, $X = \text{I}$). Orbital- and density-based quantum chemical calculations reveal dative $\text{Mo} \rightarrow M$ σ -interactions in all cases and so these complexes constitute unprecedented actinide-group 6 metal-metal bonds, where before heterobimetallic uranium-metal bonds were restricted to a few group 7-10 metals.

With a synthetic route towards actinide-cobalt complexes established future work must look towards the reduction of these complexes to result in highly reactive and polarised early-late heterobimetallic compounds. The subsequent reaction of these compounds with small molecules such as CO , CO_2 and H_2 *etc* has the potential to result in novel and unusual chemistry which can help develop our fundamental understanding of the actinides. Although the actinide-molybdenum complexes were relatively straightforward to synthesise, surprisingly, the analogous chromium and tungsten complexes were not accessible by the same method, although it has been anticipated that photolysis could be an alternative synthetic route. Photolysis could also lead to the removal of one or more of the carbonyl groups situated on the group 6 metal and result in the targeted highly reactive and polarised early-late heterobimetallic compounds suitable for the activation of small molecules.

Acknowledgements

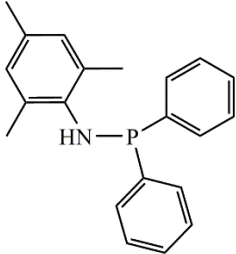
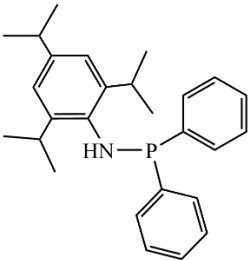
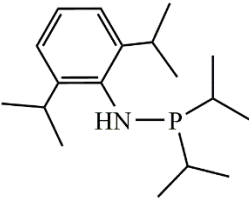
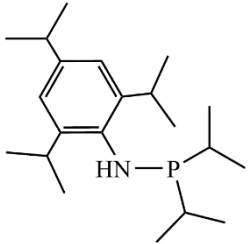
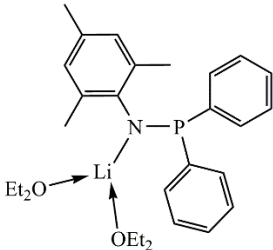
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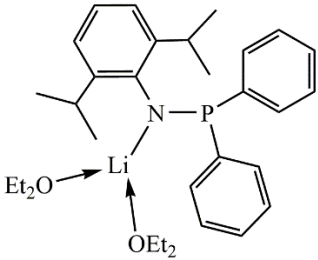
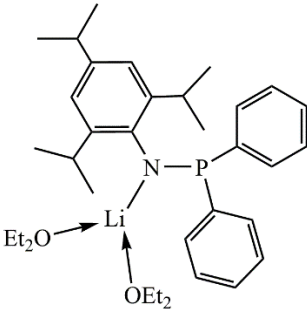
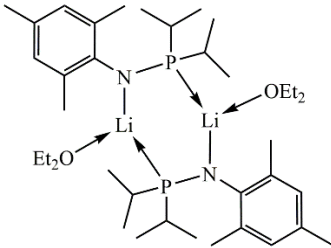
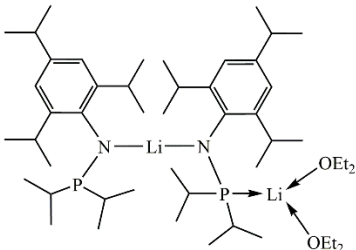
I would like to thank Prof. Eric McInnes and Dr Floriana Tuna for their contributions and expertise in SQUID magnetometry and EPR spectroscopy which are discussed throughout this work. I'd Like to thank the following researchers and Technicians for assistance during my studies: Prof. Alexander Blake and Dr William Lewis for teaching me the complexities of X-ray crystallography; Dr J. McMaster for DFT calculations; Dr Tong Liu and Stephen Boyer for elemental analysis; Dr Adrienne Davis, Kevin Butler and Shazad Azlam for NMR spectroscopy.

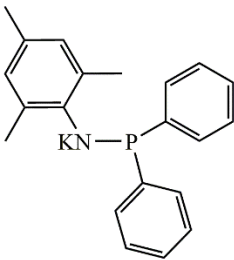
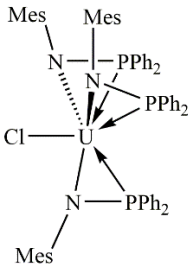
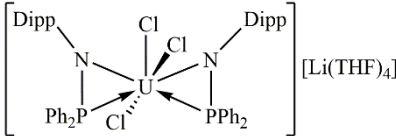
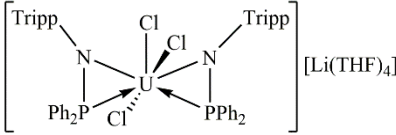
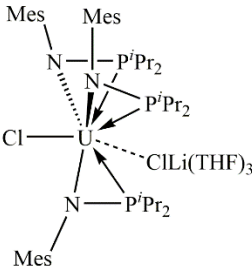
Special thanks must go to Terrence Keely who allowed me to live in his house for almost five years but sadly passed away before he got a chance to read this thesis.

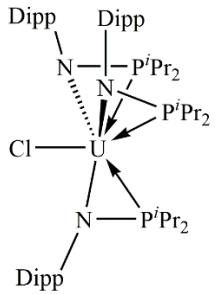
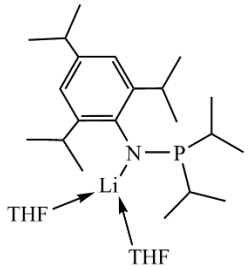
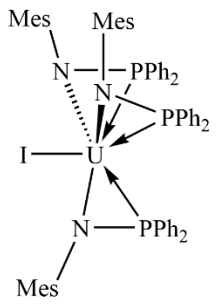
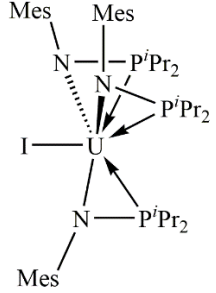
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List of New Complexes

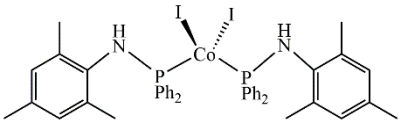
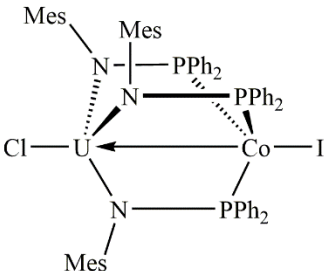
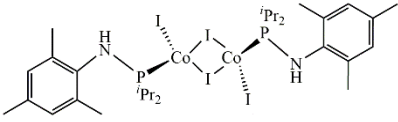
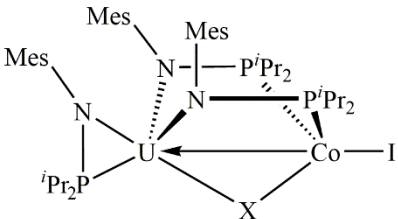
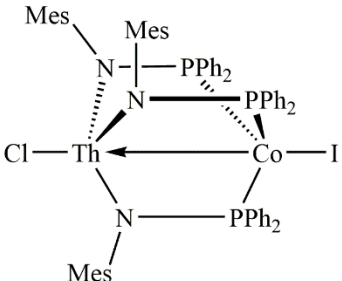
Complex	Formula	Structure	Page
145	MesN(H)PPh ₂		79
147	TrippN(H)PPh ₂		81
149	DippN(H)P ⁱ Pr ₂		82
150	TrippN(H)P ⁱ Pr ₂		82
151	[Li(MesNPPh ₂)(Et ₂ O) ₂]		84

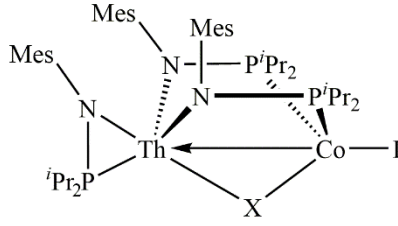
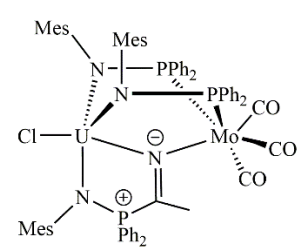
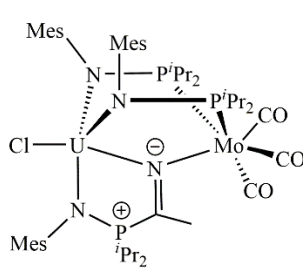
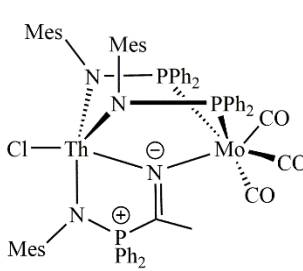
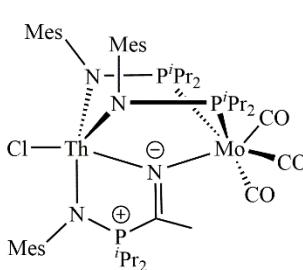
Complex	Formula	Structure	Page
152	$[\text{Li}(\text{DippNPPh}_2)(\text{Et}_2\text{O})_2]$		84
153	$[\text{Li}(\text{TrippNPPh}_2)(\text{Et}_2\text{O})_2]$		84
154	$[\{\text{LiNMes}(\text{P}^i\text{Pr}_2)(\text{Et}_2\text{O})\}]$		89
155	$[\text{LiNDipp}(\text{P}^i\text{Pr}_2)]$	??	92
156	$[(\text{P}^i\text{Pr}_2)\text{TrippN}\{\mu\text{-Li}\}\text{NTripp}(\text{P}^i\text{Pr}_2)\text{Li}\{\text{Et}_2\text{O}\}_2]$		93

Complex	Formula	Structure	Page
157	$[\text{K}(\text{MesNPPh}_2)]$		95
165	$[\text{UCl}(\text{MesNPPh}_2)_3]$		113
166	$[\text{UCl}_3(\text{DippNPPh}_2)_2]$ $[\text{Li}(\text{THF})_4]$		116
167	$[\text{UCl}_3(\text{TrippNPPh}_2)_2]$ $[\text{Li}(\text{THF})_4]$		116
168	$[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_3(\text{LiCl}\{\text{THF}\}_3)]$		121

Complex	Formula	Structure	Page
169	$[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_3]$	??	122
170	$[\text{UCl}(\text{DippNP}^i\text{Pr}_2)_3]$		123
172	$[\text{Li}(\text{TrippNP}^i\text{Pr}_2)(\text{THF})_2]$		126
173	$[\text{UI}(\text{MesNPPH}_2)_3]$		128
161	$[\text{UI}(\text{MesNP}^i\text{Pr}_2)_3]$		111

Complex	Formula	Structure	Page
174	$[\text{UI}_2(\text{DippNP}^i\text{Pr}_2)_2]$		131
175	$[\text{ThCl}(\text{MesNPPH}_2)_3]$		134
176	$[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_3]$		134
177	$[\text{ThI}(\text{MesNPPH}_2)_3]$		138
178	$[\text{ThI}(\text{MesNP}^i\text{Pr}_2)_3]$		138

Complex	Formula	Structure	Page
183	$[\text{CoI}_2\{\text{MesN}(\text{H})\text{PPh}_2\}_2]$		155
184	$[\text{UCl}(\text{MesNPPh}_2)_3\text{CoI}]$		156
185	$[\text{CoI}(\mu\text{-I})\{\text{MesN}(\text{H})\text{P}^i\text{Pr}_2\}_2]$		159
186	$[(\text{MesNP}^i\text{Pr}_2)_2\text{U}(\mu\text{-X})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$		160
187	$[\text{ThCl}(\text{MesNPPh}_2)_3\text{CoI}]$		163

Complex	Formula	Structure	Page
188	$[(\text{MesNP}^i\text{Pr}_2)\text{Th}(\mu\text{-I})$ $(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$		163
189	$[\text{UCl}(\text{MesNPPH}_2)_2$ $(\text{MesNPPH}_2\{\mu\text{-CNMe}\})\text{Mo}(\text{CO})_3]$		185
190	$[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_2$ $(\text{MesNP}^i\text{Pr}_2\{\mu\text{-CNMe}\})\text{Mo}(\text{CO})_3]$		185
191	$[\text{ThCl}(\text{MesNPPH}_2)_2$ $(\text{MesNPPH}_2\{\mu\text{-CNMe}\})\text{Mo}(\text{CO})_3]$		184
192	$[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_2(\text{MesNP}^i\text{Pr}_2\{\mu\text{-CNMe}\})\text{Mo}(\text{CO})_3]$		198

Complex	Formula	Structure	Page
193	$[(\eta^2\text{-MesNP}^i\text{Pr}_2)$ $\text{UI}(\text{MesNP}^i\text{Pr}_2)$ $(\{\mu\text{-CNMe}\}\text{MesNP}^i\text{Pr}_2)$ $\text{Mo}(\text{CO})_3]$		192
194	$[(\eta^2\text{-MesNP}^i\text{Pr}_2)$ $\text{ThI}(\text{MesNP}^i\text{Pr}_2)$ $(\{\mu\text{-CNMe}\}\text{MesNP}^i\text{Pr}_2)$ $\text{Mo}(\text{CO})_3]$		192
195	$[\text{UCl}(\text{MesNPPH}_2)_3\text{Mo}$ $(\text{CO})_3]$		196
196	$[\text{UI}(\text{MesNPPH}_2)_3\text{Mo}$ $(\text{CO})_3]$		199
197	$[\text{ThCl}(\text{MesNPPH}_2)_3\text{Mo}$ $(\text{CO})_3]$		200

Complex	Formula	Structure	Page
198	$[\text{ThI}(\text{MesNPPh}_2)_3\text{Mo}(\text{CO})_3]$		200

Abbreviations

An	Actinide
Ar	Aryl
br	Broad
d	Doublet
DFT	Density Functional Theory
Dipp	2,6-Diisopropylphenyl
Et	Ethyl
eV	Electron Volt
FTIR	Fourier Transform Infra Red
{ ¹ H}	Proton Decoupled
HOMO	Highest Occupied Molecular Orbital
ⁱ Pr	<i>iso</i> -Propyl
IR	Infrared
K	Kelvin
kJ mol ⁻¹	Kilojoules per mole
Ln	Lanthanide
M	Molar (mol dm ⁻³)
m	Multiplet
Me	Methyl
Mes	1,3,5-trimethylbenzene
MO	Molecular Orbital
NIR	Near-Infrared
nm	Nanometre (10 ⁻⁹ m)
NMR	Nuclear Magnetic Resonance
Ph	Phenyl
ppm	Parts Per Million
q `	Quartet
QTAIM	Quantum theory of atoms in molecules
s	Singlet
SCF	Self-Consistent Field

SOMO	Singly-Occupied Molecular Orbital
SQUID	Superconducting Quantum Interference Device
T	Tesla
TIP	Temperature independent paramagnetism
Tripp	2, 4, 6-Triisopropylphenyl
t	Triplet
THF	Tetrahydrofuran
TMS	Trimethylsilyl
UV	Ultra-Violet
V	Volt
XRD	X-Ray Diffraction

Table of Contents

1	Introduction	1
1.1	Background	2
1.2	Metal-Metal Complexes	11
1.3	Small Molecule Activation	55
1.4	Project Aim	67
1.5	References	68
2	Phosphinoamines and their Group One Metal Salts	77
2.1	Background	78
2.2	Phosphinoamine Proligands	79
2.3	Ligand Transfer Reagents	83
2.4	Concluding Remarks	96
2.5	Experimental Information	98
2.6	References	105
3	Tris(phosphinoamide) Actinide(IV) Halide Complexes	108
3.1	Background	109
3.2	Tris(phosphinoamide) Uranium Chlorides	112
3.3	Tris(phosphinoamide) Uranium Iodides	127
3.4	Tris(phosphinoamide) Thorium Chlorides	133
3.5	Tris(phosphinoamide) Thorium Iodides	137
3.6	Experimental	141
3.7	References	143

4	Heterobimetallic Actinide-Cobalt Complexes	150
4.1	Background	151
4.2	Heterobimetallic Actinide-Cobalt Complexes	154
4.3	Characterisation of Actinide-Cobalt Complexes	165
4.4	Concluding remarks	173
4.5	Experimental	176
4.6	References	179
5	Heterobimetallic Actinide-Molybdenum Complexes	182
5.1	Background	183
5.2	Activation of Acetonitrile	184
5.3	Paddlewheel An-Mo Complexes	196
5.4	Concluding remarks	210
5.5	Experimental	211
5.6	References	217
6	Supplementary Information	220

Chapter One

Introduction

Contents

1.1	Background	2
1.2	Metal-Metal Complexes	11
1.3	Small Molecule Activation	55
1.4	Project Aim	67
1.5	References	68

1.1 Background

General

The actinides (An) are the fourteen elements from thorium (Th) to lawrencium (Lr) situated in the f-block of the Periodic Table; they are analogous to the lanthanides (Ln) and result from the filling of the 5f orbitals moving from left to right across the period. Although the ‘parent’ element actinium (Ac) is not strictly an actinide it is often included in discussions of f-element chemistry due to its similarity in chemical characteristics. With an abundance of 2.4 parts per million (ppm) in the Earth’s crust uranium (U) is the heaviest naturally occurring element, thorium is the only other actinide that is naturally present in significant quantities (8.1 ppm). Whilst actinium and protactinium (Pa) occur naturally in small quantities (approximately 10–8 ppm) the rest of the actinides are considered to be synthetic and are products of nuclear reactions.²

Uranium was discovered in 1789 by Martin Heinrich Klaproth who demonstrated that pitchblende, previously considered to be a mixture of zinc, iron and tungsten oxides, contained the oxide of a new element uranium.³ Uranium is found in many oxide minerals, the two most important of these being pitchblende or uranite (U_3O_8) and carnotite [$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$], the main sources of these minerals are Australia, Canada, Kazakhstan, Namibia, Niger, Russia and the USA. Although the specific extraction processes are dependent on the particular ore the general procedure begins with the leaching of the ore with sulfuric acid in the presence of an oxidising agent such as MnO_2 or NaClO_3 . This ensures that all uranium present is as an acidic solution of a uranyl (UO_2^{2+}) complex of sulfate or chloride. The neutralisation of the acidic solution is typically performed with ammonia to yield a precipitate known as ‘yellow cake’, a mixture of salts and oxides with an approximate composition of $[(\text{NH}_4)_2\text{U}_2\text{O}_7]$. Heating the yellow cake to 300 °C produces uranium trioxide, UO_3 , which can be further reduced to UO_2 by heating to 700 °C in the presence of hydrogen gas. In turn, the UO_2 can be converted to UF_4 by reaction with hydrogen fluoride. Uranium metal is obtained *via* reduction of UF_4 with magnesium. Alternatively the

synthesis of UCl_4 can be achieved by the reaction of UO_3 with excess hexachloropropene; this is the primary starting material used in this project.

In 1828 Jöns Jacob Berzelius discovered the new oxide thorium from which he subsequently isolated thorium.³ The principal source of thorium is the mineral monazite; a mixed lanthanide orthophosphate (LnPO_4) which contains up to 10% ThO_2 . Monazite deposits occur in many countries, including India, Brazil, Sri Lanka South Africa, Australia and Malaysia. The abstraction of thorium from monazite begins by the dissolution of the mineral in *ca.* 70% NaOH solution for several hours followed by addition of hot water to form a slurry of crude hydrous oxides. The slurry is then added to boiling HCl until a pH of 3.5 is reached at which point crude hydrous ThO_2 is precipitated. Nitric acid is used to dissolve the hydrous ThO_2 and the resulting thorium nitrate is purified by extraction into tributylphosphate diluted with kerosene.

Application of the Actinides

All known isotopes of the actinides exhibit radioactivity with a trend towards decreasing half-life with increasing atomic number, this radioactivity lends itself to two major applications; energy and weapons. The physical process, which both of these have as their basis, is nuclear fission. Nuclear fission occurs when a larger nucleus splits into two smaller ones, this process can also result in the liberation of one or more neutrons which in turn may collide with further nuclei. For the actinides this is an exothermic process and a self-sustaining chain reaction can occur assuming that there is a sufficient mass of fissile material to prevent excessive loss of neutrons. If the mass of fissile material is in excess of the minimum “critical” mass very few neutrons can escape the surface, the chain reaction increases rapidly resulting in the possibility of a nuclear explosion. This uncontrolled chain reaction was the principal behind the first nuclear weapons developed during the Second World War. The ‘Little Boy’ bomb which was dropped on Hiroshima consisted of two subcritical masses of ^{235}U which formed a critical mass when forced together using conventional explosives.

A more peaceful application is to be found in nuclear power stations. UO_2 pellets which have been enriched to around 3% ^{235}U are stacked into fuel rods to form the fissile material for the reactor along with control rods which consist of lighter elements such as boron, carbon and nitrogen. These control rods regulate the chain reaction *via* absorbing neutrons and can be lowered into the reactor accordingly. The reaction occurs in a medium of either water or heavy water (Heavy water, formally called deuterium oxide ($^2\text{H}_2\text{O}$ or D_2O), is a form of water that contains a larger than normal amount of the hydrogen isotope deuterium) which, as well as acting as a moderator to decrease the energy of neutrons produced by ^{235}U fission resulting in a more efficient process, is used to drive steam turbines generating electricity.

Electronic Structure

The electronic configurations of free lanthanide and actinide atoms are often difficult to determine due to their complex electronic spectra and in the case of the later actinides, the difficulties in producing a significant quantity of atoms. The lanthanides and actinides exhibit seven degenerate f-orbitals which play a fundamental role in determining their physiochemical properties. There is no unique way of representing these f-orbitals but the most common set of f-orbitals is known as the *cubic* set and is appropriate for molecules in which the x, y and z axes are symmetry related *e.g.* those of which belong to the O_h and T_d point groups. These are labelled as f_z^3 , f_y^3 , f_x^3 , f_{xyz} , $f_{z(x^2-y^2)}$, $f_{y(z^2-x^2)}$ and $f_{x(z^2-y^2)}$. When non-cubic geometries are present the *general* set is used, f_z^3 , f_{xz^2} , f_{yz^2} , f_{xyz} , $f_{x(z^2-y^2)}$, $f_{x(x^2-3y^2)}$ and $f_{y(3x^2-y^2)}$.² The ground state electronic configuration for thorium is $[\text{Rn}]6d^27s^2$ and the ground state electronic configuration for uranium is $[\text{Rn}]5f^36d^17s^2$ ($[\text{Rn}]$ = electronic configuration of radon, 86 electrons). As demonstrated by uranium, the 6d and 7s orbitals are lower in energy than the 5f orbitals for the early actinides (Ac-Am).

Although the lanthanides and actinides are grouped together in the f-block they display highly divergent electronic properties. For the lanthanides the valence 4f orbitals are significantly shielded by the filled 5s and 5p core orbitals, however in the case of the actinides the 5f orbitals are not subject to the same degree of shielding by the 6s and

6p shells due to increased primary quantum numbers. This results in a greater extent of electron density far from the nucleus and an increased sensitivity to changes in valence and an increased availability for bonding than is the case for the lanthanides. A larger range of oxidation states is therefore observed for the early actinides as opposed to the lanthanides which predominately adopt the +3 oxidation state. The later actinides however are subject to a drop in energy of the 5f orbitals such that it falls below that of the 6d orbitals, this is due to their inability to efficiently shield each other from the nucleus, therefore we see the +3 oxidation state dominating and their chemistry becomes comparable to that of the lanthanides.^{3,4}

For uranium, the lowering of the 5f orbital energies compared to the 6d-orbitals results in the 5f and 6d-orbitals being remarkably close in energy compared to the rest of the actinides allowing for a degree of hybridisation. This is illustrated by the orbital energy calculations conducted by Bursten on $[AnCp_3]$ complexes ($An = Th, Pa, U, Np, Pu$; $Cp = \eta^5-C_5H_5$) (**Fig. 1**) where it can be seen that going across the actinide series the 6d orbitals (π_2 and a_1') increase in energy, whereas the 5f-orbitals (5f and a_2) fall in energy. It is also possible to observe the energy of the 5f-orbitals of the latter actinides fall to a point where they have become core like in nature.¹

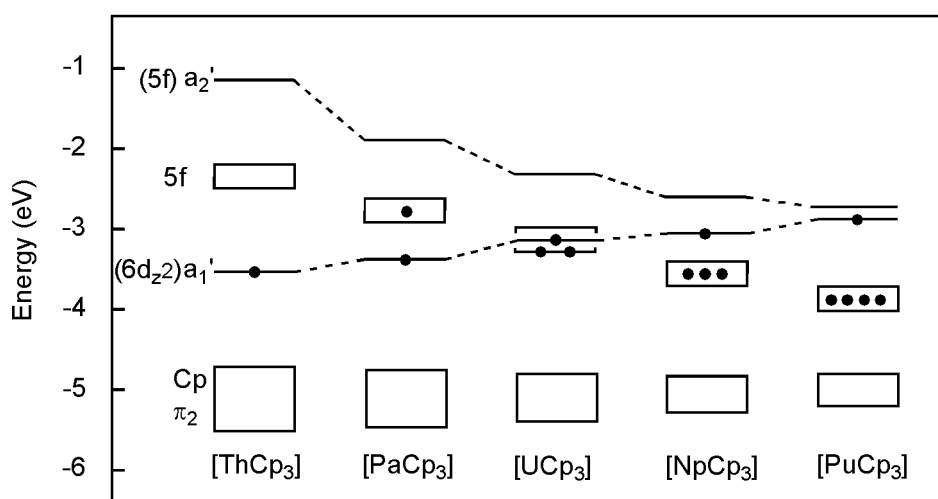
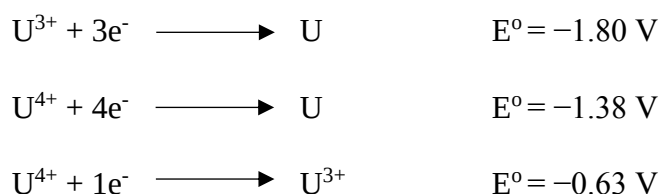


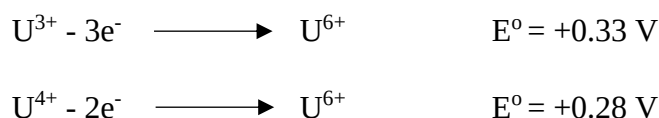
Fig. 1 - Metal-based orbital energies for the $5f^{n-1} 6d^1$ electron configurations of planar $[AnCp_3]$ complexes ($An = Th, Pa, U, Np, Pu$). Adapted from Bursten et al.¹

Whilst +4 is the predominant oxidation state for thorium compounds with only a few examples of other valences,⁵ uranium is able to access the formal oxidation states +2 to +6 via removal of valence electrons such that the electronic configuration for the U^{II} to U^{VI} ions are $5f^36d^1$ to $5f^0$ respectively. In Nature, the +6 oxidation state dominates due to the fundamental stability of the uranyl ion $[UO_2]^{2+}$. This is due partly to the overriding stability of the noble gas configuration of U^{VI} and as a consequence of the ‘inverse trans influence’. This is the reverse of what is observed in transition metal complexes where the $U=O$ bonds are significantly stabilised by virtue of the position of the oxo ligands *trans* to each other in the linear $[UO_2]^{2+}$ ion. In non-aqueous solvents the +4 and +6 valence dominates, however more recently the +2, +3 and +5 oxidation states are attracting greater attention from chemists.⁶⁻⁸

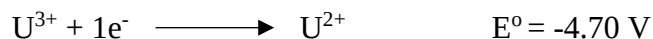
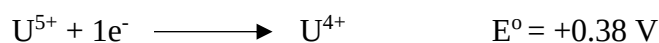
A better understanding of the stabilities and the relationships of the oxidation states can be ascertained by studying the standard reduction potentials (E^0 , in volts, V, relative to the standard hydrogen electrode, SHE)



Firstly it is found that U^{3+} is highly reducing and more reducing than U^{4+} . However, due to the small E^0 values for the reduction of U^{4+} to U^{3+} , both oxidation states have reasonable stability, with +4 being the more stable oxidation state.



Secondly in the case of U^{3+} and U^{4+} the oxidation to U^{6+} is energetically favourable.



The $\text{U}^{5+}/\text{U}^{4+}$ reduction couple suggests that whilst accessible, U^{5+} is unstable due to the energetically favourable reduction to U^{4+} . Until recently, it was thought U^{5+} was the least stable of the accessible oxidation states of uranium due to the large negative potential from U^{3+} to U^{2+} however, Evans and Meyers have recently reported the identification of the +2 oxidation state for uranium in crystalline molecular complexes.⁸⁻¹⁰

Relativity, Electronic Spectroscopy and Magnetism

Relativistic theories developed in the early part of the 20th century which at first were thought to be of little chemical importance have been shown to be very significant particularly for the heavier elements such as the actinides. The two main consequences can be divided into the necessary modification of atomic orbital energies and the effects on spin-orbit coupling. Einstein's theory of relativity states that the mass of a particle tends to infinity as its velocity tends towards the speed of light (in which the velocity cannot ever reach the speed of light), this increase of mass is known as the *relativistic mass increase*. For example a 1s electron with a given velocity will have an increased mass in comparison to when motionless. This mass increase results in a marked contraction of the 1s electron and an energetic stabilisation.

With the dependence of relativistic mass correction on atomic number the effects of relativity are generally small for the light elements, however this is not the case for the heavier elements. One effect is that the s functions, which in higher primary quantum shells are orthogonal to the 1s orbital, become stabilised as a result of the stabilisation of the 1s orbital. This is known as the *direct relativistic orbital contraction* and although smaller these effects are experienced by the p electrons. By contrast, valence

d and f electrons are expanded and destabilised as a result of increased shielding of the nucleus by the outer core s and p electrons. This is known as the *indirect relativistic orbital expansion* and in very heavy elements such as the actinides is sufficient enough to alter their chemistry in comparison with the hypothetical non-relativistic analogues. Furthermore, as the 5f orbitals are more destabilised by relativistic effects than the 4f orbitals and more weakly bound the larger range of oxidation states and their greater tendency to form covalent bonds can be attributed, in part, to the greater effects of relativity.^{3, 11-13}

Another consequence of relativistic effects becomes more apparent when studying the electronic energy levels and magnetic properties of actinide complexes. As the time-dependent Schrödinger equation is incompatible with relativity due to its different treatment of space and time, Paul Dirac suggested a different form to incorporate quantum theory with relativity. One of the aspects of Dirac's equation is that it included electron spin, which has to be treated as an 'extra' in non-relativistic quantum mechanics. When an electron is part of an atom the angular momentum associated with its spin can couple with the angular momentum generated by its orbital motion, this is known as *spin orbit coupling*. Many factors determine the magnitude of this spin-orbit coupling but in general it increases significantly with increasing atomic nuclear charge and decreases with sub-shell, in the order $p > d > f$. It is possible to define and describe the states and their corresponding energies produced by spin-orbit coupling according to their spin and orbital angular momenta in two principal ways.³

The first of which is *LS* or Russell-Saunders coupling which is used when spin-orbit coupling is weak in comparison with interelectronic repulsion. Russell-Saunders coupling assumes that all the individual orbital angular momenta of all the electrons combine into a total atomic orbital angular momentum, quantum number L . The same assumption is made of the individual spin angular momenta of the electrons and given the quantum number S . The total atomic angular momentum is given the quantum number J and is a result of the coupling of L and S with individual atomic or ionic energy levels characterised by a term symbol of general form $^{(2S+1)}L_J$.

The most significant term of an atom or ion is the most stable or ‘ground’ term which is determined by applying Hund’s rules. The ground term always has the largest value of S , this is known as maximum multiplicity. If two terms have the same multiplicity, the one with highest value of L lies lower in energy. For less than half filled electronic subshells the level with lowest value of J is lowest in energy whereas it is the highest value of J which is lowest in energy for more than half filled electronic sub shells. The Russell-Saunders coupling scheme is particularly effective at describing the electronic structure of lanthanide atoms and in particular Ln^{III} ions.

The second method, $j-j$ coupling, combines the individual orbital and spin angular momenta for each electron to give j . It is these individual j values which are coupled together to produce the total atomic angular momentum J . As a result of spin-orbit coupling not dominating interelectronic repulsions and 5f orbitals being much more sensitive to their environment compared to their 4f counterparts neither coupling scheme is particularly effective for the actinides. As a result experimental studies of actinide spin-orbit coupling, for example electronic spectroscopy and magnetic measurements are far more difficult to interpret compared to analogous lanthanide data.

As a result of the ligand environment having a greater effect on the chemistry of the actinides than with the corresponding lanthanides due to the larger bonding interactions of the 5f orbitals, it can be difficult to interpret the electronic absorption spectra of the actinides, despite this it is still feasible to draw some conclusions. As with $d \rightarrow d$ transitions, $f \rightarrow f$ transitions are forbidden by electric dipole and Laporte selection rules. However vibronic modes allow d orbitals to acquire some p type character and with $d \rightarrow p$ transitions fully allowed the formally forbidden $d \rightarrow d$ transitions gain intensity. This vibronic relaxation of the Laporte selection rule requires significant interactions between metal valence orbitals and those of the surrounding ligands therefore the heavily contracted nature of the Ln^{+3} 4f orbitals results in only weak relaxation and very weak $f \rightarrow f$ transitions ($\epsilon = 5 \text{ M}^{-1} \text{ cm}^{-1}$ $\epsilon =$ extinction coefficient, $\text{M}^{-1} = \text{dm}^3 \text{ mol}^{-1}$). In comparison vibronic coupling is greater in actinide complexes than those of the lanthanides resulting in stronger $f \rightarrow f$ transitions. This increased 5f orbital ligand interaction also results in actinide $f \rightarrow f$ bands being broader than the equivalent lanthanides. In addition to weak $f \rightarrow f$ transitions, much stronger $4f \rightarrow 5d$ and $5f \rightarrow 6d$ transitions than observed for the lanthanides and

actinides respectively. These allowed transitions are usually found in the ultra-violet region of the spectra resulting in less intense colours for the lanthanides. However, the allowed ligand to metal charge transfer transition which although normally resides in the UV tails in to the visible spectra resulting in highly intense colours for many actinide complexes.¹⁴⁻¹⁶

Paramagnetism arises in the f-elements as a result of unpaired f-electrons. In Ln^{3+} complexes the lack of interaction between metal based electrons and their ligand environment means that these compounds display very similar magnetic properties to the free metal ion. As previously stated the spin-orbit coupling can be described by the Russell-Saunders coupling scheme, where each atomic or ionic term is split into a series of levels denoted by their J values. For most Ln^{3+} complexes their magnetic behaviour is dictated by the ground level due to the magnitude of the f orbital spin orbit coupling being sufficiently large enough so that the excited levels are thermally inaccessible. The effective magnetic moment (μ_{eff}) of this ground level is given by the following equations.

$$\mu_{\text{eff}} = g_J \sqrt{J(J+1)}$$

$$\text{Where } g_J = 3/2 + S(S+1) - L(L+1)/2J(J+1)$$

This is remarkably similar to the equation used for first row transition metal compounds where only S is required as in these compounds the orbital contribution to μ_{eff} is quenched by the interaction of the d-orbitals with the surrounding ligands. The replacement of S by J is necessary because the surrounding ligands fail to quench the orbital contribution due to the contracted nature of the 4f orbitals.^{3, 11}

As with the increased complexity of the electronic absorption spectra of the actinides compared to the lanthanides the same can be said about their complicated magnetic behaviour. The above equation is much less applicable to actinides with a much greater temperature dependence on their magnetic susceptibilities. This is demonstrated by UF_6 and certain uranyl complexes which should be diamagnetic due to their $5f^0$ metal

configuration and $^1S_0$ ground state. However, these compounds exhibit temperature independent paramagnetism (TIP) as a consequence of the mixing of paramagnetic excited levels with the ground level. U^{4+} is one of the most widely studied actinide ions with its magnetic data usually interpreted by considering the $^3H_4$ ground level. However, unlike the Ln^{3+} ions, the effects of surrounding ligands must be taken into consideration. The $^3H_4$ ground level is split by the ligand crystal field into a number of thermally accessible energy levels, dependent on coordination number and geometry. In a regular octahedral field there is no mixing of the higher energy paramagnetic levels so there is no contribution to the magnetic susceptibility from temperature dependent contributions. A small distortion in this regular octahedral field results in the splitting of the first excited state, ^1T_g . Despite this split, the energy gap between the states is still too large for any thermal population and no temperature dependence is observed. It is only when the distortion of the octahedral field increases that a significant enough decrease in the energy gap occurs to allow thermal population of non-singlet magnetic states and the susceptibility starts to become increasingly temperature-dependent. The μ_{eff} of U^{4+} complexes in theory should tend towards zero as the temperature approaches absolute zero since the two unpaired electrons have the potential to spin couple at low temperatures.^{3, 11, 17, 18}

1.2 Metal-Metal Complexes

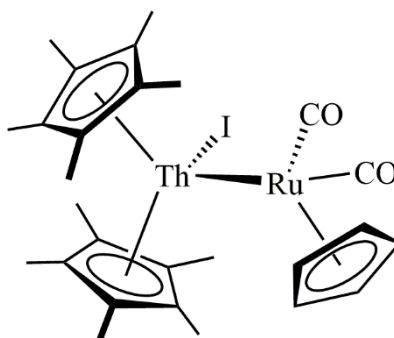
Many major advances in our fundamental chemical knowledge have emerged from novel metal-metal chemistry as demonstrated by the landmark Re–Re,¹⁹ Zn–Zn,²⁰ Cr–Cr,²¹ Mg–Mg²² and hexa-indium complexes.²³ Such complexes, exhibiting metal-metal interactions, have provided excellent tools for developing our understanding of chemical structure and bonding, catalysis, metal surface chemistry and bioinorganic chemistry.^{24, 25} However, whilst metal-metal bonding is now well understood in the p-^{23, 26-28} and d-²⁴ blocks and to some extent the s-block²² of the Periodic Table very little is known, in comparison, about that for the f-block and especially the actinide elements.²⁹⁻³²

Traditionally the chemistry of molecular f-element compounds has been dominated by the use of carbon, nitrogen, oxygen and halogen based ligands with the implementation of metal-based fragments as ligands considerably less developed. For example, the uranyl $[\text{UO}_2]^{2+}$ unit accounts for over 60% of all structurally characterised molecular uranium complexes.³³

Actinide-Transition Metal Complexes

The first proposal for the synthesis of an actinide-transition metal complex containing a metal-metal bond was made by Stone in 1971, in which he reported the compound $[\text{U}\{\text{Mn}(\text{CO})_5\}_4]$ (**1**).³⁴ However, this compound was reportedly extremely air sensitive and decomposed during analysis. For example, attempts to record IR spectra in chloroform exhibited ν_{CO} bands consistent with $[\text{Mn}(\text{CO})_5\text{Cl}]$ and the only identifiable fragments in the mass spectrum were $[\text{Mn}(\text{CO})_n]^+$. With no definitive X-ray diffraction data obtained the presence of uranium-manganese bonds must remain in doubt as the likelihood of iso-carbonyl bridging to the oxophilic uranium(IV) centre must be regarded as high.

In 1985, Marks and co-workers described the synthesis of the first definitive, structurally characterised, actinide-transition metal complex $[\text{Th}(\text{Cp}^*)_2(\text{I})\{\text{Ru}(\text{Cp})(\text{CO})_2\}]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (**2**) (**Fig. 2**) which was prepared *via* the salt elimination reaction of $[\text{Th}(\text{Cp}^*)_2(\text{I})_2]$ with $[\text{Na}\{\text{Ru}(\text{Cp})(\text{CO})_2\}]$.³⁵ Complex **2** was shown by an X-ray diffraction study to have a Th-Ru bond length of 3.028(2) Å, which is approximately equal to the sum of the covalent radii for thorium and ruthenium (3.00 Å)³⁶. The FTIR ν_{CO} bands at 2023 and 1959 cm^{-1} are comparable to the ν_{CO} bands observed of the related rare earth complex $[\text{Lu}(\text{Cp})_2(\text{THF})\{\text{Ru}(\text{Cp})(\text{CO})_2\}]$ (**3**). Marks also reported several complexes of the general form $[\text{An}(\eta^5\text{-C}_5\text{H}_4\text{R})_3\{\text{M}(\text{Cp})(\text{CO})_2\}](\text{An} = \text{Th, U; R} = \text{H, Me; M} = \text{Fe, Ru})$.³⁷ These were not characterised by single crystal X-ray diffraction studies, however the FTIR data were consistent with **2** and **3**, suggestive of the formation of similar complexes and the formation of metal-metal bonds.



2

Fig. 2 - Structure of $[Th(Cp^*)_2(I)\{Ru(Cp)(CO)_2\}]$ (**2**)

The complex $[Th(Cp^*)_2(\mu-PPh_2)_2Ni(CO)_2]$ (**4**) (**Fig. 3**) was reported by Ryan *et al.* Complex **4** was isolated from the reaction between $[Th(Cp^*)_2(PPh_2)_2]$ and $[Ni(COD)_2]$ (COD = cyclooctadiene) under an atmosphere of carbon monoxide.³⁸ The bridged Th-Ni interaction was determined by a single-crystal X-ray diffraction study to have a bond length of 3.206(2) Å which is larger than the sum of the covalent radii of thorium and nickel (2.85 Å).³⁶ The Th-P-Ni bond angle was determined to be approximately 76°, this is especially acute and provides further evidence for a Th-Ni interaction as complexes where no metal-metal bond is present exhibit significantly larger M-P-M' angles (>100°).³⁶ Ryan and co-workers also reported the complex $[Th(Cp^*)_2(\mu-PPh_2)_2Pt(PMe_3)]$ (**5**) (**Fig. 3**).³⁹ Complex **5** was prepared by the reaction between $[Th(Cp^*)_2(PPh_2)_2]$ and $[Pt(COD)_2]$ in the presence of trimethylphosphine. A single-crystal X-ray diffractions study revealed a Th-Pt bond distance of 2.984(1) Å, which is well within the sum of the covalent radii of thorium and platinum (3.42 Å), as well as a significantly acute Th-P-Pt angle (69.1°) further suggesting a supported Th-Pt bond.⁴⁰ *Ab initio* calculations performed on **5** suggested that the Th-Pt interaction is dative in character, with donation of electron density from platinum to thorium.

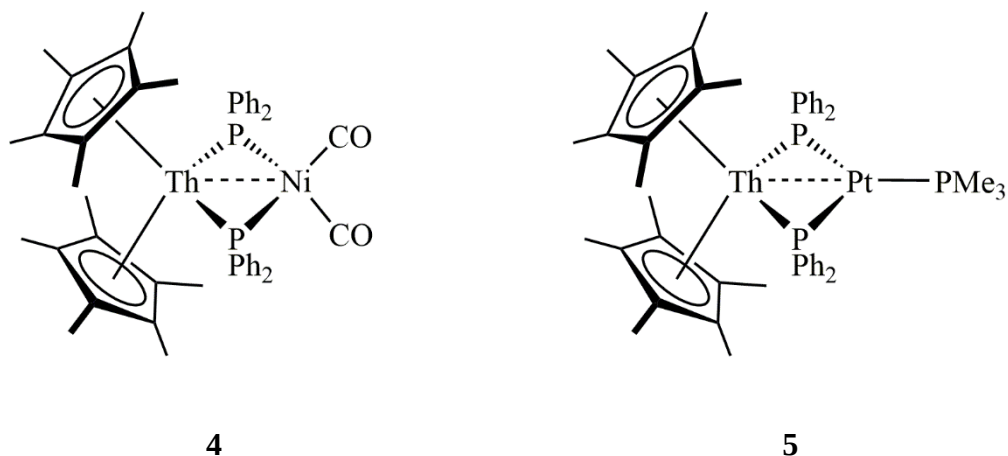
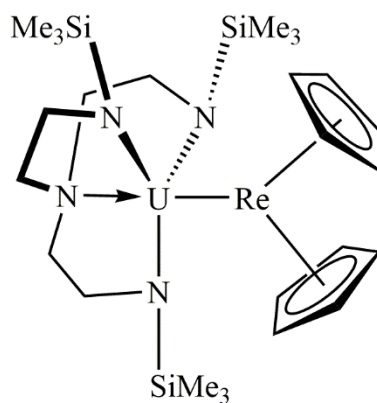


Fig. 3 - Structure of $[Th(Cp^*)_2(\mu-PPh_2)_2Ni(CO)_2]$ (**4**) and $[Th(Cp^*)_2(\mu-PPh_2)_2Pt(PMe_3)]$ (**5**)

The first structurally authenticated molecular uranium-transition metal bond was reported by Liddle *et al* in 2009.⁴¹ $[U(Tren^{TMS})\{Re(Cp)_2\}]$ [$Tren^{TMS} = N(CH_2CH_2NSiMe_3)_3$] (**6**) (**Fig. 4**) was prepared from the salt elimination reaction between $[U(Tren^{TMS})(I)(THF)]$ and $[K\{Re(Cp)_2\}]$.



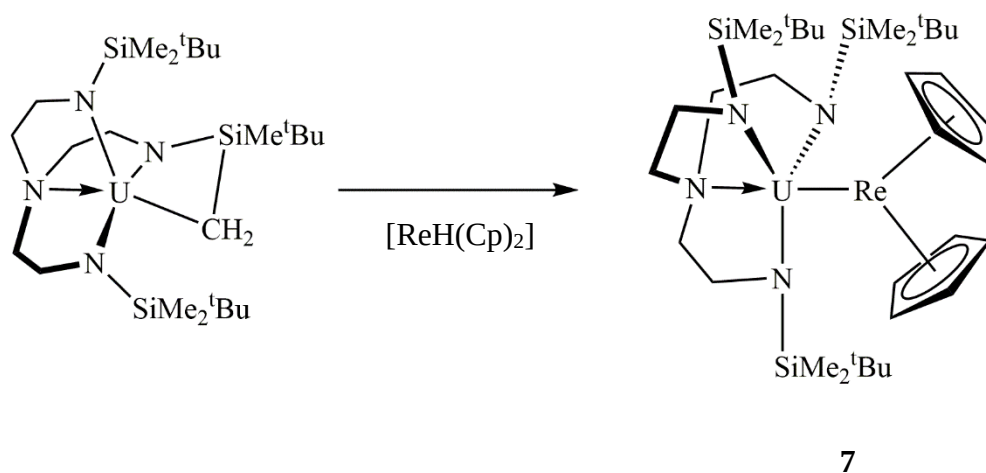
6

Fig. 4 - Structure of $[U(TrenTMS)\{Re(Cp)_2\}]$ (**6**)

A single-crystal X-ray diffraction study performed on a red crystal of **6** revealed a U–Re bond distance of 3.0475(4) Å which lies just outside the sum of the covalent radii of uranium and rhenium (2.95 Å).³⁶ The FTIR spectrum of the solid compound

contains no features in the region where bridging hydrides would be expected and treatment of **6** with CCl_4 did not result in the formation of CHCl_3 as judged by ^1H NMR spectroscopy. The room temperature magnetic moment of **6** ($2.88 \mu_{\text{B}}$) (μ_{B} = Bohr magneton) is within the range of other reported uranium(IV) compounds of 2.5-2.9 μ_{B} , but is lower than the theoretical free ion value of 3.58 μ_{B} expected for the $^3\text{H}_4$ ground state of f^2 uranium(IV).^{42, 43} A DFT (DFT = density functional theory) study concluded that although the U-Re interaction is predominantly electrostatic, there is a weak π -type donation of electron density from molecular orbitals principally composed of Re $5d_{yz}$ into a principally empty $5f_{x^2y}$ orbitals on uranium.

Continuing on from the success of synthesising the first actinide-transition metal bond *via* salt elimination, Liddle sought to expand the methods used to target such linkages by employing alkane elimination. The reaction of $[\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2^t\text{Bu})_2(\text{CH}_2\text{CH}_2\text{NSiMe}^t\text{BuCH}_2)\}]$ with $[\text{ReH}(\text{Cp})_2]$ in toluene, after work up and crystallisation, afforded red crystals of $[\text{U}(\text{Tren}^{\text{DMSB}})\{\text{Re}(\text{Cp})_2\}]$ (**7**) (**Scheme 1**) $[\text{Tren}^{\text{DMSB}} = \text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2^t\text{Bu})_3]$.⁴⁴



Scheme 1 - Synthesis of $[\text{U}(\text{TrenDMSB})\{\text{Re}(\text{Cp})_2\}]$ (**7**)

Despite the more sterically demanding $\text{Tren}^{\text{DMSB}}$ ligand compared to Tren^{TMS} the uranium-rhenium distance in **7** of 3.0479(6) Å is essentially identical to that of the uranium-rhenium distance in **6** whilst the room temperature magnetic moment of **7** ($2.86 \mu_{\text{B}}$) is also comparable with **6**. A DFT study of **7** showed that the uranium-

rhodium interaction is predominately ionic; however, as with that of **6**, there is a weak π component contributing to the bonding.

Liddle also demonstrated that uranium-rhodium bonds could be targeted *via* amine elimination.⁴⁵ Treatment of $[(Ts^{Xy})(THF)U(NCy_2)][Ts^{Xy} = HC(SiMe_2NAr)_3$; Ar = 3,5-Me₂C₆H₃; Cy = cyclohexyl] with $[ReH(Cp)_2]$ in THF afforded, after workup, $[U(Ts^{Xy})(THF)Re(Cp)_2]$ (**8**) (**Fig. 5**) as red crystals. Alternatively reaction of THF-free $[(Ts^{Xy})U(N\{SiMe_3\}_2)]$ with $[ReH(Cp)_2]$ in toluene, afforded after work up, red blocks of $[U(Ts^{Xy})Re(Cp)_2]$ (**9**) (**Fig. 5**).

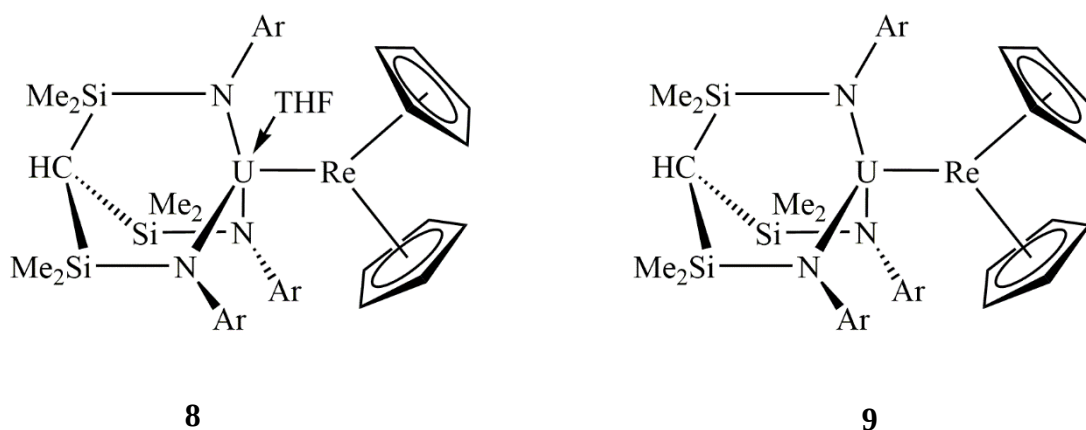


Fig. 5 - Structure of $[U(Ts^{Xy})(THF)Re(Cp)_2]$ (**8**) and $[U(Ts^{Xy})Re(Cp)_2]$ (**9**)

Both **8** and **9** were fully characterised by single crystal X-ray diffraction and DFT studies to allow for direct comparison of the effect of the ancillary ligands on the uranium-rhodium bond in complexes **6-9**. The uranium-rhodium bond distance of 3.0021(8) Å for **8** is representative of a contraction of ~0.04 Å from **6**. Following the loss of the THF ligand, the uranium-rhodium bond distance contracts by a further ~0.07 Å (2.9307(8) Å). This represents a total contraction of ~0.11 Å from **6-9**, a trend which was qualitatively matched by DFT calculations. From the analysis of the frontier orbitals it was observed that the removal of the Lewis base ancillaries increased the contribution to the σ -bonds from uranium- and rhenium-based orbitals. However, the total contribution from uranium- and rhenium based orbitals to the U-Re π -interactions remains the same. Therefore, upon moving from **6** to **9** the uranium

becomes more electron deficient, alleviated by strengthening of the uranium-rhenium σ -bond.

Liddle also recently reported the first structurally-characterised series of uranium-ruthenium complexes.⁴⁶ A salt elimination methodology was used to react four different uranium halide complexes with $[K\{Ru(Cp)(CO)_2\}]$ to afford the four new uranium-ruthenium complexes $[U(Tren^{TMS})\{Ru(Cp)(CO)_2\}]$ (**10**), $[U(Tren^{DMSB})\{Ru(Cp)(CO)_2\}]$ (**11**), $[U(Ts^{Tol})(THF)\{Ru(Cp)(CO)_2\}]$ (**12**) and $[U(Ts^{Xy})(THF)\{Ru(Cp)(CO)_2\}]$ (**13**) ($Ts^{Tol} = HC(SiMe_2NAr)_3$; $Ar = 4-MeC_6H_4$) (**Fig. 6**).

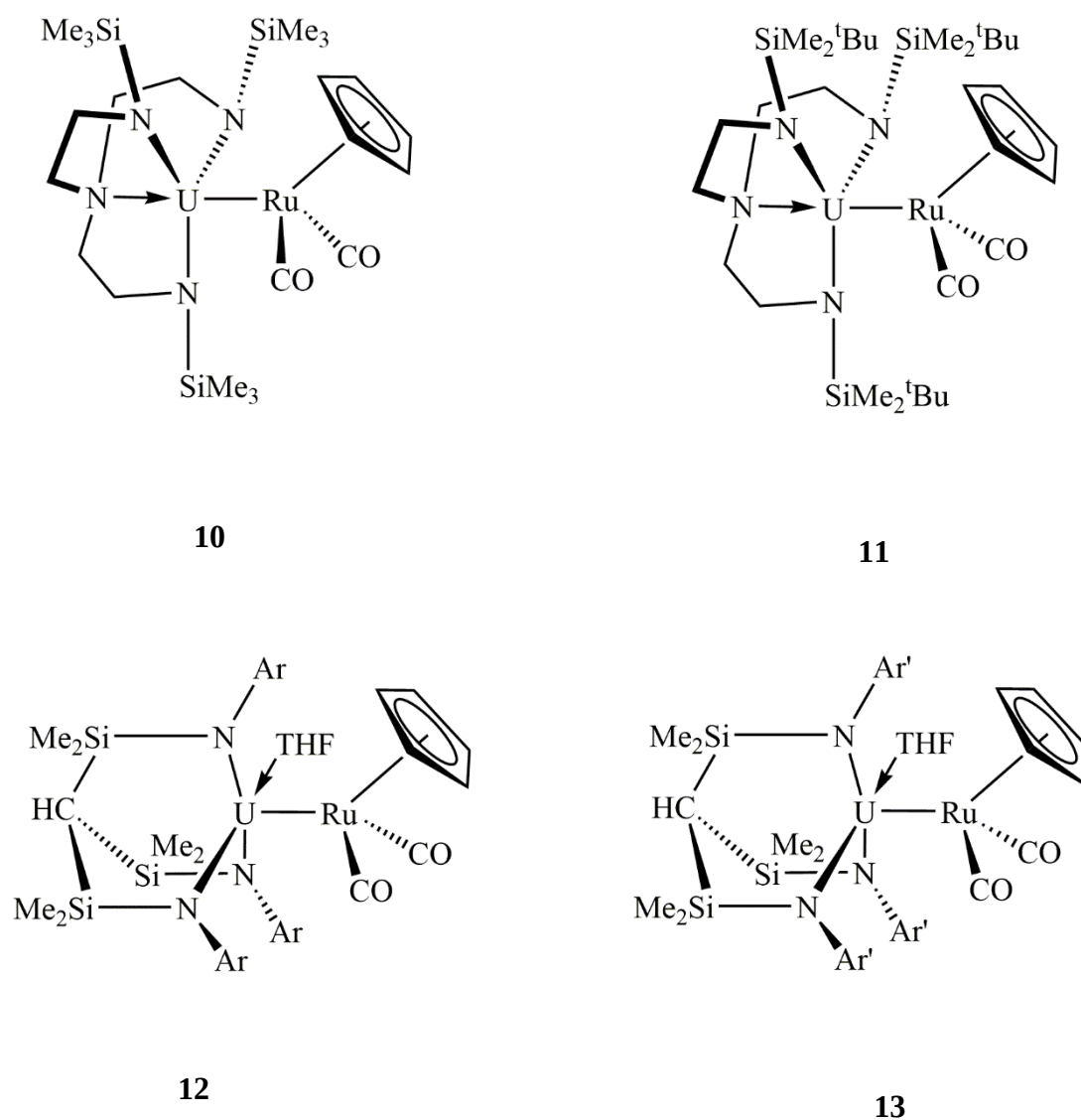
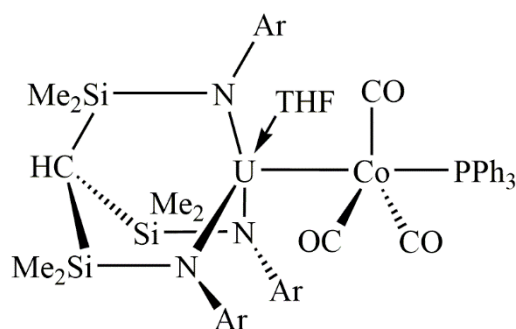


Fig. 6 - Structure of $[U(Tren^{TMS})\{Ru(Cp)(CO)_2\}]$ (**10**), $[U(Tren^{DMSB})\{Ru(Cp)(CO)_2\}]$ (**11**), $[U(Ts^{Tol})(THF)\{Ru(Cp)(CO)_2\}]$ (**12**) and $[U(Ts^{Xy})(THF)\{Ru(Cp)(CO)_2\}]$ (**13**)

Single crystal X-ray diffraction experiments performed on **10-13** confirmed the presence of unsupported uranium-ruthenium bonds with the bond distances spanning the range 2.9885(3)-3.0925(3) Å, which fall just outside the sum of the covalent radii of uranium and ruthenium (2.95 Å).³⁶ DFT studies conducted on **10-13** revealed that the interaction between the two metal centres is dominated by electrostatic contributions. Complexes **10-13** exhibit two ν_{CO} bands averaging 1947 and 1874 cm^{-1} and are typical of terminal rather than bridging carbonyl ligands which is supportive of the X-ray diffraction data.

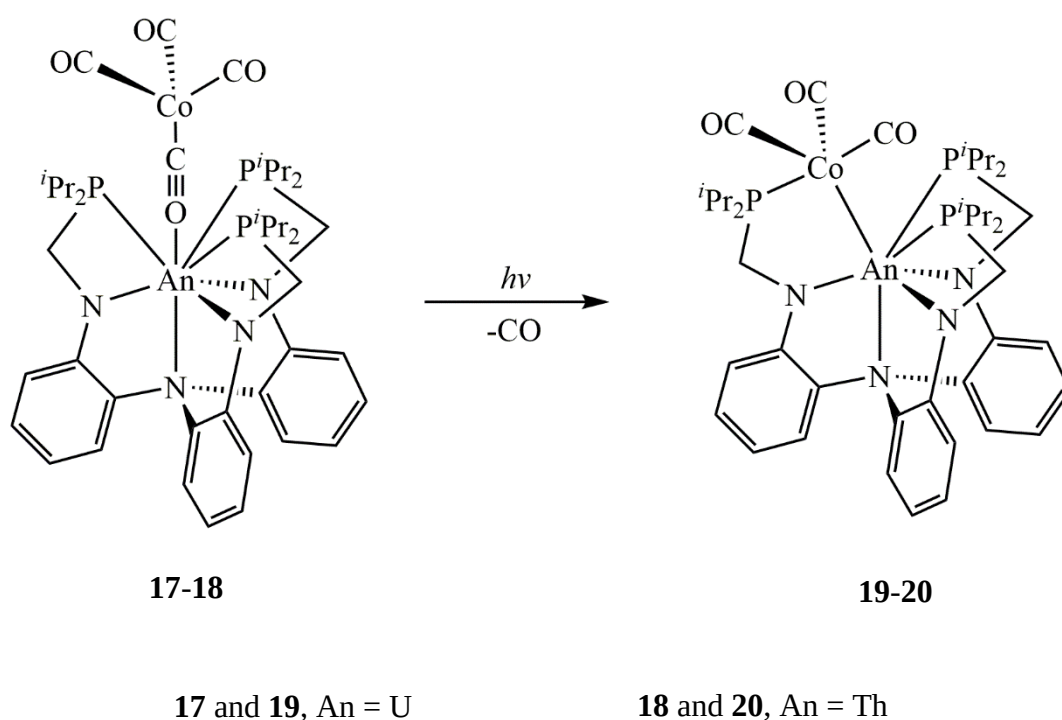
The complex $[\text{U}(\text{Ts}^{\text{Xy}})\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}]$ (**14**) (**Fig. 7**), the first to feature a uranium-cobalt bond, was reported by Liddle.⁴⁷ The treatment of the inverse sandwich arene complex $[\{\text{U}(\text{Ts}^{\text{Xy}})\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_5\text{Me})]$ with one equivalent of the cobalt dimer $[\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2]$ afforded **14** in 59% yield. Unlike all other uranium-transition metal complexes which were afforded by alkane, amine or salt elimination reactions this reaction proceeded *via* the reductive cleavage of $[\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2]$ by the inverse sandwich arene complex. This was important because attempts at synthesising **14** *via* salt elimination were all unsuccessful. An X-ray diffraction study of **14** revealed a uranium-cobalt bond distance of 2.9450(9) Å; this distance lies outside the sum of the covalent radii for uranium and cobalt (2.81 Å).³⁶ The U-Co interaction was analysed by a DFT study which concluded that it was largely ionic in nature.



14

Fig. 7 - Structure of $[\text{U}(\text{Ts}^{\text{Xy}})\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}]$ (**14**)

As recently as 2014 Arnold reported a series of uranium-cobalt and thorium-cobalt heterobimetallic complexes *via* a photochemical route.⁴⁸ The complexes, which utilise a binucleating ligand, $[\text{UCl}(\text{N}\{\sigma\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4\}_3)]$ (**15**) and $[\text{ThCl}(\text{N}\{\sigma\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4\}_3)]$ (**16**) were reacted with $[\text{Na}\{\text{Co}(\text{CO})_4\}]$ to form the respective carbonyl bridged complexes $[\text{U}(\text{N}\{\sigma\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4\}_3)(\mu\text{-OC})\text{Co}(\text{CO})_3]$ (**17**) and $[\text{Th}(\text{N}\{\sigma\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4\}_3)(\mu\text{-OC})\text{Co}(\text{CO})_3]$ (**18**). Irradiation of the resulting isocarbonyls with ultraviolet light resulted in the new actinide-cobalt species $[\text{U}(\text{N}\{\sigma\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4\}_3)\text{Co}(\text{CO})_3]$ (**19**) and $[\text{Th}(\text{N}\{\sigma\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4\}_3)\text{Co}(\text{CO})_3]$ (**20**) (**Scheme 2**) containing metal-metal interactions.



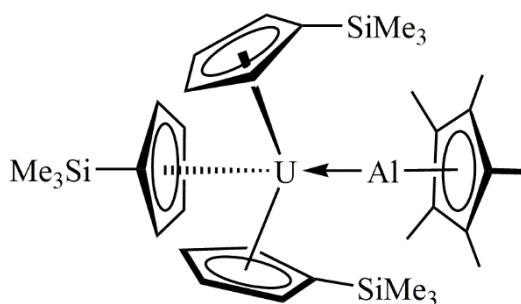
Scheme 2 - Synthesis of $[\text{U}(\text{N}\{\sigma\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4\}_3)(\mu\text{-OC})\text{Co}(\text{CO})_3]$ (**19**) and $[\text{Th}(\text{N}\{\sigma\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4\}_3)(\mu\text{-OC})\text{Co}(\text{CO})_3]$ (**20**)

Characterisation of **17-20** by single crystal X-ray diffraction experiments revealed the elimination of the bridging carbonyl and formation of the metal-metal bond which was accompanied by the coordination of a pendant phosphine arm of the triphosphinetriamide ligand to the cobalt centre upon irradiation. Additionally actinide-cobalt bonds of 3.0319(7) Å and 3.0771(5) Å in **19** and **20**, respectively, were observed which are within the range of previously reported uranium-cobalt

complexes.⁴⁷ It was concluded that the secondary coordination sphere incorporated into the ligand framework was crucial to the formation of the actinide-metal bonds as without it, upon photolysis, the resulting coordinatively unsaturated $\text{Co}(\text{CO})_3$ complex would be susceptible to decomposition.

Actinide-Main Group Metal Complexes

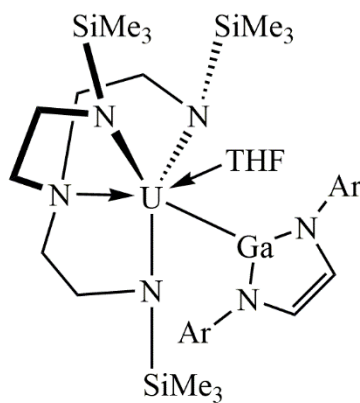
The first actinide-Group 13 metal complex, $[\text{U}(\text{Cp}')_3\text{Al}(\text{Cp}^*)]$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$) (**21**) (**Fig. 8**) was reported in 2008 by Arnold.⁴⁹ Reaction of one molar equivalent of $[\text{U}(\text{Cp}')_3]$ with a quarter molar equivalent of $[\{\text{Al}(\text{Cp}^*)\}_4]$ in toluene at 60 °C yielded, after work up, brown crystals. An X-ray diffraction study revealed a uranium-aluminium bond distance of 3.117(3) Å (sum of the covalent radii of uranium and aluminium 2.96 Å).⁴⁰ Neither NMR nor FTIR spectra revealed signals which could be assigned to bridging hydrides whilst addition of CCl_4 did not result in the formation of CHCl_3 . The room temperature magnetic moment of 3.0(1) μ_B is consistent with a $^4\text{I}_{9/2}$ ground state for $5f^3$ U(III). Using the model complex $[\text{U}(\text{Cp})_3\text{Al}(\text{Cp})]$ a DFT study revealed a uranium-aluminium donor-acceptor bonding interaction which was essentially σ -bonding in character with no observable π -bonding.



21

Fig. 8 - Structure of $[\text{U}(\text{Cp}')_3\text{Al}(\text{Cp}^*)]$ (**21**)

In 2009 Liddle and Jones reported the first structurally characterised actinide-Group 13 complex to exhibit both σ - and π -bonding character. The reaction between $[\text{U}(\text{Tren}^{\text{TMS}})(\text{I})(\text{THF})]$ and the gallium(I) heterocycle $[\text{Ga}(\text{NArCH})_2][\text{K}(\text{tmeda})]$ afforded the complex $[\text{U}(\text{Tren}^{\text{TMS}})\{\text{Ga}(\text{NArCH})_2(\text{THF})\}]$ (**22**) (**Fig. 9**).⁵⁰ As with **21** the NMR and FTIR spectra of **22**, suggested that no bridging hydrides were present. A single crystal X-ray diffraction study revealed two independent molecules of **22** in the asymmetric unit which were almost structurally identical except for the uranium gallium bonds [3.221(2) and 3.298(2) Å]. These bond lengths fall outside the sum of the covalent radii of 2.94 Å, possibly as a result of the sterically demanding ligands utilised.³⁶ A DFT study on the model complex $[\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiH}_3)_3\}\{\text{Ga}[\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{CH}]_2\}(\text{OMe}_2)]$ revealed not just the expected σ -bonding but also a weak π -component to the U-Ga bond. Although the uranium orbital contribution to the U-Ga π bond is *ca.* 20% in **22** compared to the 2% orbital contribution of yttrium in the complex $[\text{Y}(\text{BIPM})\{\text{Ga}(\text{NArCH})_2(\text{THF})_2\}]$ (**17**) ($\text{BIPM} = \{\text{C}(\text{PPh}_2\text{NSiMe}_3)_2\}^{2-}$) it should be kept in mind that the U-Ga interaction is predominately electrostatic in nature with only 28% of the total attractive interaction attributed to the orbital contribution.⁵¹

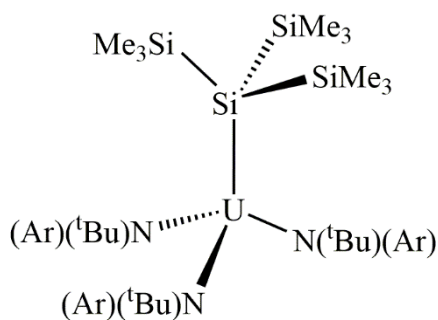


22

Fig. 9 - Structure of $[\text{U}(\text{Tren}^{\text{TMS}})\text{Ga}\{\text{NArCH}\}_2(\text{THF})]$ (**22**)

The compounds $[M(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_3\text{Ga}(\text{Cp}^*)]$ ($M = \text{U}$, **23**; $M = \text{Nd}$, **24**) which are isostructural to **21** were prepared in an analogous manner by Arnold in 2009.⁵² A single crystal X-ray diffraction study of **23** revealed two independent molecules of **23** in the asymmetric unit with U-Ga bond lengths of 3.0648(12) Å and 3.0800(13) Å respectively. To allow for direct comparison between the uranium-Group 13 metal interactions of **21** and **23** with the lanthanides Arnold attempted to synthesise the analogous Nd-Al, Nd-Ga, Ce-Al and Ce-Ga complexes. Only the Nd-Ga complex was structurally authenticated whilst the others were characterised *via* alternative spectroscopic methods. Despite the fact that **24** could only be isolated in relatively low yields and co-crystallising with $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Nd}(\mu\text{-OH})_2]$, structural comparisons were still able to be made, with the Nd-Ga bond length of 3.1536(6) Å in **24** being shorter than the respective Nd-Ga bond length in $[\text{Nd}(\text{L}')(\text{N}'')\{\text{Ga}(\text{NArCH})_2\}(\text{THF})]$ (**25**) ($\text{L}' = \text{'BuNCH}_2\text{CH}_2\{\text{C}(\text{NCSiMe}_3\text{CHN}'\text{Bu})\}$; $\text{N}'' = \text{N}(\text{SiMe}_3)_2$). DFT calculations on these complexes revealed that the $[\text{Al}(\text{Cp}^*)]$ fragment is a slightly better donor than $[\text{Ga}(\text{Cp}^*)]$ whereas quantitative ^1H NMR spectroscopic studies reveal that uranium is a better acceptor for soft σ -donating ligands than neodymium by an order of magnitude. ^1H NMR spectroscopy was also used to monitor competition reactions which showed that both $[\text{Al}(\text{Cp}^*)]$ and $[\text{Ga}(\text{Cp}^*)]$ preferentially bind to 5f uranium over 4f neodymium with excellent selectivity. However, DFT calculations suggested that this selectivity arises not from the back bonding of 5f uranium electrons but has its origins in a particularly strong σ -interaction.

The first and only structurally characterised uranium-silicon bond was reported by Cummins. Reaction between $[\text{U}(\text{I})\{\text{N}(3,5\text{-Me}_2\text{C}_6\text{H}_3)(\text{'Bu})\}_3]$ and $[\text{Li}\{\text{Si}(\text{SiMe}_3)_3\}(\text{THF})_3]$ afforded the complex $[\text{U}\{\text{N}(3,5\text{-Me}_2\text{C}_6\text{H}_3)(\text{'Bu})\}_3\{\text{Si}(\text{SiMe}_3)_3\}]$ (**26**) (**Fig. 10**) as red crystals.⁵³ A single crystal X-ray diffraction study of **26** revealed a uranium-silicon bond length of 3.091(3) Å, which is slightly longer than the sum of the covalent radii of uranium and silicon (3.07 Å).⁴⁰ A DFT study on the model complex $[\text{U}(\text{H}_2\text{N})_3(\text{SiH}_3)]$ revealed a uranium silicon bonding orbital composed mainly of silicon $3p_z$ (49 %) and uranium $6d_z^2$ (15 %) orbitals.



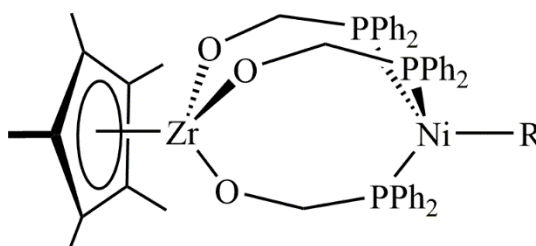
26

Fig. 10 - Structure of $[U\{N(3,5\text{-Me}_2\text{C}_6\text{H}_3)(t\text{Bu})\}_3\{\text{Si}(\text{SiMe}_3)_3\}]$ (26)

Supported Heterobimetallic Complexes

Although a number of f-element-metal complexes have been described their number is very small in comparison to the rest of the periodic table due to not only their inherent instability but also until recently a distinct lack of synthetic pathways. In recent years dinuclear species containing a metal-metal bond between two different transition metal centres bridged by a supporting ligand structure have rapidly been gaining interest, as they would be expected to exhibit different reactivity to those of monometallic or homobimetallic complexes. Early/late heterobimetallic complexes, featuring metal-metal interactions between a hard, Lewis acidic metal centre and a softer more Lewis basic metal centre, have received particular attention due to their two very different reaction sites, inherent bond polarity and between the two centres resulting in unique reactivity. This has potential applications in the activation of small molecules, homogeneous catalysis, and as bifunctional catalysts.^{25, 54-56}

In 1985 Wolczanski reported an early/late, Zr-Ni, heterobimetallic complex using an alkoxyalkyl phosphine ($\text{OCH}_2\text{Ph}_2\text{P}$) ligand system in an attempt to model the electron rich late metals and early metal oxide surfaces found in Fischer-Tropsch catalyst systems.⁵⁷ Although it was clear that an important role of the metal oxide support was to keep the electron-rich metal dispersed, these cocatalysts have potential to play a more direct role in the forming or breaking of C-C bonds.⁵⁸⁻⁶¹ The complex $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_3\text{Ni}(\text{PPh}_2\text{CH}_2\text{OH})]$ (**27**) (**Fig. 11**) was afforded from the reaction of equimolar quantities of $[\text{Ni}(\text{PPh}_2\text{CH}_2\text{OH})_4]$ and $[\text{Zr}(\text{Cp}^*)\text{Me}_3]$. Due to the high solubility of **27** purification was hampered, therefore derivatisation was accomplished *via* exposure to excess PMe_3 , P(OMe)_3 and CO to afford $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_3\text{Ni}(\text{PMe}_3)]$ (**28**), $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_3\text{Ni}(\text{P(OMe)}_3)]$ (**29**) and $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_3\text{Ni}(\text{CO})]$ (**30**) respectively. A single crystal X-ray diffraction study was performed on **30** revealing a Ni-Zr distance of the 4.049(1) Å which is much greater than the sum of the covalent radii of the metals (2.64 Å).³⁶ ruling out the possibility of a metal-metal interaction. It was envisaged that in order to observe any bimetallic chemistry that one of the bridging $\mu\text{-OCH}_2\text{Ph}_2\text{P}$ must be cleaved however this was not achieved.



27, R = $\text{PPh}_2\text{CH}_2\text{OH}$

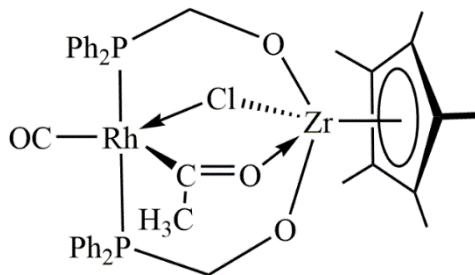
28, R = PMe_3

29, R = P(OMe)_3

30, R = CO

Fig. 11 - Structures of $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_3\text{Ni}(\text{PPh}_2\text{CH}_2\text{OH})]$ (**27**), $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_3\text{Ni}(\text{PMe}_3)]$ (**28**), $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_3\text{Ni}(\text{P(OMe)}_3)]$ (**29**) and $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_3\text{Ni}(\text{CO})]$ (**30**)

Wolczanski expanded the range of heterobimetallics supported by the alkoxyalkylphosphine ($\text{OCH}_2\text{Ph}_2\text{P}$)⁻ ligand system by reaction of $[(\text{Cp}^*)\text{ZrMe}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2]$ with half a molar equivalent of $[\{\text{RhCl}(\text{CO})_2\}_2]$ to afford the $\mu_2:\eta^2$ -acetyl “a-frame” complex $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2\{\mu_2:\eta^2\text{-OC}(\text{CH}_3)_3\})(\mu\text{-Cl})\text{Rh}(\text{CO})]$ (**31**) (**Fig. 12**) whose NMR and IR spectra were consistent with the structure indicated in **Fig. 12**.⁶²



31

Fig. 12 - Structure of $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2\{\mu_2:\eta^2\text{-OC}(\text{CH}_3)_3\})(\mu\text{-Cl})\text{Rh}(\text{CO})]$ (**31**)

Exposure of **31** to the electrophile HCl resulted in the formation of acetaldehyde and the complex $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2(\mu\text{-Cl})_2\text{Rh}(\text{CO})]$ (**32**). Alternatively **32** could be more easily obtained via refluxing of a CHCl_3 solution of **31**. The mixed halide derivative $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2(\mu\text{-Cl})(\mu\text{-I})\text{Rh}(\text{CO})]$ was synthesised via reaction of **31** with one equivalent of MeI with the formation of acetone as a side product.

In 1988 Woczanski extended the library of heterobimetallics utilising the alkoxyalkyl phosphine ($\text{OCH}_2\text{Ph}_2\text{P}$)⁻ ligand system to include several complexes which exhibited Rh-Zr bonds.⁶³ Treatment of $[(\text{Cp}^*)\text{ZrMe}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2]$ with $[\text{RhMe}(\text{PPh}_3)_3]$ in toluene resulted in the Rh-Zr complex $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2\text{RhMe}_2]$ (**33**) (**Fig. 13**). A single crystal X-ray diffraction study revealed a significantly short Rh-Zr distance of $2.444(1) \text{ \AA}$ (sum of covalent radii of Rh and Zr = $2.79 \text{ \AA}$)³⁶ hinting at multiple bonding. The complex $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_3\text{RhMe}]$ (**34**) (**Fig. 13**) was also generated via an unknown disproportionation pathway. **34** was independently synthesised in an 81% yield by an *in situ* alcoholysis of $[(\text{Cp}^*)\text{ZrMe}_3]$ with three

equivalents of $(\text{HOCH}_2\text{Ph}_2\text{P})$ to provide $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_3]$, followed by the addition of $[\text{RhMe}(\text{PPh}_3)_3]$. Several spectroscopic features suggested that **33** contained an unanticipated Rh-Zr bond although **33** did not react with CO_2 or N_2O as anticipated. This was contrary to the expected behaviour of a polarised Rh-Zr bond but is consistent with extensive steric shielding by the ancillary ligands of both metals.

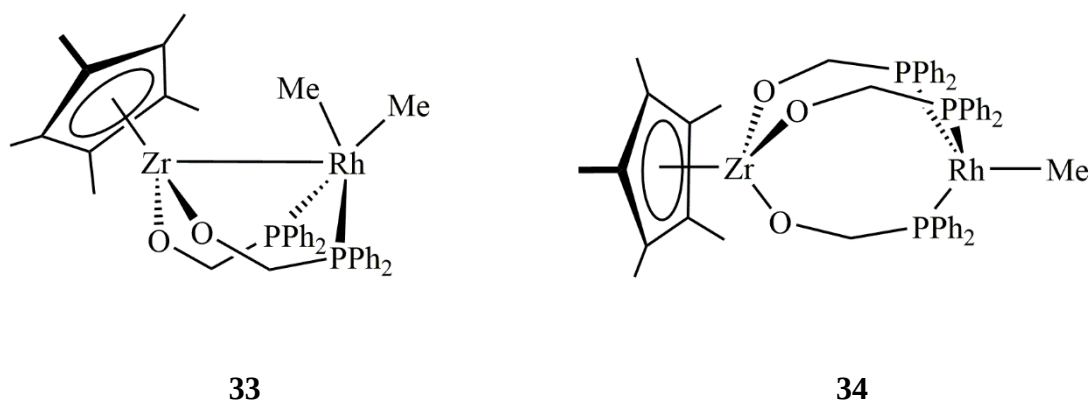
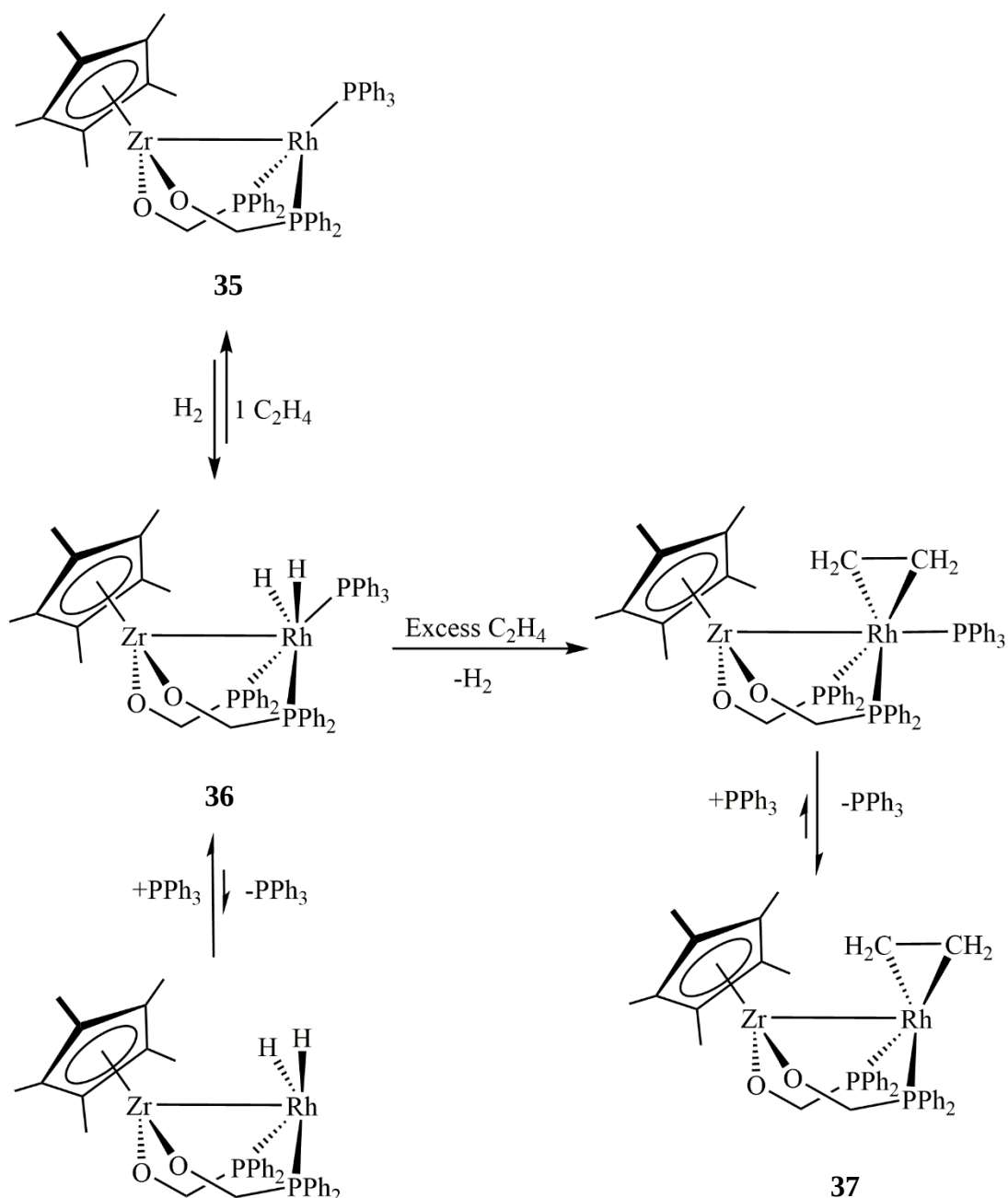


Fig. 13 - Structures of $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2\text{RhMe}_2]$ (**33**) and $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_3\text{RhMe}]$ (**34**)

In order to synthesise a less sterically encumbered metal-metal bond $[(\text{Cp}^*)\text{ZrMe}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2]$ was treated with $[\text{RhH}(\text{PPh}_3)_3]$ resulting in the immediate evolution of methane and the formation of the complex $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2\text{Rh}(\text{PPh}_3)]$ (**35**) (Scheme 3). The reaction of **35** with H_2 produced $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2\text{RhH}_2(\text{PPh}_3)]$ (**36**) (Scheme 3) in a near quantitative yield by ^1H NMR spectroscopy. Exposure of **36** to one equivalent of ethylene resulted in the reversal of this reaction. As there were problems with PPh_3 as an impurity, **36** was prepared in an alternate fashion through the hydrogenation of **33** in the presence of just one equivalent of PPh_3 . At room temperature the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the product of this reaction exhibited a sharp signal at δ 31.56 ppm attributed to the ligand bridges accompanied by a broad PPh_3 dependent signal, indicative of PPh_3 loss (Scheme 3). Whereas only complex mixtures were obtained from the reaction of **36** with small molecules CO , CO_2 , HCl and MeI , the reaction of **36** with ethylene resulted in its slow hydrogenation to ethane and the formation of **35**. Alternatively exposure of **36** to an excess of ethylene gave the ethylene adduct $[(\eta^5\text{-Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2\text{Rh}(\eta^2\text{-C}_2\text{H}_4)]$ (**37**) (Scheme 3).

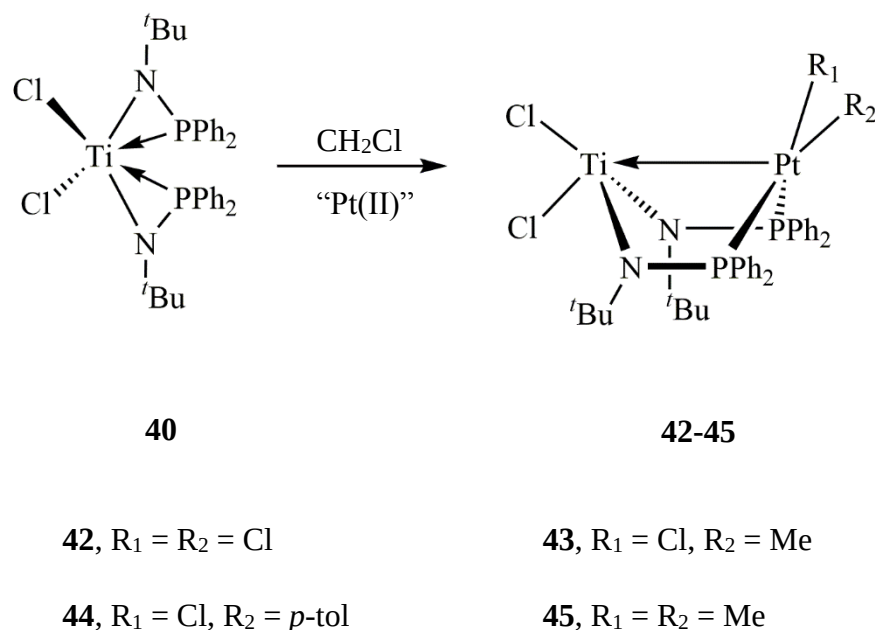


Scheme 3 - Synthesis of $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2\text{Rh}(\text{PPh}_3)]$ (**35**), $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2\text{RhH}_2(\text{PPh}_3)]$ (**36**) and $[(\text{Cp}^*)\text{Zr}(\mu\text{-OCH}_2\text{Ph}_2\text{P})_2\text{Rh}(\eta^2\text{-C}_2\text{H}_4)]$ (**37**)

More recently Nagashima reported a range of titanium complexes supported by the phosphinoamide ligand, $(\text{RNPPH}_2)^-$ ($\text{R} = \text{alkyl}$), to act as bidentate metalloligands for late transition metal centres.⁶⁴ Treatment of the lithium phosphinoamides, $[\text{Li}(\text{RNPPH}_2)]$ ($\text{R} = \text{'Bu}$, **38**; 'Pr , **39**), with TiCl_4 in a 2:1 molar ratio results in the

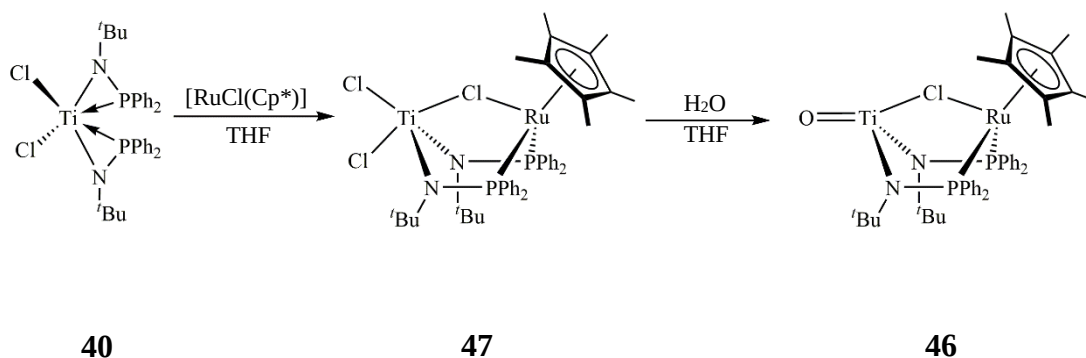
formation of the titanium bis(phosphinoamides)dichlorides, $[\text{TiCl}_2(\text{RNPPH}_2)_2]$ ($\text{R} = \text{}^t\text{Bu}$, **40**; $\text{}^i\text{Pr}$ **41**). Single crystal X-ray diffraction studies on both **40** and **41** revealed covalent bonding between the titanium centre and the two nitrogen atoms, whereas the two phosphorus atoms are datively coordinated to the metal centre intramolecularly. Variable-temperature ^1H NMR spectroscopic studies suggested reversible dissociation of the phosphines from the titanium in solution. It is these dissociated phosphines in complex **40** that effectively react with the platinum(II) species $[(\eta^4\text{-COD})\text{PtCl}_2]$, $[(\eta^4\text{-COD})\text{Pt}(\text{R})(\text{Cl})]$ ($\text{R} = \text{Me}$; *p*-Tol) or $[\{\text{PtMe}_2(\mu\text{-SMe}_2)\}_2]$ to afford the corresponding Ti-Pt heterobimetallic complexes $[\text{TiCl}_2(\text{}^t\text{BuNPPH}_2)_2\text{PtCl}_2]$ (**42**), $[\text{TiCl}_2(\text{}^t\text{BuNPPH}_2)_2\text{PtClMe}]$ (**43**), $[\text{TiCl}_2(\text{}^t\text{BuNPPH}_2)_2\text{PtCl}(p\text{-tol})]$ (**44**) and $[\text{TiCl}_2(\text{}^t\text{BuNPPH}_2)_2\text{PtMe}_2]$ (**45**) (Scheme 4).

The molecular structures of all four of these complexes were determined by single crystal X-ray diffraction studies with all four complexes adopting similar boat conformations, in which two nitrogen atoms are bonded to the titanium atom, whereas two phosphorus atoms are coordinated to the platinum centre. The 6-membered ring is in the boat conformation with the two metal atoms occupying apical locations. The four titanium-platinum distances in **42-45** range from 2.8358(8) Å to 2.6860(11) Å, which all fall outside the sum of the covalent radii of titanium and platinum (2.59 Å).³⁶ The two chloride and two amide centres coordinated to the titanium atoms in **42-45** are distorted significantly from a tetrahedral geometry, presumably as a result of the possible dative interaction. The ligand arrangement around the platinum atom is square planar; however, the platinum centre is distorted out of the plane. The contraction of the platinum-titanium distance moving from **42** to **45** was explained by considering the electron density on the platinum atom; the increased electron density donating ability of Me over Cl⁻ renders the platinum centre more electron rich resulting in a greater degree of electron donation to the Lewis acidic titanium centre and an accompanying contraction of the Ti-Pt distance.



Scheme 4 - $[\text{TiCl}_2(\text{tBuNPPPh}_2)_2\text{PtCl}_2]$ (**42**), $[\text{TiCl}_2(\text{tBuNPPPh}_2)_2\text{PtClMe}]$ (**43**), $[\text{TiCl}_2(\text{tBuNPPPh}_2)_2\text{PtCl}(p\text{-tol})]$ (**44**) and $[\text{TiCl}_2(\text{tBuNPPPh}_2)_2\text{PtMe}_2]$ (**45**)

Nagashima subsequently expanded the range of phosphinoamide supported heterobimetallics to include titanium-ruthenium complexes. **40** reacted with 0.25 equivalents of $[(\text{RuCl})_4]$ to produce two Ti-Ru species.⁶⁵ Fractional crystallisation of the crude reaction mixture allowed isolation of $[\text{TiO}(\text{tBuNPPPh}_2)_2(\mu\text{-Cl})\text{Ru}(\text{Cp}^*)]$ (**46**) (**Scheme 50**) exclusively and was characterised by a single crystal X-ray diffraction study. Both the titanium and ruthenium centres in **46** adopt a pseudo-tetrahedral coordination geometry linked by the two phosphinoamide ligands. This results in the formation of two fused 5-membered metallacycles. The long Ti-Ru distance of 3.093(2) Å excludes any metal-metal interaction as metal-metal bonds between titanium and ruthenium are usually shorter than 3 Å.^{55, 66-69} The chloride atom bridges over the Ti-Ru axis, and the interaction of its lone pair electrons compensates for the Lewis acidity of the titanium centre instead of the dative bond seen in the Ti-Pt heterobimetallic complex.

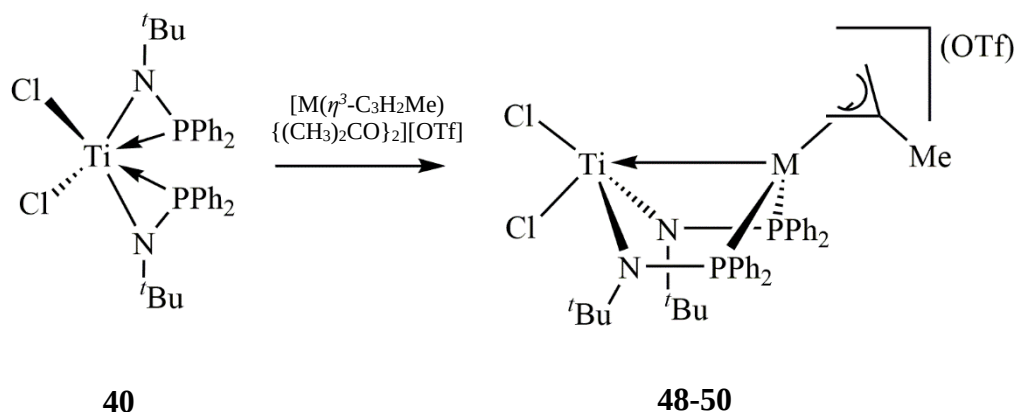


Scheme 5- Synthesis of $[\text{TiCl}_2(\text{tBuNPPPh}_2)_2(\mu\text{-Cl})\text{Ru}(\text{Cp}^*)]$ (**46**) and $[\text{TiO}(\text{tBuNPPPh}_2)_2(\mu\text{-Cl})\text{Ru}(\text{Cp}^*)]$ (**47**)

Although the product expected from the reaction of **40** and $[(\text{RuCl}(\text{Cp}^*))_4]$ is the trichloride $[\text{TiCl}_2(\text{tBuNPPPh}_2)_2(\mu\text{-Cl})\text{Ru}(\text{Cp}^*)]$ (**47**) the only product identified crystallographically was the oxide complex **46**. The trichloride species **47** was very unstable and only detectable at the initial stages of the reaction, however, careful experiments which excluded all water in a sealed NMR tube provided spectroscopic evidence for **47** which was extremely moisture sensitive and readily converted to the oxide in the presence of H_2O . This instability towards water was attributed to the intra-molecular interaction of the lone pair electrons of the bridging chloride atom at the apical position with the Lewis acidic titanium centre, of which the trans-influence destabilises the bond between the titanium and the apical terminal chlorine atom which in turn becomes susceptible to nucleophilic attack of water.

In 2009 Nagashima reported a series of titanium-Group 10 complexes with an η^3 -methallyl ligand bound to the Group 10 metal centres.⁷¹ Complexes of the form $[\text{TiCl}_2(\text{tBuNPPPh}_2)_2\text{M}(\eta^3\text{-C}_3\text{H}_2\text{Me})][\text{OTf}]$ ($\text{M} = \text{Ni}$ **48**; Pd **49**; Pt **50**) ($\text{OTf} = \text{CF}_3\text{SO}_3^-$) were afforded from the reaction of **40** with $[\text{M}(\eta^3\text{-C}_3\text{H}_2\text{Me})\{(\text{CH}_3)_2\text{CO}\}_2][\text{OTf}]$ ($\text{M} = \text{Ni}$; Pd ; Pt) (**Scheme 6**). **48**, **49** and **50** were all structurally characterised and as in **46-49**, the six membered metallocycle adopts a boat conformation with the two metal atoms again occupying the apical locations. Computational studies on **48-50** using density functional theory (DFT) revealed that the HOMO for **48** and **50** or the HOMO-1 for **49** may involve some Ti-M bonding interaction *via* donation of electron density from the d_{z^2} and d_{yz} orbitals of the group ten metal atom to the titanium centre. This polarisation of electron density away from the Group 10 metal centre enhances the

electrophilicity of the η^3 -methallyl ligand in **48-50**. This was demonstrated experimentally by the increased reactivity of the η^3 -methallyl fragment towards Et₂NH compared to the dppp (dppp= diphenylphosphinepropyl) analogues in the formation of diethylmethallylamine which in contrast exhibited no reaction.



48 M = Ni

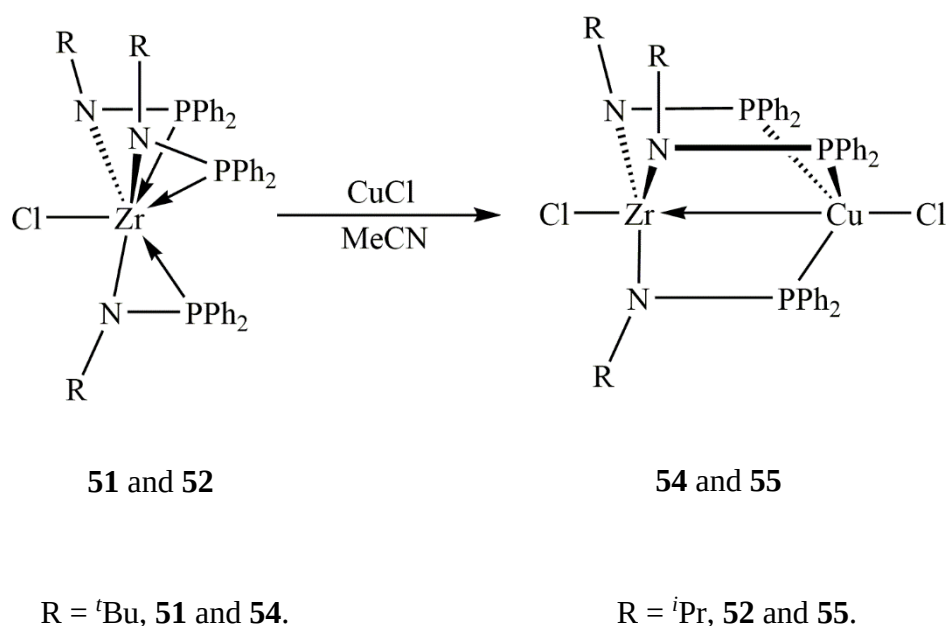
49, M = Pt

50, M = Pd

Scheme 6 - Synthesis of $[\text{TiCl}_2(\text{tBuNPPPh}_2)_2\text{Ni}(\eta^3\text{-C}_3\text{H}_2\text{Me})][\text{OTf}]$ (**48**), $[\text{TiCl}_2(\text{tBuNPPPh}_2)_2\text{Pt}(\eta^3\text{-C}_3\text{H}_2\text{Me})][\text{OTf}]$ (**49**) and $[\text{TiCl}_2(\text{tBuNPPPh}_2)_2\text{Pd}(\eta^3\text{-C}_3\text{H}_2\text{Me})][\text{OTf}]$ (**50**)

In 2007 Nagashima reported the synthesis of tripodal zirconium(IV) tris(phosphinoamide) complexes as metalloligands envisaged to be a route towards zirconium-late transition metal heterobimetallic complexes.⁷² Treatment of three equivalents of **38** and **39** with zirconium tetrachloride afforded the respective tris(phosphinoamide)zirconium chloride complexes $[\text{ZrCl}(\text{tBuNPPPh}_2)_3]$ (**51**) and $[\text{ZrCl}(\text{tPrNPPPh}_2)_3]$ (**52**) in high yields. As with the bis(phosphinoamide)titanium complexes, single crystal X-ray diffraction studies revealed the three nitrogen atoms bonded covalently to the zirconium centre whereas the three phosphines were datively bound. Although all three phosphorus atoms are bonded to the zirconium centre in the solid state, NMR spectroscopic studies suggested a dynamic coordination/dissociation process similar to that which is observed in the related bis(phosphinoamide)titanium complexes **40** and **41** and the zirconium(phosphinoamide) complex $[\text{Zr}(\text{Ph}_2\text{PNPh})_4]$ (**53**).⁷³

The fluxional behaviour of **51** and **52** suggested their suitability as a *fac*-P₃ tripodal type metalloligands for complexes with tetrahedral or octahedral geometry. Reaction of **51** and **52** with one equivalent of CuCl in acetonitrile afforded the respective Zr-Cu heterobimetallic complexes [ZrCl(^tBuNPPPh₂)₃CuCl] (**54**) and [ZrCl(ⁱPrNPPPh₂)₃CuCl] (**55**) (**Scheme 7**). Both complexes were characterised by NMR spectroscopy with a single peak in the ³¹P{¹H} NMR spectra at -30.6 and -11.2 ppm respectively and with ¹H NMR spectroscopy hinting at six magnetically equivalent phenyl groups adopting a C_{3v} symmetric structure. This was confirmed by single crystal X-ray diffraction analysis revealing the two metal centres are linked by three phosphinoamide ligands. The copper atom adopts a *pseudotetrahedral* coordination geometry with tripodal phosphorus moieties and a chloride atom, whereas the ligand arrangement around the zirconium atom is trigonal bipyramidal.



*Scheme 7 - Synthesis of [ZrCl(^tBuNPPPh₂)₃CuCl] (**54**) and [ZrCl(ⁱPrNPPPh₂)₃CuCl] (**55**)*

Reaction of **52** with the octahedrally arranged molybdenum precursor [Mo(CO)₃(MeCN)₃] resulted in the displacement of the MeCN ligands by the three phosphines in **52** to give the Zr-Mo heterobimetallic complex [ZrCl(ⁱPrNPPPh₂)₃Mo(CO)₃] (**56**) (**Fig. 14**). The ¹H NMR spectrum of **56** showed signals for three magnetically equivalent ⁱPrNPPPh₂ moieties with the ³¹P{¹H} NMR

spectrum displaying a singlet at 36.3 which is shifted down field by 20 ppm relative to $[(\text{trisphos})\text{Mo}(\text{CO})_3]$ (**57**) [$\text{trisphos} = 1,1,1\text{-tris}\{(\text{diphenylphosphanyl})\text{methyl}\}\text{ethane}$].⁷⁴ The IR spectrum shows two characteristic CO stretching bands at 1987 and 1913 cm^{-1} which represents a hypsochromic shift of ca. 60 cm^{-1} relative to **57**. This weaker back-donation from molybdenum to the π^* orbital of the CO ligands was attributed to either direct through-space interaction between the Lewis acidic zirconium and the molybdenum atoms or by a through-bond interaction *via* the Zr-N-P-Mo bond. A single crystal X-ray diffraction study revealed the two metal centres to be connected by the three phosphinoamide bridging ligands and the three phosphorus atoms are coordinated to the molybdenum centre in a *fac*- P_3 fashion. The Mo-P bond lengths in **56** are slightly longer relative to those found in **57**, whereas the C-O bond lengths are more closely comparable, with a relatively large Mo-Zr distance of 2.9741(5) Å suggesting that the previously described shift of the ν_{CO} band to higher frequencies can be better explained by through-bond interactions.

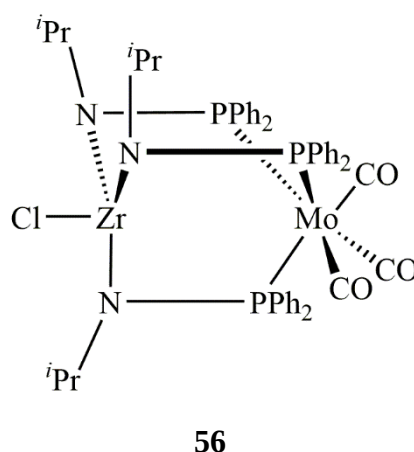
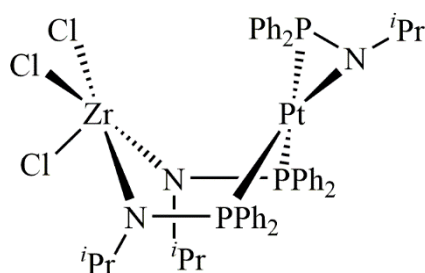


Fig. 14 - Structure of $[\text{ZrCl}(\text{iPrNPPH}_2)_3\text{Mo}(\text{CO})_3]$ (**56**)

To resolve the question of what would occur if the second metal complex fragment does not have the required geometry for *fac*- P_3 tripodal type coordination Nagashima treated **52** with the square planar Pt(II) precursor $[\text{PtCl}_2(\text{COD})]$ to afford the novel Zr-Pt heterobimetallic complex $[\text{ZrCl}_3(\text{iPrNPPH}_2)_2\text{Pt}(\text{iPrNPPH}_2)]$ (**58**) (**Fig. 15**). In contrast to the C_{3v} symmetric structures of the Zr-Cu and Zr-Mo complexes **54**, **55** and **56**

which each give a single $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic resonance, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **58** clearly demonstrates that the three $^i\text{PrNPPh}_2$ ligands in **58** are magnetically inequivalent and the complex has C_1 symmetry on the NMR timescale in solution.



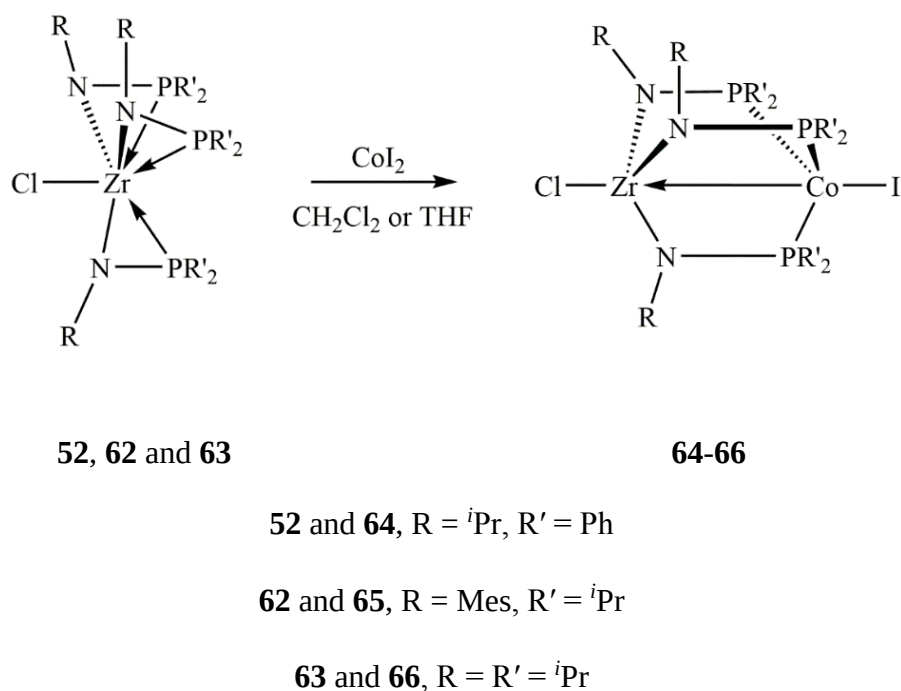
58

Fig. 15 - Structure of $[\text{ZrCl}_3(^i\text{PrNPPh}_2)_2\text{Pt}(^i\text{PrNPPh}_2)]$ (**58**)

The molecular structure of **58** revealed two metal centres linked by two phosphinoamide bridges in a boat conformation similar to that observed for the related Ti-Ru (**42-45**) and Ti-Group 10 (**48-50**) complexes. The ligand arrangement indicates that **66** is formally considered to have a zwitterionic form with Zr(IV)^- and Pt(II)^+ centres. This unusual ligand rearrangement is likely to occur intermolecularly with the close proximity in which the Zr and Pt exists facilitating the reaction pathway whereby the ring strain of the primarily formed intermediates created by the square planar geometry of the platinum centre and the tripodal ligand system is released to form the zwitterionic Zr-Pt heterobimetallic complex.

As a result of the shifted CO stretching frequencies by 50-70 cm^{-1} , of the Zr-Mo complex **56** compared to the $[(\text{trisphos})\text{Mo}(\text{CO})_3]$ (**57**), as a consequence of weaker back bonding into CO π^* orbitals, in 2009 Thomas investigated what effect coordination of a Lewis acidic early transition metal would have on a potentially redox-active late transition metal.⁷⁵ Lithiation of the phosphinoamine precursors $^i\text{PrN}(\text{H})\text{PPh}_2$ (**59**), $\text{MesN}(\text{H})\text{P}^i\text{Pr}_2$ (**60**) and $^i\text{PrN}(\text{H})\text{P}^i\text{Pr}_2$ (**61**) [$\text{Mes} = \text{C}_6\text{H}_2(\text{CH}_3)_3$] followed by the *in situ* treatment with 1/3 equivalent of ZrCl_4 led to the isolation of

the previously known tris(phosphinoamide)zirconium chloride complex $[\text{ZrCl}(\text{}^i\text{PrNPPh}_2)_3]$ (**52**) and the analogous tris(phosphinoamide)zirconium chloride complexes $[\text{ZrCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**62**) and $[\text{ZrCl}(\text{}^i\text{PrNP}^i\text{Pr}_2)_3]$ (**63**). Thomas demonstrated, using variable temperature ^1H NMR spectroscopy, that the reversible phosphine dissociation observed in **52** occurred in solution at room temperature for **62** and **63** making them viable metalloligands. Reaction of **52**, **62** and **63** with one equivalent of CoI_2 resulted in the isolation of the heterobimetallic complexes $[\text{ZrCl}(\text{}^i\text{PrNPPh}_2)_3\text{CoI}]$ (**64**) $[\text{ZrCl}(\text{MesNP}^i\text{Pr}_2)_3\text{CoI}]$ (**65**) and $[\text{ZrCl}(\text{}^i\text{PrNP}^i\text{Pr}_2)_3\text{CoI}]$ (**66**) (**Scheme 8**) and the formal reduction from Co^{II} to Co^{I} as confirmed by solution magnetic studies.

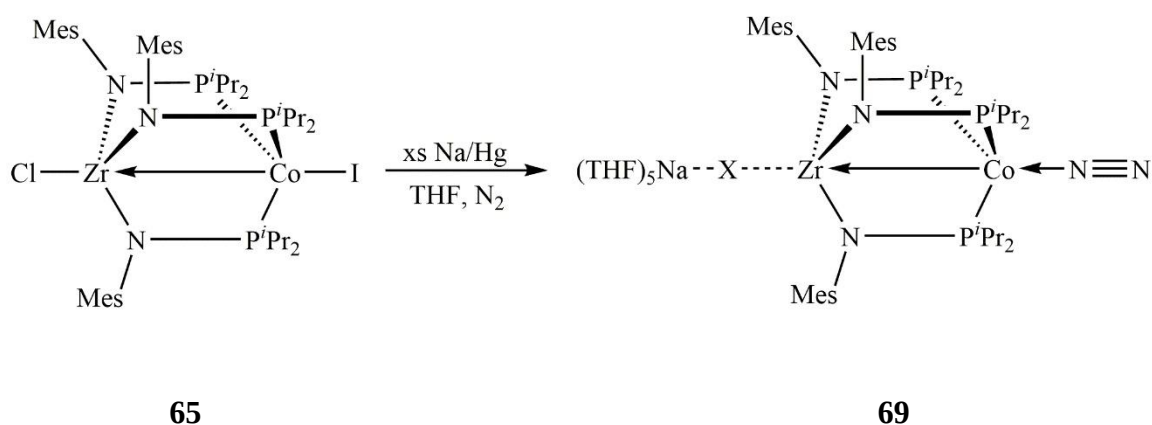


Scheme 8 - Synthesis of $[\text{ZrCl}(\text{}^i\text{PrNPPh}_2)_3\text{CoI}]$ (**64**) $[\text{ZrCl}(\text{MesNP}^i\text{Pr}_2)_3\text{CoI}]$ (**65**) and $[\text{ZrCl}(\text{}^i\text{PrNP}^i\text{Pr}_2)_3\text{CoI}]$ (**66**)

Single-crystal X-ray diffraction studies of **64-66** revealed Zr-Co bonds with interatomic distances of 2.7315(5) Å, 2.6280(5) Å and 2.6309(5) Å, respectively, which lie close to, or within the sum of the covalent radii for zirconium and cobalt (2.65 Å) and within the range of previously structurally characterised Zr-Co bonds.^{36,}

⁷⁰ The variation in interatomic distance was attributed to the electron donating

properties of the phosphine ligands; increased donation of electron density onto the cobalt was thought to give rise to a stronger cobalt-zirconium interaction accounting for a shortened bond distance. Treatment of CoI_2 with two equivalents of **59**, resulted in the formation of the cobalt(II) bis(phosphinoamine)diiodide complex $[\text{CoI}_2\{\text{}^i\text{PrN(H)PPh}_2\}_2]$ (**67**). The monoiodo Co^{I} analogue, $[\text{CoI}\{\text{}^i\text{PrN(H)PPh}_2\}_3]$ (**68**) could only be afforded in the presence of the reducing agent elemental zinc indicating that reduction of the Co^{II} to Co^{I} in the formation of the heterobimetallic complexes **64-66** only occurs in the presence of the bound zirconium centre. Cyclic voltammetry studies on complexes **64-66** indicated that all three compounds could undergo two electron reduction processes.

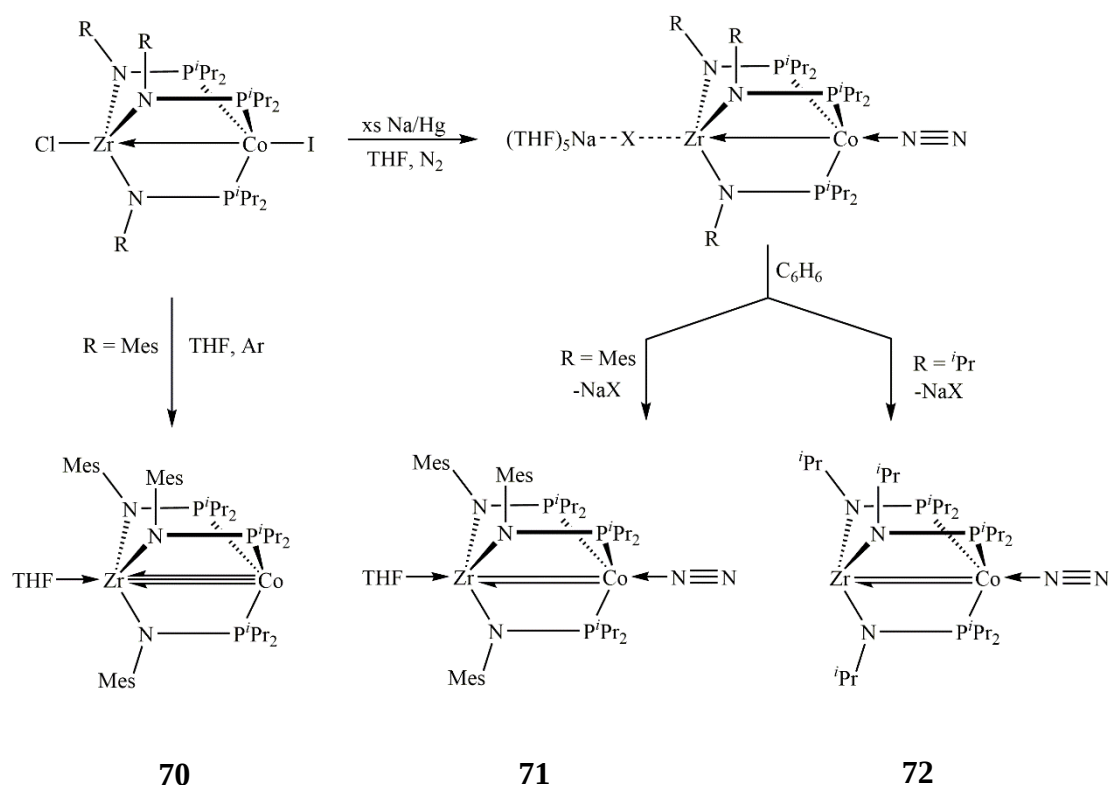


Scheme 9 - Synthesis of $[\text{Na}(\text{THF})_5(\mu\text{-X})\{\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\}\text{Co}(\eta^1\text{-N}_2)]$

(X = 73% I, 27% Cl) (**69**)

This was demonstrated experimentally by the chemical reduction of **65** with an excess of Na/Hg amalgam to form the product of a two electron reduction and dinitrogen coordination, $[\text{Na}(\text{THF})_5(\mu\text{-X})\{\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\}\text{Co}(\eta^1\text{-N}_2)]$ (X = 73% I, 27% Cl) (**69**) (**Scheme 9**). A single-crystal X-ray diffraction study performed on **69** showed that upon the two electron reduction there was a significant contraction of the Zr-Co bond distance from 2.6280(5) Å to 2.4112(3) Å compared to **65**. This was attributed to the increase in electron density upon reduction of the cobalt leading to a stronger donation from the cobalt centre to the zirconium centre. Both the relatively short N-N distance

of 1.1220(2) Å and relatively high ν_{N_2} stretching frequency of 2023 cm^{-1} suggested very little activation of the N_2 unit.⁷⁶ This was attributed to the involvement of the filled cobalt d-orbitals in the donation to the zirconium, disfavours backbonding into the N-N antibonding orbitals of the coordinated N_2 , and was supported by DFT calculations.



Scheme 10 - The synthesis of $[\text{Zr}(\text{THF})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}]$ (**70**), $[\text{Zr}(\text{THF})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\eta^1\text{-N}_2)]$ (**71**) and $[\text{Zr}(i\text{PrNP}^i\text{Pr}_2)_3\text{Co}(\eta^1\text{-N}_2)]$ (**72**)

The reduction of the Zr-Co complexes **65** and **66** was further investigated by Thomas.⁷⁷ Reduction of **65** with an excess of Na/Hg amalgam under an atmosphere of argon resulted in the formation of $[\text{Zr}(\text{THF})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}]$ (**70**) (**Scheme 10**), which features an unoccupied coordination site on the trigonal monopyramidal cobalt centre. The absence of an apical ligand at Co dramatically strengthened the bond between Co and Zr, shortening the bond length from 2.6280(5) in **65** to 2.14(1) Å in **70**. $[\text{Zr}(\text{THF})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\eta^1\text{-N}_2)]$ (**71**) and $[\text{Zr}(i\text{PrNP}^i\text{Pr}_2)_3\text{Co}(\eta^1\text{-N}_2)]$ (**72**) (**Scheme 10**) were afforded from the reduction of their corresponding Zr-Co complexes **65** and

66 with an excess of Na/Hg amalgam under an atmosphere of nitrogen followed by the precipitation of the labile NaX salt and, in the case of **71**, coordination of a THF molecule. The geometry about the Zr centre for **72** is trigonal monopyramidal, and is the first example of Zr adopting this type of coordination geometry. Examination of the highest occupied molecular orbitals of **71** and **72** revealed substantial Co-Zr bond character consisting of both σ - and π - interactions through overlap of the d_{z^2} (σ) and the d_{xz} and d_{yz} orbitals (π) of Co and Zr. This is in contrast to the CO-Zr bonding character of the dihalide precursor **65** which is predominately σ in nature. The Zr-Co distance in **72** is moderately shorter than that in **71** [2.33(1) Å and 2.36(1) Å respectively], this was attributed to a decrease in backbonding from the Co to the N₂ in **72** which was indicated by an increase in the ν_{N_2} by 30 cm⁻¹ with respect to **71**, with stronger involvement of the d_{xz} and d_{yz} orbitals in the Co-Zr bonding interaction in the absence of sigma donation from THF to Zr. The electronic structure of **70** revealed the clear formation of one σ and two π bonds between the metal centres and this increase in metal-metal multiple bonding character is reflected in the drastic contraction of the Co-Zr distance in **70** relative to **65**.

With this series of coordinatively unsaturated heterobimetallic Zr-Co complexes featuring metal-metal multiple bonds in hand Thomas then went on to thoroughly investigate their reactivity, the results of which are briefly described here. Treatment of **71** with one equivalent of I₂ resulted in a mixture of two products, [ZrI(MesNPⁱPr₂)₃CoI] (**73**) and [(MesNPⁱPr₂)Zr(μ -I)(MesNPⁱPr₂)₂CoI] (**74**) (**Fig.16**).⁷⁸ Despite its paramagnetism, **73** was easily identified by the similarity of its ¹H NMR spectrum to the related dihalide complex **65**. An X-ray diffraction study on single crystals of **74** revealed that one of the phosphinoamide ligands is dissociated from Co in the solid state and binds in an η^2 fashion to the zirconium centre to accommodate a bridging iodide ligand.

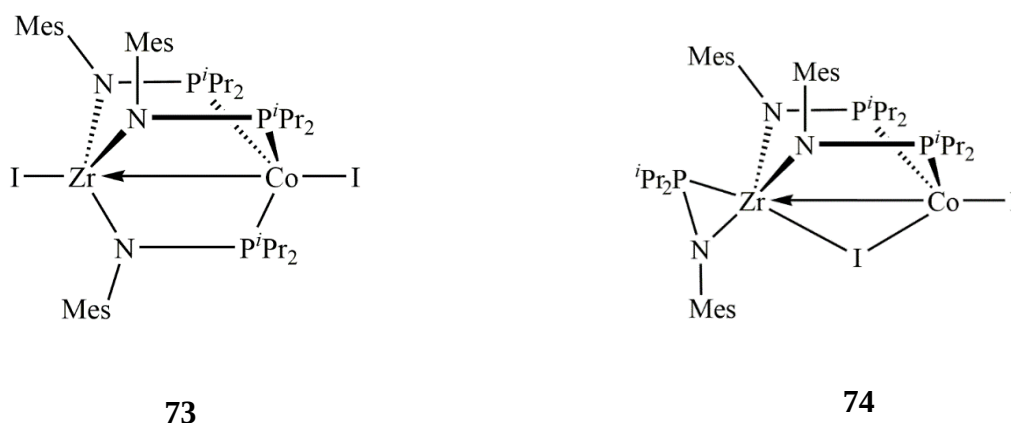


Fig. 16 - Structures of $[ZrI(MesNP^iPr_2)_3CoI]$ (**73**) and $[(MesNP^iPr_2)_2Zr(\mu-I)(MesNP^iPr_2)_2CoI]$ (**74**)

In contrast to its reactivity with I_2 , treatment of **71** with MeI exclusively generated the bridging methyl product $[(MesNP^iPr_2)_2Zr(\mu-CH_3)(MesNP^iPr_2)_2CoI]$ (**75**) (**Fig. 17**) in which the methyl group has oxidatively added across the Zr-Co bond and a phosphinoamide ligand has dissociated from Co.⁷⁸ The methyl group adopts a bridging mode *via* an agostic interaction. Anticipating a similar oxidative addition product Thomas treated **71** with one equivalent of 2-iodopropane. However, rather than the an iso-propyl bridged species, an intramolecular C-H activation product $[(\eta^3-P^iPr_2N\{C_6(CH_3)_2H_2(CH_2)\})Zr(MesNP^iPr_2)_2CoI]$ (**76**) (**Fig. 17**) was isolated. Complex **76** was also generated when **71** was treated with ethyl iodide, and a similar product, $[(\eta^3-P^iPr_2N\{C_6(CH_3)_2H_2(CH_2)\})Zr(MesNP^iPr_2)_2CoI]$ (**77**), was formed upon addition of cyclohexyl chloride to **71**.

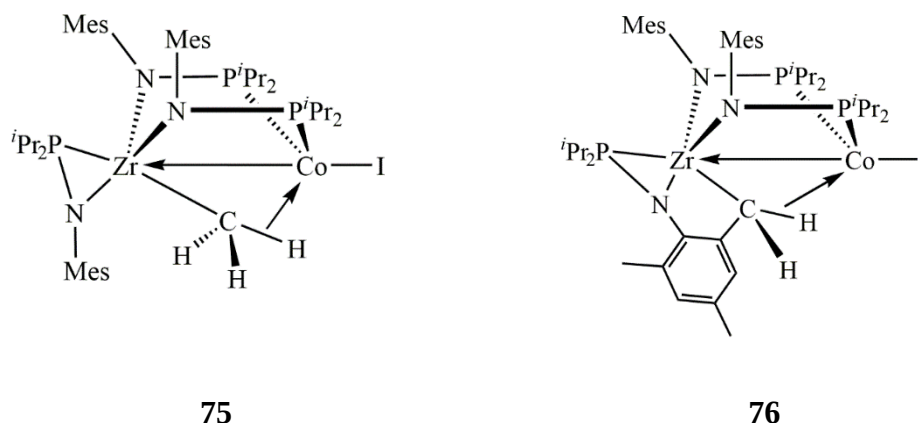
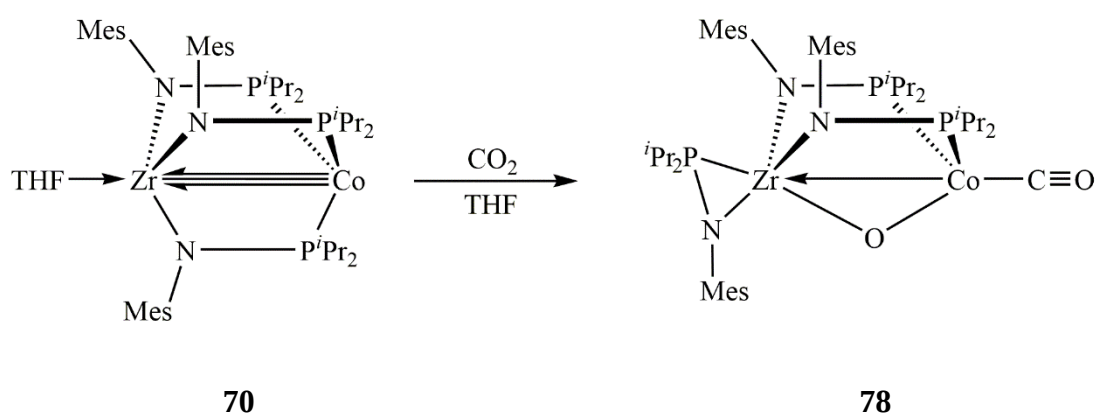


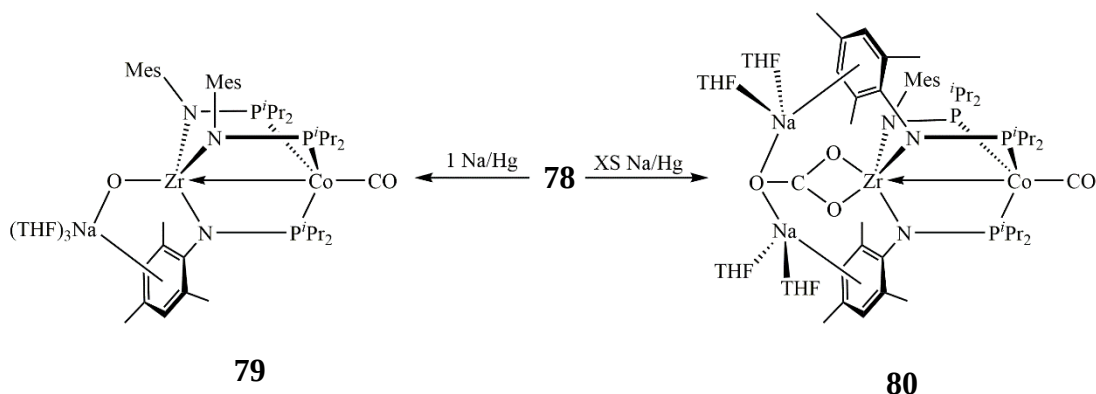
Fig. 17 - Structures of $[(MesNP^iPr_2)_2Zr(\mu-CH_3)(MesNP^iPr_2)_2CoI]$ (**75**) and $[(\eta^3-P^iPr_2N\{C_6(CH_3)_2H_2(CH_2)\})Zr(MesNP^iPr_2)_2CoI]$ (**76**)

The reactivity of the coordinatively unsaturated complex **70** towards CO₂ was investigated by Thomas. Exposure of **70** to exactly one equivalent of CO₂ resulted in oxidative insertion of the Co centre into one of the C=O bond and the formation of [(MesNP^{*i*}Pr₂)Zr(μ-O)(MesNP^{*i*}Pr₂)₂Co(CO)] (**78**) (**Scheme 11**). Complex **78** is a paramagnetic, *S* = 1, complex with a characteristic infrared ν_{CO} at 1926 cm⁻¹. A single crystal X-ray diffraction study revealed that one of the phosphinoamide ligands has decoordinated from Co and has bound to the Zr in an η² fashion to accommodate the bridging oxo ligand. Treatment of **70** with an excess of CO₂ lead to an intractable mixture of products. Cyclic voltammetric studies revealed a fully reversible reduction.



Scheme 11 - Synthesis of [(MesNP^{*i*}Pr₂)Zr(μ-O)(MesNP^{*i*}Pr₂)₂Co(CO)] (**78**)

The chemical reduction of **78** with one equivalent of a Na/Hg amalgam resulted in the formation of the unusual Zr-oxoanion [(THF)₃NaOZr(MesNP^{*i*}Pr₂)₃Co(CO)] (**79**) (**Scheme 12**). A single crystal X-ray diffraction study revealed a 3-fold arrangement of the ligand environment with the oxo ligand occupying an axial position on the Zr *trans* to the Co centre. The Zr-O distance of 2.074(4) Å is elongated by comparison to Parkin's terminal Z=O, [(η⁵-C₅Me₄R)₂Zr(O)(NC₅H₅)] (R = Me, Et) 1.804(4) Å,⁷⁹ and Stephan's Zr oxide anion, [{(Cp*)₂ZrH(OLi{THF})}]₂ 1.847(9) Å,^{79, 80} owing to the strong interaction of the O atom with Na⁺ in **79**. Reduction of **78** with an excess of Na/Hg amalgam resulted in a mixture of products including **79** and Zr-carbonate complex [(THF)₄Na₂(CO₃)Zr(MesNP^{*i*}Pr₂)₃Co(CO)] (**80**) (**Scheme 12**). **80** has a slightly lower ν_{CO} stretching frequency than **79**, (1884 cm⁻¹ and 1899 cm⁻¹), as a result of its more electron dense Co centre.



Scheme 12 - Synthesis of $[(\text{THF})_3\text{NaOZr}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**79**) and $[(\text{THF})_4\text{Na}_2(\text{CO}_3)\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**80**)

In addition to the reduction chemistry of **78**, the functionalisation of the $\mu\text{-O}$ was investigated. Complex **78** was treated with phenylsilane to afford $[\text{Zr}(\text{OSiH}_2\text{Ph})(^i\text{Pr}_2\text{PNMes})_3\text{CoH}(\text{CO})]$ (**81**) (**Fig.18**) which was also structurally characterised and revealed phenyl siloxane and cobalt hydride functionalities resulting from silation of the oxo group and hydride transfer to cobalt.

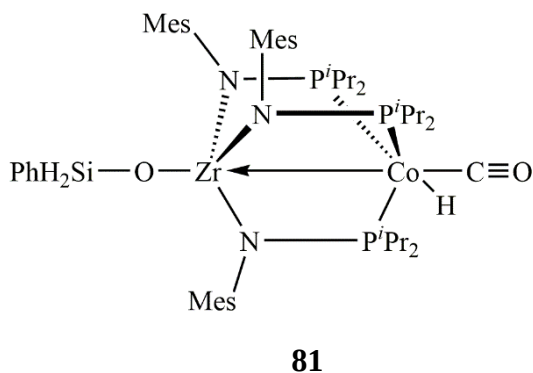
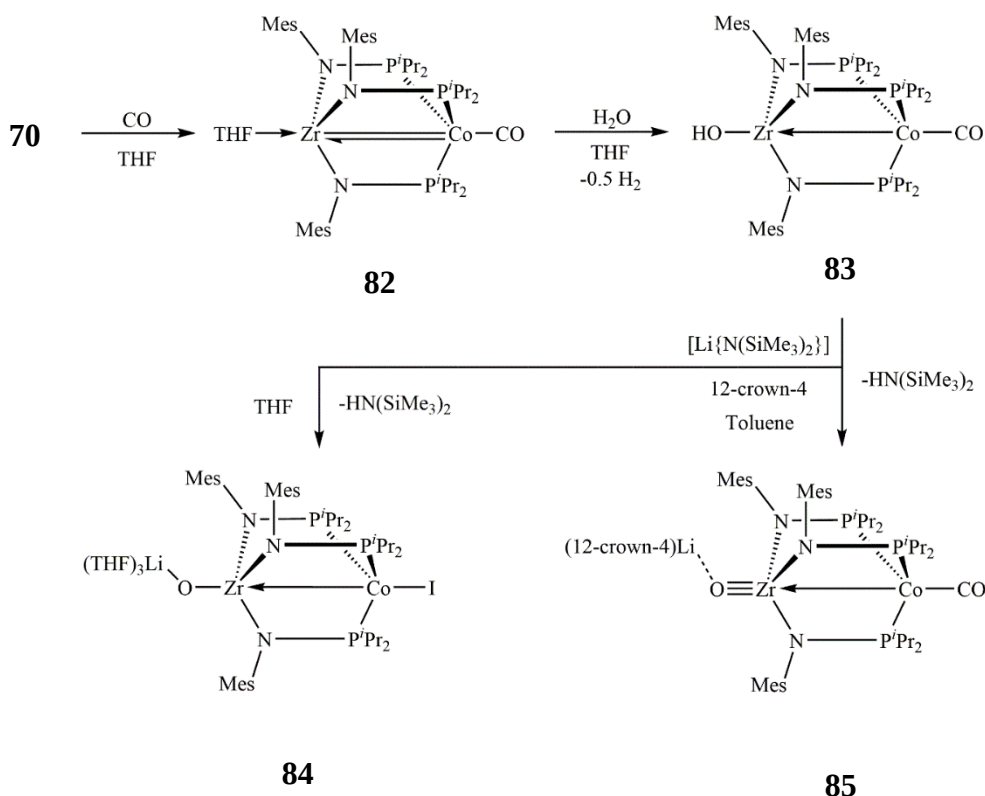


Fig. 18 - Structure of $[\text{Zr}(\text{OSiH}_2\text{Ph})(^i\text{Pr}_2\text{PNMes})_3\text{CoH}(\text{CO})]$ (**81**)

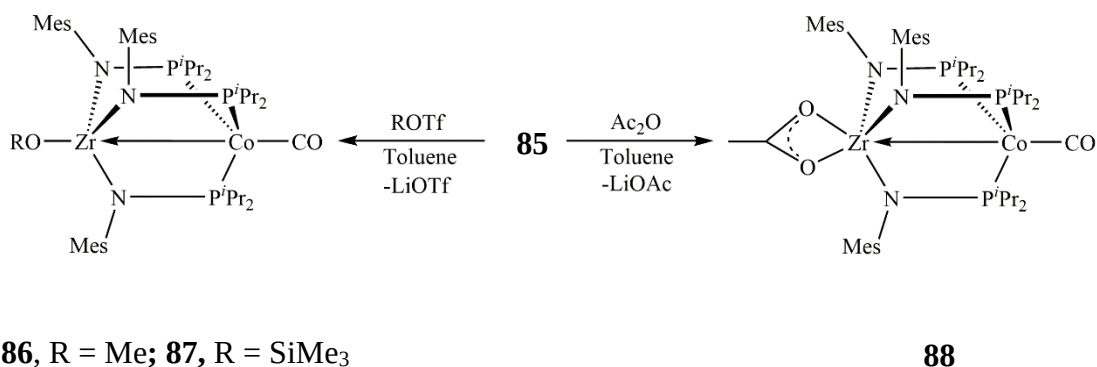
As a result of the very few structurally characterised Zr-oxoanions in the literature and the study of the reactivity of these species, coupled with the low yield of **79** (despite alternative reducing agents such as Mg^0 and $\text{Na}(\text{naphthalenide})$ not resulting in a cleaner, more selective reaction) an alternative high yielding synthetic route was devised to form the Zr-oxoanion (**Scheme 13**).⁸¹



Scheme 13 - Synthesis of $[\text{Zr}(\text{THF})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**82**), $[\text{Zr}(\text{OH})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**83**), $[\text{Li}(\text{THF})_3][\text{ZrO}(\text{MesNP}^i\text{Pr}_2)_3\text{CoI}(\text{CO})]$ (**84**) and $[\text{Li}(12\text{-crown-4})][\text{ZrO}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**85**)

Firstly **70** was treated with an excess of CO to form the diamagnetic complex $[\text{Zr}(\text{THF})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**82**) (**Scheme 13**). Addition of one equivalent of H₂O to **82** resulted in the immediate evolution of H₂ and a colour change from red to yellow. A single-crystal X-ray diffraction study identified the new compound as the Zr-hydroxide complex $[\text{Zr}(\text{OH})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**83**) (**Scheme 13**) whose ¹H NMR spectrum exhibits a singlet resonance at -41 ppm assigned to the hydroxide proton. To generate the desired anionic oxo species, **83** was treated with one equivalent of lithium hexamethyldisilazide, $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$, to form the new species $[\text{Li}(\text{THF})_3][\text{ZrO}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**84**) (**Scheme 13**). In an attempt to sequester the lithium cation, deprotonation of **83** with $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$ was performed in the presence of 12-crown-4 ether. This, however, resulted in the formation of $[\text{Li}(12\text{-crown-4})][\text{ZrO}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**85**) (**Scheme 13**). Single-crystal X-ray diffraction studies were performed on both **84** and **85** and revealed significant structural differences between the two anions.

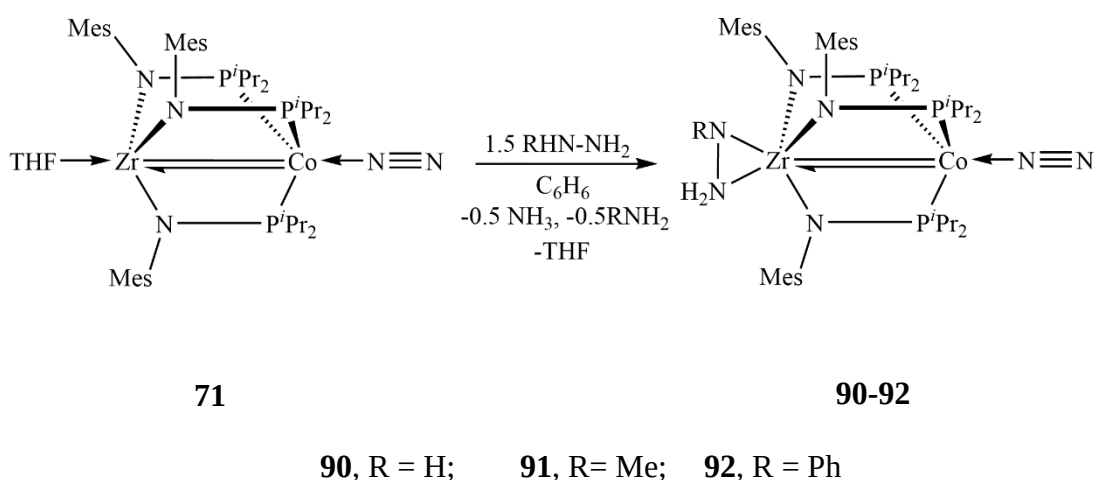
The Zr-O distance in **85** of 1.8328(11) Å is ~0.3 Å shorter than that in **84**, and the Zr-Co distance in **85** is elongated to 2.9236(3) Å compared to the Zr-Co distance of 2.5375(3) Å in **84**. These changes in structure and the local 3 fold symmetry at the zirconium centre allow for one σ and two π bonding interactions between the oxide and zirconium centres, with the assignment of a formal Zr-O bond order of three.



Scheme 14 - Synthesis of $[\text{Zr}(\text{MeO})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**86**),
 $[\text{Zr}(\text{Me}_3\text{SiO})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**87**) and $[\text{Zr}(\text{AcO})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**88**)

Reactivity studies were performed on **85** using the electrophiles MeOTf, Me₃SiOTf (Tf = F₃CSO₂) and acetic anhydride (**Scheme 14**).⁸¹ Reaction of **85** with MeOTf and Me₃SiOTf resulted in the formation of the corresponding methoxide $[\text{Zr}(\text{MeO})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**86**) and trimethylsiloxide $[\text{Zr}(\text{Me}_3\text{SiO})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**87**) complexes respectively. The reaction of **85** with acetic anhydride also proceeded *via* the electrophilic attack of the oxo anion to produce the complex $[\text{Zr}(\text{AcO})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**88**). Solid state structures of all three compounds **86-88** were determined by single crystal X-ray diffraction studies. Complex **85** was also shown to react with one equivalent of CO₂ to form the monoanionic Zr-carbonate $[\text{Li}(12\text{-crown-4})][\text{Zr}(\kappa^2\text{-CO}_3)(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})]$ (**89**). The binding of the CO₂ to **85** was shown to be reversible *via* a ¹³C isotope labelling study.

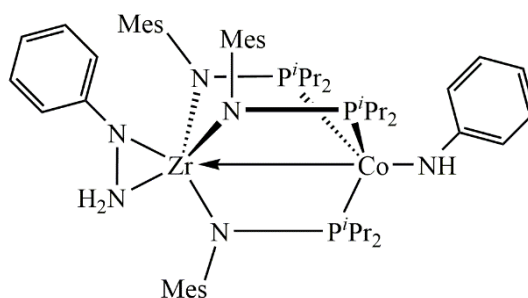
The activation of N-H bonds is an important step in catalytic C-N bond forming reactions.^{82, 83} Therefore in 2013 Thomas investigated the N-H bond chemistry of the heterobimetallic complex **71**.⁸⁴ Complex **71** was shown not to react with primary amines or anilines but readily reacted with hydrazines (**Scheme 15**). The complexes $[\text{Zr}(\text{RNHNH}_2)(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{N}_2)]$ [$\text{R} = \text{H}$ (**90**); $\text{R} = \text{Me}$ (**91**); $\text{R} = \text{Ph}$ (**92**)] were synthesised from the reaction of **71** with 1.5 equivalents of hydrazine, methylhydrazine and phenylhydrazine respectively.



Scheme 15 - Synthesis of $[\text{Zr}(\text{NH}_2\text{NH}_2)(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{N}_2)]$ (**90**),
 $[\text{Zr}(\text{MeNHNH}_2)(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{N}_2)]$ (**91**) and $[\text{Zr}(\text{PhNHNH}_2)(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{N}_2)]$ (**92**)

X-ray diffraction studies performed on single crystals of **90** and **92** revealed substitution of the zirconium-bound THF ligand with a η^2 diamine ligand. ^1H NMR spectroscopic analysis of the volatile components isolated from the reaction mixtures revealed the formation of ammonia and the corresponding amine RNH_2 as by-products; this was attributed to the reduction of the hydrazine by the proton extruded from the formation of **90-92**. This one electron oxidative process is in contrast with the two electron oxidative processes described previously. This one-electron transfer process is highly unusual for Zr, as is the activation of N-H bonds by an early transition metal fragment.⁸⁵⁻⁸⁸ The metal-metal bonding in complex **71** appears to promote σ -bond activation at Zr remotely, without effecting the immediate coordination sphere of Co or the C_3 -symmetric core of the bimetallic unit. When **71** was treated with an

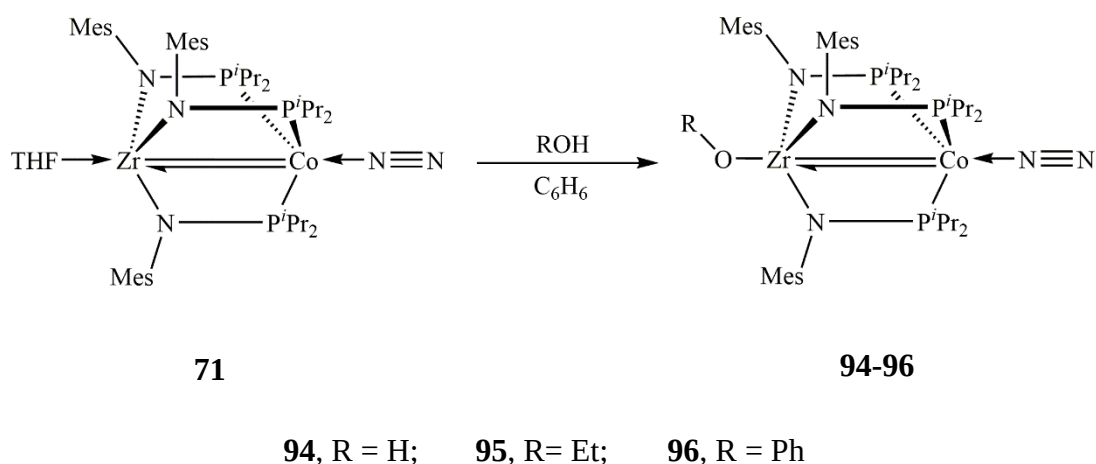
excess of PhNHNH₂ a new product arising from a two electron oxidation [Zr(PhNHNH₂)(MesNPⁱPr₂)₃Co(NHPh)] (**93**) (**Fig. 19**) formed and the solution magnetic measurements confirmed a S = 1 spin ground state consistent with a Zr^{IV}/Co^I product.



93

Fig. 19 - Structure of [Zr(PhNHNH₂)(MesNPⁱPr₂)₃Co(NHPh)] (**93**)

The reactivity of **71** with small molecules was further investigated by Thomas *via* the activation of O-H, S-H, S-S and O-O bonds.⁸⁹ Complex **71** was shown to readily react with stoichiometric quantities of H₂O, EtOH and PhOH to form [Zr(OR)(MesNPⁱPr₂)₃Co(N₂)] (R = H, **94**; Et, **95**; Ph **96**) (**Scheme 16**), respectively. Complexes **94-96** are the result of O-H bond cleavage with magnetic moments measured in solution indicative of S = ½ ground states, consistent with a one electron oxidation of the Zr/Co bimetallic unit. In the case of **94** its ¹H NMR spectrum features a dramatically shifted resonance for the Zr-OH unit consistent with the shift observed for the Zr-OH proton in complex **82**. Single crystal X-ray diffraction studies were performed for **94** and **96** to confirm their structure.



Scheme 16 - Synthesis of $[\text{Zr}(\text{OH})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{N}_2)]$ (**94**)

$[\text{Zr}(\text{OEt})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{N}_2)]$ (**95**) and $[\text{Zr}(\text{OPh})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{N}_2)]$ (**96**)

In contrast to the activation of O-H bonds, reaction with two equivalents of PhSH or one equivalent of PhSSPh resulted in the same product $[\text{Zr}(\text{MesNP}^i\text{Pr}_2)(\mu\text{-SPh})(\text{MesNP}^i\text{Pr}_2)_2\text{Co}(\text{SPh})]$ (**97**) (**Fig. 20**). The IR spectrum of **97** did not show any evidence for a cobalt-bound dinitrogen ligand and the ^1H NMR spectrum exhibited sixteen broad paramagnetically shifted resonances which indicated two inequivalent phosphanylamine ligand sets. The solution magnetic moment was indicative of an $S = 1$ spin state, consistent with a two electron oxidation of the Zr/Co bimetallic unit. Repeated attempts to structurally characterise **97** were unsuccessful so S-H bond activation was investigated using the analogous Zr/Co complex **72** which formed the complex $[\text{Zr}(^i\text{PrNP}^i\text{Pr}_2)(\mu\text{-SPh})(^i\text{PrNP}^i\text{Pr}_2)_2\text{Co}(\text{SPh})]$ (**98**).

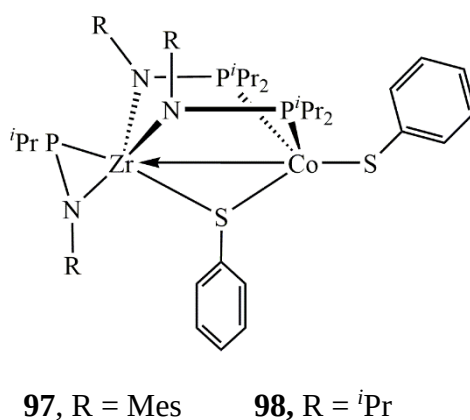


Fig. 20 - Structure of $[\text{Zr}(\text{MesNP}^i\text{Pr}_2)(\mu\text{-SPh})(\text{MesNP}^i\text{Pr}_2)_2\text{Co}(\text{SPh})]$ (**97**) and $[\text{Zr}(^i\text{PrNP}^i\text{Pr}_2)(\mu\text{-SPh})(^i\text{PrNP}^i\text{Pr}_2)_2\text{Co}(\text{SPh})]$ (**98**)

To investigate whether the reactivity of peroxides was comparable to that of the disulfides, **71** was treated with one equivalent of diethyl peroxide. Instead of the product of a two electron oxidation, analogous to **97**, the product of the O-O bond activation was the ethoxide complex **95**. However treatment of **71** with an excess of diethyl peroxide resulted in further reactivity and the complex $[\text{Zr}(\text{EtO})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{OEt})]$ (**99**) (**Fig. 21**) as a result of a two electron oxidation. A Single crystal X-ray diffraction study confirmed the identity of **99** and the solution magnetic measurements confirmed the $S = 1$ spin state consistent with a $\text{Zr}^{\text{IV}}/\text{Co}^{\text{I}}$ product. More sterically hindered peroxides such as dicumyl peroxide or di-*tert*-butyl peroxide did not react with **71** under ambient conditions, but upon photolysis di-*tert*-butyl peroxide did react to form $[\text{Zr}(^t\text{BuO})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{N}_2)]$ (**100**) (**Fig. 21**). This lack of reaction until the O-O bond is homolysed is indicative of an inner sphere dissociative electron-transfer pathway. A similar mechanism was thought to be operative in the case of the reactivity of **71** and **72** with thiophenol or diphenyl disulfide, however, in this case a second one electron process occurs in stepwise fashion leading to the two-electron oxidised products **97** and **98**.^{90, 91}

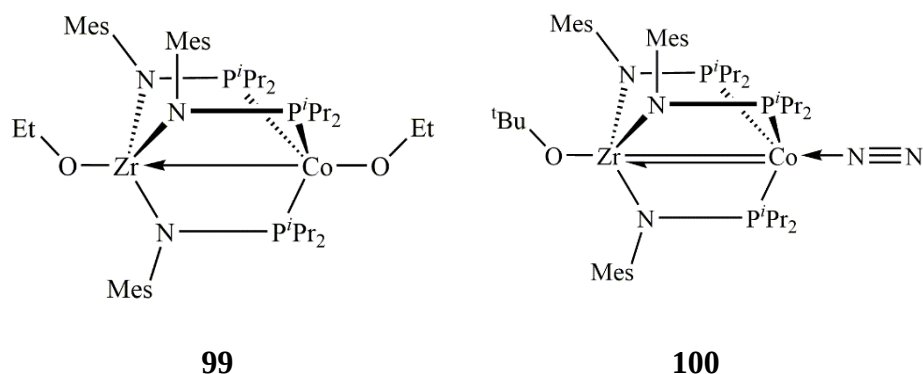
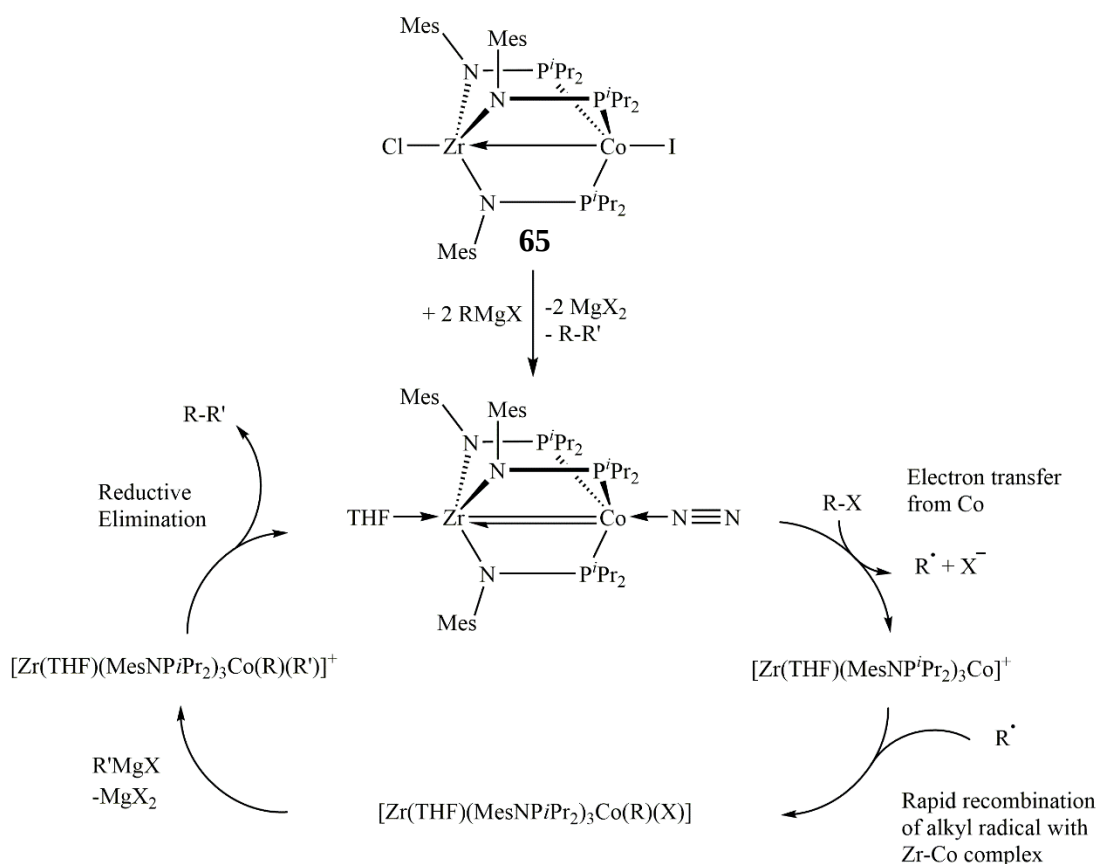


Fig. 21 - Structure of $[\text{Zr}(\text{EtO})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{OEt})]$ (**99**) and $[\text{Zr}(^t\text{BuO})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{N}_2)]$ (**100**)

Cross-coupling reactions to form carbon-carbon bonds are some of the most common catalytic processes in organic synthesis.⁹²⁻⁹⁶ Under appropriate reaction conditions, cobalt complexes can be utilised as catalysts for the formation of C-C bonds from organic halides and Grignard reagents; a reaction known as Kumada Corriu Tamao, or simply Kumada coupling.⁹⁷⁻¹⁰¹ In 2011 Thomas screened the heterobimetallic

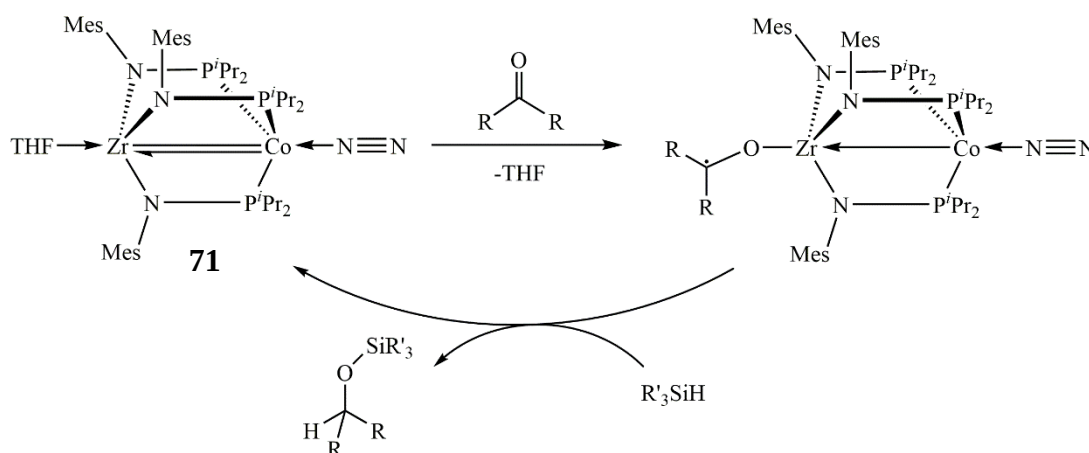
complexes **64-66** as catalysts for the Kumada coupling of alkyl halides with *n*-octyl magnesium bromide with % yields of 62.9, 81.9 and 83.3 respectively (**Scheme 17**). Optimisation of the reaction conditions suggested that catalytic performance was better in THF than in Et₂O and the optimal catalyst was 5 mol%. An addition of 30 mol% of TMEDA was necessary to obtain high yields of coupled products. Both primary and secondary substrates, including iodides, bromides and chlorides were investigated with all three heterobimetallic complexes with varying success (from 1.7% to 99.1% yield). Notably, the Ph₂P-substituted precatalyst **64** showed significantly diminished activity from that of the other precatalysts, this is likely a result of both the less electron rich nature of **64** as well as the difference in the nature and reactivity of the two electron-reduction products of **65** and **66**.⁷⁸



Scheme 17 - Kumada coupling of alkyl halides using $[\text{ZrCl}(\text{MesNP}^i\text{Pr}_2)_3\text{CoI}]$ (**65**)

These catalysts perform not only moderately better than the comparable monometallic cobalt complexes towards primary and secondary alkyl bromides, but, more importantly the Zr-Co heterobimetallic complexes increases the yield of coupling products with chlorides at room temperature compared to monometallic Co complexes, which in most cases are completely inactive towards these substrates.

Hydrosilylation is a fundamental organometallic transformation for the reduction of alkenes, carbonyl and imine functionalities.⁹² Whilst the most common ketone hydrosilylation catalysts feature noble metals,^{102, 103} as well as a variety of variety of first row metals,¹⁰⁴⁻¹⁰⁷ there were no reported zirconium-based hydrosilylation catalysts and limited cobalt-based carbonyl catalysts.¹⁰⁸⁻¹¹¹ In 2013 Thomas reported the catalytic hydrosilylation of ketones using complex **71** (**Scheme 18**).¹¹² In an initial test reaction it was found that acetophenone was cleanly hydrosilylated by PhSiH₃ in the presence of 5 mol% of **71** after six hours at room temperature to afford the corresponding alcohol after acidic workup. A wide range of alkyl and aryl ketones was screened to investigate the catalytic reaction all resulting in good to excellent yields over a time scale of six to twenty four hours over a temperature range, from room temperature to 65 °C. To determine the role of the Co and the Zr and the potential cooperative reactivity between these two metals, monometallic analogues of complex **71** were also screened as catalysts. The complex [ZrCl(MesNPⁱPr₂)₃] (**62**) did not show any hydrosilylation activity whereas the complex [CoI(MesNPⁱPr₂)₃] (**101**) did afford the hydrosilylation product, but in low yield (30%). These reactions imply that both the Zr and the Co are playing an important role in the catalytic hydrosilylation reaction.



Scheme 18 - Catalytic hydrosilylation of ketones using $[\text{Zr}(\text{THF})(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{N}_2)]$ (**71**)

In an attempt to gain some insight into the mechanism, stoichiometric reactions were attempted.¹¹³ It was initially proposed that the reaction proceeded via oxidative addition of the silane to the metal centres followed by insertion of the ketone into an M-Si or M-H bond. However, no reaction occurred when **71** was treated with one equivalent of PhSiH₃ at room temperature based on ¹H NMR spectroscopy. Reaction of **71** with benzophenone yielded the radical coupling product [$\{Co(N_2)(MesNP^iPr_2)_3Zr\}_2\{\mu-OCPh_2CH(C_2H_2)_2CC(Ph)O\}$] (**102**) (**Fig. 22**) implying the intermediacy of a Zr bound ketyl radical fragment. Therefore, a radical based hydrosilylation involving hydrogen atom transfer from PhSiH₃ to the Zr bound ketyl radical mechanism was proposed.

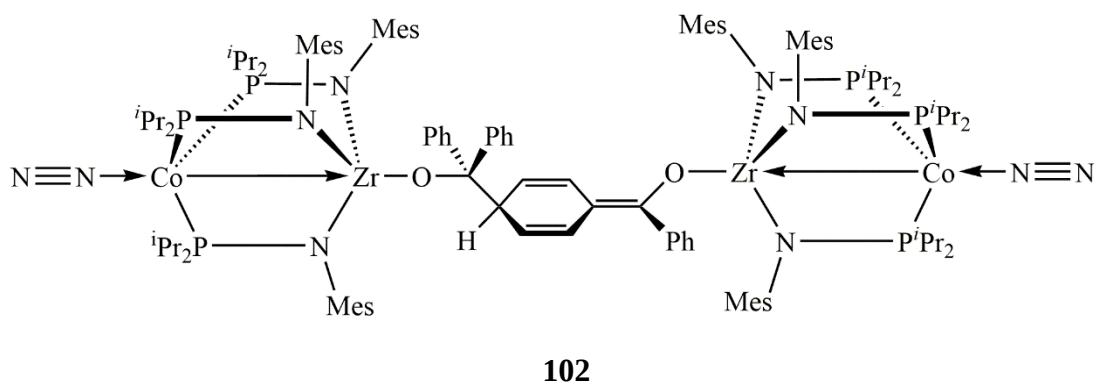


Fig. 22 - Structure of [$\{Co(N_2)(MesNP^iPr_2)_3Zr\}_2\{\mu-OCPh_2CH(C_2H_2)_2CC(Ph)O\}$] (**102**)

In an attempt to favour the monomeric ketyl radical species and probe for an equilibrium complex **102** was heated to 70 °C for 20 minutes in benzene. This resulted in the unexpected isolation of a rare terminal cobalt carbene complex [$Zr(\eta MesNP^iPr_2)(\mu-O)(MesNP^iPr_2)_2Co(CPh_2)$] (**103**) (**Fig. 23**) via an unusual reductive C=O bond cleavage.¹¹⁴⁻¹¹⁶ The complex [$Zr(Ph_2\{^iPr_2P\})(\mu-NMes)(MesNP^iPr_2)_2Co$] (**104**) was also identified as a by-product of this reaction. Fractional crystallisation was used to separate these two products and their respective structures verified by single crystal X-ray diffraction studies.

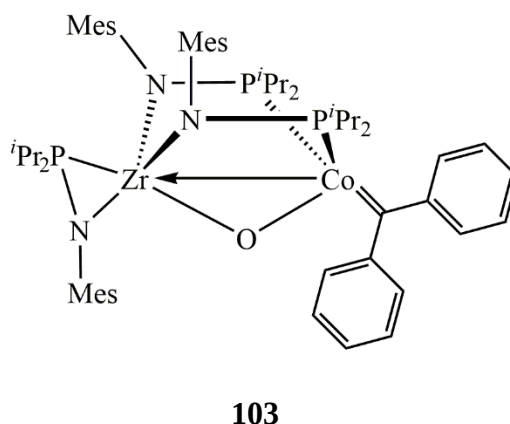
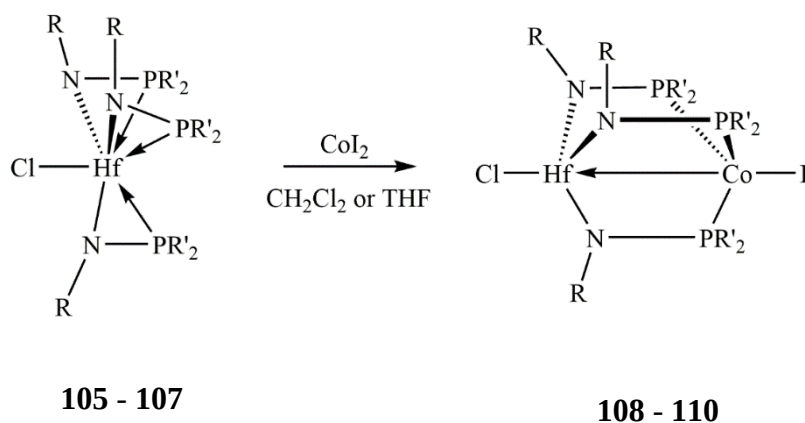


Fig. 23 - Structure of $[Zr(MesNP^iPr_2)(\mu-O)(MesNP^iPr_2)_2Co(CPh_2)]$ (**103**)

To allow for direct comparison with the Zr-Co complexes **63-65** the analogous Hf-Co complexes were prepared by Thomas.¹¹⁷ The tris(phosphinoamide)hafnium chloride metalloligands $[HfCl(^iPrNPPh_2)_3]$ (**105**) $[HfCl(MesNP^iPr_2)_3]$ (**106**) and $[HfCl(^iPrNP^iPr_2)_3]$ (**107**) were synthesised using the same procedure as reported previously for their Zr equivalents. The metalloligands **105-107** were then treated with one equivalent of CoI_2 to generate the corresponding Hf-Co heterobimetallic complexes $[HfCl(^iPrNPPh_2)_3CoI]$ (**108**) $[HfCl(MesNP^iPr_2)_3CoI]$ (**109**) and $[HfCl(^iPrNP^iPr_2)_3CoI]$ (**110**), respectively (**Scheme 19**).



105 and **108**, $R = ^iPr$, $R' = Ph$; **106** and **109**, $R = Mes$, $R' = ^iPr$;

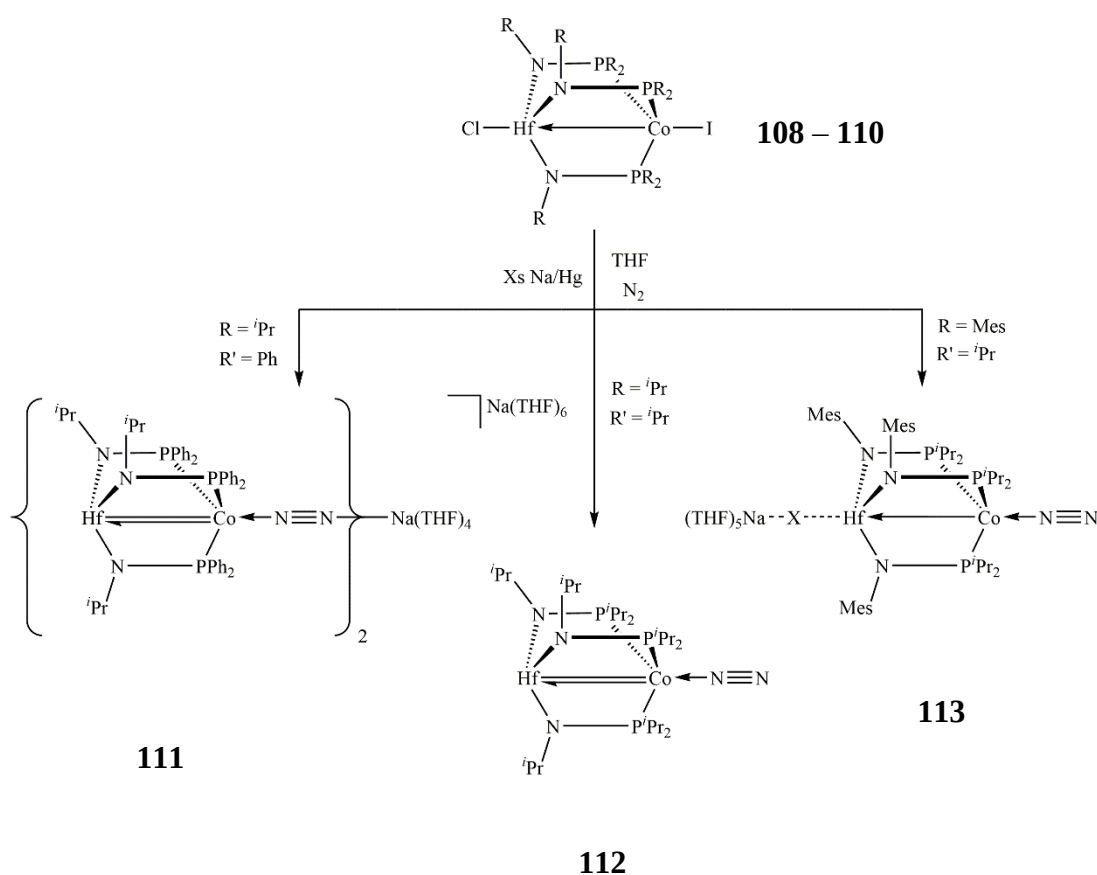
107 and **110**, $R = R' = ^iPr$

Scheme 19 - Synthesis of $[HfCl(^iPrNPPh_2)_3CoI]$ (**108**) $[HfCl(MesNP^iPr_2)_3CoI]$ (**109**) and $[HfCl(^iPrNP^iPr_2)_3CoI]$ (**110**)

Single crystal X-ray diffraction experiments performed on **108-110** revealed very little notable differences in structure upon comparison with **64-66** except for an increased metal-metal bond length of ~ 0.06 Å for **109** compared to **65**. The redox behaviour of **108-110** was examined by cyclic voltammetry and compared to **64-66**. The cyclic voltammogram of complex **108** is nearly identical to that of **64**, characterised by a reversible two-electron reduction at -1.66 V. Whilst the reductive features of complex **109** are shifted to slightly more negative potentials than the corresponding reduction events observed for **65**, the reductive processes in the CV of complex **110** are shifted to more positive potentials than those of **66**. The shift of the redox events of **109** to more negative potentials than those of its Zr analogue is consistent with the slightly longer M-Co distance and a weaker Co-Hf dative donation.

Complexes **108-110** were chemically reduced with an excess of Na/Hg amalgam to compare their reduction products with the analogous Zr complexes. Reduction of complex **108** led to a dinitrogen-bound salt $[(\text{THF})_4\text{Na}\{\text{N}_2\text{Co}(\text{}^i\text{PrNPPh}_2)_3\text{HfCl}\}_2][\text{Na}(\text{THF})_6]$ (**111**) (**Scheme 20**). A single crystal X-ray diffraction study confirmed that one THF-bound Na^+ cation associates with the lone pairs on the distal nitrogens of two symmetry related N_2 molecules, while a second THF-bound Na^+ cation remains in an outersphere location. The Hf-Co distance in **111** has contracted to 2.5470(3) Å from 2.7548(5) Å in **108**, implying a substantial increase in Hf-Co bond order. Whilst a solid state structure of the Zr-Co analogue could not be obtained, the similarity in spectroscopic features suggest an analogous structure for the Zr and Hf derivatives. Reduction of **110** with excess Na/Hg led to a diamagnetic N_2 -bound Hf-Co species $[\text{Hf}(\text{}^i\text{PrNP}^i\text{Pr}_2)_3\text{Co}(\eta^1\text{-N}_2)]$ (**112**) (**Scheme 20**) analogous to the corresponding Zr complex **72**. Although crystals of sufficient quality were not obtained for a diffraction study an absence of resonances corresponding to bound THF in the ^1H NMR spectrum implies an open coordination site at the Hf centre. In contrast to the reduction of **108** and **110**, the reduction of **109** resulted in substantial differences. Reduction of **109** with an excess of Na/Hg resulted in the monoanionic N_2 bound complex $[\text{Na}(\text{THF})_5(\mu\text{-X})\{\text{Hf}(\text{MesNP}^i\text{Pr}_2)_3\}\text{Co}(\eta^1\text{-N}_2)]$ ($\text{X} = 24\% \text{ I}, 76\% \text{ Cl}$) (**113**) (**Scheme 20**). However, while the Zr-Co analogue **69** undergoes rapid loss of NaX upon dissolution of benzene, the Hf-Co complex **113** is insoluble in benzene and entirely inert towards loss of NaX. While the differences in (N_2) stretching frequency for **111** and **112**, compared to their Zr analogues, are negligible,

the ν_{N_2} of complex **113** is $\sim 30\text{ cm}^{-1}$ lower in energy than that for **115**. The increase in π -backbonding from Co to N₂ in **112** suggests that less Co-derived electron density is involved in π -donation to Hf. This weaker metal-metal interaction is also consistent with the loss of lability of the NaX moiety as Co exerts less of a *trans* influence at Hf relative to Zr. Structural characterisation confirmed this with an elongated Hf-Co distance of 2.455(5), an increase of $\sim 0.04\text{ \AA}$ compared to the Zr-Co bond length of 77.



Scheme 20 - Synthesis of $[(\text{THF})_4\text{Na}\{\text{N}_2\text{Co}(\text{iPrNPPh}_2)_3\text{HfCl}\}_2][\text{Na}(\text{THF})^6]$ (**111**), $[\text{Hf}(\text{iPrNP}^i\text{Pr}_2)_3\text{Co}(\eta^1\text{-N}_2)]$ (**112**) and $[\text{Na}(\text{THF})_5(\mu\text{-X})\{\text{Hf}(\text{MesNP}^i\text{Pr}_2)_3\}\text{Co}(\eta^1\text{-N}_2)]$ ($X = 24\% \text{ I}, 76\% \text{ Cl}$) (**113**)

The reactivity of **113** towards oxidative addition was examined *via* treatment with MeI. Unlike the bridging methyl species **75** which is formed when the Zr analogue is treated with MeI, reaction of **113** with MeI results in the one electron oxidised product $[\text{HfCl}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\eta^1\text{-N}_2)]$ (**114**) (**Scheme 21**). Although complex **114** was

1.3 Small Molecule Activation

If nuclear energy is to contribute significantly towards ‘low-carbon’ energy production then there needs to be a greater understanding of the fundamental chemistry of uranium. During the nuclear energy cycle uranium will interact with numerous other elements and understanding the chemistry of uranium and its compounds is critically important in the development of a more efficient and environmentally cleaner nuclear industry. In recent years the field of uranium-mediated small molecule activation has flourished as a result, with the new and often unexpected reactivity of uranium compounds towards small molecules helping to develop our knowledge of the chemistry accessible to uranium.¹¹⁸⁻¹²²

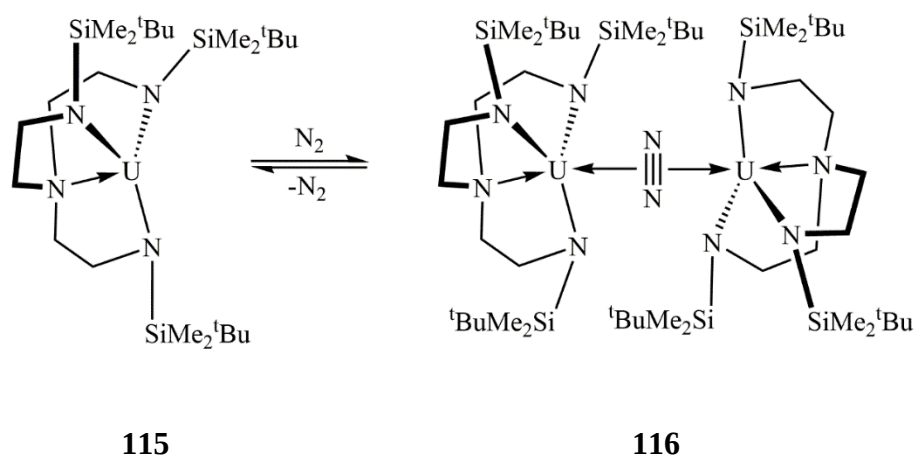
The classical reactivity, oxidative addition and reductive elimination, that is normally associated with the organometallic chemistry of the transition metals is far less common for uranium. Due to the highly polarising character of the actinide centre and the bonding nature of the 5f orbitals the typical reactivity observed for organometallic uranium compounds is that of migratory insertion, σ -bond metathesis and redox activity. It is this reactivity that is responsible for the often unpredictable chemistry of uranium towards small molecules.¹²³ Although the field of small molecule activation is still a burgeoning research area selected literature highlights concerning the activation of dinitrogen (N_2), carbon monoxide (CO) and carbon dioxide (CO_2) by uranium complexes will be featured.

Activation of N_2 by Uranium Complexes

In spite of the very strong N-N bond in dinitrogen ($945.33 \pm 0.59 \text{ kJ mol}^{-1}$)¹²⁴ it remains the primary source of nitrogen in both industrial and biological contexts with the reduction of N_2 in the presence of hydrogen using heterogeneous Transition Metal catalysts in the Haber-Bosch process are responsible for the production of over one hundred million tons of ammonia per year.¹²⁵ Dinitrogen is a weak σ -donor/ π -acceptor and binds to metal centres in a number of modes: terminal or bridging and end-on or side-on. For lanthanide complexes, $M \rightarrow L$ π -donation would not be expected due to

the highly contracted nature of the Ln 4f orbitals preventing any significant orbital overlap. Despite this, for uranium the increased 5f orbital extension could lead to increased covalent bonding character in this context.¹²⁶

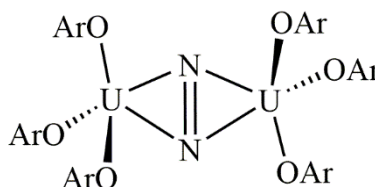
Whilst the coordination, reduction and cleavage of dinitrogen for transition metal systems^{76, 127, 128} and now even the lanthanides¹²⁹ are well established, examples of such behaviour for uranium are uncommon, and exist only for uranium(III).¹²² The first example of dinitrogen complexed to an actinide element was published in 1998 when Scott reported a dinitrogen-bridged diuranium complex.¹³⁰ Exposure of a saturated pentane solution of $[\text{U}(\text{Tren}^{\text{DMBS}})]$ [$\text{Tren}^{\text{DMBS}} = \{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2^t\text{Bu})_3\}^{3-}$] (**115**) to one atmosphere of dinitrogen resulted in the side-on bound uranium dinitrogen complex $[\{\text{U}(\text{Tren}^{\text{DMBS}})\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$ (**116**) (**Scheme 22**)



Scheme 22 - Synthesis of $[\{\text{U}(\text{Tren}^{\text{DMBS}})\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$ (**116**)

Initial analysis by Scott of **116** suggested that the coordination of dinitrogen to **115** did not result in an increase in the formal oxidation state of the uranium centres and the reported N-N bond length of 1.109(7) Å in **116** that is essentially the same as the N-N bond length in free N₂ (1.0975 Å),¹²⁷ was suggestive of the dinitrogen ligand in **116** being weakly bound and unreduced. However, more recent work by Arnold resulted in the robust dinitrogen bound uranium tris(aryloxide) complexes $[\{\text{U}(\text{OAr})_3\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$ (Ar = 2,6-^tBu₂-C₆H₃, **117**; Ar = 2,4,6-^tBu₃-C₆H₂, **118**) (**Fig. 24**). All the experimental and computational evidence collected for **117** and **118**

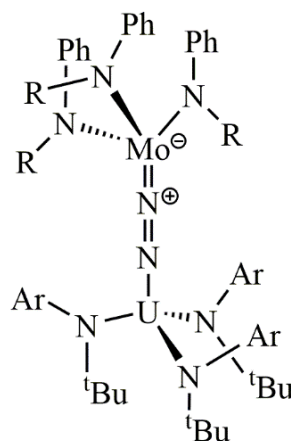
indicated a formal oxidation oxidation of the uranium centers to U^{IV} with concomitant reduction of the dinitrogen ligand to N_2^{2-} . The average N-N bond length of 1.189 Å in **117** and the N-N bond lengths of 1.190(18) Å (crystallised from n-hexane) and 1.236(5) Å (crystallised from toluene) in **118** are consistent with a large degree of reduction from free N_2 (1.0975 Å) to diazenido N_2^{2-} .¹²⁷ Raman spectroscopy of **118** showed a strong band at 1451 cm^{-1} which corresponded well to the calculated theoretical value of 1486 cm^{-1} compared to the value for free N_2 (2454 cm^{-1}). DFT calculations on the model complex $[\{U(OAr)_3\}_2(\mu-\eta^2:\eta^2-N_2)]$ also revealed a degree of π -backbonding which is in contrast to the essentially σ -bonding system first proposed by Scott in **116**.



117, Ar = 2,6- t Bu₂-C₆H₃ **118**, Ar = 2,4,6- t Bu₃-C₆H₂

Fig. 24 - Structure of $[\{U(OAr)_3\}_2(\mu-\eta^2:\eta^2-N_2)]$ (Ar = 2,6- t Bu₂-C₆H₃, **117**; 2,4,6- t Bu₃-C₆H₂, **118**)

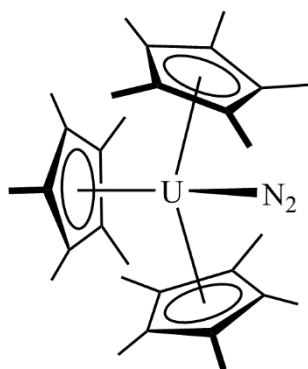
The first uranium heterodinuclear complexes to exhibit an end-on bound dinitrogen ligand was reported by Cummins in 1998.¹³¹ The heteroleptic U^{III} *tris*(amide) complex $[U\{N(tBu)Ar\}_3(THF)]$ (Ar = 3,5-Me₂-C₆H₃) was treated with the Mo(III) *tris*(amide) complexes $[Mo\{N(R)Ph\}_3]$ (R = t Bu; 1-adamantyl or Ad,) affording $[U\{Ar(tBu)N\}_3(\mu-\eta^1:\eta^1-N_2)Mo\{N(R)Ph\}_3]$, (R = t Bu, **119**; Ad, **120**) (**Fig. 25**). A single crystal X-ray diffraction study of **119** revealed an N-N distance of 1.232(11) Å, 0.13 Å longer than that of free nitrogen and mean U-N_{amide} distances (av. 2.257 Å) that are characteristic of U^{IV} amides; which together is suggestive for the reduction of N_2 . The formal oxidation state of +4 was assigned for both metal centres, with molybdenum acting as the more effective π -donor to the complexed bridging diazenide ligand.



119, R = ^tBu **120**, R = Ad

Fig. 25 - Structure of $[U\{Ar(^tBu)N\}_3(\mu-\eta^1:\eta^1-N_2)Mo\{N(R)Ph\}_3]$, (R = ^tBu, **119**; Ad, **120**)

The complex $[U(Cp^*)_3(\eta^1-N_2)]$ (**121**) (**Fig. 26**) was reported by Evans from the treatment of $[U(Cp^*)_3]$ with N_2 .¹³² Compound **121** exhibits a remarkable η^1 -coordinated dinitrogen ligand and was the first example of a monometallic f-element complex of N_2 . However, a pressure of eighty psi (psi = pounds per square inch) of N_2 was required to stabilise the complex and lowering of the pressure to one psi for a solution of **121** resulted in the release of N_2 and the regeneration of the starting material $[U(Cp^*)_3]$. The dinitrogen binding to uranium in **121** was therefore determined to be reversible and the weakness of this association was emphasised by an X-ray diffraction study showing virtually no change in the $[U(Cp^*)_3]$ fragment upon complexation of dinitrogen. Furthermore, an N–N bond distance in **121** of 1.120(14) Å is indistinguishable from that in free N_2 (1.0975 Å).¹²⁷



121

Fig. 26 - Structure of $[U(Cp^*)_3(\eta^1-N_2)]$ (**121**)

Activation of CO by Uranium Complexes

Despite possessing the strongest bond between two elements in the Periodic Table with a bond enthalpy of $1076.5 \pm 0.4 \text{ kJ mol}^{-1}$,¹²⁴ carbon monoxide remains a key C_1 feedstock for conversion into alkanes and alkenes in the Fischer-Tropsch process. Like the Haber process, the reduction of CO in the presence of H_2 is extremely energy intensive and catalysed by heterogeneous cobalt or iron catalysts with milder alternatives extremely desirable but yet to be developed. Transition Metals are known to bind CO in a twofold synergic fashion. Formally this interaction is characterised by the transfer of electron density from filled CO orbitals of σ symmetry into vacant metal orbitals with a second bonding interaction of π symmetry involving donation of electron density from filled or partially filled metal-based orbitals into the vacant CO π^* orbitals. This second interaction is the origin of the stability of transition metal carbonyl complexes with this bonding very well established for the d-block elements with thousands of reported examples.

In 1986, Andersen reported CO binding reversibly to $[U(Cp')_3]$ ($Cp' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$) forming the proposed CO adduct “ $[U(Cp')_3(CO)]$ ” (**122**). Although no structure was crystallographically determined it was observed that green solutions of $[U(Cp')_3]$ turned dark red on exposure to one atmosphere of ^{12}CO , ^{13}CO or C^{18}O with volumetric

studies revealing approximately one equivalent of CO gas was absorbed by the metallocene solution whilst experimental infrared spectra matched well to theoretical data.¹³³ Carmona and Andersen then proceeded to isolate and crystallographically characterise the carbonyl complex $[U(C_5Me_4H)_3(CO)]$ (**123**) (**Fig. 26**) from the reaction of $[U(C_5Me_4H)_3]$ and CO.^{134, 135} The purple-black crystals were grown under an atmosphere of CO to avoid the dissociation of the CO ligand. Compound **123** exhibits a near-linear U–C–O unit with a relatively short U–C(O) bond distance of 2.383(6) Å, suggesting a significant U–CO interaction, although the C–O bond length of 1.142(7) Å is very close to that of free CO (1.128 Å). More recently, Evans reported the carbonyl complex $[U(Cp^*)_3(CO)]$ (**124**) (**Fig. 27**) via an analogous synthetic strategy to Carmona and Andersen. The solid state structure revealed a linear U–C–O unit with a U–C(O) bond distance of 2.485(9) Å that is much longer than that in **123** as a result of the increased steric demand of the Cp* ligands and a C–O bond length of 1.13(1) Å, indistinguishable from that in both **123** and free CO. **124** exhibits a ν_{CO} band at 1922 cm⁻¹, which is lower than in **122** (1976 cm⁻¹) and is consistent with the greater electron-donating ability of the Cp* ligand relative to Cp'. However the ν_{CO} for **124** is *ca.* 40 cm⁻¹ higher in energy than that in complex **123**, which was attributed to the abnormally long U–C(O) bond in complex **124** at the time and supported later by *ab initio* calculations.^{136, 137}

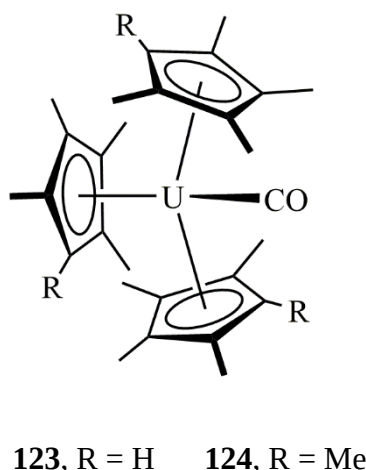
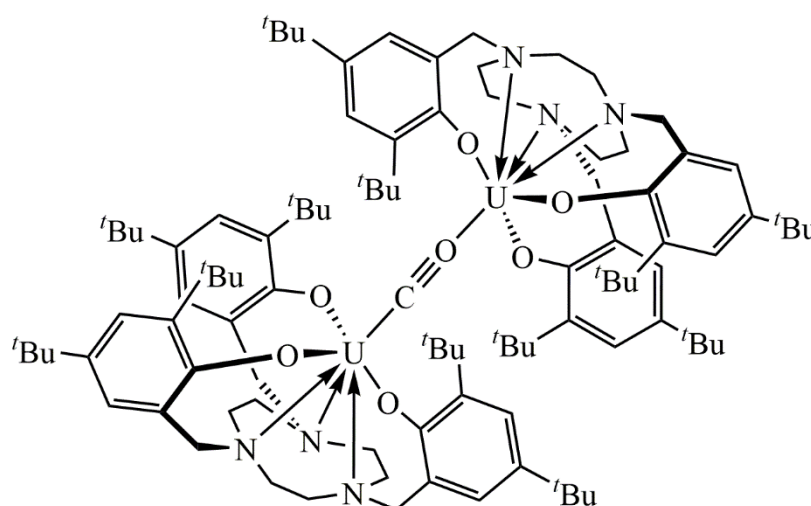


Fig. 27 - Structure of $[U(C_5Me_4H)_3(CO)]$ (**123**) and $[U(Cp^*)_3(CO)]$ (**124**)

In 2005 Meyer reported the first example of a single molecule of CO being reductively activated by two U^{III} complexes. The sterically demanding U^{III} complex $[U\{(tBuArO)_3tacn\}]$ [$(tBuArO)_3tacn = \{C_6H_{12}N_3(CH_2C_6H_2-3,5-tBu_2-6-O)_3\}^{3-}$] reacted with CO forming the dinuclear bridged-CO complex $[(U\{(tBuArO)_3tacn\})_2(\mu-\eta^1:\eta^1-CO)]$ (**125**) (**Fig. 28**). It can be seen that the CO is formally singly reduced, manifesting as both a carbonyl and isocarbonyl in the product. Complex **125** exhibits a relatively high energy ν_{CO} band at 2092 cm^{-1} , suggestive of coordinated CO, however the CO bridging unit is centred on a crystallographic inversion centre and is fully disordered, precluding a meaningful discussion of the bond distances in the U–CO–U fragment.



125

Fig. 28 - Structure of $[(U\{(tBuArO)_3tacn\})_2(\mu-\eta^1:\eta^1-CO)]$ (**125**)

Although there are numerous examples of d-block and lanthanide complexes which are known to coordinate and reductively couple carbon monoxide, only a select few uranium complexes have demonstrated controlled C-C coupling of two metal coordinated CO ligands. The first example was reported by Cloke by the trivalent uranium complex $[U(Cp^*)(COT'')]$ [$COT'' = \{\eta^8-1,4-(Si^iPr_3)_2-C_8H_6\}$] (**126**). Reaction of **126** with one equivalent of CO resulted in a colour change from dark purple to dark red with a single crystal X-ray diffraction study revealing the resulting complex to be $[\{U(Cp^*)(COT'')\}_2(\mu-\eta^1:\eta^2-C_3O_3)]$, (**127**) (**Fig. 29**), featuring a reductively homologated, CO trimer coordinated between two formal uranium(IV) centres.

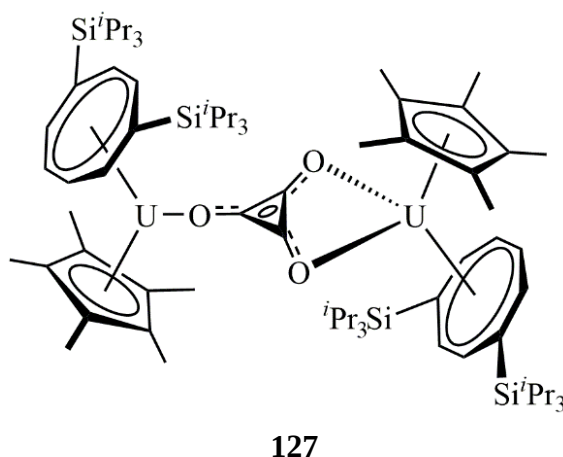


Fig. 29 - Structure of $[\{U(Cp^*)(COT'')\}_2(\mu-\eta^1:\eta^2-C_3O_3)]$, (**127**)

The formation of the D_{3h} symmetric cyclo- $(C_3O_3)^{2-}$ dianion from CO alone was unprecedented. The planar deltate unit in **127** is bound unsymmetrically in an $\eta^1:\eta^2$ mode and noticeably distorted with two short C–C bonds [av. 1.379(6) Å] and one longer C–C bond [1.436(7) Å]. **126** was also found to be capable of reductively coupling exactly 0.9 equivalents of CO per U centre to afford the dinuclear U^{IV} compound $[\{U(Cp^*)(COT'')\}_2(\mu-\eta^1:\eta^1-C_2O_2)]$, (**128**). Although structural authentication was not possible, **126** reacts with the same quantity of ^{13}CO to yield the isotopically labelled analogue of **128**, $[\{U(Cp^*)(COT'')\}_2(\mu-\eta^1:\eta^1-^{13}C_2O_2)]$ (**129**) (**Fig. 30**). The linear diuranium ethynediolate was the first of its kind to be structurally characterised with a C–C bond distance of 1.177(12) Å, confirming the presence of a C–C triple bond.^{138, 139}

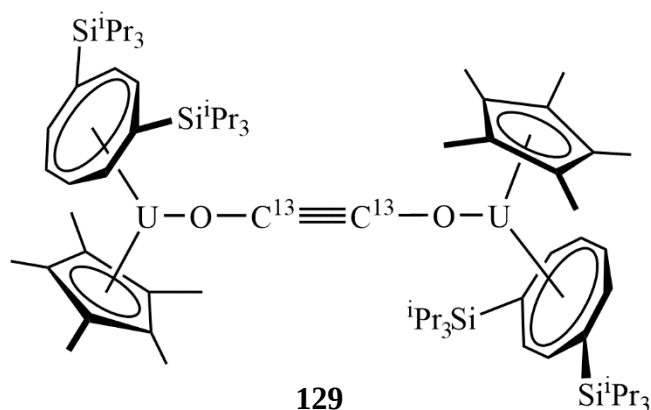
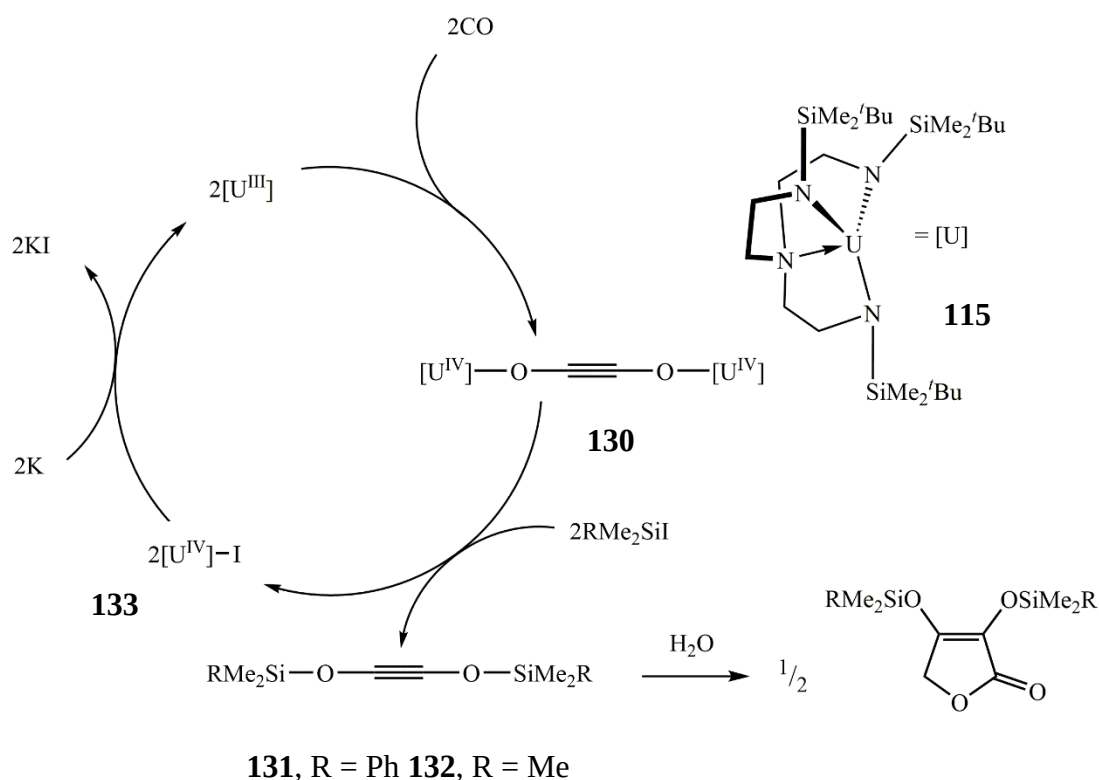


Fig. 30 - Structure of $[\{U(Cp^*)(COT'')\}_2(\mu-\eta^1:\eta^1-^{13}C_2O_2)]$ (**129**)

In 2012 Liddle demonstrated that the trivalent uranium complex $[\text{U}(\text{Tren}^{\text{DMBS}})]$ (**115**) could selectively achieve the reductive homologation of two molecules of CO at ambient temperatures and pressures to result in the dinuclear uranium(IV)-ethynediolate complex $[\{\text{U}(\text{Tren}^{\text{DMBS}})\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-OCCO})]$ (**130**) (**Scheme 23**).¹⁴⁰ Reaction of **130** with the organosilyl iodides Me_3SiI and PhMe_2SiI resulted in the liberation of the functionalised acetylenes $\text{RMe}_2\text{SiOCCOSiMe}_2\text{R}$ ($\text{R} = \text{Ph}$, **131**; Me , **132**) along with the direct precursor to **115**, $[\text{UI}(\text{Tren}^{\text{DMBS}})]$ (**133**).¹⁴¹ Treatment of **133** with the reducing agents potassium successfully closed the synthetic cycle via the regeneration of **115**.¹⁴² A DFT study suggested that the sterically demanding nature of **115** may contribute to this unusually straightforward liberation chemistry. The C_2 -bis(ether)acetylenes that were produced underwent facile conversion to C_4 -furanones both of which are precursors to diols and furans that are produced industrially on mega-tonne scales.¹⁴³



Scheme 23 - Synthetic cycle for the reductive homologation and functionalisation of CO

Activation of CO₂ by Uranium Complexes

Like carbon monoxide, carbon dioxide has received the attention of coordination chemists for many years. As one of the major greenhouse gases and as a potentially inexpensive C₁ feedstock material, the controlled chemical activation and subsequent functionalisation of CO₂ is a highly desirable target. Despite being highly sought after, the strong C=O bonds in CO₂ generally require a highly reactive metal centre in order to overcome its thermodynamic and kinetic stability.¹⁴⁴⁻¹⁴⁷ Despite the formation of carbonate complexes of transition metals and lanthanum¹⁴⁸⁻¹⁵⁰ and the adsorption of CO₂ onto metal surfaces¹⁵¹ the activation of carbon dioxide by the f-elements has not been well documented and remains a relatively unexplored area.^{152, 153}

The trivalent uranium complex [U{(AdArO)₃tacn}] (**134**) [(AdArO)₃tacn = {C₆H₁₂N₃(CH₂C₆H₂-3-*t*Bu-5-Ad-6-O)₃}³⁻] was shown, by Meyer, to react with CO₂ to afford [U{(AdArO)₃tacn}(η¹-OCO)] (**135**) (**Fig. 31**). **135** exhibited an unprecedented end-on bound CO₂ unit with the [U]O–C bond length of 1.122(4) Å within the reported range of C=O double bonds, whilst the terminal (O)C–O distance can be considered activated with a length of 1.277(4) Å. The structural and spectroscopic evidence strongly supported a molecular structure featuring a charge-separated CO₂^{•-} radical anion, U^{IV}–(OCO^{•-}). Such an electronic structure would result from a metal-centred one electron oxidation upon CO₂ coordination. In contrast, treatment of the sterically less demanding [U(^tBuArO)₃tacn] (**136**) with CO₂ resulted in the complete, two electron, reduction of CO₂ and the formation of the μ-oxo bridged dimer [{U(^tBuArO)₃tacn}₂(μ-O)] (**137**).^{154, 155}

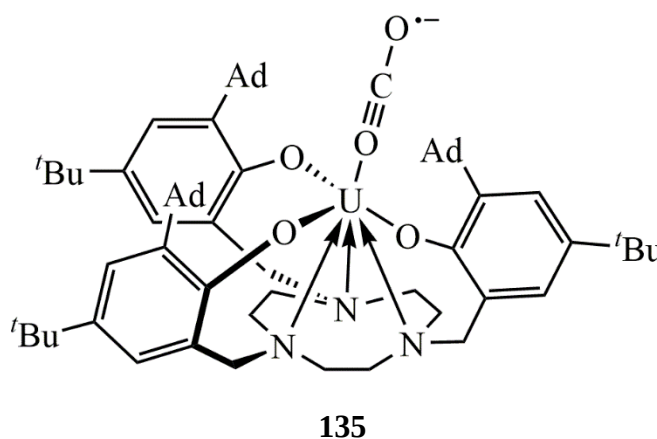


Fig. 31- Structure of [U{(AdArO)₃tacn}(η¹-OCO)] (**135**)

Cloke had previously demonstrated the reactivity of the mixed-sandwich uranium(III) complexes $[U(\eta^5\text{-C}_5\text{Me}_4\text{R})(\text{COT}'')(\text{THF})]$ ($\text{R} = \text{Me}$, **138**; H , **139**) towards CO , and subsequently investigated the reactivity of these complexes with CO_2 . Upon exposure of **138** and **139** to CO_2 , the dinuclear bridging carbonate species $[\{U(\eta^5\text{-C}_5\text{Me}_4\text{R})(\text{COT}'')\}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO}_3)]$ ($\text{R} = \text{Me}$, **140**; H , **141**) (**Fig. 32**) were afforded. A single crystal X-ray diffraction study revealed the first example of a $\mu\text{-}\eta^1\text{:}\eta^2\text{-}$ carbonate binding mode to be observed with uranium despite uranyl carbonates being relatively common in nature, with spectroscopic data confirming the assignment of a $\text{U}^{\text{IV}}\text{-CO}_3^{2-}\text{-U}^{\text{IV}}$ complex. Free CO was observed to evolve from the reactions, confirming that CO_2 has been reductively disproportionated forming carbonate and carbon monoxide.^{156, 157}

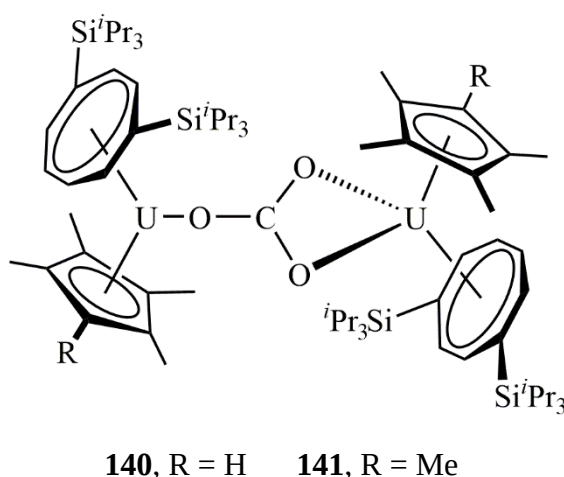
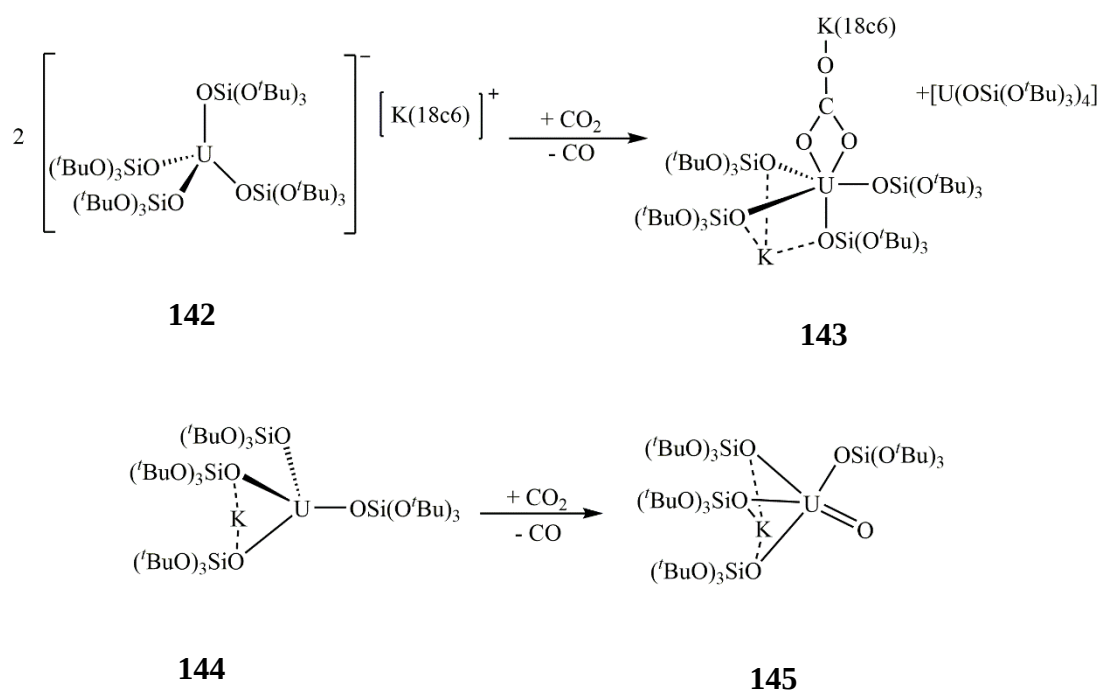


Fig. 32 - Structure of $[\{U(\eta^5\text{-C}_5\text{Me}_4\text{R})(\text{COT}'')\}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO}_3)]$
($\text{R} = \text{Me}$, **140**; H , **141**)

More recently, Mazzanti and co-workers have reported that the presence of potassium at a U, K site supported by sterically demanding tris(tert-butoxy)siloxide ligands induces a large cooperative effect in the reduction of CO_2 . The ion pair complex $[K(18\text{c}6)][U\{\text{OSi}(\text{O}^t\text{Bu})_3\}_4]$ (**142**) promotes the selective reductive disproportionation of CO_2 to yield CO and the mononuclear uranium(V) carbonate complex $[U\{\text{OSi}(\text{O}^t\text{Bu})_3\}_4(\mu\text{-}\kappa^2\text{:}\kappa^1\text{-CO}_3)K_2(18\text{c}6)]$ (**143**) (**Scheme 24**). In contrast, the heterobimetallic complex $[U\{\text{OSi}(\text{O}^t\text{Bu})_3\}_4K]$ (**144**) promotes the potassium-assisted two-electron reductive cleavage of CO_2 , yielding CO and the U(V) terminal oxo complex $[UO\{\text{OSi}(\text{O}^t\text{Bu})_3\}_4K]$ (**145**) (**Scheme 24**) thus providing an example of two-electron transfer in U(III) chemistry.¹⁵⁸

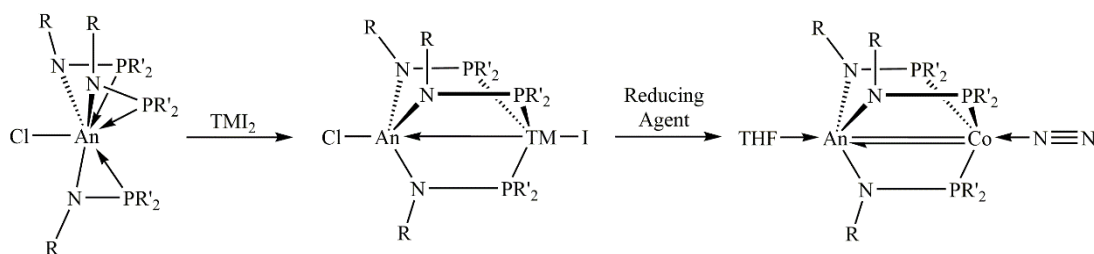


Scheme 24 - Synthesis of $[\text{U}\{\text{OSi}(\text{O}^t\text{Bu})_3\}_4(\mu\text{-}\kappa^2\text{:}\kappa^1\text{-CO}_3)\text{K}_2(18\text{c6})]$ (**143**) and $[\text{UO}\{\text{OSi}(\text{O}^t\text{Bu})_3\}_4\text{K}]$ (**145**)

1.4 Project Aim

Compounds containing metal-metal bonds can be found practically across the entire Periodic Table and have played a fundamentally important role in developing our chemical knowledge. However, in spite of this the chemistry of f-block metal-metal bonds is considerably less well developed in contrast to the s- p- and d-blocks. This is surprising as the large ionic radii, variable oxidation states and potential availability of f-orbitals for the actinides could potentially result in unique examples of chemical bonding, magnetism and reactivity. However, this scarcity of examples is testament to the practical difficulties of stabilising such linkages.

With respect to the success of bifunctional ligands containing hard and soft donor centres, such as phosphinoalkoxides $[\text{Ph}_2\text{PCH}_2\text{O}]^-$ employed by Wolczanski^{57, 62, 63} and particularly the phosphinoamides $[\text{RNPR}_2]^-$ utilised by Nagashima^{64, 65, 71, 72} and Thomas,^{56, 75, 77, 78, 81, 84, 89, 112, 113, 117} in stabilising early-late transition metal heterobimetallic complexes it is the aim of this project to extend this chemistry into the f-block. Using phosphinoamide ligands, with their extensive scope for steric and electronic modification, supported actinide-transition metal complexes containing dative metal-metal bonds will be targeted. Given the high reactivity of the reduced early-late transition metal heterobimetallic complexes coupled with the often unusual reactivity of low valent uranium towards small molecules such as N_2 , CO and CO_2 , chemical reduction and subsequent reaction with small molecules of any isolated actinide-transition metal complexes will be highly desirable.



Scheme 25 - Potential Synthesis of a reduced actinide-transition metal heterobimetallic complex

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Chapter Two

Phosphinoamines and their Group One Metal Salts

Contents

2.1	Background	78
2.2	Phosphinoamine Proligands	79
2.3	Ligand Transfer Reagents	83
2.4	Concluding Remarks	96
2.5	Experimental Information	98
2.6	References	105

2.1 Background

As has been outlined in chapter one metal-metal linkages will be targeted using the supportive phosphinoamide ligand system as a result of the extensive scope for steric and electronic modification. Once deprotonated the phosphinoamine proligands, of type $\text{RN}(\text{H})\text{PR}'_2$, would provide sufficient steric protection of any metal-metal interaction as well as the ability to systematically modify the electron donating capacity of the phosphine. As early as 1961 Sisler and Smith reported several *N*-substituted aminodiphenylphosphines as a result into their research on the hydrazine analogue, monoaminophosphine (PH_2NH_2).¹⁻³

Initial work regarding lithium phosphinoamides conducted by Ashby in the 1990s was concerning the nature of the N-P bond in these systems.^{4,6} The phosphinoamine $\text{PhN}(\text{H})\text{PPh}_2$, reacted with one equivalent of $^n\text{BuLi}$ in Et_2O to form the lithium salt $[\{\text{LiNPh}(\text{PPh}_2)(\text{Et}_2\text{O})\}_2]$ (**144**) that could be described as either a phosphinoamide or an iminophosphide (**Fig. 31**). The phosphorus atom in both resonance forms is in the P^{+3} oxidation state; however the resonance form of the phosphinoamide has a formal negative charge on the nitrogen atom, whereas for the iminophosphide the negative charge is located on the phosphorus atom. The phosphinoamide is expected to predominate if the greater electronegativity of the nitrogen atom is the dominant factor; however the iminophosphide, in which the phosphorus has expanded its octet, results in additional stabilisation due to resonance delocalisation of the charge and N-P multiple bonding.

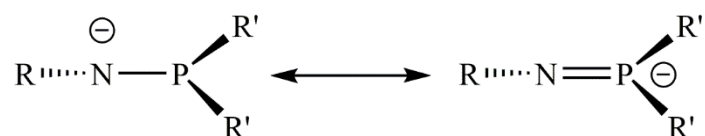
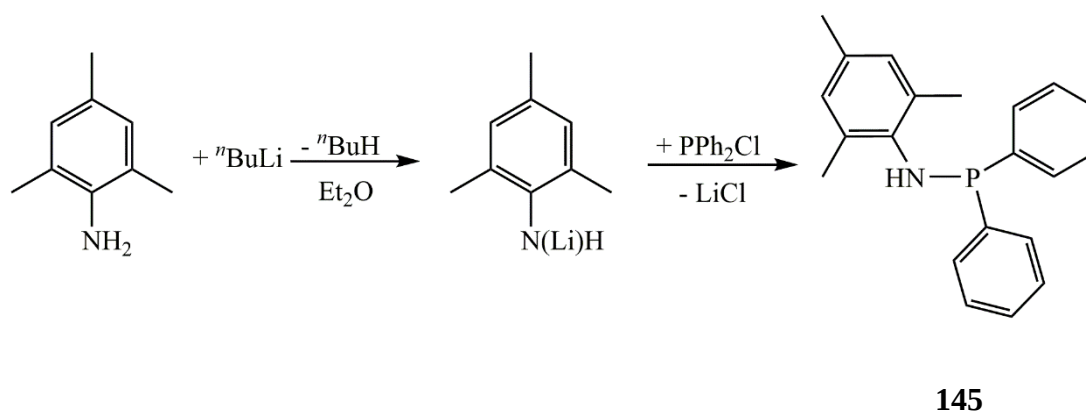


Fig. 31 – The resonance forms of the phosphinoamide (left) and iminophosphide (right) anions

Ashby reported several more lithium salts of phosphinoamines with N-P distances in the range of 1.659(4) to 1.672(2) Å which fall somewhere between the expected double bond lengths of the P(IV) phosphazenes (1.58-1.64 Å)⁷⁻⁹ and the reported single bond lengths of aminophosphines (1.62-1.74 Å)¹⁰⁻¹⁷ as well as the expected N-P single-bond length calculated using the Schomaker-Stevenson approach of 1.76 Å.¹⁸ Although direct comparison is complicated due to the apparent sensitivity of N-P bond lengths to substituents, the relatively short N-P distances reported by Ashby is suggestive of partial N-P multiple bond character with the RNPR'₂ anion viewed as a resonance hybrid phosphinoamide/imino phosphide.

It is with slight modifications of these literature procedures that Nagashima¹⁹⁻²² and Thomas²³⁻³⁵ prepared suitable ligands to support their transition metal linkages and it is these procedures that will be used to synthesise ligands in an attempt to stabilise actinide-transition metal interactions.

2.2 Phosphinoamine Proligands



Scheme 25 – Synthesis of MesN(H)PPh₂ (**145**)

Treatment of 2,4,6-trimethylaniline (NH₂Mes) with one equivalent of ⁿBuLi at 0 °C followed by heating to reflux for thirty minutes (to ensure the reaction had reached completion) resulted in the formation of a white precipitate. The stirring slurry was

then added drop wise to PPh_2Cl at $-78\text{ }^\circ\text{C}$ to yield, following work up, MesN(H)PPh_2 (**145**) (**Scheme 25**) as a pale yellow solid in 86% yield. Colourless crystals of **145** suitable for an X-ray diffraction study were grown from THF and the molecular structure is shown in **Fig. 32** with selected bond lengths and angles. Complex **145** crystallised as a discrete monomeric species in the space group $\text{P2}_1/\text{c}$. The P(1)-N(1) bond length of $1.7011(13)\text{ \AA}$ in **145** is comparable to the previously reported P-N bond length of $1.730(2)\text{ \AA}$ for the phosphinoamine $\text{Mes}^*\text{N(H)PPh}_2$ ($\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$).⁴ The conformation about the N-P bond renders the lone pair of the nitrogen approximately trans to the P(1)-C(16) bond, an orientation that favours $\text{N(n}\sigma\text{)} \rightarrow \text{P(1)-C(16)}\sigma^*$ negative hyperconjugation. Such donation is evidenced by the slight lengthening of the P(1)-C(16) bond of $1.8375(14)$ compared to the P(1)-C(10) bond of $1.8268(15)\text{ \AA}$.

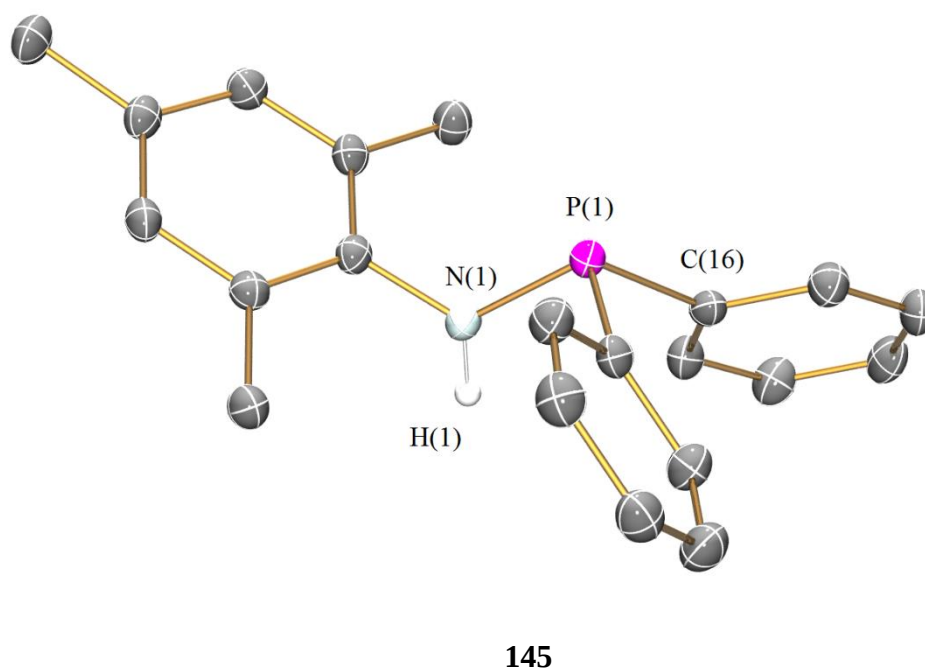
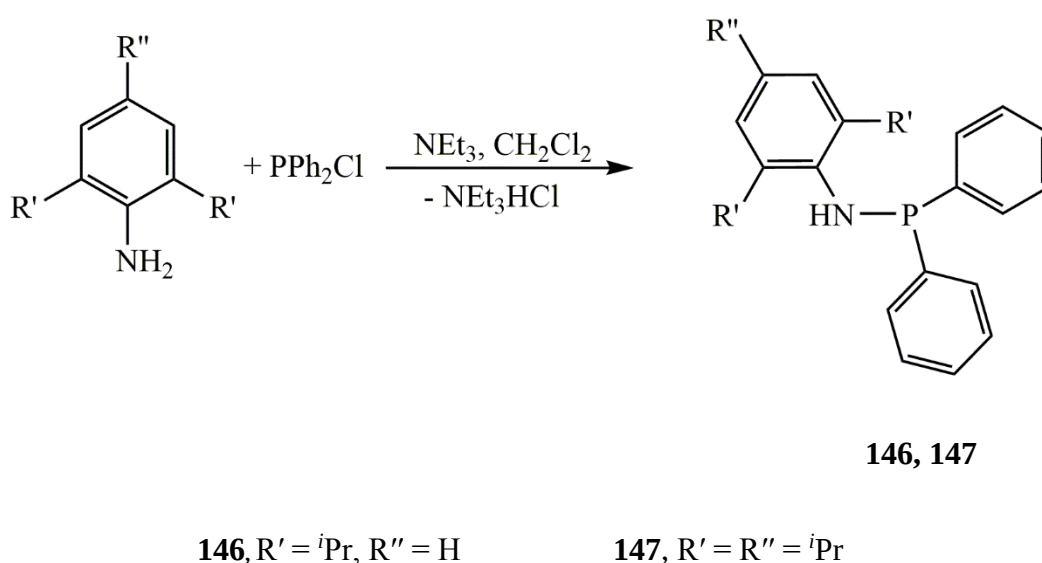


Fig. 32 – Structure of MesN(H)PPh_2 (**145**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity except H(1). Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$) P(1)-N(1) $1.7011(13)$, P(1)-C(10) $1.8268(15)$, P(1)-C(16) $1.8375(14)$, N(1)-C(1) $1.4313(18)$, N(1)-P(1)-C(10) $102.90(7)$, N(1)-P(1)-C(16) $103.51(6)$, C(1)-N(1)-P(1) $118.78(10)$.

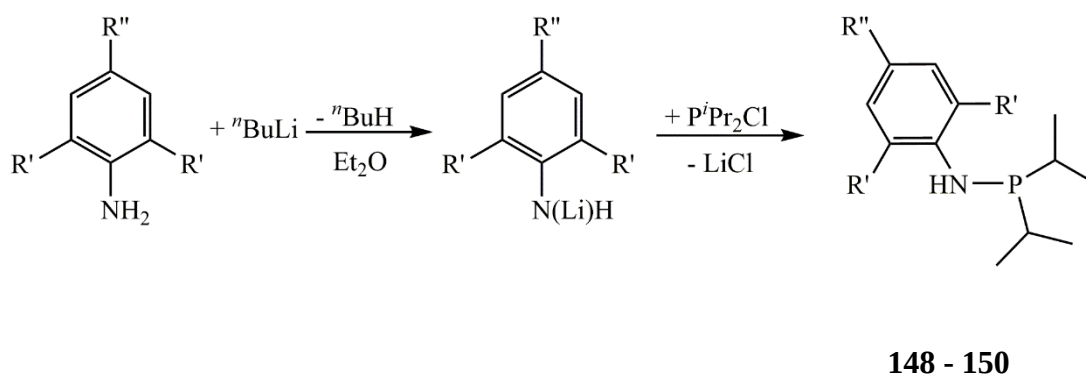
The ^1H NMR spectrum of **145** exhibits resonances in the range 7.19 to 7.60 ppm which are typical for the PPh_2 group. A doublet resonance which integrates to one proton at 3.65 ppm is assigned to the NH proton and is split into a doublet by ^2J coupling with the phosphorus atom. Resonances at 2.20, 2.25 and 6.86 ppm are attributed to the two CH_3 and one CH of the Mes group respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibits a single resonance at 36.07 ppm.

In a slight adaptation of the literature procedure employed by Baysal to synthesise the aminophosphine DippN(H)PPh_2 (**146**) during his investigations into Heck and Suzuki cross coupling reactions, the sterically encumbered phosphinoamine TrippN(H)PPh_2 (**147**) (**Scheme 26**) was synthesised.³⁶ The reaction of 2,4,6-triisopropylaniline (NH_2Tripp) with PPh_2Cl in the presence of triethylamine in CH_2Cl_2 resulted in the aminolysis product **147** as a pale yellow solid in a 97% yield. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **147** were consistent with the formation of the phosphinoamine. The ^1H NMR spectrum of **147** exhibits resonances in the range 7.11 to 7.50 ppm which are typical for the PPh_2 group. A doublet resonance which integrates to one proton at 3.83 ppm is assigned to the NH proton and, like in the ^1H NMR spectrum of **145**, is split into a doublet by ^2J coupling with the phosphorus atom. Resonances at 1.17 and 1.24 ppm are attributed to the CH_3 groups of the $i\text{Pr}$ with resonances at 2.81 and 3.24 ppm assigned to the CH protons of the $i\text{Pr}$. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibits a single resonance at 42.10 ppm.



Scheme 26 – Synthesis of DippN(H)PPh_2 (**146**) and TrippN(H)PPh_2 (**147**)

To allow for systematic modification of the electron donating capacity of the phosphine whilst keeping the amido portions constant the corresponding previously reported aminophosphine MesN(H)PⁱPr₂ (**148**) as well as the novel aminophosphines DippN(H)PⁱPr₂ (**149**) and TrippN(H)PⁱPr₂ (**150**) (**Scheme 27**) were synthesised using slight modifications of literature procedures.



148, R' = R'' = CH₃

149, R' = ⁱPr, R'' = H

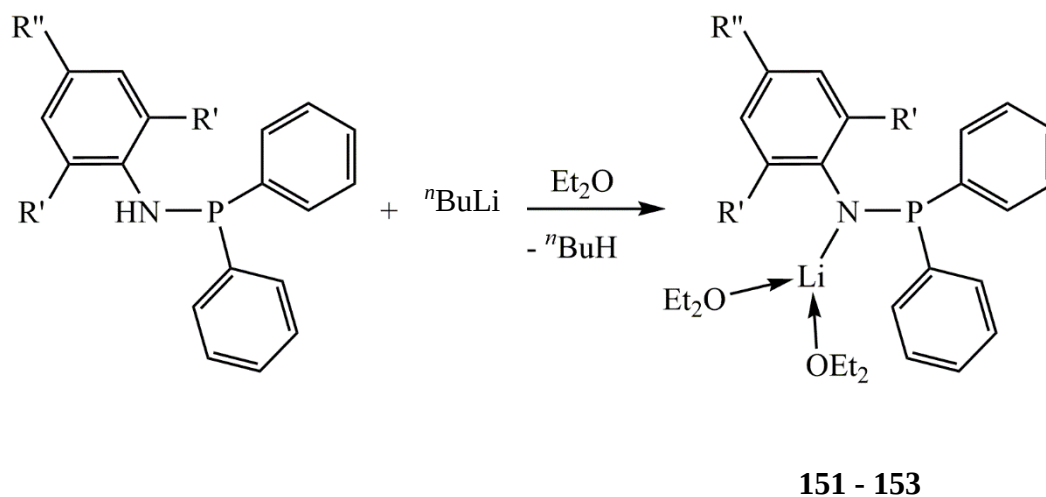
150, R' = R'' = ⁱPr

Scheme 27 – Synthesis of MesN(H)PⁱPr₂ (**148**), DippN(H)PⁱPr₂ (**149**) and TrippN(H)PⁱPr₂ (**150**)

Treatment of 2,6-diisopropylaniline (NH₂Dipp) with one equivalent of ⁿBuLi at room temperature in hexane resulted in the formation of a white precipitate. This white precipitate was added dropwise as a slurry to PⁱPr₂Cl at -78 °C to yield, following work up, **149** as a pale yellow oil in an 81% yield (**Scheme 27**). The ¹H and ³¹P{¹H} NMR spectra of **149** were consistent with the formation of the phosphinoamine. The ¹H NMR spectrum of **149** exhibits resonances in the range 7.01 to 7.14 ppm which is typical for the CH groups of the Dipp substituent. Septets at 3.66 and 1.61 ppm which both integrate to two protons each are assigned to the CH of the ⁱPr groups. A doublet resonance which integrates to one proton at 3.54 ppm is assigned to the NH proton and is split into a doublet by ²J coupling by the phosphorus atom. Resonances between 1.01 and 1.29 ppm are attributed to the four CH₃ groups of the ⁱPr substituents. The ³¹P{¹H} NMR spectrum exhibits a single resonance at 67.14 ppm.

In an analogous manner, treatment of 2,4,6-triisopropylaniline (NH_2Tripp) with one equivalent of $^n\text{BuLi}$ at room temperature in hexane resulted in the formation of a white precipitate. This white precipitate was added dropwise as a slurry to $\text{P}^i\text{Pr}_2\text{Cl}$ at $-78\text{ }^\circ\text{C}$ to yield, following work up, **150** as a pale yellow oil in a 92% yield (**Scheme 27**). The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **150** were consistent with the formation of the phosphinoamine. The ^1H NMR spectrum of **150** exhibits a resonance at 7.11 ppm which corresponds to the CH groups of the Tripp substituent. Septets at 3.69, 2.83 and 1.62 ppm are assigned to the CH of the ^iPr groups. A doublet resonance which integrates to one proton at 3.44 ppm is assigned to the NH proton and is split into a doublet by ^2J coupling by the phosphorus atom. Resonances between 1.00 and 1.34 ppm are attributed to the five CH_3 groups of the ^iPr substituents. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibits a single resonance at 66.37 ppm.

2.3 Ligand Transfer Reagents



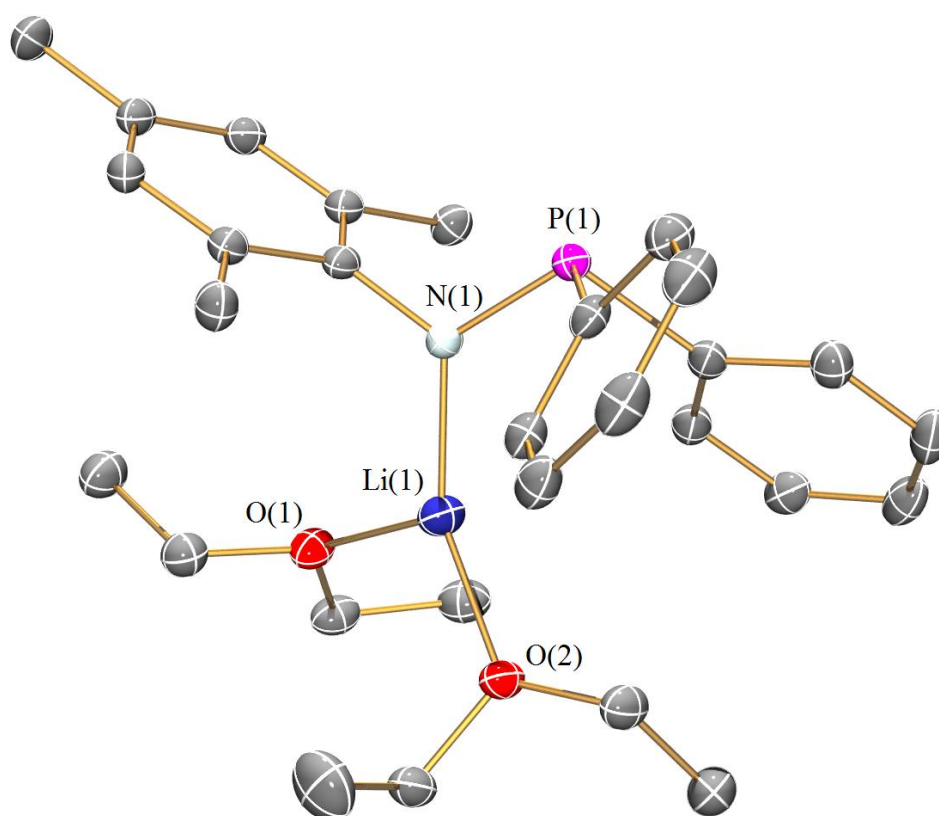
151, $\text{R}' = \text{R}'' = \text{CH}_3$

152, $\text{R}' = ^i\text{Pr}$, $\text{R}'' = \text{H}$

153, $\text{R}' = \text{R}'' = ^i\text{Pr}$

Scheme 28 – Synthesis of $[\text{Li}(\text{MesNPPH}_2)(\text{Et}_2\text{O})_2]$ (**151**), $[\text{Li}(\text{DippNPPH}_2)(\text{Et}_2\text{O})_2]$ (**152**) and $[\text{Li}(\text{TrippNPPH}_2)(\text{Et}_2\text{O})_2]$ (**153**)

The subsequent step required deprotonation to produce the phosphinoamide alkali metal salts to act as ligand-transfer reagents. Treatment of **145** with one equivalent of $^n\text{BuLi}$ in Et_2O afforded the complex $[\text{Li}(\text{MesNPPH}_2)(\text{Et}_2\text{O})_2]$ (**151**) (**Scheme 28**) in 79 % yield as a colourless crystalline solid. Single crystals of **151** suitable for an X-ray diffraction study were grown from cold ($-30\text{ }^\circ\text{C}$) Et_2O over seventy two hours and the molecular structure is shown in **Fig. 33** with selected bond lengths and angles.



151

Fig. 33 – Structure of $[\text{Li}(\text{MesNPPH}_2)(\text{Et}_2\text{O})_2]$ (**151**)

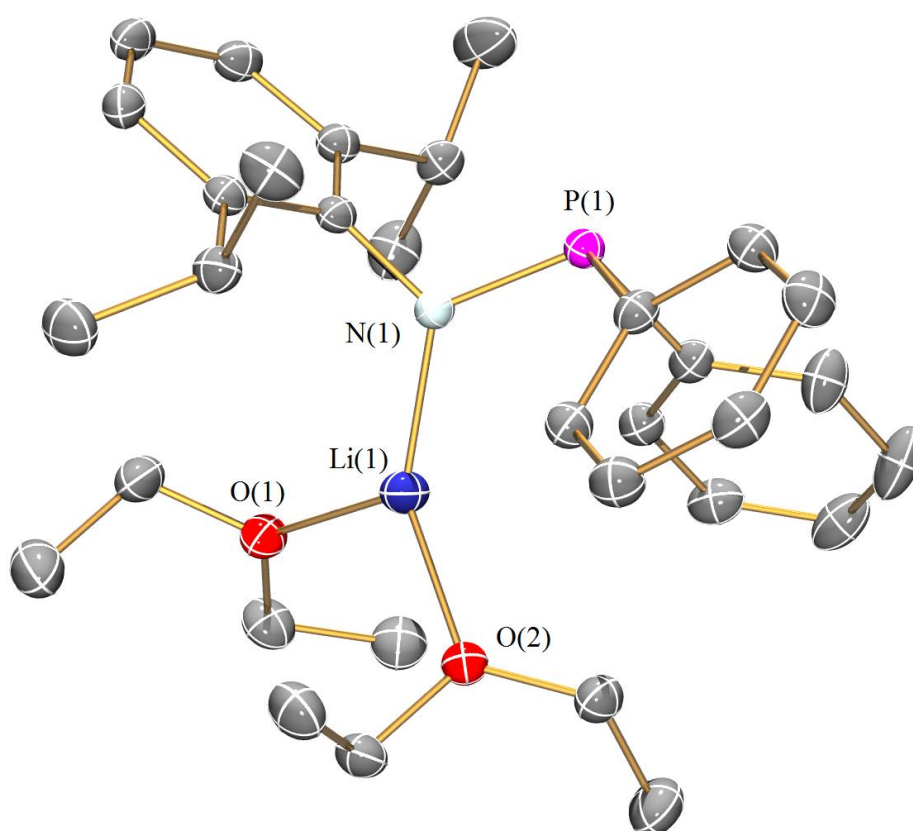
Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) P(1)-N(1) 1.6580(10), P(1)-C(10) 1.8523(12), P(1)-C(16) 1.8642(12), N(1)-C(1) 1.4191(14), N(1)-Li(1) 1.922(2), N(1)-P(1)-C(10) 102.22(5), N(1)-P(1)-C(16) 106.45(5), C(1)-N(1)-P(1) 115.79(8), C(1)-N(1)-Li(1) 117.48(10), P(1)-N(1)-Li(1) 125.77(9).

Complex **151** crystallised as a discrete monomeric species in the space group *P21/c*. Complex **151** exhibits a *trans* conformation of substituents about the N(1)-P(1) bond, and only one other example of this exists in the literature.⁴ In contrast to the majority of the structurally-characterised phosphinoamide complexes **151** is not a dimer in the solid state which is presumably due to the sterically demanding mesityl substituent on the nitrogen centre. The N(1)-P(1) distance of 1.658(10) Å is shorter by 0.042 Å compared to **145** and is comparable to previously structurally characterised lithium phosphinoamides suggesting partial N-P double bond character. The lithium cation is ligated by the phosphinoamide through the N(1) and analogously to lithium(2,4,6-tri-*tert*-butylphenyl)(diphenylphosphino)amide there appears to be no Li-P interaction as is often observed for *cis*-lithium phosphinoamides. The coordination sphere of the lithium is completed by two Et₂O ligands and adopts a distorted trigonal planar geometry [sum of angles at Li = 357.02(34)°] which is typical for a 3-coordinate lithium centre. The Li(1)-O(1) and Li(1)-O(2) distances of 1.930(2) Å and 1.932(2) Å are unexceptional.³⁷

The ¹H NMR spectrum of **151** exhibits resonances in the range 7.13 to 7.81 ppm which are typical for the *PPh*₂ group. Resonances at 0.78 and 3.00 ppm are assigned to the CH₃ and CH₂, respectively, groups of the coordinated Et₂O molecules and those at 2.22, 2.33 and 6.95 ppm were attributed to the two CH₃ and one CH of the Mes group, respectively. The ³¹P{¹H} NMR spectrum of **151** exhibits a single resonance at 45.03 ppm, shifted downfield by 8.96 ppm compared to **145**. The ⁷Li{¹H} NMR spectrum of **151** exhibits a single resonance at 1.13 ppm.

Treatment of **146** with one equivalent of ⁿBuLi in Et₂O gave the complex [Li(DippNPPH₂)(Et₂O)₂] (**152**) (**Scheme 28**) in 72% yield as a colourless crystalline solid. Single crystals of **152** suitable for an X-ray diffraction study were grown from cold (-30 °C) Et₂O over twenty four hours and the molecular structure is shown in **Fig. 34** with selected bond lengths and angles. Complex **152** crystallised as a discrete monomeric species in the space group *Pbca*. As with **151**, **152** is monomeric in the solid state and the substituents around the N(1)-P(1) bond adopt a *trans* conformation. This is again attributed to the high steric demands of the Dipp group. The N(1)-P(1) distance of 1.6617(9) Å is unremarkable. The lithium cation is ligated by the phosphinoamide through N(1) and unlike the reported *cis*-lithium phosphinoamides

there is no interaction between the lithium and the phosphorus centre. The coordination sphere of the lithium atom is completed by two Et₂O ligands and Li(1) adopts a trigonal planar geometry [sum of angles at Li = 357.83(29)°] which is typical for a 3-coordinate lithium centre. The Li(1)-O(1) and Li(1)-O(2) distances of 1.9669(19) Å and 1.946(2) Å are slightly longer than in **146** but are still unexceptional.³⁷



152

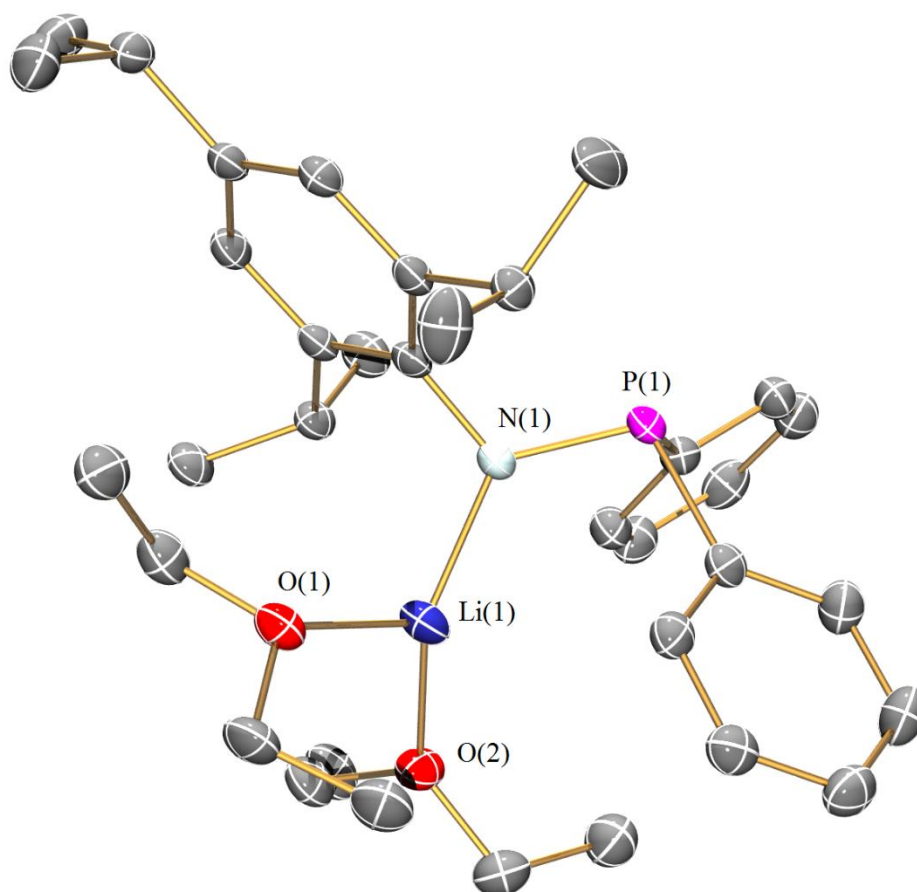
Fig. 34 – Structure of [Li(DippNPPPh₂)(Et₂O)₂] (**152**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) P(1)-N(1) 1.6617(9), P(1)-C(13) 1.8525(11), P(1)-C(19) 1.8559(10), N(1)-C(1) 1.4151(12), N(1)-Li(1) 1.956(2), N(1)-P(1)-C(13) 102.27(5), N(1)-P(1)-C(19) 107.13(4), C(1)-N(1)-P(1) 115.37(6), C(1)-N(1)-Li(1) 120.00(8), P(1)-N(1)-Li(1) 123.26(7).

The ^1H NMR spectrum of **152** exhibits resonances in the range 7.25 to 7.78 ppm which are typical for the PPh_2 group. Resonances at 0.98 and 3.18 ppm are assigned to the CH_3 and CH_2 groups, respectively of the coordinated Et_2O molecules and those at 1.16 and 3.95 ppm are attributed to the CH_3 and CH of the ^iPr groups respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **152** exhibits a single resonance at 43.54 ppm, shifted downfield by 0.88 ppm compared to **146**. The $^7\text{Li}\{^1\text{H}\}$ NMR spectrum of **152** exhibits a single resonance at 1.17 ppm.

Treatment of **147** with one equivalent of $^n\text{BuLi}$ in Et_2O afforded the complex $[\text{Li}(\text{TrippNPPH}_2)(\text{Et}_2\text{O})_2]$ (**153**) (**Scheme 28**) in 68% yield as a colourless crystalline solid. Single crystals of **153** suitable for an X-ray diffraction study were grown from cold ($-30\text{ }^\circ\text{C}$) Et_2O over eighty six hours and the molecular structure is shown in **Fig. 35** with selected bond lengths and angles. Complex **153** crystallised as a discrete monomeric species in the space group $P-1$. As with the lithiated phosphinoamides discussed previously, **153** is an example of a lithiated phosphinoamide crystallising in the solid state as a monomeric unit in the *trans* conformation around the $\text{N}(1)\text{-P}(1)$ bond. The $\text{N}(1)\text{-P}(1)$ distance of $1.6654(12)\text{ \AA}$ is comparable to previously structurally characterised lithium phosphinoamides, **151** and **152**. The lithium cation is ligated by the phosphinoamide through the $\text{N}(1)$ with no interaction between the lithium and the phosphorus, this is comparable to **151** and **152**. The coordination sphere of the lithium centre is completed by two Et_2O ligands, and adopts a trigonal planar geometry [sum of angles at $\text{Li} = 355.85(42)^\circ$]. The $\text{Li}(1)\text{-O}(1)$ and $\text{Li}(1)\text{-O}(2)$ distances of $1.942(3)\text{ \AA}$ and $1.995(3)\text{ \AA}$ are unexceptional for Li coordinated Et_2O units.³⁷

The ^1H NMR spectrum of **153** exhibits resonances in the range 7.15 to 7.71 ppm which are typical for that of the PPh_2 group. Resonances at 1.07 and 3.24 ppm are assigned to the CH_3 and CH_2 groups of the coordinated Et_2O respectively. Resonances at 1.29 and 1.31 ppm are assigned to the CH_3 of the ^iPr groups and resonances at 2.87 and 4.08 ppm are assigned to the CH of the ^iPr groups. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **153** exhibits a single resonance at 61.83 ppm shifted downfield by 24.27 ppm compared to **147**. The $^7\text{Li}\{^1\text{H}\}$ NMR spectrum of **153** exhibits a single resonance at 0.78 ppm.

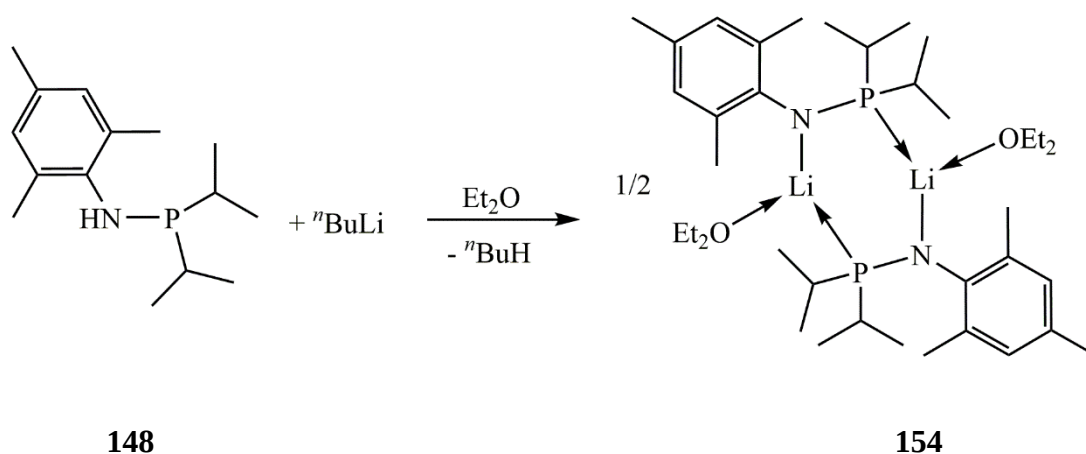


153

Fig. 35 – Structure of $[Li(TrippNPPPh_2)(Et_2O)_2]$ (**153**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) P(1)-N(1) 1.6654(12), P(1)-C(16) 1.8508(16), P(1)-C(22) 1.8563(16), N(1)-C(1) 1.4186(19), N(1)-Li(1) 1.943(3), N(1)-P(1)-C(16) 101.30(7), N(1)-P(1)-C(22) 106.83(7), C(1)-N(1)-P(1) 117.02(9), C(1)-N(1)-Li(1) 112.89(12), P(1)-N(1)-Li(1) 127.43(11).

Although the preparation of $[LiNMes(P^iPr_2)(Et_2O)]_2$ (**154**) has been reported by Thomas in 2009, no single crystal X-ray diffraction study was performed to authenticate the structure.²⁹ Treatment of **148** with one equivalent of $nBuLi$ in Et_2O produced the dimeric complex $[LiNMes(P^iPr_2)(Et_2O)]_2$ (**154**) (**Scheme 29**) in 78% yield as a colourless crystalline solid. Single crystals of **154** suitable for an X-ray diffraction study were grown from cold ($-30\text{ }^\circ\text{C}$) Et_2O over twenty four hours and the molecular structure is shown in **Fig. 36** with selected bond lengths and angles.

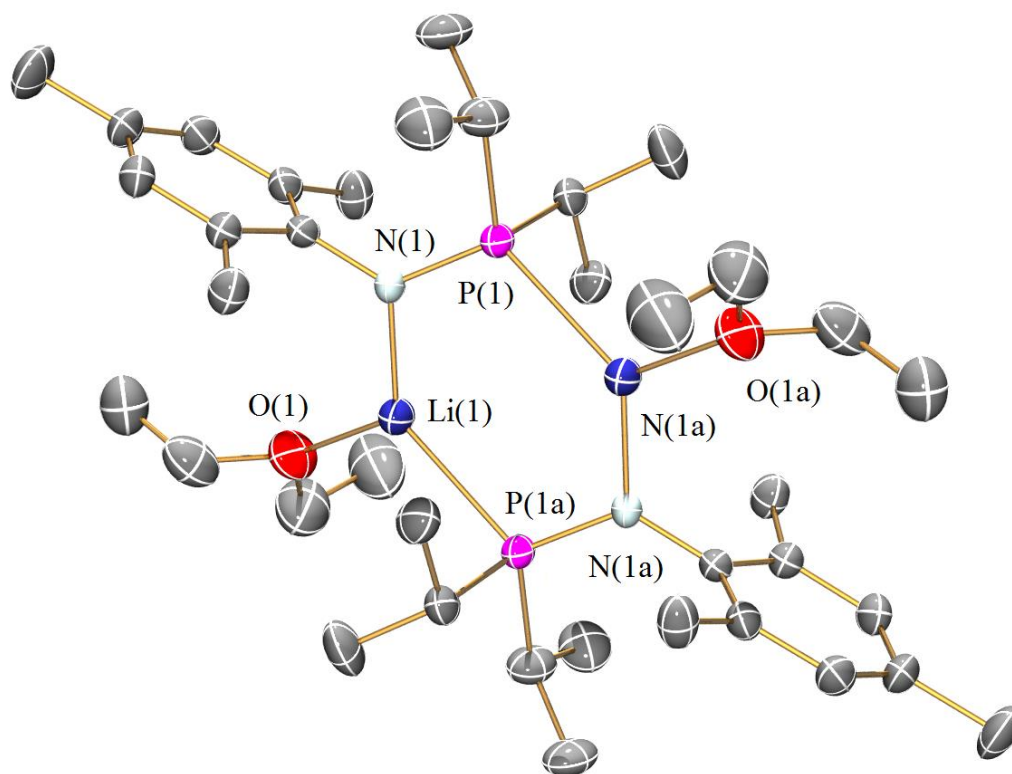


Scheme 29 – Synthesis of $[\{LiNMes(P^iPr_2)(Et_2O)\}_2]$ (**154**)

Complex **154** crystallised in the space group $P2_1/c$ with two crystallographically independent molecules in the asymmetric unit, although despite this the two units are structurally almost identical. In contrast to the lithium phosphinoamides **151-153**, **154** forms a centrosymmetric dimeric species in the solid state more commonly found in the literature than the monomeric complexes.^{4, 5} This has been attributed to the less sterically demanding substituents of the phosphinoamide which adopt a *cis* conformation about the N(1)-P(1) bond. The N-P bond lengths of 1.6490(14) Å and 1.6570(15) Å are statistically identical and are comparable to the previously structurally characterised lithium phosphinoamides **151-153** and to those found in the literature. The lithium cation is ligated by the both of the heteroatoms of opposing phosphinoamides with the coordination sphere completed by an Et_2O ligand adopting a distorted trigonal planar geometry [sum of angles at Li = 359.93(75)° and 359.99(46)°] for the two Li atoms respectively.

The ^1H NMR spectrum of **154** exhibits a multiplet resonance at 6.52 ppm and is attributed to the *CH* protons of the Mes group whereas resonances at 2.06 and 2.32 ppm are assigned to the CH_3 protons of the Mes group. A septet at 1.42 ppm and multiplets between 0.91 and 1.10 are assigned to the *CH* and CH_3 protons of the *i*Pr groups respectively. The $^{31}P\{^1H\}$ NMR spectrum of **154** exhibits a single resonance at 73.29 ppm, shifted downfield by 15.59 ppm compared to **148**. The $^7Li\{^1H\}$ NMR spectrum of **154** also exhibits a single peak at -1.40 ppm. There are no resonances that

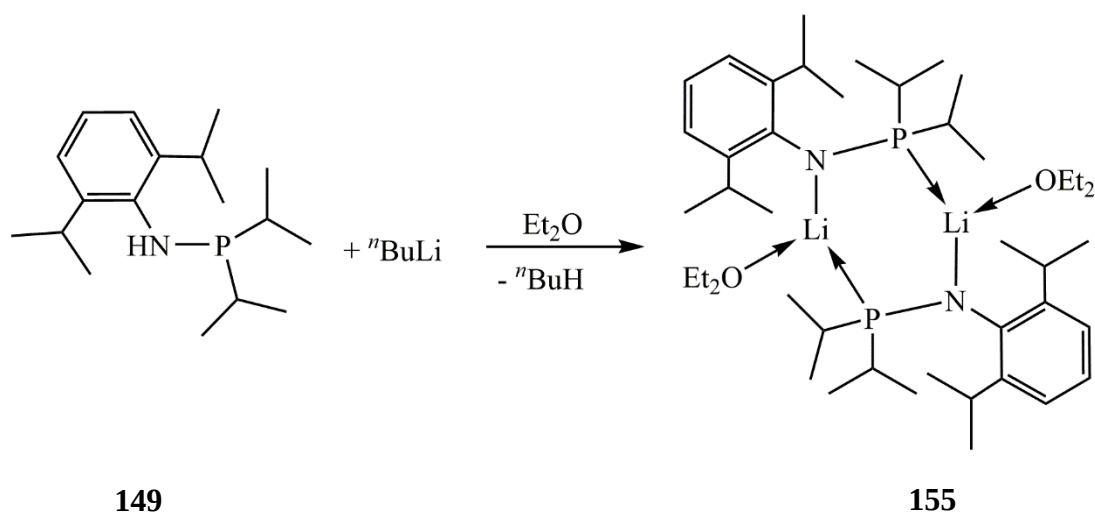
can be attributed to Et₂O molecules, either coordinated or otherwise, in the ¹H NMR spectrum, this is confirmed by elemental microanalysis. The coordinated Et₂O in the solid state structure of **154** was therefore removed under vacuum when crystals of **154** are isolated.



154

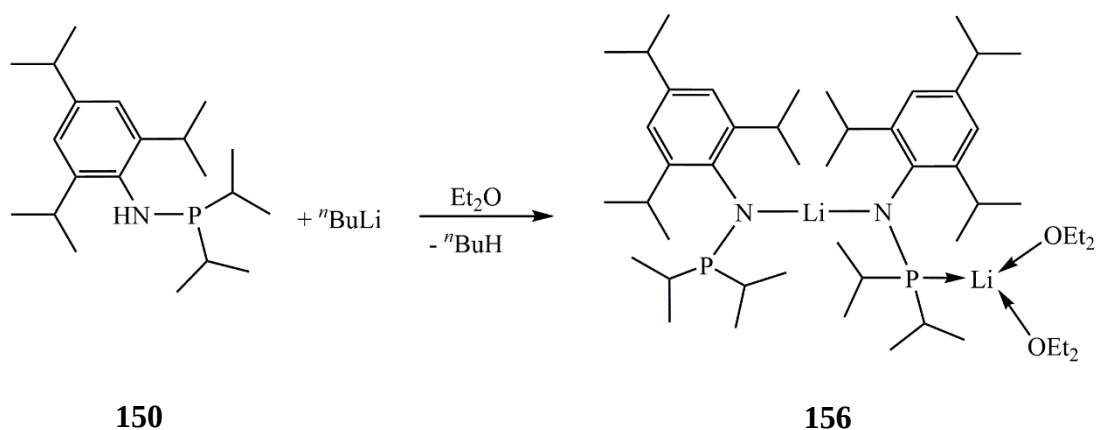
Fig. 36 – Structure of $[\{\text{LiNMes}(\text{P}^i\text{Pr}_2)(\text{Et}_2\text{O})\}_2]$ (**154**)

Thermal ellipsoids set at 40% probability. Disorder components, one of the two crystallographically unique units and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) P(1)-N(1) 1.6490(14), P(1)-C(10) 1.878(2), P(1)-C(13) 1.8817(19), N(1)-C(1) 1.415(2), N(1)-Li(1) 1.928(3) Li(1)-P(1) 2.593(3), P(1)-N(1)-Li(1) 114.11(12), C(1)-N(1)-Li(1) 117.77(14), C(1)-N(1)-P(1) 126.82(12), N(1)-P(1)-C(10) 112.82(13), N(1)-P(1)-C(13) 111.26(8).



Scheme 30 – Potential synthesis of “[LiNDipp(PⁱPr₂)]” (**155**)

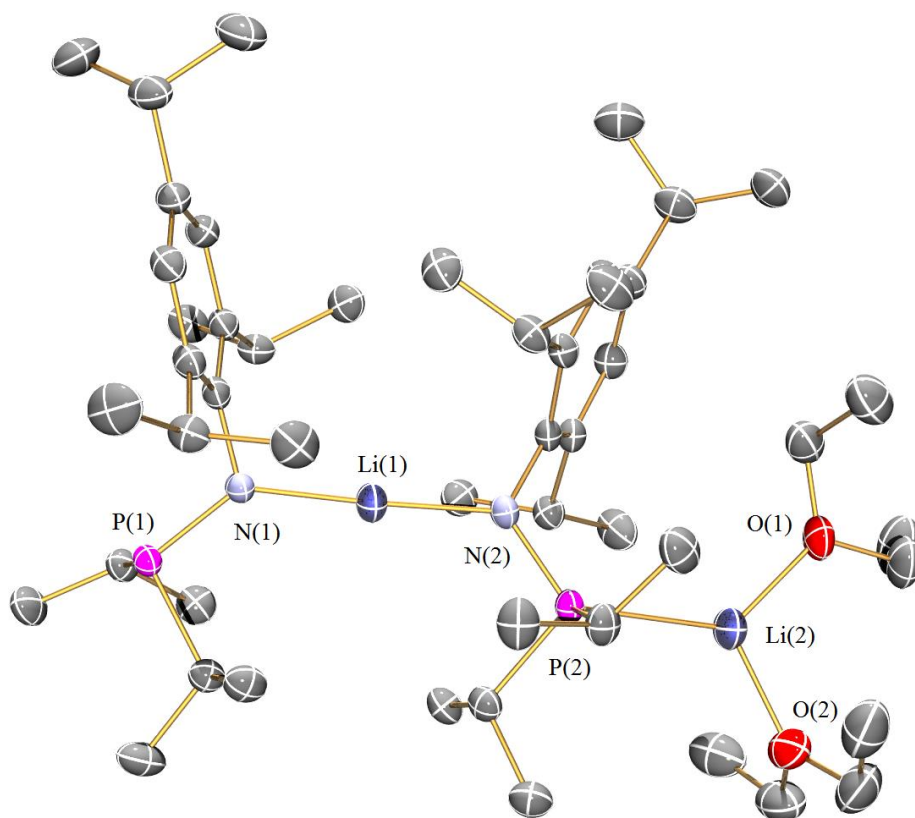
Treatment of **149** with one equivalent of ⁿBuLi in Et₂O gave the complex “[LiNDipp(PⁱPr₂)]” (**155**) (**Scheme 30**) in 81% yield as a colourless crystalline solid. Due to its increased air sensitivity **155** was not structurally characterised as it decomposed during analysis. Although it is possible that **155**, like **154**, adopts a *cis*-conformation in the solid state the increased steric demands of the Dipp amine group could potentially result in a different geometry, unfortunately without a single crystal X-ray diffraction study it is only possible to speculate. The ¹H NMR spectrum of **155** exhibits resonances in the range 6.42 to 6.75 ppm which is typical for the CH groups of the Dipp substituent. Septets at 4.20 and 1.48 ppm which both integrate to two protons each are assigned to the CH of the ⁱPr groups. Resonances between 0.98 and 1.11 ppm are attributed to the four CH₃ groups of the ⁱPr substituents. The ³¹P{¹H} NMR spectrum of **155** exhibits a single resonance at 84.69 ppm, shifted downfield by 17.55 ppm compared to **147**. The ⁷Li{¹H} NMR spectrum of **155** also exhibits a single peak at -1.50 ppm. As with complex **154**, **155** has no resonances in the ¹H NMR spectrum that can be assigned to Et₂O so, it is assumed that any coordinated Et₂O was labile enough to be removed under vacuum when isolating the crystals.



Scheme 31 – Synthesis of $[(P^iPr_2)TrippN\{\mu-Li\}NTripp(P^iPr_2)Li\{Et_2O\}_2]$ (**156**)

Treatment of **150** with one equivalent of $nBuLi$ in Et_2O resulted in, after work up and crystallisation, a colourless crystalline solid in 88% yield. A single crystal X-ray diffraction study was performed which revealed the product to be $[(P^iPr_2)TrippN\{\mu-Li\}NTripp(P^iPr_2)Li\{Et_2O\}_2]$ (**156**), and the molecular structure is illustrated in **Fig. 37** with selected bond lengths and angles.

Complex **156** crystallised as a discrete monomeric species in the space group $P-1$. Unlike **151**, complex **156** adopt a *trans* conformation about the N(1)-P(1) bonds of the phosphinoamide units. The two phosphinoamides bond through their respective nitrogen centres to what appears to be a two coordinate lithium centre in a near linear geometry [N(1)-Li(1)-N(2) 177.17(18)°], there are however, several agostic type interactions stabilising this geometry. The second lithium centre is coordinated to the phosphorus centre of the second phosphinoamide with two Et_2O molecules completing the coordination sphere in a more orthodox distorted trigonal planar geometry [sum of angles = 356.89(44)°] observed in **151-153**. The N-P bond lengths of 1.6829(12) and 1.6612(13) Å are comparable to the previously reported lithium phosphinoamides as are the N-Li bond lengths of 1.898(3) and 1.923(3) Å. The P(2)-Li(2) bond length of 2.538(3) Å is similar to the P-Li bond length found in **154** whilst The Li(2)-O(1) and Li(2)-O(2) distances of 1.879(3) and 1.949(3) Å are unexceptional.³⁷



156

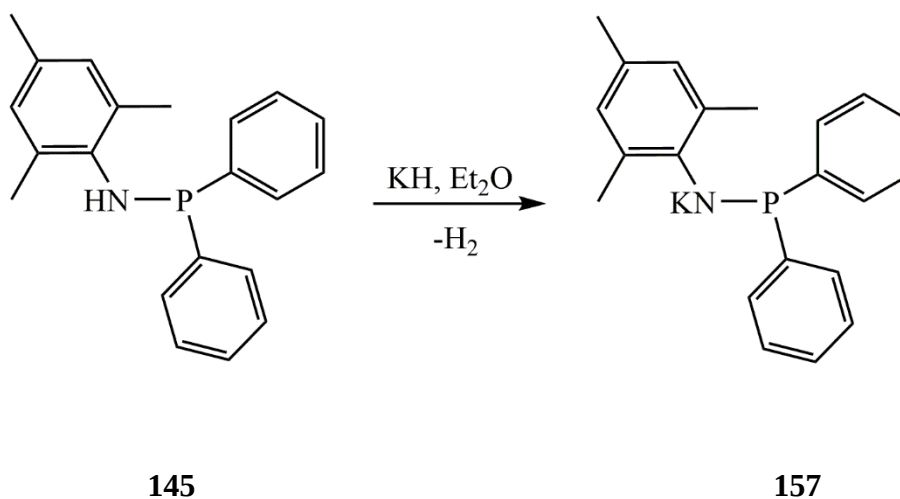
Fig. 37 – Structure of $[(P^iPr_2)TrippN\{\mu-Li\}NTripp(P^iPr_2)Li\{Et_2O\}_2]$ (**156**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) P(1)-N(1) 1.6829(12), N(1)-Li(1) 1.898(3), N(2)-Li(1) 1.923(3), P(2)-N(2) 1.6612(13), P(2)-Li(2) 2.538(3), O(1)-Li(2) 1.879(3) O(2)-Li(2) 1.949(3), C(1)-N(1)-P(1) 114.44(9), P(1)-N(1)-Li(1) 134.51(11), N(1)-Li(1)-N(2) 177.17(18), O(1)-Li(2)-P(2) 126.81(15).

The ^1H NMR spectrum of **156** exhibits a resonance at 6.67 ppm which corresponds to the CH groups of the Tripp substituent. Septets at 4.22, 2.68 and 1.47 ppm are assigned to the CH of the ^iPr groups. Resonances between 0.99 and 1.20 ppm are attributed to the five CH_3 groups of the ^iPr substituents. The $^{31}P\{^1H\}$ NMR spectrum of **156** exhibits a single resonance at 85.78 ppm, shifted downfield by 19.41 ppm compared to **150**. The $^7Li\{^1H\}$ NMR spectrum of **156** also exhibits a single peak at 0.49 ppm. Despite the two different phosphorus and lithium environments in the solid state the single resonances in their respective NMR spectra suggests that in solution this is

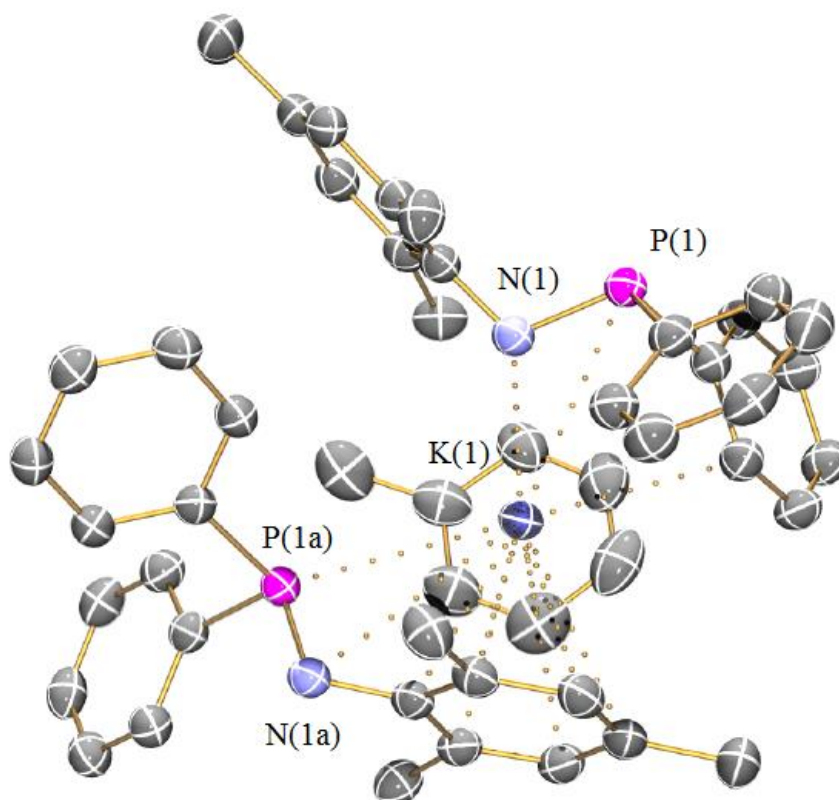
disrupted. As with complex **154** and **155**, **156** has no resonances in the ^1H NMR spectrum that can be assigned to Et_2O and it is assumed that any coordinated Et_2O was labile enough to be removed under vacuum when isolating the crystals.

In an attempt to isolate the potassium salt MesN(K)PPh_2 (**157**), **145** was treated with one equivalent of KH in Et_2O resulting in a white precipitate, which following work up, yielded the potassium salt $[\text{K}(\text{MesNPPH}_2)]$ (**157**) in 76% yield (**Scheme 32**). Single crystals of **157** suitable for an X-ray diffraction study were grown from toluene at room temperature over twenty four hours and the molecular structure is shown in **Fig. 38** with selected bond lengths and angles.



Scheme 32 - Synthesis of $[\text{K}(\text{MesNPPH}_2)]$ (**157**)

Complex **157** crystallised as an infinite polymeric chain in the space group C_2/c with a *trans* conformation about the P(1)-N(1) bond. The potassium cation is ligated by both the heteroatoms of the phosphinoamine as well as a toluene molecule. The softer potassium cation, in comparison to the harder lithium cation, results in more favourable arene interactions with the Mes substituent in the adjacent aminophosphide to form the polymeric chain. The P(1)-N(1) bond length of 1.6589(15) is comparable to the previously reported complexes. The ^1H NMR spectrum of **157** exhibits resonances in the range 7.02 to 7.62 ppm which is typical for the PPh_2 group. Resonances at 2.08, 2.20 and 6.56 ppm are attributed to the two CH_3 and one CH of the Mes group respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibits a single resonance at 45.36 ppm.



157

Fig. 38 - Structure of $[K(\text{MesNPPh}_2)].(\text{C}_7\text{H}_8)$ (**157**)

Thermal ellipsoids set at 40% probability, disorder components and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) P(1)-N(1) 1.6589(15), P(1)-C(10) 1.8515(18), P(1)-C(16) 1.8532(17), C(1)-N(1) 1.406(2), K(1)-P(1) 3.3978(6), K(1)-N(1) 2.7143(15), K(1)-C(26) 3.424(10), N(1)-P(1)-C(16) 102.96(8), N(1)-P(1)-C(10) 109.07(8), P(1)-N(1)-K(1) 114.02(7), C(1)-N(1)-K(1) 126.68(11), C(1)-N(1)-P(1) 113.38(11).

2.4 Concluding remarks

The novel phosphinoamines MesN(H)PPh₂ (**145**), TrippN(H)PPh₂ (**147**), DippN(H)PⁱPr₂ (**149**) and TrippN(H)PⁱPr₂ (**150**) have been successfully synthesised to accompany the previously reported phosphinoamines DippN(H)PPh₂ (**146**) and MesN(H)PⁱPr₂ (**148**). Compound **145** was structurally characterised by a single crystal X-ray diffraction study. All six phosphinoamines were successfully deprotonated using ⁿBuLi to afford the corresponding lithium derivatives. The three new lithium salts [Li(MesNPPh₂)(Et₂O)₂] (**151**), [Li(DippNPPh₂)(Et₂O)₂] (**152**) and [Li(TrippNPPh₂)(Et₂O)₂] (**153**) were all structurally characterised. Whilst the lithium phosphinoamide [{LiNMes(PⁱPr₂)(Et₂O)}₂] (**154**) has been previously reported by Thomas this is the first report of its solid state structure as authenticated by a single crystal X-ray diffraction study. Although crystals of “[LiNDipp(PⁱPr₂)]” (**155**) were too sensitive to allow for a single crystal X-ray diffraction study, all other analytical data supported its formation. A single crystal X-ray diffraction study on the lithium salt of **150** revealed an unusual structure with two different lithium centres, [(PⁱPr₂)TrippN{μ-Li}NTripp(PⁱPr₂)Li{Et₂O}₂] (**156**). Finally, treatment of **145** with KH resulted in the formation of [K(MesNPPh₂)] (**157**) which crystallised as an infinite polymeric chain. The N-P bond distances for **151** to **154**, **156** and **157** fall in the range of 1.6490(14) to 1.6829(12) Å and are consistent with the assumption of a resonance hybrid phosphinoamide/iminophosphide anion with some partial N-P bond character.

An *ab initio* molecular orbital study of the phosphinoamide/iminophosphide anion conducted by Ashby suggested that there is sufficient hyperconjugative bonding to enforce two ground-state conformations, *cis* and *trans*, with a calculated energy barrier for interconversion to be in the range of 7-32 kcal/mol, where the larger barriers are associated with derivatives with substituents that are relatively electron withdrawing.

⁶ Ashby concluded from detailed comparison of molecular structures that negative hyperconjugation does indeed influence the molecular structure of the phosphinoamide and the sterically unfavourable *cis* conformation about the N-P bond can be enforced as observed with **154**. Ashby also demonstrated that employing more sterically demanding substituents could promote the *trans* geometry. Although less common in

the literature the sterically encumbered nature of **151-153**, **156** and **157** results in them all adopting the *trans* geometry.

The Group one metal salts of phosphinoamides **151-157** offer a range of ligand transfer reagents with the potential to systematically alter the sterics and the electron donating properties of both the amide and the phosphine portions. This variety is vitally important when working with the actinides as their chemistry is often unexpected and unpredictable.

2.5 Experimental Information

General

All manipulations described in this thesis were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques, or an MBraun UniLab glovebox operating under an atmosphere of dry nitrogen with H₂O and O₂ < 0.1 ppm. All glassware was dried either by overnight storage in an oven at 150 °C or by flame-drying with subsequent cooling under 10⁻³ mm Hg vacuum followed by repeated alternate evacuation and purging with nitrogen. Oxygen-free nitrogen gas cylinders were supplied by BOC Gases UK. The solvents THF, diethyl ether, toluene, hexanes and pentane were dried by passage through activated alumina towers and degassed before use. 1,2-dimethoxyethane (DME) and benzene were distilled from potassium. Dichloromethane (DCM) was distilled calcium hydride. All solvents were stored over potassium mirrors except for DCM, and ethers which were stored over activated 4 Å sieves. Deuterated NMR solvents (d⁶-benzene, d⁸-toluene, d⁶-dimethylsiloxane) were purchased from Goss Scientific Ltd and were distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under nitrogen prior to use. Nujol was purchased from Sigma-Aldrich and used as received.

Preparation of MesN(H)PPh₂ (**145**)

A solution of 2,4,6-trimethylaniline (6.76 g, 50.0 mmol) in Et₂O (100 ml) was cooled to 0 °C. To this was added ⁿBuLi (22 ml, 2.5 M in hexanes, 55 mmol), the resulting solution was allowed to warm slowly to room temperature then heated to reflux (50 °C) for 30 minutes. The resulting slurry was added to a stirring solution of PPh₂Cl (11.03 g, 50 mmol) in Et₂O (100 ml) at -78 °C. The solution was allowed to warm slowly to room temperature and stirred for a further hour where upon the solution turned a pale yellow with a white precipitate. The reaction mixture was filtered away from the LiCl and the volatiles were removed in *vacuo* to leave **145** as an analytically pure, pale yellow solid. Colourless crystals of **145** suitable for a single crystal X-ray diffraction study were obtained from storage of a concentrated Et₂O solution at -30 °C for 72 hours. Yield: 13.73 g, 86 %. Anal. Calc'd for C₂₁H₂₂NP: C, 78.97; H, 6.94;

N, 4.39 %. Found: C, 78.99; H, 7.09; N, 4.28 %. ^1H NMR (C_6D_6 , 295 K): δ (ppm) 2.20 (6H, s, Mes- CH_3), 2.25 (3H, s, Mes- CH_3), 3.65 (1H, d, $J_{\text{PH}} = 8.0$ Hz, NH), 6.86 (2H, s, Ar-CH), 7.19 (6H, m, Ar-CH), 7.60 (4H, m, Ar-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 19.07 (d, $J_{\text{PC}} = 6.20$ Hz, Mes- CH_3), 20.53 (Mes- CH_3), 128.46 (d, $J_{\text{PC}} = 6.20$ Hz, Ar-CH), 128.74 (Ar-CH), 129.67 (Ar-CH), 130.70 (d, $J_{\text{PC}} = 3.40$ Hz, Ar-CH), 131.41 (Ar-C), 131.69 (Ar-C), 140.57 (d, $J_{\text{PC}} = 14.65$ Hz, Ar-C), 142.49 (d, $J_{\text{PC}} = 16.34$ Hz, Ar-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 36.07 (s). FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}) 516 (w), 556 (m), 566 (m), 581 (m), 619 (w), 695 (s), 740 (s), 852 (m), 936 (w), 961 (w), 1067 (m), 1157 (m), 1180 (m), 1220 (m), 1246 (m), 1304 (m), 1365 (m), 1412 (s), 1480 (m).

Preparation of TrippN(H)PPh₂ (147)

To a stirring solution of 2,4,6-triisopropylaniline (4.39 g, 20 mmol) and triethylamine (2.02 g 20 mmol) in DCM at 0 °C was added PPh₂Cl (4.41g 20 mmol). The reaction was allowed to warm slowly to room temperature and stirred for a further 3 hours and the volatiles were then removed *in vacuo*. The pale yellow solid was extracted into Et₂O filtered from the NEt₃HCl and volatiles removed *in vacuo* to leave **147** as a pale yellow solid. Yield: 7.82 g, 97 %. Anal. Calc'd for C₂₇H₃₄NP: C, 80.36; H, 8.49; N, 3.47 %. Found. ^1H NMR (C_6D_6 , 295 K): δ (ppm) 1.17 (12H, d, $J_{\text{HH}} = 8.0$ Hz, Tripp- CH_3), 1.24 (6H, d, $J_{\text{HH}} = 8.0$ Hz, Tripp- CH_3), 2.81 (1H, st, $J_{\text{HH}} = 8.0$ Hz, Tripp-CH), 3.24 (2H, m, Tripp-CH), 3.83 (1H, d, $J_{\text{PH}} = 12.0$ Hz, NH), 7.09 (2H, M, Ar-CH), 7.11 (4H, M, Ar-CH), 7.12 (2H, M, Ar-CH), 7.50 (4H, M, Ar-CH).. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 42.10 (s).).

Preparation of DippN(H)PⁱPr₂ (149)

A solution of 2,6-diisopropylaniline (1.77 g, 10.0 mmol) in hexanes (30 mL) was cooled to 0 °C. To this was added ⁿBuLi (4.4 mL, 2.5 M in hexanes, 11 mmol), the resulting solution was allowed to warm slowly to room temperature then stirred for 16 hours. The white precipitate was isolated *via* filtration and to the DippNHLi was added Et₂O (30 mL). The resulting slurry was added to a stirring solution of PⁱPr₂Cl (1.52 g, 10 mmol) in Et₂O (30 mL at -78 °C. The solution was allowed to warm slowly to room temperature and stirred for a further hour to afford a pale yellow solution and a white

precipitate. The reaction mixture was filtered away from the LiCl and the volatiles were removed *in vacuo* to give **149** as a pale yellow oil. Yield: 2.61 g, 89%. ^1H NMR (C_6D_6 , 295 K): δ (ppm) 1.01 (12H, m, $^i\text{Pr-CH}_3$), 1.29 (12H, d, $J_{\text{HH}} = 8.0$ Hz, $^i\text{Pr-CH}_3$), 1.61 (2H, m, $^i\text{Pr-CH}$), 3.54 (1H, d, $J_{\text{PH}} = 8.0$ Hz, NH), 3.66 (2H, m, $^i\text{Pr-CH}$), 7.01-7.14 (3H, m, Ar-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 17.17 (d, $J_{\text{PC}} = 10.0$ Hz, $^i\text{Pr-CH}_3$), 18.62 (d, $J_{\text{PC}} = 16.0$ Hz $^i\text{Pr-CH}_3$), 23.82 ($^i\text{Pr-CH}$), 28.10 ($^i\text{Pr-CH}$), 122.45 (Ar-CH), 123.90 (Ar-CH), 139.58 (Ar-C), 141.3 (d, $J_{\text{PC}} = 7.0$ Hz (Ar-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 67.14 (s).

Preparation of TrippN(H)P ^{i} Pr $_2$ (**150**)

A solution of 2,4,6-triisopropylaniline (2.19 g, 10.0 mmol) in hexanes (30 mL) was cooled to 0 °C. To this was added $n\text{BuLi}$ (4.4 mL, 2.5 M in hexanes, 11 mmol), the resulting solution was allowed to warm slowly to room temperature then stirred for 16 hours. The white precipitate was isolated *via* filtration and to the TrippNHLi was added Et_2O (30 mL). The resulting slurry was added to a stirring solution of $\text{P}^i\text{Pr}_2\text{Cl}$ (1.52 g, 10 mmol) in Et_2O (30 mL at -78 °C. The solution was allowed to warm slowly to room temperature and stirred for a further hour to afford a pale yellow solution and a white precipitate. The reaction mixture was filtered away from the LiCl and the volatiles were removed *in vacuo* to give **150** as a pale yellow oil. Yield: 3.11 g, 92%. ^1H NMR (C_6D_6 , 295 K): δ (ppm) 1.00-1.06 (12H, m, $^i\text{pr-CH}_3$), 1.26 (6H, d, $J_{\text{HH}} = 6.0$ Hz, $^i\text{pr-CH}_3$), 1.34 (12H, d, $J_{\text{HH}} = 9.0$ Hz, $^i\text{pr-CH}_3$), 1.62 (2H, m, $^i\text{pr-CH}$), 2.83 (1H, m, $^i\text{pr-CH}$), 3.44 (1H, d, $J_{\text{PH}} = 6.0$ Hz, NH), 3.69 (2H, m, $^i\text{pr-CH}$) 7.11 (2H, s, Ar-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 17.30 (d, $J_{\text{PC}} = 42.0$ Hz, $^i\text{Pr-CH}_3$), 18.61 (d, $J_{\text{PC}} = 66.0$ Hz, $^i\text{Pr-CH}_3$) 23.96 ($^i\text{Pr-CH}_3$), 24.32 ($^i\text{Pr-CH}_3$), 27.94 ($^i\text{Pr-CH}$), 28.18 ($^i\text{Pr-CH}$), 28.24 ($^i\text{Pr-CH}$), 34.17 ($^i\text{Pr-CH}$), 121.61 (Ar-CH), 139.04 (Ar-C), 139.70 (Ar-C), 142.19 (Ar-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 66.37 (s).

Preparation of [Li(MesNPPPh₂)(Et₂O)₂] (**151**)

A solution of MesN(H)PPh₂ (7.25 g, 22.7 mmol) in Et₂O (75 ml) was cooled to -78 °C. To this was added ⁿBuLi (10 ml, 2.5 M in hexanes, 25 mmol). The resulting yellow solution was allowed to warm slowly to room temperature and stirred for 3 hours. The reaction mixture was concentrated *in vacuo* and cooled to -30 °C to afford **151** as a colourless crystalline solid. Colourless crystals of **151** suitable for a single crystal X-ray diffraction study were obtained from storage of a concentrated Et₂O solution at -30 °C for 72 hours. Yield: 9.34 g, 79 %. Anal. Calc'd for C₂₉H₄₁LiNO₂P: C, 73.55; H, 8.73; N, 2.96 %. Found: C, 73.68; H, 8.65; N, 3.04 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) 0.78 (12H, t, J_{HH} = 8.0 Hz, Et₂O-CH₃), 2.22 (6H, s, Mes-CH₃), 2.33 (3H, s, Mes-CH₃), 3.00 (8H, q, J_{HH} = 8.0 Hz, Et₂O-CH₂), 6.95 (2H, s, Ar-CH), 7.13 (2H, m, Ar-CH), 7.21 (4H, m, Ar-CH), 7.81 (4H, m, Ar-CH). ¹³C{¹H} NMR (C₆D₆, 295 K): δ (ppm), 13.95 (Et₂O-CH₃), 20.52 (Mes-CH₃), 21.34 (d, J_{PC} = 3.35 Hz, Mes-CH₃), 65.08 (Et₂O-CH₂), 128.18 (Ar-CH), 128.6 (d, J_{PC} = 6.70 Hz, Ar-CH), 129.73 (Ar-CH), 132.2 (Ar-CH), 132.4 (Ar-C), 133.4 (d, J_{PC} = 6.20 Hz, Ar-CH), 146.9 (d, J_{PC} = 22.3 Hz, Ar-CH), 152.8 (Ar-C). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 45.03 (s). ⁷Li{¹H} NMR (C₆D₆, 295 K): δ (ppm) 1.13 (s). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 535 (w), 578 (w), 614 (w), 625 (w), 698 (m), 739 (m), 749 (m), 856 (m), 924 (m), 965 (m), 1069 (m), 1090 (s), 1159 (m), 1230 (s), 1298 (m), 1414 (m), 1432 (m), 1501 (m).

Preparation of [Li(DippNPPPh₂)(Et₂O)₂] (**152**)

A solution of DippN(H)PPh₂ (7.18 g, 19.9 mmol) in Et₂O (75 mL) was cooled to -78 °C. To this was added ⁿBuLi (9 mL, 2.5 M in hexanes, 22 mmol). The resulting yellow solution was allowed to warm slowly to room temperature and stirred for 3 hours. The reaction mixture was concentrated *in vacuo* and cooled to -30 °C to afford **152** as a colourless crystalline solid. Colourless crystals of **152** suitable for a single crystal X-ray diffraction study were obtained from storage of a concentrated Et₂O solution at -30 °C for 72 hours. Yield: 7.38 g, 72 %. Anal. Calc'd for C₃₂H₄₇LiNO₂P: C, 74.54; H, 9.19; N, 2.72 %. Found: C, 74.38; H, 9.21; N, 2.76 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) 0.98 (12H, t, J_{HH} = 8.0 Hz, Et₂O-CH₃), 1.16 (12H, m, ⁱpr-CH₃), 3.18 (8H, q, J_{HH} = 8.0 Hz, Et₂O-CH₂), 3.95 (2H, m, ⁱpr-CH), 7.12 (1H, m, Ar-CH), 7.25 (8H, m,

Ar-CH), 7.78 (4H, m, Ar-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 12.92 ($\text{Et}_2\text{O}-\text{CH}_3$), 22.58 ($^i\text{Pr}-\text{CH}_3$), 25.53 ($^i\text{Pr}-\text{CH}$), 63.53 ($\text{Et}_2\text{O}-\text{CH}_2$), 115.41 (Ar-CH), 120.25 (Ar-CH), 123.79 (Ar-CH), 125.11 (Ar-CH), 129.38 (Ar-CH), 142.41 (Ar-C), 150.91 (Ar-C), 154.69 (Ar-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 43.54 (br, s). ^7Li NMR (C_6D_6 , 295 K): δ (ppm) 1.17 (s). FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}). 511 (m), 554 (w), 599 (w), 736 (m), 747 (m), 782 (m), 820 (w), 1000 (w), 1026 (w), 1052 (w), 1091 (m), 1149 (w), 1194 (m), 1238 (m), 1311 (m), 1421 (m), 1433 (m), 1585 (w).

Preparation of **[Li(TrippNPPH₂)(Et₂O)₂] (153)**

A solution of TrippN(H)PPh₂ (7.48 g, 18.5 mmol) in Et₂O (75 mL) was cooled to -78 °C. To this was added ⁿBuLi (8.5 mL, 2.5 M in hexanes, 21 mmol). The resulting yellow solution was allowed to warm slowly to room temperature and stirred for 3 hours. The reaction mixture was concentrated in *vacuo* and cooled to -30 °C to afford **153** as a colourless crystalline solution. Colourless crystals of **153** suitable for a single crystal X-ray diffraction study were obtained from storage of a concentrated Et₂O solution at -30 °C for 72 hours. Yield: 7.01 g, 68 %. Anal. Calc'd for C₃₅H₅₃LiNO₂P: C, 75.37; H, 9.58; N, 2.51 %. Found: C, 75.14; H, 9.38; N, 2.42 %. ^1H NMR (C_6D_6 , 295 K): δ (ppm) 1.07 (12H, t, $J_{\text{HH}} = 8.0$ Hz, $\text{Et}_2\text{O}-\text{CH}_3$), 1.29 (12H, m, $^i\text{Pr}-\text{CH}_3$), 1.31 (6H, m, $^i\text{Pr}-\text{CH}_3$), 2.87 (1H, m, $^i\text{Pr}-\text{CH}$), 3.24 (8H, q, $J_{\text{HH}} = 8.0$ Hz, $^i\text{Pr}-\text{CH}_2$), 4.08 (2H, m, $^i\text{Pr}-\text{CH}$), 7.00 (2H, s, Ar-CH), 7.15 (4H, m, Ar-CH), 7.17 (2H, m, Ar-CH), 7.71 (4H, m, Ar-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 22.63 ($^i\text{Pr}-\text{CH}_3$), 25.29 ($^i\text{Pr}-\text{CH}$), 32.22 ($^i\text{Pr}-\text{CH}$), 117.98 (Ar-CH), 123.67 (Ar-CH), 125.03 (Ar-CH), 129.40 (Ar-CH), 135.06 (Ar-C), 142.08 (Ar-C), 151.23 (Ar-C), 152.38 (Ar-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 61.83 (s). ^7Li NMR (C_6D_6 , 295 K): δ (ppm) 0.78 (s). FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}). 797 (m), 841 (w), 876 (w), 924 (w), 950 (m), 1032 (w), 1051 (m), 1065 (w), 1102 (w), 1116 (w), 1174 (m), 1211 (m), 1301 (m), 1322 (w), 1358 (w), 1435 (m).

Preparation of [$\text{LiNMes}(\text{P}^i\text{Pr}_2)(\text{Et}_2\text{O})$] $_2$ (**154**)

A solution of $\text{MesN}(\text{H})\text{P}^i\text{Pr}_2$ (7.53 g, 30.0 mmol) in Et_2O (75 ml) was cooled to -78°C . To this was added $^n\text{BuLi}$ (13.2 ml, 2.5 M in hexanes, 33 mmol). The resulting yellow solution was allowed to warm slowly to room temperature and stirred for 3 hours. The reaction mixture was concentrated in *vacuo* and cooled to -30°C to afford **154** as a colourless crystalline solid. Colourless crystals of **154** suitable for a single crystal X-ray diffraction study were obtained from storage of a concentrated Et_2O solution at -30°C for 72 hours. Yield: 7.75 g, 78 %. Anal. Calc'd for $\text{C}_{15}\text{H}_{25}\text{LiNP}$: C, 70.03; H, 9.79; N, 5.44 %. Found: C, 70.08; H, 9.91; N, 5.58 %. ^1H NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 0.91 (6H, m, $^i\text{Pr-CH}_3$), 1.10 (6H, m, $^i\text{Pr-CH}_3$), 1.42 (2H, m, $^i\text{Pr-CH}$), 2.06 (3H, s, Mes-CH_3), 2.32 (6H, s, Mes-CH_3), 6.52 (3H, s, Ar-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 16.21 (d, $J_{\text{PC}} = 11.0$ Hz, $^i\text{Pr-CH}_3$), 17.33 (d, $J_{\text{PC}} = 19.0$ Hz, $^i\text{Pr-CH}_3$), 17.95 (Mes- CH_3), 19.73 (d, $J_{\text{PC}} = 11.0$ Hz, Mes- CH_3), 27.54 (d, $J_{\text{PC}} = 22.0$ Hz, $^i\text{Pr-CH}$), 119.71 (Ar- CH), 126.8 (Ar-C), 128.58 (Ar-C), 155.83 (Ar-C). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 73.29 (s). ^7Li NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) -1.40 (s). FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}) 447 (w), 564 (s), 611 (m), 660 (m), 782 (s), 857 (m), 906 (s), 956 (m), 1007 (m), 1155 (s), 1223 (s), 1289 (s), 1414 (m), 1605 (w).

Preparation of “[$\text{LiNDipp}(\text{P}^i\text{Pr}_2)$]” (**155**)

A solution of $\text{DippN}(\text{H})\text{P}^i\text{Pr}_2$ (2.21 g, 7.5 mmol) in Et_2O (75 mL) was cooled to -78°C . To this was added $^n\text{BuLi}$ (3.3 mL, 2.5 M in hexanes, 8.3 mmol). The resulting yellow solution was allowed to warm slowly to room temperature and stirred for 3 hours. The reaction mixture was concentrated in *vacuo* and cooled to -30°C to afford **155** as a colourless crystalline solid. All attempts at a single crystal X-ray diffraction study resulted in decomposition during preparation of sample. Yield: 2.26 g, 81 %. Anal. Calc'd for $\text{C}_{18}\text{H}_{31}\text{LiNP}$: C, 72.22; H, 10.44; N, 4.68%. Found: C, 72.12; H, 10.32; N, 4.58 %. ^1H NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 0.98 (6H, m, $^i\text{Pr-CH}_3$), 1.11 (18H, m, $^i\text{Pr-CH}_3$), 1.48 (2H, sp $^2J_{\text{H}} = 8.0$ Hz, $^i\text{Pr-CH}$), 4.20 (2H, m, $^i\text{Pr-CH}$), 6.42 (1H, t, $^2J_{\text{H}} = 8.0$ Hz, Ar- CH), 6.75 (2H, d, $^2J_{\text{H}} = 8.0$ Hz, Ar- CH). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 16.52 (d, $J_{\text{PC}} = 13.0$ Hz, $^i\text{Pr-CH}_3$), 17.14 (d, $J_{\text{PC}} = 19.0$ Hz, $^i\text{Pr-CH}_3$), 24.64 (d, $J_{\text{PC}} = 8.0$ Hz, $^i\text{Pr-CH}$), 27.49 (d, $J_{\text{PC}} = 23.0$ Hz, $^i\text{Pr-CH}$), 113.53 (Ar- CH), 120.74 (Ar- CH), 140.54 (d, $J_{\text{PC}} = 4.0$ Hz, Ar-C), 155.26 (d, $J_{\text{PC}} = 13.0$ Hz Ar-C).

$^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 84.69 (s). ^7Li NMR ($\text{D}_8\text{-THF}$), 295 K): δ (ppm) -1.50 (s). FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}) 553 (w), 589 (w), 617 (w), 656 (w), 693 (w), 790 (m), 817 (m), 879 (w), 917 (m), 1041 (w), 1101 (w), 1143 (w), 1185 (w), 1233 (w), 1309 (m), 1421 (m).

Preparation of $[(\text{P}^i\text{Pr}_2)\text{TrippN}\{\mu\text{-Li}\}\text{NTripp}(\text{P}^i\text{Pr}_2)\text{Li}\{\text{Et}_2\text{O}\}_2]$ (**156**)

A solution of $\text{TrippN}(\text{H})\text{P}^i\text{Pr}_2$ (2.52 g, 7.5 mmol) in Et_2O (75 mL) was cooled to -78°C . To this was added $^n\text{BuLi}$ (3.3 mL, 2.5 M in hexanes, 8.3 mmol). The resulting yellow solution was allowed to warm slowly to room temperature and stirred for 3 hours. The reaction mixture was concentrated in *vacuo* and cooled to -30°C to afford **156** as a colourless crystalline solid. Colourless crystals of $[(\text{P}^i\text{Pr}_2)\text{TrippN}\{\mu\text{-Li}\}\text{NTripp}(\text{P}^i\text{Pr}_2)\text{Li}\{\text{Et}_2\text{O}\}_2]$ suitable for a single crystal X-ray diffraction study were obtained from storage of a concentrated Et_2O solution at -30°C for 72 hours. Yield: 2.26 g, 88%. Anal. Calc'd for $\text{C}_{18}\text{H}_{31}\text{LiNP}$: C, 73.87; H, 10.92; N, 4.10 %. Found: C, 74.25; H, 11.02; N, 4.45 %. ^1H NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 0.99 (6H, m, $^i\text{Pr-CH}_3$), 1.06-1.20 (24H, m, $^i\text{Pr-CH}_3$), 1.47 (2H, sp, $^2J_{\text{H}} = 6.0$ Hz, $^i\text{Pr-CH}$) 2.68 (1H, sp, $^2J_{\text{H}} = 6.0$ Hz, $^i\text{Pr-CH}$), 4.22 (2H, m, $^i\text{Pr-CH}$), 6.67 (2H, s, Ar-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 18.61 ($^i\text{Pr-CH}_3$), 19.09 ($^i\text{Pr-CH}_3$), 26.51 ($^i\text{Pr-CH}$), 29.46 ($^i\text{Pr-CH}$), 33.88 ($^i\text{Pr-CH}$) 120.35 (Ar-CH), 134.85 (Ar-C), 142.16 (Ar-C), 154.66 (Ar-C). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 85.78 (s). ^7Li NMR ($\text{D}_8\text{-THF}$), 295 K): δ (ppm) 0.49 (s). FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}) 700 (m), 736 (m), 843 (w), 878 (w), 912 (w), 927 (w), 1088 (m), 1176 (m), 1211 (m), 1305 (w), 1434 (m).

Preparation of $[\text{KMesN}(\text{PPh}_2)]$ (**157**)

To a stirring mixture of $\text{MesN}(\text{H})\text{PPh}_2$ (3.20 g, 10 mmol) and KH (0.40 g, 10 mmol) at -78°C was added Et_2O (40 mL). The reaction mixture was allowed to warm slowly to room temperature and stirred for 12 hours. Volatiles were removed in *vacuo* and the resulting colourless solid was extracted into toluene to afford **157** as a colourless crystalline solid. Colourless crystals of **157** suitable for a single crystal X-ray

diffraction study were obtained from storage of a concentrated toluene solution at -30°C for 72 hours. Yield: 2.71 g, 76 %. Anal. Calc'd for $\text{C}_{21}\text{H}_{21}\text{KNP}$ C, 70.56; H, 5.92; N, 3.92 %. Found: C, 70.43; H, 5.82; N, 3.91 %. ^1H NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 2.08 (3H, s, Mes- CH_3), 2.20 (6H, s, Mes- CH_3), 6.56 (2H, s, Ar- CH), 7.02 (2H, m, Ar- CH), 7.14 (4H, m, Ar- CH), 7.62 (4H, t, $^2J_{\text{H}} = 4.0$ Hz, Ar- CH). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 19.90 (Mes- CH_3), 20.54 (Mes- CH_3), 125.07 (Ar- CH), 126.74 (d, JPC = 5.0 Hz (Ar- CH), 127.94 (Ar- CH), 128.30 (Ar- CH), 128.71 (Ar-C), 130.41 (Ar-C), 130.6 (Ar- CH), 137.47 (Ar-C). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 295 K): δ (ppm) 45.36 (s). FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}). 701 (w), 739 (w), 767 (m), 862 (m), 902 (w), 961 (m), 1082 (m), 1150 (m), 1239 (w), 1295 (m), 1413 (m).

2.6 References

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Chapter three

Tris(phosphinoamide) Actinide(IV) Halide Complexes

Contents

3.1	Background	109
3.2	Tris(phosphinoamide) Uranium Chlorides	112
3.3	Tris(phosphinoamide) Uranium Iodides	127
3.4	Tris(phosphinoamide) Thorium Chlorides	133
3.5	Tris(phosphinoamide) Thorium Iodides	137
3.6	Experimental	141
3.7	References	143

3.1 Background

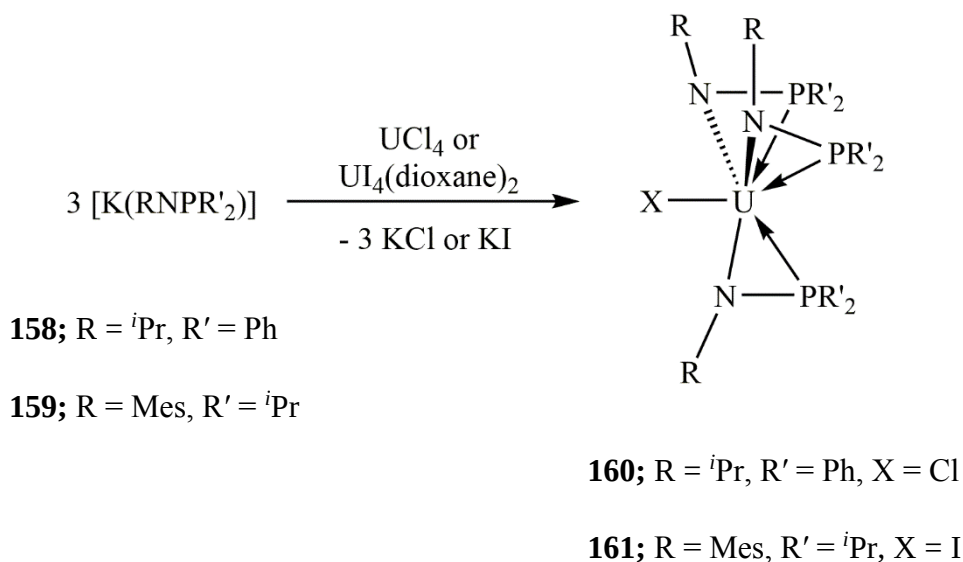
As outlined in chapter one the next step towards the preparation of metal-metal linkages is the formation of tris(phosphinoamide) actinide halide ‘metalloligand’ complexes. Nagashima first identified the potential of $[\text{TiCl}_2(\text{RNPPH}_2)_2]$ ($\text{R} = \text{'Bu}$, **40**; 'Pr **41**) to act as a metalloligand towards the formation of heterobimetallic complexes. Complexes **40** and **41** resonate as singlets in their $^{31}\text{P}\{^1\text{H}\}$, and are shifted upfield compared to the resonances observed for the respective free pro-ligands indicating coordination of the phosphorus to the metal centre in solution as observed in the solid state. The coordination of the titanium centre by the RNPPH_2^- ligands makes the two phenyl groups appear inequivalent but in solution the signal assigned to the phenyl groups are suggestive of magnetically equivalent phenyl groups. Broadening of the ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ resonances at low temperature suggested that whilst the phosphines are unequivocally bound to the titanium centre in the solid state and at low temperature, reversible phosphine dissociation occurs in solution at room temperature. This dynamic behaviour led to the conclusion that **40** and **41** would be viable precursors for heterobimetallic complexes.¹

Nagashima also synthesised the tris(phosphinoamide) zirconium complexes $[\text{ZrCl}(\text{RNPPH}_2)_3]$ ($\text{R} = \text{'Bu}$, **51**; 'Pr **52**) as tripodal metalloligands. As with **40** and **41**, solid state structures of **51** and **52** showed that the three phosphorus atoms were coordinated to the zirconium centre, whereas variable temperature NMR studies indicated a reversible coordination/dissociation process in solution.² It was proposed that in an analogous methodology to the synthesis of **51** and **52** reaction of the ligand transfer reagents **151-157** ($[\text{Li}(\text{MesNPPH}_2)(\text{Et}_2\text{O})_2]$ (**151**), $[\text{Li}(\text{DippNPPH}_2)(\text{Et}_2\text{O})_2]$ (**152**) and $[\text{Li}(\text{TrippNPPH}_2)(\text{Et}_2\text{O})_2]$ (**153**) $[\{\text{LiNMes}(\text{P}^i\text{Pr}_2)(\text{Et}_2\text{O})\}_2]$ (**154**) “ $[\text{LiNDipp}(\text{P}^i\text{Pr}_2)]$ ” (**155**) $[(\text{P}^i\text{Pr}_2)\text{TrippN}\{\mu\text{-Li}\}\text{NTripp}(\text{P}^i\text{Pr}_2)\text{Li}\{\text{Et}_2\text{O}\}_2]$ (**156**) and $[\text{K}(\text{MesNPPH}_2)]$ (**157**)) with the appropriate actinide(IV) halide starting materials, in a 3:1 ratio would result in the synthesis of the desired tris(phosphinoamide) actinide(IV) halide complexes.

At the outset of this work, actinide phosphinoamide chemistry was unknown. However, Thomas has recently reported a series of tris(phosphinoamide) supported uranium-cobalt heterobimetallic complexes featuring dative U-Co interactions.³

Whilst this work was conducted simultaneously there is very little overlap in results, and accordingly it would be prudent to discuss these results here.

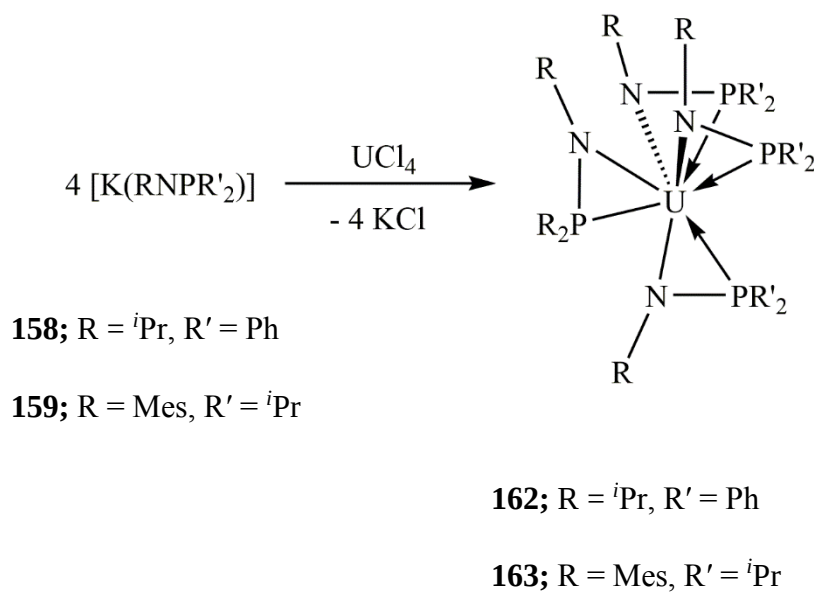
The reaction of three equivalents of the potassium salts $[K(^i\text{PrNPPh}_2)]$ (**158**) and $[K(\text{MesNP}^i\text{Pr}_2)]$ (**159**) with either UCl_4 or $[\text{UI}_4(1,4\text{-dioxane})_2]$ respectively, resulted in the formation of the tris(phosphinoamide) uranium halide complexes $[\text{UCl}(^i\text{PrNPPh}_2)_3]$ (**160**) and $[\text{UI}(\text{MesNP}^i\text{Pr}_2)_3]$ (**161**) (**Scheme 33**). Analysis of **160** and **161** by ^1H NMR spectroscopy revealed broad, paramagnetically shifted resonances indicative of C_3 -symmetric uranium species in solution. A single crystal X-ray diffraction study on **161** revealed a seven coordinate uranium centre with a distorted capped trigonal antiprismatic geometry.



Scheme 33 – Synthesis of $[\text{UCl}(^i\text{PrNPPh}_2)_3]$ (**160**) and $[\text{UI}(\text{MesNP}^i\text{Pr}_2)_3]$ (**161**)

Addition of four equivalents of **158** and **159** to a THF solution of UCl_4 resulted in the synthesis of the homoleptic uranium tetra(phosphinoamide) species $[\text{U}(^i\text{PrNPPh}_2)_4]$ (**162**) and $[\text{U}(\text{MesNP}^i\text{Pr}_2)_4]$ (**163**) (**Scheme 34**). These complexes were characterised by ^1H NMR spectroscopy which revealed paramagnetically broadened and shifted resonances with equivalent phosphinoamide ligands in solution. A single crystal X-ray diffraction study on **162** revealed the eight-coordinate uranium(IV) tetra(phosphinoamide) complex in a distorted square antiprismatic geometry with a C_2

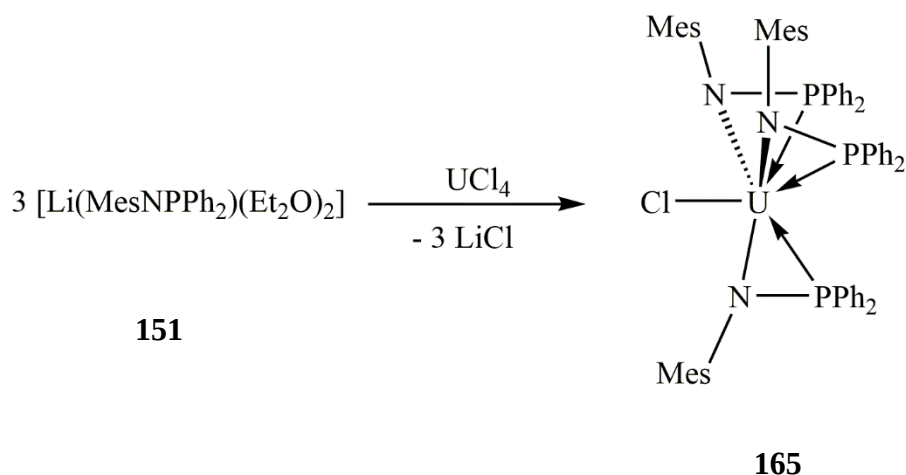
rotation axis. The uranium-nitrogen distances of 2.316(6) and 2.322(6) Å are comparable to those in the homoleptic uranium(IV) amides found in the literature whilst the uranium phosphine distances of 2.8882(16) and 2.9195(16) Å are shorter than those previously reported.⁴⁻⁶ This was attributed to coordinative unsaturation of the U(IV) centre as well as the η^2 -coordination imposed by the phosphinoamide framework.



Scheme 34 – Synthesis of $[\text{U}(\textit{i}\text{PrNPPH}_2)_4]$ (**162**) and $[\text{U}(\text{MesNP}^i\text{Pr}_2)_4]$ (**163**)

3.2 Tris(phosphinoamide) Uranium Chlorides

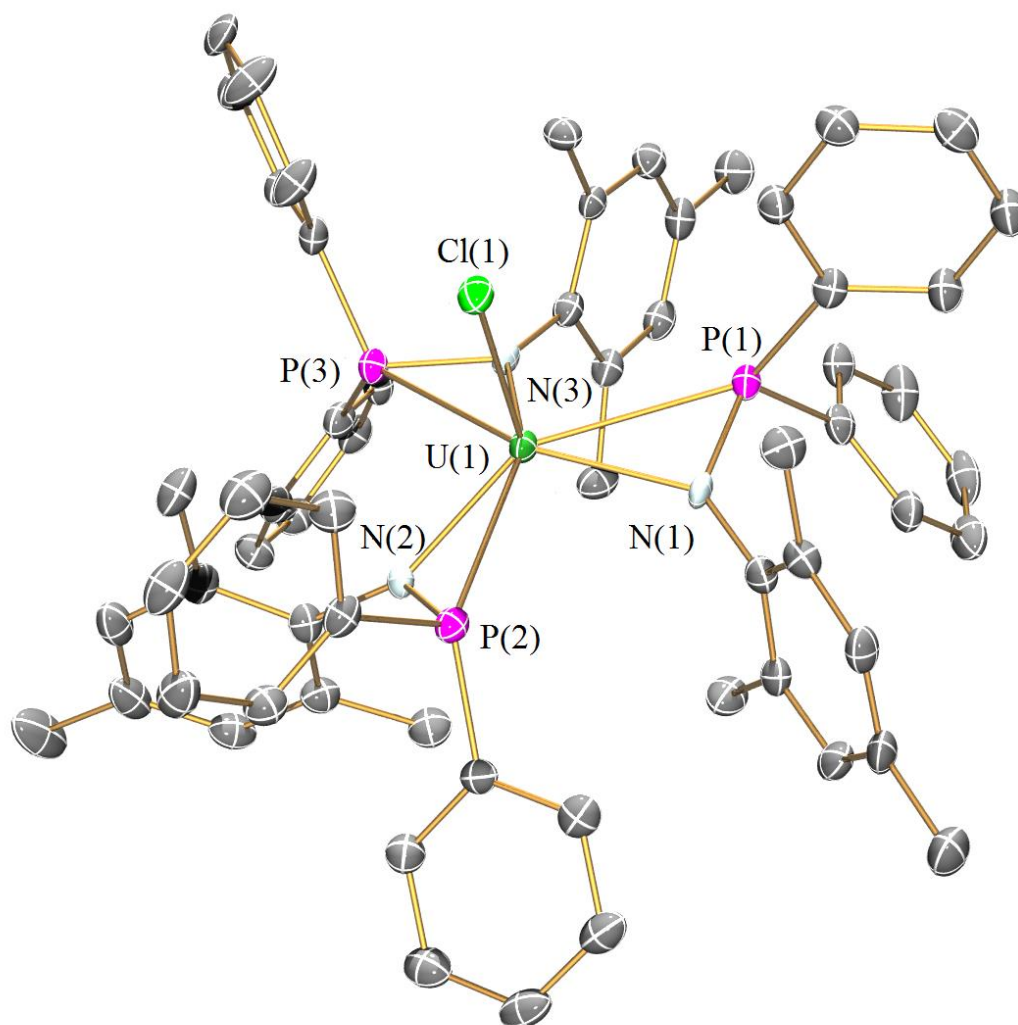
Treatment of uranium tetrachloride with three molar equivalents of $[\text{Li}(\text{MesNPPh}_2)(\text{Et}_2\text{O})_2]$ (**151**) in THF afforded a brown solution. Following work-up and recrystallisation, light brown crystals of $[\text{UCl}(\text{MesNPPh}_2)_3]$ (**165**) were isolated in 66% yield (**Scheme 35**)



Scheme 35 – Synthesis of $[\text{UCl}(\text{MesNPPh}_2)_3]$ (**165**)

The analytical data are consistent with the proposed formulation with the ^1H NMR spectrum exhibiting paramagnetically broadened and shifted resonances in the range +12 to –12 ppm and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra revealing one resonance at 1973 ppm. These are consistent with the uranium(IV) formulation and an averaged C_{3v} symmetry on the NMR timescale. Also consistent with the uranium(IV) formulation is the effective magnetic moment of $2.38 \mu_{\text{B}}$ in benzene solution at 298 K; although this value is lower than the theoretical magnetic moment of $3.58 \mu_{\text{B}}$ for $^3\text{H}_4$ uranium(IV) it is consistent with typical uranium(IV) effective magnetic moments.⁷⁻¹⁰ The molecular structure of **165** was determined by a single crystal X-ray diffraction study and is illustrated in **Fig. 38**. Complex **165** crystallises as a discrete monomeric species in the space group $P2_1/n$ with two toluene solvent molecules in the crystal lattice per uranium centre. Each phosphinoamide ligand coordinates in a bidentate manner, to afford a 7-coordinate uranium centre that adopts a distorted capped trigonal antiprismatic geometry analogous to **161**. The U-N bond distances of 2.256(4), 2.261(4) and

2.287(3) Å are typical of uranium(IV)-amide distances and are almost identical to the U-N distances found in **161**.¹¹ The U-P distances of 2.8786(11), 2.9334(12) and 2.9486(11) Å are comparable to the U-P distances of **161** and to those typically observed in η^5 -phospholide-uranium complexes (2.93 Å).¹²



165

Fig. 38 - Structure of $[UCl(MesNPPPh_2)_3]$ (**165**)

Thermal ellipsoids set at 40% probability. Solvent molecules and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) U(1)-N(1) 2.256(4), U(1)-N(2) 2.261(4), U(1)-N(3) 2.287(3), U(1)-P(1) 2.8786(11), U(1)-P(2) 2.9334(12), U(1)-P(3) 2.9486(11), P(1)-N(1) 1.693(4), U(1)-Cl(1) 2.5967(11), N(1)-U(1)-P(1) 34.87(10), N(1)-U(1)-Cl(1) 103.00(10), Cl(1)-U(1)-P(1) 94.69(3).

Confirmation of the uranium(IV) assignment was sought *via* variable temperature SQUID magnetometry. The results of the variable temperature SQUID magnetometry for **165** dispersed in eicosane are shown in **Fig. 39** as a plot of μ_{eff} versus temperature over the range 300 to 1.8 K. The magnetic moment at 300 K was found to be $2.62 \mu_{\text{B}}$ which is within the range for reported uranium(IV) complexes.⁷⁻¹⁰ The value of μ_{eff} decreases smoothly as the temperature is lowered from 300 K to ~ 30 K, where it begins to decrease more sharply and at 1.8 K the magnetic moment is $0.53 \mu_{\text{B}}$. The magnetisation trace tends to 0 at this temperature, which is consistent with a $5f^2$ configuration and the presence of $^3\text{H}_4$ uranium(IV).

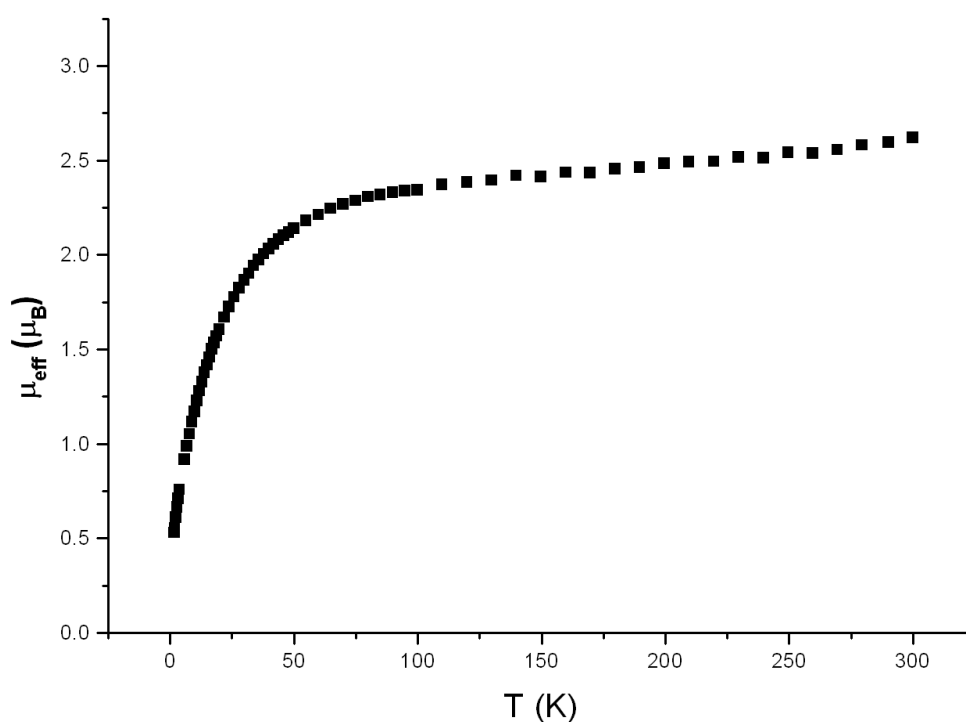
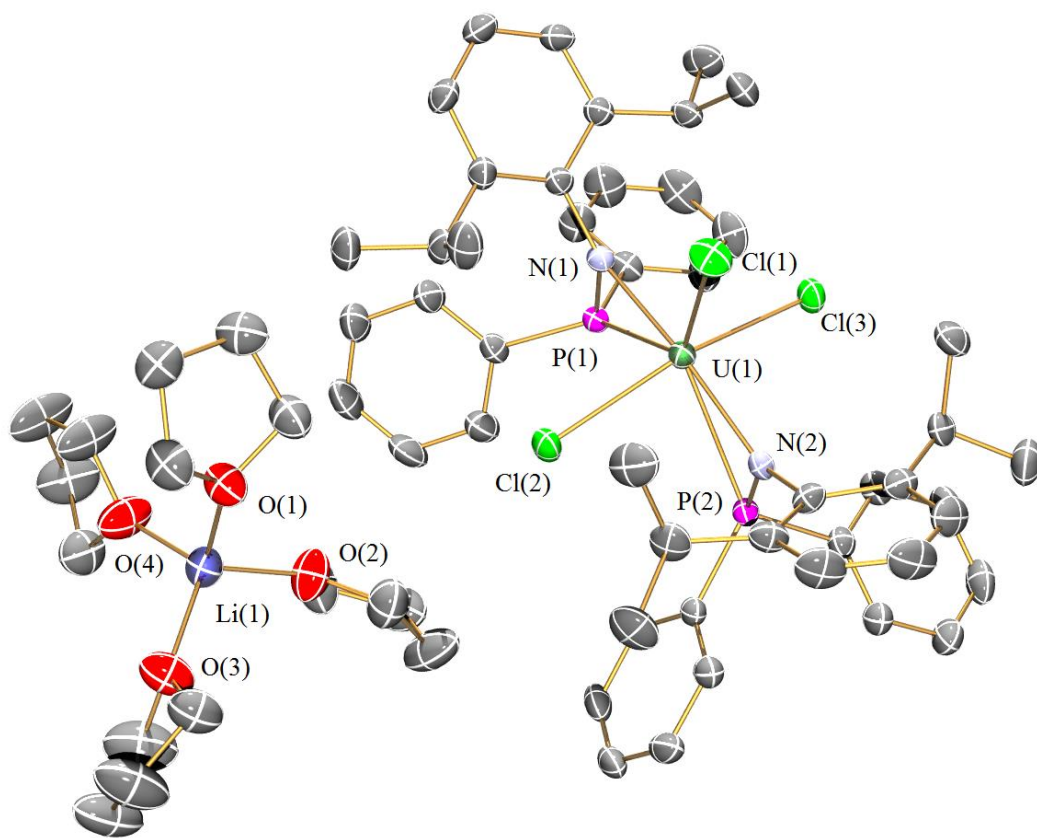


Fig. 39 - Plot of μ_{eff} (μ_{B}) versus temperature (K) for **165**

bond distance of 2.310(3) Å is slightly longer, by approximately 0.4 Å, than the average U-N bond distances in **161** and **165**, but still unexceptional for a uranium-amide bond length,¹¹ this can be attributed to the bulkier nature of the Dipp group and because **161** and **165** are neutral complexes. The U-P bond lengths of 2.841(2) and 2.840(1) Å are slightly shorter than those observed in **161** and **165** (by ~0.05 Å) and are a potential result of the coordinative unsaturation of U(IV) as well as the η^2 -coordination imposed by the phosphinoamide framework. The [Li(THF)₄]⁺ cation is unexceptional in terms of its structural features.



166

Fig. 40 – Structure of [UCl₃(DippNPPh₂)₂][Li(THF)₄] (**166**)

Thermal ellipsoids set at 40% probability. Lattice solvent molecules, minor disorder components and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) U(1)-N(1) 2.307(3), U(1)-P(1) 2.8408(7), U(1)-Cl(1) 2.6237(8), P(1)-N(1) 1.682(3), O(1)-Li(1) 1.922(6), N(1)-U(1)-Cl(1) 93.20(8), Cl(1)-U(1)-P(1) 129.34(2), O(1)-Li(1)-O(2) 107.2(3).

The ^1H NMR spectrum of **166** exhibits broad resonances in the range of -43.58 to +21.69 ppm. Variable-temperature SQUID measurements were used to confirm the uranium(IV) assignment. The results of the variable temperature SQUID magnetometry for **166** dispersed in eicosane are shown in **Fig. 41** as a plot of μ_{eff} (μ_{B}) versus temperature over the range 300 to 1.8 K. The effective magnetic moment of the solid sample of **166** at 300 K was found to be $1.95 \mu_{\text{B}}$. The value of μ_{eff} decreases smoothly as the temperature is lowered from 300 K to ~ 30 K, where it begins to decrease more sharply and at 1.8 K the effective magnetic moment is $0.46 \mu_{\text{B}}$. The magnetisation trace tends to 0 at this temperature, which is consistent with a $5f^2$ configuration and the presence of $^3\text{H}_4$ uranium(IV). This lower than expected magnetic moment of **166** suggests that the orbital angular momentum contribution to the magnetic moment at 300 K at the uranium centre may be partially suppressed due to its charged formation.¹³ This is closely comparable to previous work published by the Liddle group where the lower than expected magnetic moment for $[\text{U}(\text{Tren}^{\text{TMS}})(\text{THF})_2][\text{BPh}_4]$ was attributed to its cationic nature.¹⁴

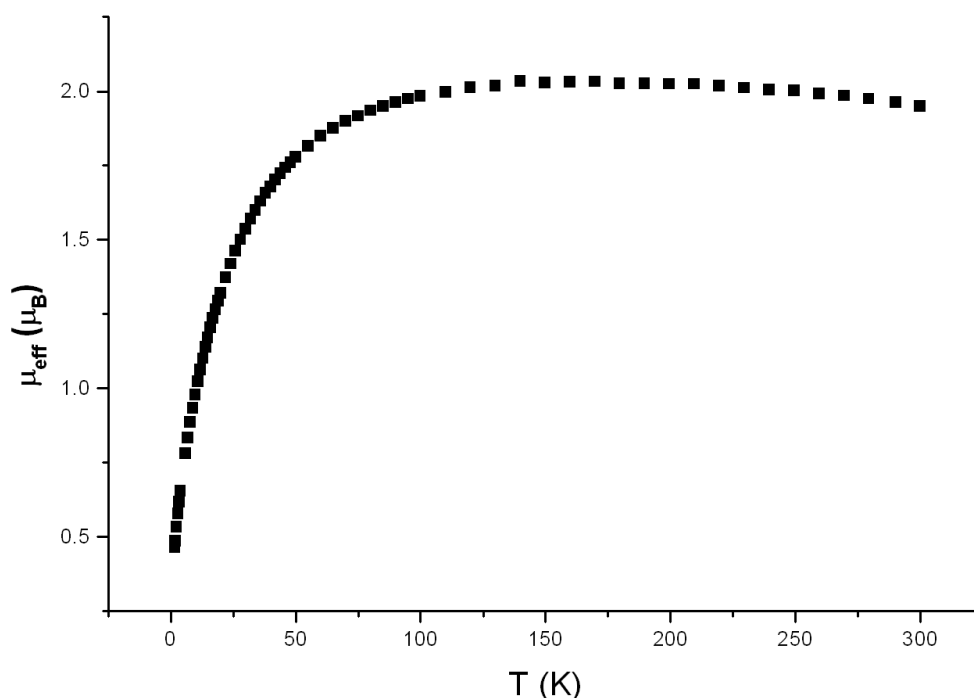
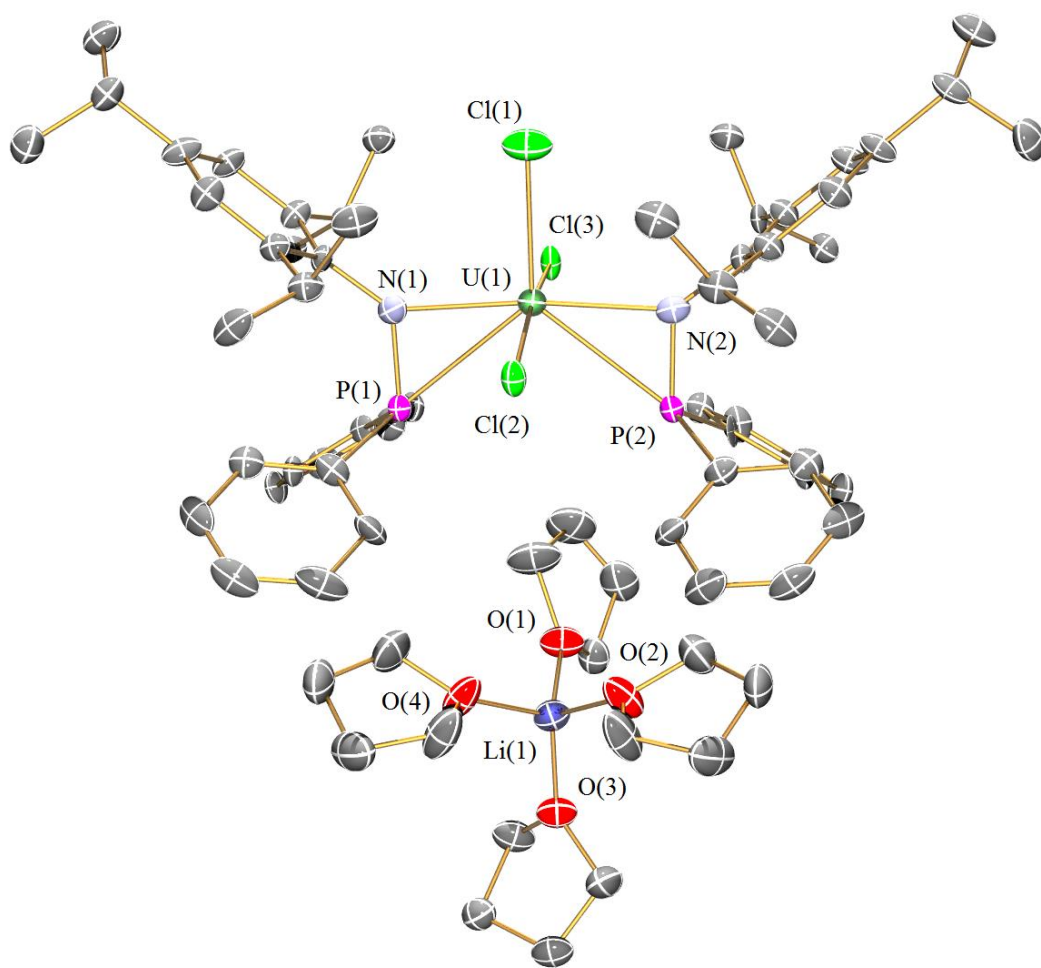


Fig. 41 - Plot of μ_{eff} (μ_{B}) versus temperature (K) for **166**

Analogously to complex **166**, the attempted synthesis of “[UCl(TrippNPPh₂)₃]” resulted in the isolation of the solvent separated ion pair [UCl₃(TrippNPPh₂)₂][Li(THF)₄] (**167**) (**Scheme 36**). A single crystal X-ray diffraction study was carried out on a brown crystal of **167** and the molecular structure of **167** is illustrated in **Fig. 42**. A complete discussion of the metrical data acquired for **167** is meaningless due to the poor quality of the data but the overall structure is unambiguous.



167

Fig. 42 – Structure of [UCl₃(TrippNPPh₂)₂][Li(THF)₄] (**167**)

Thermal ellipsoids set at 40% probability. Lattice solvent molecules, minor disorder components and H atoms omitted for clarity.

Complex **167** crystallises as a solvent separated ion pair in the space group $P2_1/n$. Each phosphinoamide ligand coordinates in a bidentate manner, whilst three chloride atoms complete the coordination sphere to afford a 7-coordinate uranium centre that adopts a distorted trigonal prismatic, square face monocapped geometry analogous to **166**. The lithium cation is coordinated by four THF molecules in a tetrahedral geometry.

Similarly to **166** the ^1H NMR spectrum of **167** exhibits broad resonances in the range of -43.11 to +21.72 ppm. Variable-temperature SQUID measurements were used to confirm the uranium(IV) assignment. The results of the variable temperature SQUID magnetometry for **167** dispersed in eicosane are shown in **Fig. 43** as a plot of μ_{eff} (μ_{B}) versus temperature over the range 300 to 1.8 K. The effective magnetic moment of the solid sample of **167** at 300 K was found to be $1.95 \mu_{\text{B}}$. The value of μ_{eff} decreases smoothly as the temperature is lowered from 300 K to ~ 30 K, where it begins to decrease more sharply and at 1.8 K the effective magnetic moment is $0.51 \mu_{\text{B}}$. The magnetisation trace tends to 0 at this temperature, which is consistent with a $5f^2$ configuration and the presence of $^3\text{H}_4$ uranium(IV). Like for complex **166**, complex **167** exhibits a lower than expected effective magnetic moment which suggests that the orbital angular momentum contribution to the magnetic moment at 300 K at the uranium centre may also be partially suppressed by its charged nature.

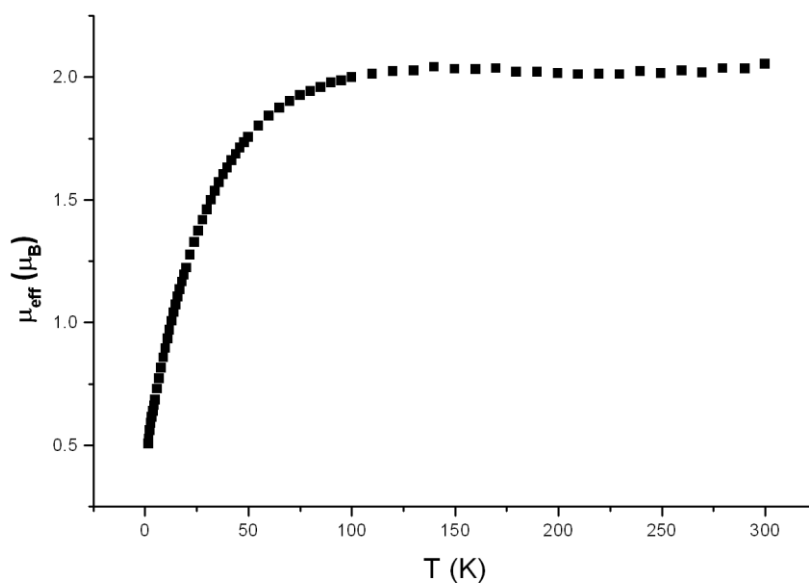
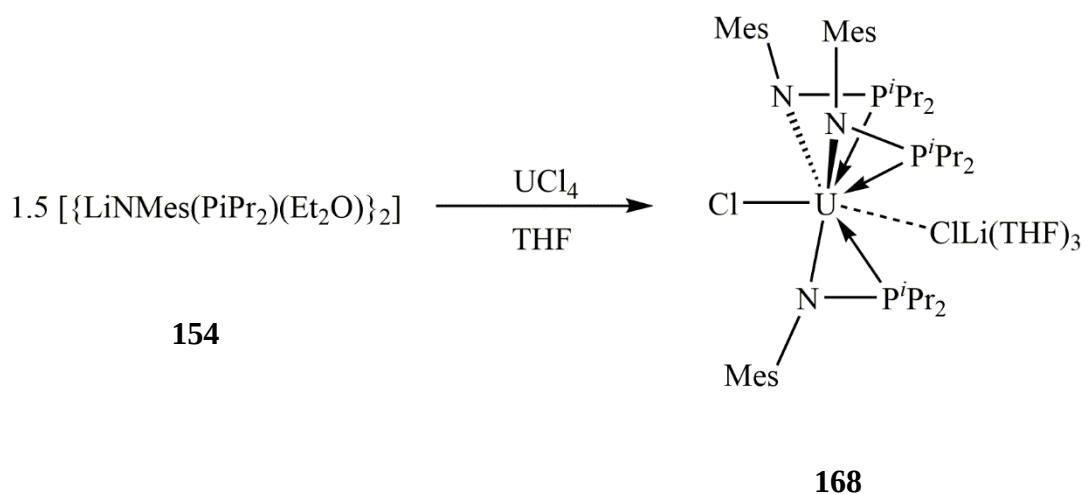


Fig. 43 - Plot of μ_{eff} (μ_{B}) versus temperature (K) for **167**

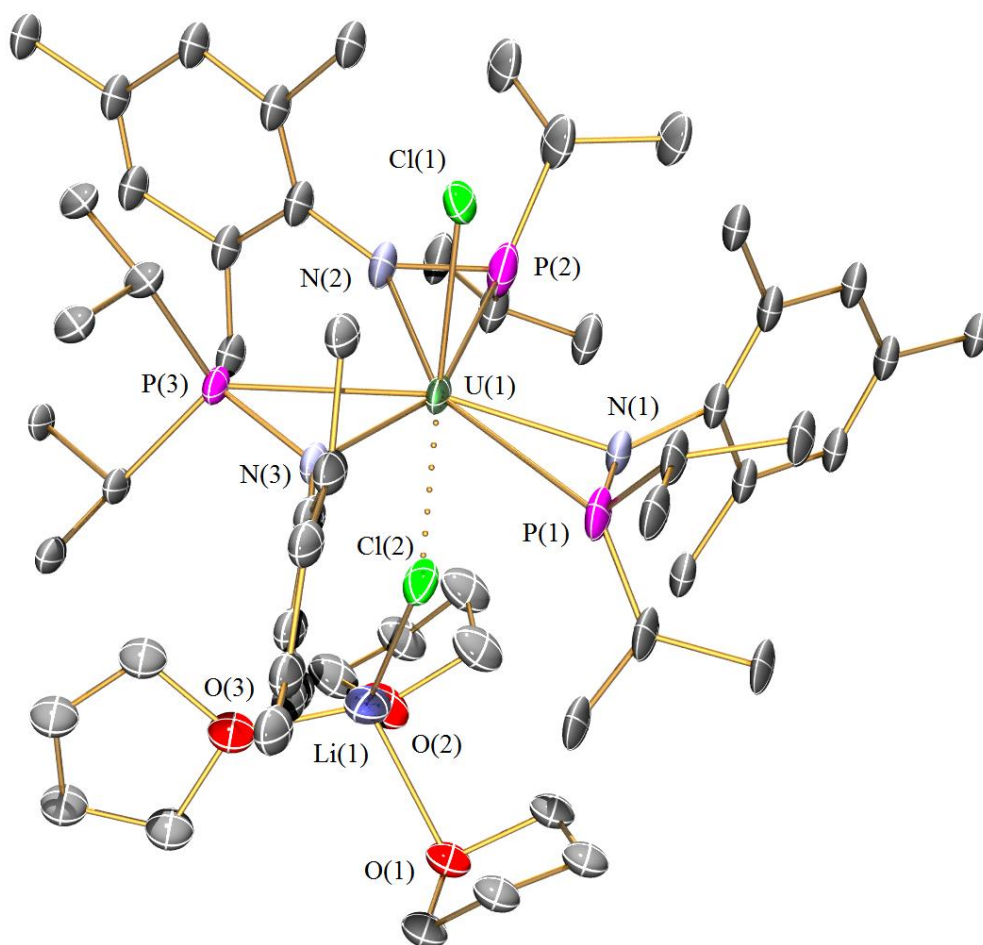
To allow for systematic modification of the electron donating capacity of the phosphine whilst keeping the amido portions constant the diisopropyl-phosphine analogues were targeted.



Scheme 37 – Synthesis of $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_3(\mu\text{-Cl})\text{Li}(\text{THF})_3]$ (**168**)

One and a half equivalents of dimeric [$\{\text{LiNMes}(\text{P}^i\text{Pr}_2)(\text{Et}_2\text{O})\}_2$] (**154**) were reacted with UCl_4 at room temperature in THF to give, after work up and crystallisation a light green crystalline solid in 56 % yield (**Scheme 37**). A single crystal X-ray diffraction study was performed which revealed the product to be $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_3(\mu\text{-Cl})\text{Li}(\text{THF})_3]$ (**168**). The molecular structure of **168** is illustrated in **Fig. 44** and although a complete discussion of the metrical data acquired for **168** is meaningless due to the poor quality of the data the overall structure is beyond doubt.

Complex **168** crystallises as a discrete monomeric species in the space group $C2$ with one THF solvent molecule per uranium in the crystal lattice. U(1) is coordinated by three phosphinoamide ligands each through nitrogen and phosphorus centres in a bidentate manner. Two Cl centres, one of which forms part of the $\{\text{LiCl}(\text{THF})_3\}$ moiety, complete the coordination sphere of the eight coordinate uranium centre which adopts what can be best described as a distorted hexagonal bipyramidal geometry. The Li(1) centre adopts a distorted tetrahedral geometry.



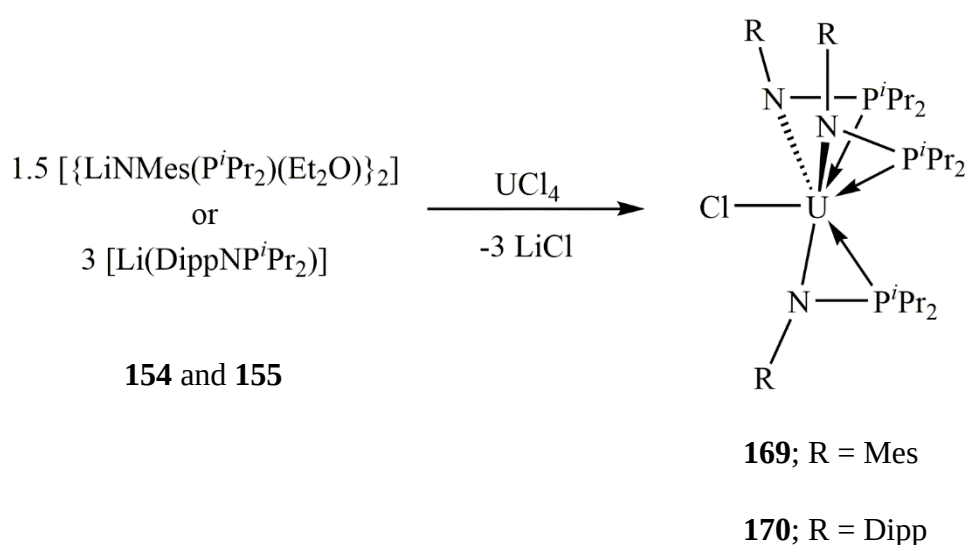
168

Fig. 44 – Structure of $[UCl(MesNP^iPr_2)_3(\mu-Cl)Li(THF)_3]$ (**168**)

Thermal ellipsoids set at 40% probability. Solvent molecules, disorder components and H atoms omitted for clarity.

Extraction of complex **168** in toluene led to the extrusion and precipitation of the labile LiCl resulting in the isolation of pale brown crystals of $[UCl(MesNP^iPr_2)_3]$ (**169**) (**Scheme 38**). Crystals of **169** isolated thus far have proven unsuitable for single crystal X-ray diffraction to confirm the proposed structure. The ^1H NMR spectrum of **169** exhibits six broad resonances in the range of +13 to -5 ppm and the $^{31}P\{^1H\}$ NMR spectra reveal a singlet resonance at 1949 ppm. Like for **165**, the NMR spectra of **169**

are consistent with an averaged C_{3v} symmetry on the NMR timescale and with the uranium(IV) formulation. The ^1H NMR data are consistent with the proposed formulation. The Evans method effective magnetic moment of a solution of **169** in benzene at 298 K was found to be $2.27 \mu_B$ which is within the range for reported uranium(IV) complexes.⁷⁻¹⁰ The proposed structure of **169** was also confirmed by elemental microanalysis.



Scheme 38 – Synthesis of $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**169**) and $[\text{UCl}(\text{DippNP}^i\text{Pr}_2)_3]$ (**170**)

Confirmation of the uranium(IV) assignment was sought via variable temperature squid magnetometry. The results of the variable temperature squid magnetometry for **169** dispersed in eicosane are shown in **Fig. 45** as a plot of $\mu_{\text{eff}} (\mu_B)$ versus temperature over the range 300 to 1.8 K. The magnetic moment at 300 K was found to be $2.78 \mu_B$ which is within the range for reported uranium(IV) complexes.⁷⁻¹⁰ The value of μ_{eff} decreases smoothly as the temperature is lowered from 300 K to ~ 30 K, where it begins to decrease more sharply and at 1.8 K the magnetic moment is $0.54 \mu_B$. The magnetisation trace tends to 0 at this temperature, which is consistent with an f^2 configuration and the presence of $^3\text{H}_4$ uranium(IV).

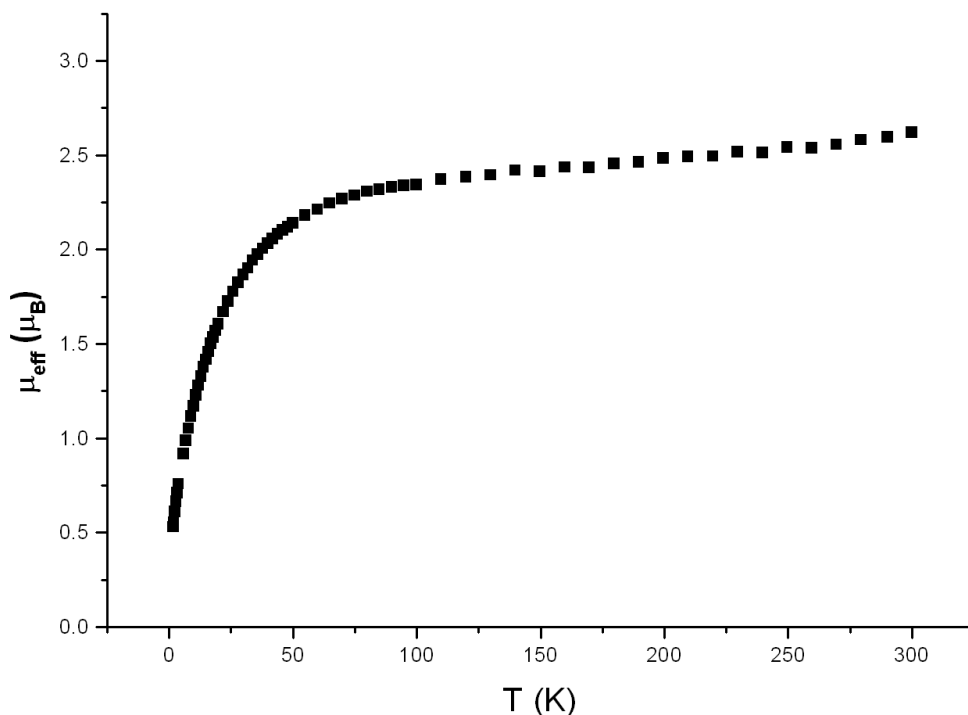
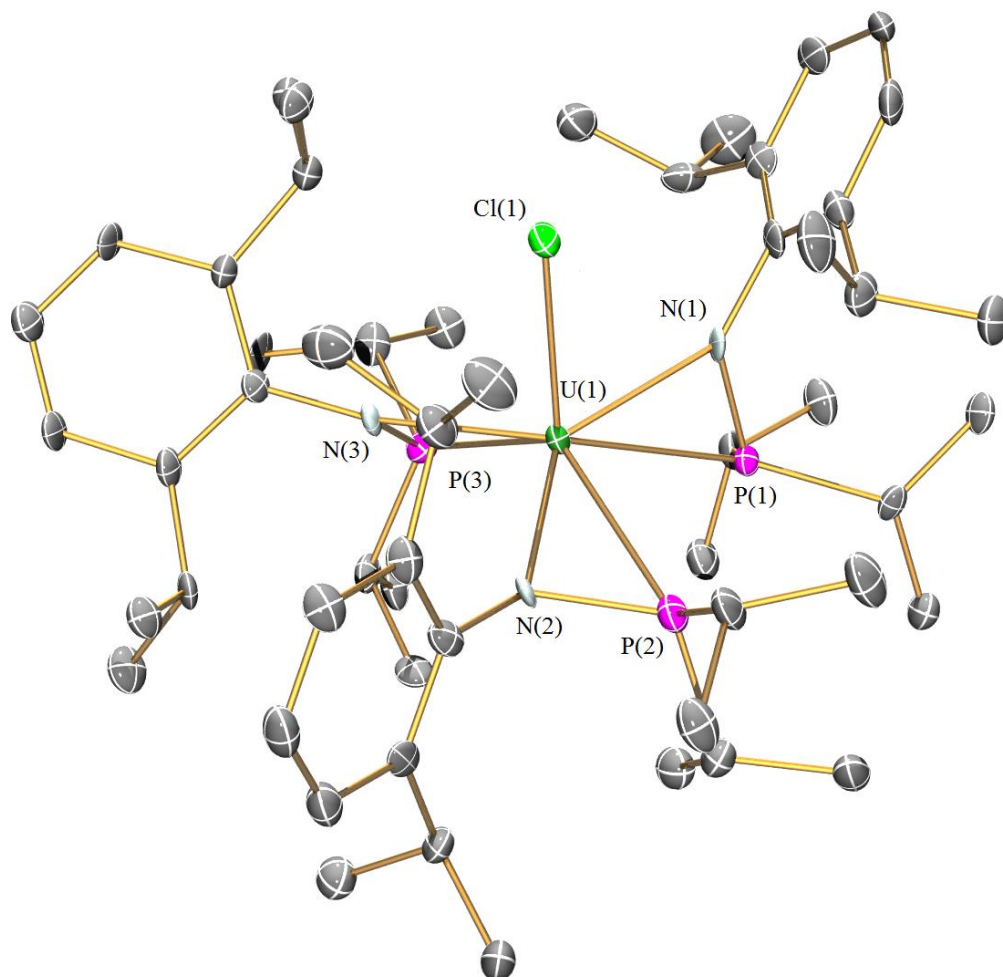


Fig. 45 - Plot of μ_{eff} (μ_B) versus temperature (K) for **169**

Whilst the encumbered nature of the (DippNPPH₂)[−] and (TrippNPPH₂)[−] phosphinoamide ligands resulted in the isolation of the solvent separated ion pair complexes **166** and **167** and not the desired tris(phosphinoamide)uranium chloride complexes, it was envisaged that the decreased steric nature of the diisopropylphosphine group would potentially result in the addition of three phosphinoamide ligands to the coordination sphere of uranium.

Indeed, three molar equivalents of [Li(DippNPⁱPr₂)] (**155**) reacted with UCl₄ at room temperature in THF to give, after work up and crystallisation from n-hexanes light brown crystals of [UCl(DippNPⁱPr₂)₃] (**170**) (**Scheme 38**) in 49 % yield. Whilst the ¹H NMR spectrum for **170** features resonances that are far more broad than the spectra observed for **165** and **169** these data are still supportive of a uranium(IV) formulation and an averaged C_{3v} symmetry on the NMR time scale in solution. Also consistent with the uranium(IV) formulation is the room temperature effective magnetic moment in benzene solution of 2.59 μ_B , although this is once again lower than the theoretical magnetic moment of 3.58 μ_B for ³H₄ uranium(IV) but still comparable to typical uranium(IV) complexes and to **165** and **169**.⁷⁻¹⁰



170

Fig. 46 – Structure of $[UCl(DippNP^iPr_2)_3]$ (**170**)

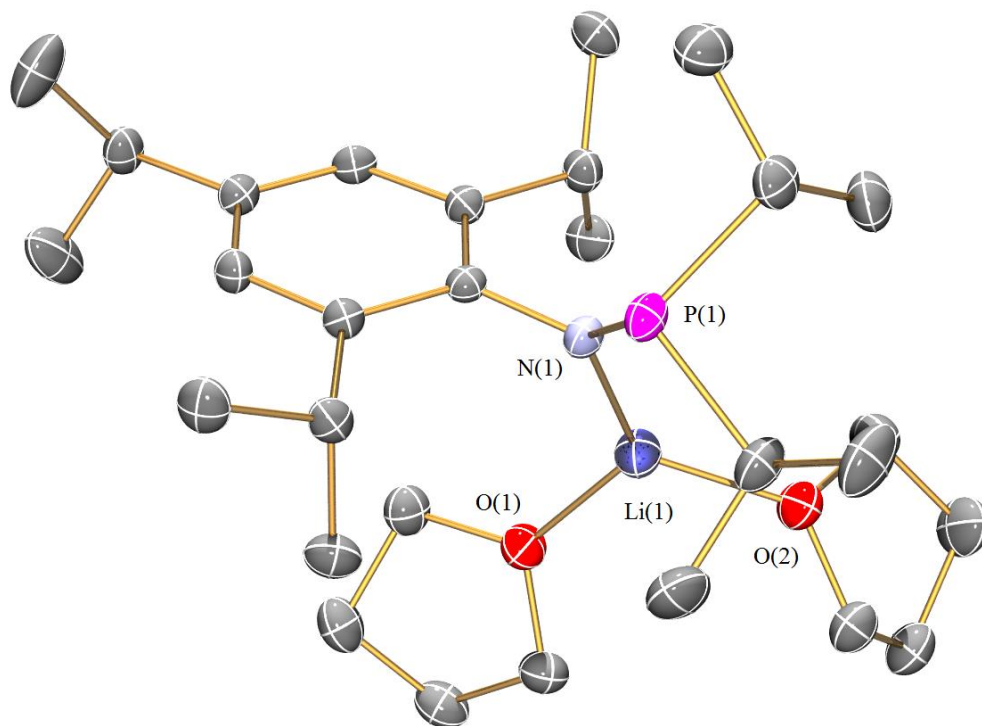
Thermal ellipsoids set at 40% probability. Solvent molecules and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) U(1)-N(1) 2.378(8), U(1)-P(1) 2.859(3), P(1)-N(1) 1.688(8), U(1)-Cl(1) 2.589(3), N(1)-U(1)-P(1) 36.1(2), N(1)-U(1)-Cl(1) 109.2(2), Cl(1)-U(1)-P(1) 112.66(9).

The molecular structure of **170** was determined by a single crystal X-ray diffraction study and is illustrated in **Fig. 46** with selected bond lengths and angles. Complex **170** crystallises as a discrete monomeric species in the space group $P2_1/n$. As for complexes **161** and **165**, each phosphinoamide ligand coordinates in a bidentate manner, to afford a 7-coordinate uranium centre that adopts a distorted capped trigonal antiprismatic geometry.³ Although this geometry is analogous to both **161** and **165** the increased steric nature of the *Dipp* group has resulted in a greater distortion of the capped trigonal antiprismatic geometry and in the solid state there is no longer a 3-

fold axis of symmetry along the U-Cl bond vector. The U-N bond distances of 2.359(8), 2.360(8) and 2.378(8) Å are on average *ca.* 0.1 Å longer than found in **161** and **165** (average ~0.1 Å), this can be once again attributed to the steric demands of the *Dipp* group versus *Mes*. The U-N bond lengths are still however comparable to typical uranium(IV)-amide distances.¹¹ The U-P distances of 2.839(3), 2.857(3) and 2.859(3) are slightly shorter than those found in **165** but are more closely comparable to **161** as a result of the greater electron donating capacity of the diisopropyl versus diphenyl of the substituents.³

In an attempt to isolate the tris(phosphinoamide) uranium chloride complex [UCl(TrippNP^{*i*}Pr₂)₃] (**171**) treatment of three molar equivalents of “[LiNDipp(P^{*i*}Pr₂)]” (**155**) with uranium tetrachloride resulted in a largely intractable mixture of products except for a small crop of [Li(TrippNP^{*i*}Pr₂)(THF)₂] (**172**). The molecular structure of **172** was determined by a single crystal X-ray diffraction study and is illustrated in **Fig. 47** with selected bond lengths and angles.

Complex **172** crystallises as a discrete monomeric species in the space group *P2₁2₁2₁*. As with complexes **151-153**, complex **172** exhibits a *trans* confirmation of substituents about the N(1)-P(1) bond. In contrast to the structure of [(P^{*i*}Pr₂)TrippN{μ-Li}NTripp(P^{*i*}Pr₂)Li{Et₂O}₂] (**156**) and all other structurally characterised phosphinoamide complexes containing a diisopropylphosphine fragment, **172** is not a dinuclear in a solid state; this is presumably a result of the solvent effects of THF compared to Et₂O. The N(1)-P(1) bond distance of 1.6782(14) Å is comparable to the N-P bond distances observed in the previously reported complexes **151-156** and is suggestive of partial N-P double bond character. The lithium cation is ligated by the phosphinoamide through the N(1) and analogously to **151-153** there appears to be no Li-P interaction as is often observed for *cis*-lithium phosphinoamides. The coordination sphere of the lithium is completed by two THF ligands and adopts a distorted trigonal planar geometry [sum of angles at Li = 359.92(50)°] which is typical for a 3-coordinate lithium centre. The Li(1)-O(1) and Li(1)-O(2) distances of 1.934(3) Å and 1.956(3) Å are unexceptional.



172

Fig. 46 – Structure of $[\text{Li}(\text{TrippNP}^i\text{Pr}_2)(\text{THF})_2]$ (**172**)

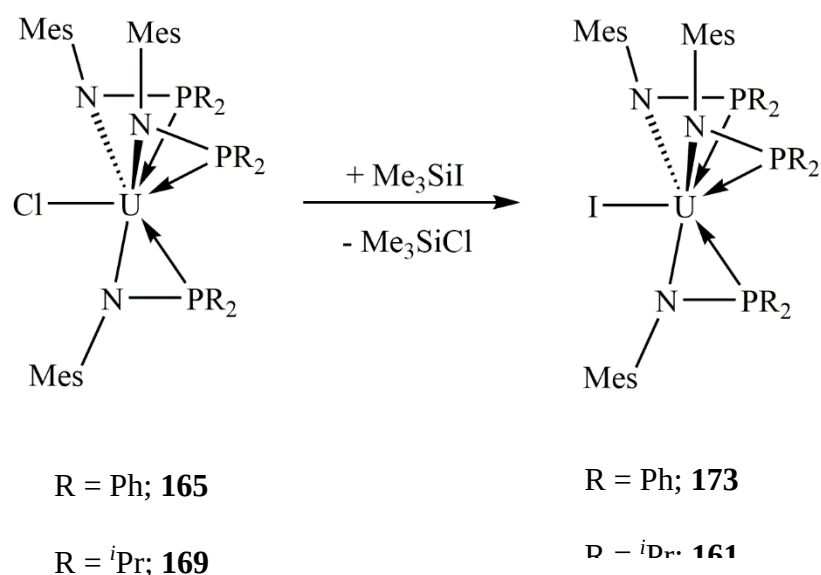
Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$) P(1)-N(1) 1.6782(14), P(1)-C(16) 1.8664(18), P(1)-C(19) 1.890(2), N(1)-C(1) 1.406(2), N(1)-Li(1) 1.918(3), N(1)-P(1)-C(16) 102.22(5), N(1)-P(1)-C(16) 99.61(8), C(1)-N(1)-P(1) 121.70(11), C(1)-N(1)-Li(1) 110.03(14), P(1)-N(1)-Li(1) 127.03(12).

The NMR and IR spectroscopic data for **172** is identical to that for **156** suggesting that in hydrocarbon solutions they are likely to adopt the same lithium phosphinoamide formulation of type “[Li(TrippNPⁱPr₂)]”, with accompanying decoordination of THF from **172**. The isolation of unreacted lithium phosphinoamide is suggestive of, but not conclusive proof, that the steric demands of the phosphinoamide (TrippNPⁱPr₂)[−] are too large to allow for the coordination of three ligands to the uranium centre and only two equivalents of the ligand transfer reagent have reacted with the uranium centre. With no uranium complexes isolated the product distribution is poorly defined, this is due to likely decomposition of product upon warming the solution to room temperature, this arises from extreme steric congestion and kinetic barrier to reactivity.

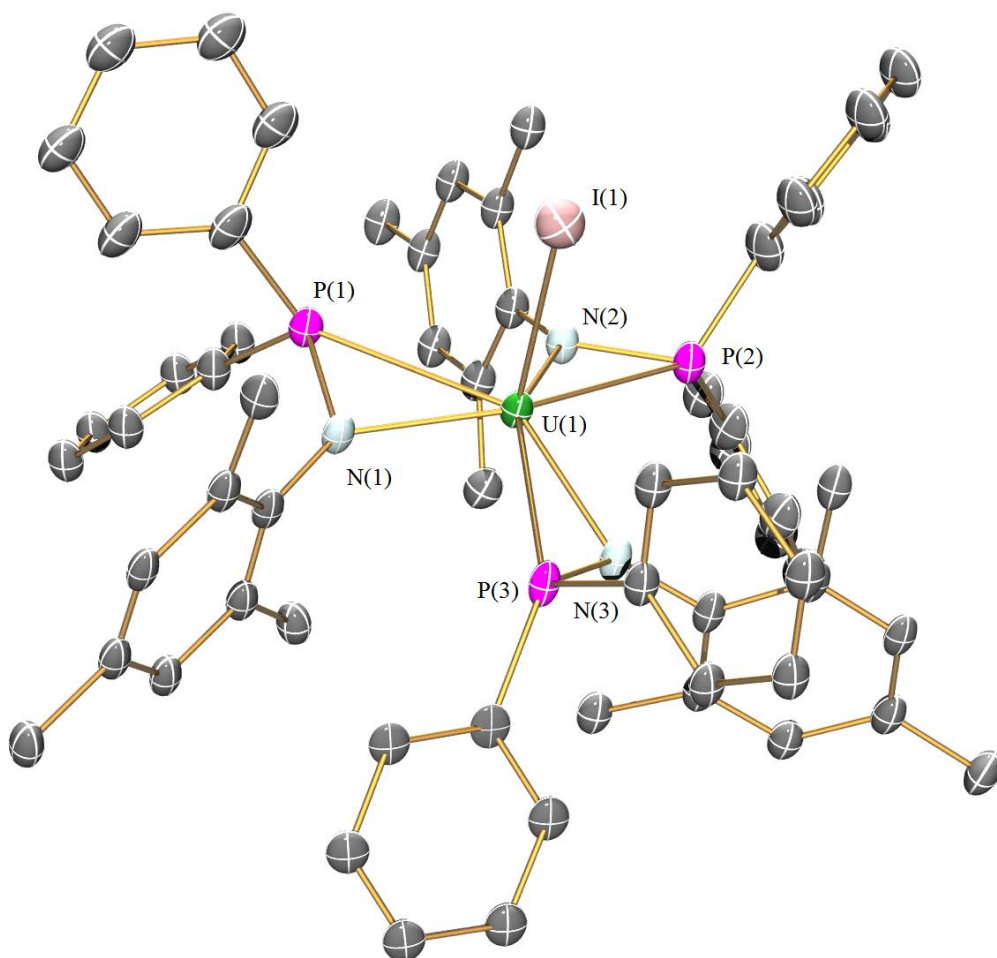
3.3 Tris(phosphinoamide) Uranium Iodides

In an attempt to synthesis the tris(phosphinoamide) uranium iodide complex $[UI(MesNPPh_2)_3]$ (**173**), three molar equivalents of the potassium salt $[K(MesNPPh_2)]$ (**157**) was reacted with $[UI_4(OEt_2)_2]$ in an analogous methodology to the salt metathesis route that had proven successful in the synthesis of the tris(phosphinoamide) uranium chloride complexes. Following work up, a mixture of products was suggested by the ^1H NMR spectrum of the reaction mixture. Due to intractable reaction mixture an alternative halide exchange route was proposed utilising trimethylsilyl iodide (Me_3SiI).

Complex **165** was treated with one equivalent of Me_3SiI at room temperature in toluene to form a green precipitate which after work up and crystallisation from toluene afforded a green crystalline solid in 72% yield (**Scheme 39**). A single crystal X-ray diffraction study was performed which revealed the product to be **173** and, although the molecular structure is illustrated in **Fig. 49**, a complete discussion of the metrical data acquired for **173** is meaningless due to the poor quality of the data; the overall structure is however unambiguous.



Scheme 39 – Synthesis of $[UI(MesNPPh_2)_3]$ (**173**) and $[UI(MesNP^iPr_2)_3]$ (**161**)



173

Fig. 49 – Structure of $[UI(MesNPPPh_2)_3]$ (**173**)

Thermal ellipsoids set at 40% probability. Solvent molecules and H atoms omitted for clarity.

Complex **173** crystallises as a discrete monomeric species in the space group $P2_1/n$ with two toluene solvent molecules per uranium in the crystal lattice. Each of the three phosphinoamide ligands coordinate in a bidentate manner, with an iodide ligand completing the coordination sphere, to afford a 7-coordinate uranium centre that adopts a distorted capped trigonal antiprismatic geometry analogous to **165**. The ^1H NMR spectrum of **173** exhibits broad resonances in the range of ± 13 ppm which is similar to the ^1H NMR resonances for **165** although they are shifted 1-3 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **173** exhibits a single broad resonance at 2048 ppm, a downfield shift of 75 ppm compared to **165**. The Evans method effective magnetic

moment **173** in benzene at 298 K was found to be 2.46 μB which is within the range for reported uranium(IV) complexes.⁷⁻¹⁰

As crystals isolated of **169** have thus far proven unsuitable for X-ray diffraction studies, the iodide derivative $[\text{UI}(\text{MesNP}^i\text{Pr}_2)_3]$ (**161**) was targeted from the treatment of **169** with Me_3SiI (Scheme 39). Note however the synthesis of complex **161**, has already been reported previously *via* an alternative synthetic pathway, (namely the treatment of $[\text{UI}_4(\text{dioxane})_2]$ with three equivalents of $[\text{K}(\text{MesNP}^i\text{Pr}_2)]$ (**159**) (Scheme 33)). Complex **161** was targeted in this way to verify the synthesis of **169** and extend the palette of halide metathesis chemistry. Crystals suitable for a single crystal X-ray diffraction study were grown from hexane with the molecular structure illustrated in Fig. 50 with selected bond lengths and angles.

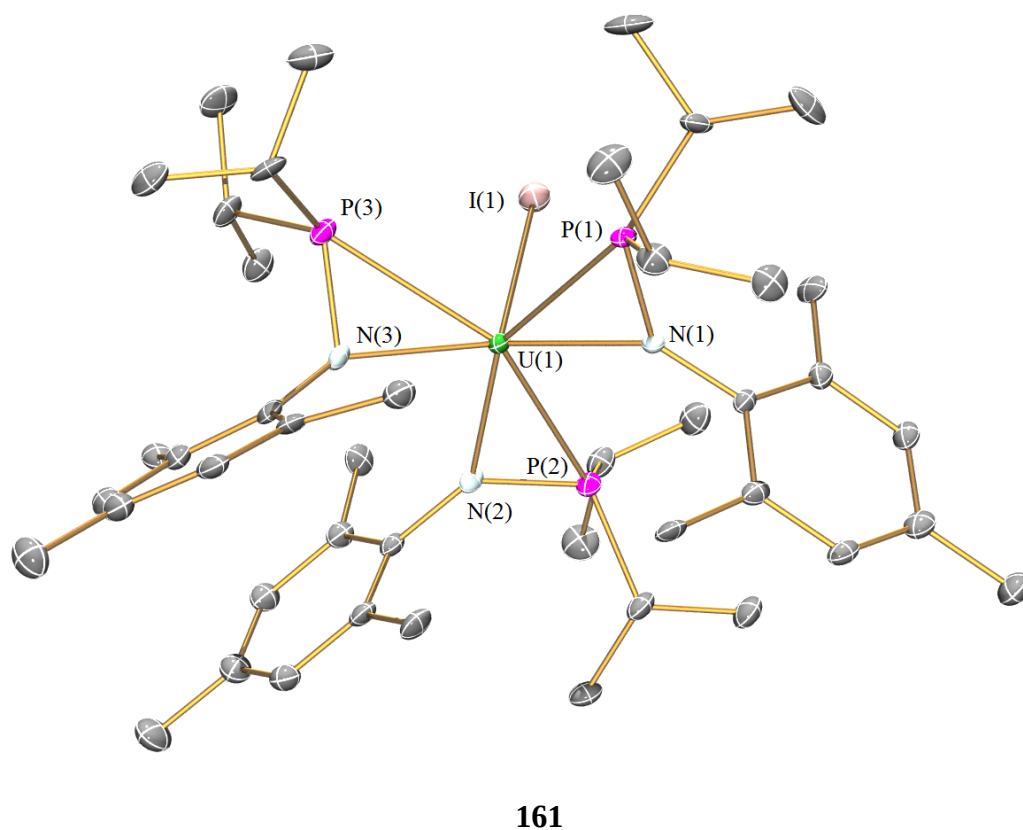
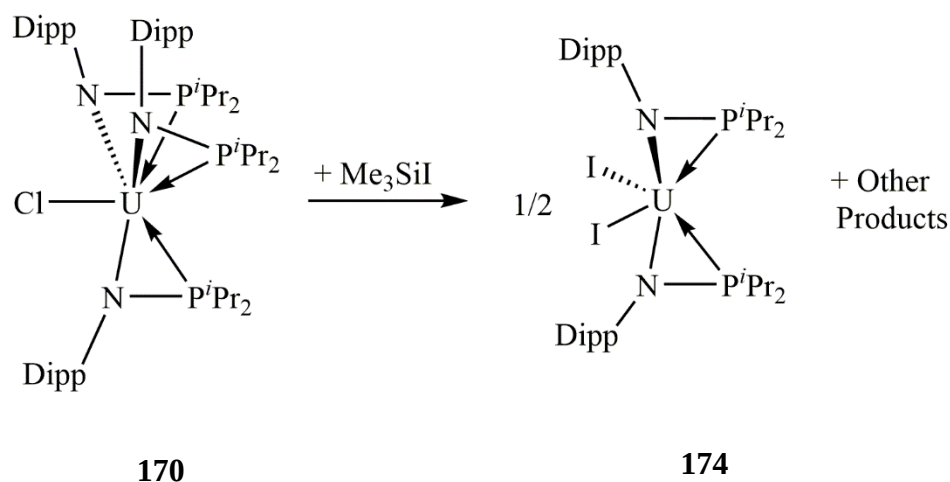


Fig. 50 – Structure of $[\text{UI}(\text{MesNP}^i\text{Pr}_2)_3]$ (**161**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$) U(1)-N(1) 2.283(8), U(1)-N(2) 2.272(8), U(1)-N(3) 2.318(8), U(1)-P(1) 2.861(3), U(1)-P(2) 2.845(3), U(1)-P(3) 2.826(3), P(1)-N(1) 1.669(8), U(1)-I(1) 3.0122(10), N(1)-U(1)-P(1) 35.7(2), N(1)-U(1)-I(1) 101.3(2), I(1)-U(1)-P(1) 94.47(6).

Complex **161** crystallises as a discrete monomeric species in the space group $P2_1/n$. As with the previously reported tris(phosphinoamide) uranium halides the X-ray structure of **161** reveals each phosphinoamide ligand coordinating in a bidentate manner, with an iodide ligand completing the coordination sphere, to afford a 7-coordinate uranium centre that adopts a distorted capped trigonal antiprismatic geometry. In contrast to complexes **165** and **173**, the approximate C_3 symmetry through the U-I bond vector has been broken. This is more likely to be a crystal-packing/steric effect and not of any real chemical significance. The U-N bond distances of 2.283(8), 2.272(8) and 2.318(8) Å are essentially identical to those observed in **165**, **170** and **173** and are almost identical to the U-N bond lengths reported by Thomas in **161**. The U-P bond distances of 2.861(3), 2.845(3) and 2.826(3) Å are shorter, by *ca.* 0.075 Å, than the corresponding distances in **165** and **173** and are more closely comparable to the corresponding distances in **170**, this is most likely a reflection of the stronger electron donor capacity of the dialkyl phosphines in (MesNP^{*i*}Pr₂)⁻ compared to the diaryl phosphines (MesNPPh₂)⁻. Although the U-P distances reported by Thomas in **161** are almost identical to those reported here, slight differences are ascribed to crystal packing effects. The ¹H NMR spectrum of **161** exhibits six broad resonances in the range of +12 to - 6 ppm mirroring the reported assignment. The ³¹P{¹H} NMR spectrum of **161** exhibits a single broad resonance at 2106 ppm, downfield by 157 ppm compared to **169**. The Evans method effective magnetic moment of a solution of **161** in benzene at 298 K was found to be 2.50 μ_B which is within the range for reported uranium(IV) complexes and once again comparable to the reported effective magnetic moment of 2.67 μ_B.³

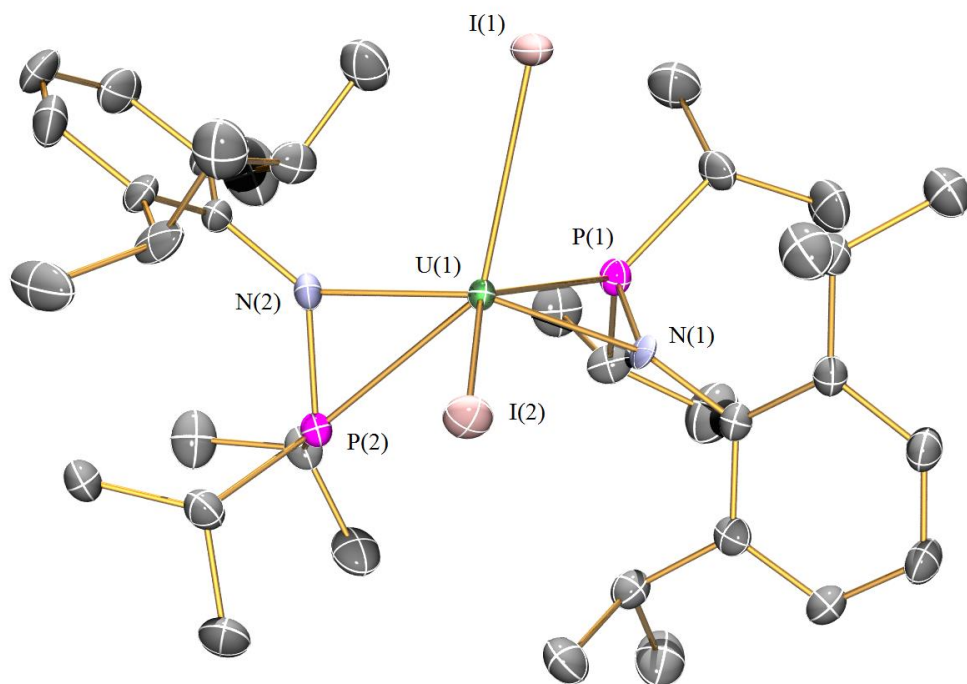
Treatment of the complex [UCl(DippNP^{*i*}Pr₂)₃] (**170**) with Me₃SiI proved to be less straightforward. Analysis of ¹H NMR spectrum of the reaction mixture showed a significant quantity of starting material along with unknown products. A small crop of crystals was isolated from the NMR tube and were subject to a single crystal X-ray diffraction study which revealed the bis(phosphinoamide)uranium diiodide, [UI₂(DippNP^{*i*}Pr₂)₂] (**174**) (**Scheme 40**) with the molecular structure illustrated in **Fig. 51** with selected bond lengths and angles.



Scheme 40 – Synthesis of $[\text{UI}_2(\text{DippNP}^i\text{Pr}_2)_2]$ (**174**)

The high steric strain in complex **170**, as a result of the encumbered nature of the phosphinoamide ($\text{DippNP}^i\text{Pr}_2$)[−], which is evidenced by the slightly longer U-N bond distances has potentially resulted in this slightly different chemistry. The addition of Me_3SiI to complex **170** resulted not only in the exchange of a chloride ligand for an iodide ligand but also the loss of a phosphinoamide ligand, with the potential formation of a $\text{DippN}(\text{SiMe}_3)\text{P}^i\text{Pr}_2$, in an attempt to relieve the steric strain.

One complete molecule and two half molecules of **174** are present in the asymmetric unit which crystallises in the space group $C2c$; the inversion centre is located on the uranium centre. Two phosphinoamide ligands coordinate in a bidentate manner, two iodide ligands complete the coordination sphere to afford a 6-coordinate uranium centre that adopts a distorted trigonal prismatic geometry. The U-N bond distances of 2.212(6) - 2.233(6) Å are shorter than the corresponding U-N bond distances in **170** (0.15 Å) as a result of the decrease in steric strain upon the reduction of the number of phosphinoamide ligands from three to two, but are still typical of uranium(IV) amide distances. The U-P bond distances of 2.803(2) - 2.852(2) Å are once again shorter than those U-P bond distances seen in **170** but are still comparable to the dialkyl phosphine derivative **161**.



174

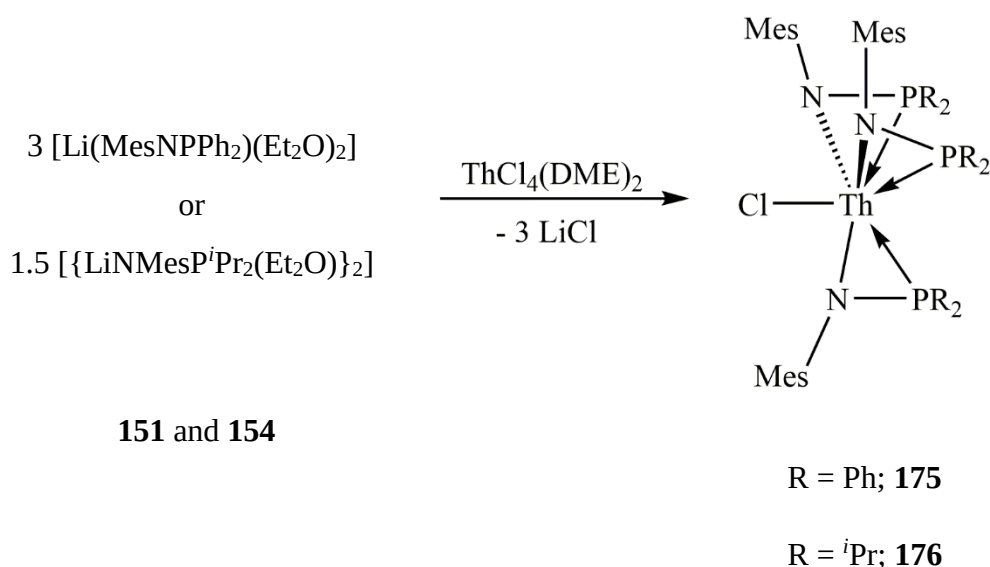
Fig. 51 – Structure of $[UI_2(DippNP^iPr_2)_2]$ (**174**)

Thermal ellipsoids set at 40% probability, one molecule of **174** is shown and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$) U(1)-N(1) 2.219(6), U(1)-N(2) 2.233(6), U(1)-P(1) 2.8234(19), U(1)-P(2) 2.811(2), U(1)-I(1) 2.9961(6), U(1)-I(2) 2.9906(6), P(1)-N(1) 1.714(7), I(2)-U(1)-I(1) 104.409(19), N(1)-U(1)-N(2) 133.4(3), N(1)-U(1)-I(1) 105.59(19), N(1)-U(1)-P(1) 37.38(18).

The ^1H NMR spectrum of **174** exhibits extremely broad resonances which are reminiscent of the ^1H NMR resonances for **170** and although they are slightly shifted, in a similar manner to the change of shifts observed in **173** and **161**, they are still typical for a paramagnetic uranium(IV) species.

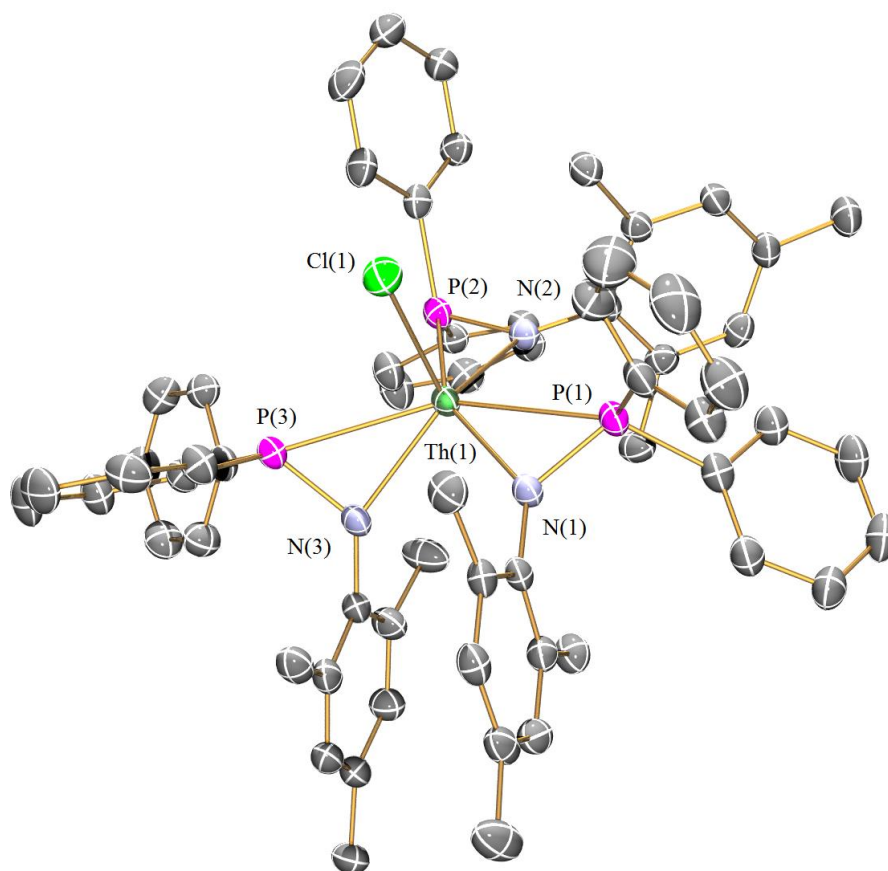
3.4 Tris(phosphinoamide) Thorium Chloride Complexes

It is of importance to synthesise the analogous thorium complexes to determine the role that any *f*-electrons play in any potential actinide-transition metal interactions. Unlike the ground electronic state of uranium(IV) which has two 5*f*-electrons, the ground electron state of thorium(IV) has no *f*-electrons. Therefore, any potential phenomenon observed in a uranium-transition metal complex that is not observed in the analogous thorium-transition metal complex may be attributed to the presence of *f*-electrons of uranium. On a side note thorium(IV) is also diamagnetic making the reaction progress easier to monitor *via* NMR spectroscopy.



Scheme 41 – Synthesis of $[\text{ThCl}(\text{MesNPPH}_2)_3]$ (**175**) and $[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**176**)

Treatment of thorium tetrachloride with three molar equivalents of $[\text{Li}(\text{MesNPPH}_2)(\text{Et}_2\text{O})_2]$ (**151**) in THF afforded a clear yellow solution. Following work-up and recrystallisation, colourless crystals of $[\text{ThCl}(\text{MesNPPH}_2)_3]$ (**175**) were isolated in 66% yield (**Scheme 41**). The analytical data are consistent with the proposed formulation, with the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra consistent with an averaged C_3 symmetry on the NMR timescale and with the thorium(IV) formulation. The molecular structure of **175** was determined by a single crystal X-ray diffraction study and is illustrated in **Fig. 52** with selected bond lengths and angles.



175

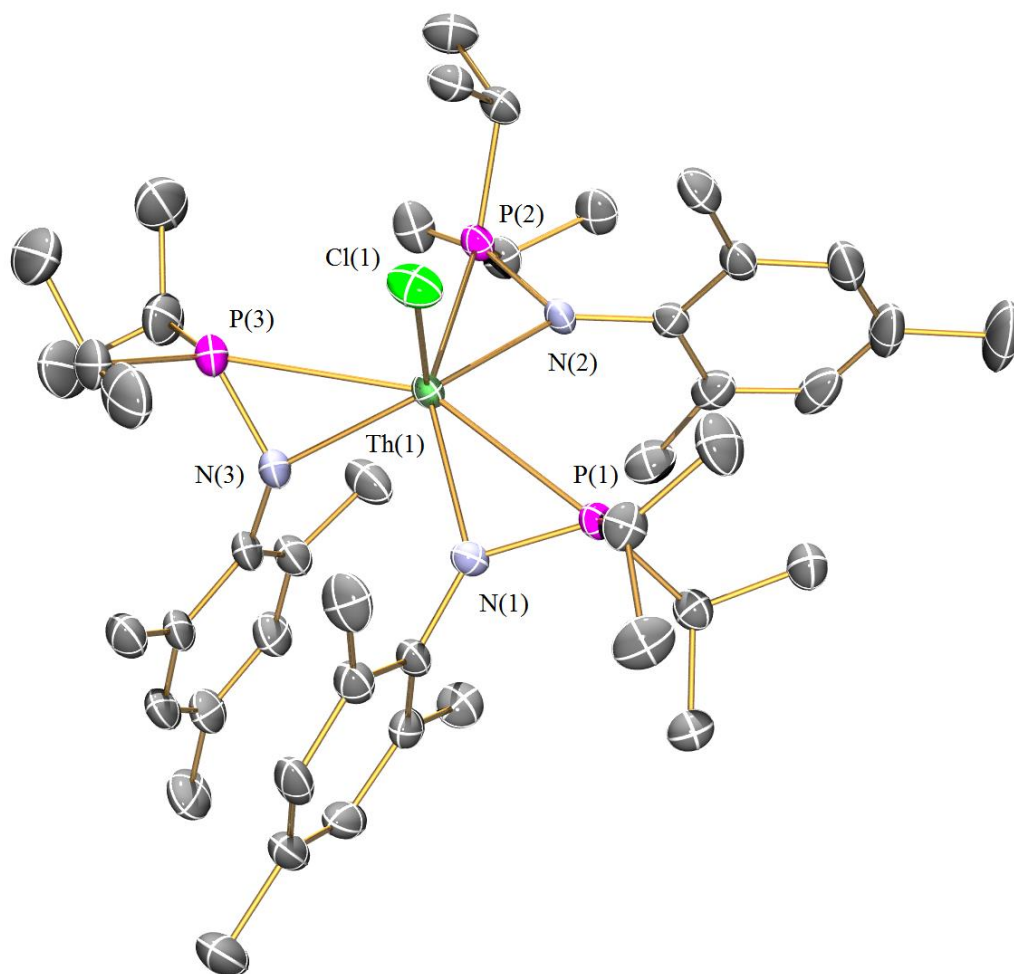
Fig. 52 – Structure of $[ThCl(MesNPPH_2)_3]$ (**175**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) Th(1)-N(1) 2.345(2), Th(1)-N(2) 2.335(2), Th(1)-N(3) 2.356(2), Th(1)-P(1) 2.9612(6), Th(1)-P(2) 2.9469(6), Th(1)-P(3) 2.8700(6), P(1)-N(1) 1.687(2), Th(1)-Cl(1) 2.6686(6), N(1)-Th(1)-P(1) 34.66(5), N(1)-Th(1)-Cl(1) 108.56(5), Cl(1)-Th(1)-P(1) 101.26(2).

Complex **175** crystallises as a discrete monomeric species in the space group $P2_1/n$. Each phosphinoamide ligand coordinates in a bidentate manner, to afford a 7-coordinate thorium centre that adopts a distorted capped trigonal antiprismatic geometry analogous to **165**. Although there are similarities between the geometry of complex **175** and complex **165**, the overall approximate C_3 symmetry observed in **165**

has been lost in the thorium analogue **175**. This is a solid state effect which can be potentially attributed to the differences in crystallographic symmetry. As would be expected, the Th-N bond distances of 2.345(2), 2.335(2), and 2.356(2) Å are slightly longer than the corresponding U-N bond distances but are within the range of reported thorium-amide bond distances. The Th-P bond distances of 2.9612(6), 2.9469(6) and 2.8700(6) Å are comparable to the previously reported U-P bond distances in the diaryl phosphine derivatives **165** and **173**.

In an analogous methodology to the preparation of **169**, one and a half equivalents of dimeric [$\{\text{LiNMes}(\text{P}^i\text{Pr}_2)(\text{Et}_2\text{O})\}_2$] (**154**) was reacted with $[\text{ThCl}_4(\text{DME})_2]$ at room temperature in THF to give, after work up and crystallisation a colourless crystalline solid in 91% yield (**Scheme 41**). A single crystal X-ray diffraction study revealed the product to be the tris(phosphinoamide)thorium chloride complex $[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**176**) with the molecular structure illustrated in **Fig. 53** with selected bond lengths and angles. Complex **176** crystallises in the space group *P*-1 as a discrete monomeric species. Each phosphinoamide ligand coordinates in a bidentate manner, to afford a 7-coordinate thorium centre that adopts a distorted capped trigonal antiprismatic geometry that is more comparable to **161** and **175** as there is no approximate C_3 symmetry at the thorium centre. The Th-N bond distances of 2.397(4), 2.330(3) and 2.348(3) Å are once again slightly longer than the corresponding U-N bond distances in complex **161** but are comparable to expected thorium-amide distances and the Th-N bond distances observed in **175**. The Th-P bond distances of 2.8924(11), 2.9224(10) and 2.9782(10) are comparable to the previously reported actinide-phosphorous(III) bond lengths. The analytical data is also consistent with the proposed formulation with the ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ spectra consistent with an averaged C_{3v} symmetry on the NMR timescale and with the thorium(IV) formulation.



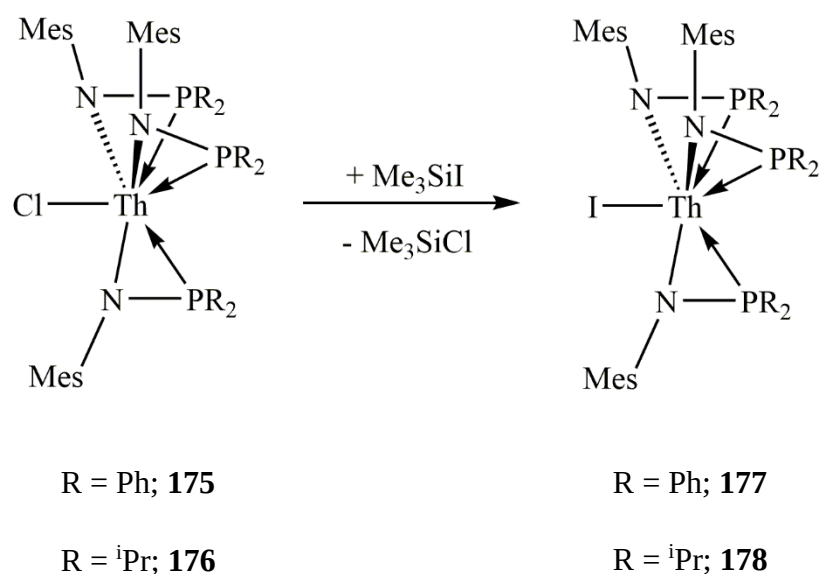
176

Fig. 53 – Structure of $[ThCl(MesNP^iPr_2)_3]$ (**176**)

Thermal ellipsoids set at 40% probability. Solvent molecules and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) Th(1)-N(1) 2.397(4), Th(1)-N(2) 2.330(3), Th(1)-N(3) 2.348(3), Th(1)-P(1) 2.8924(11), Th(1)-P(2) 2.9224(10), Th(1)-P(3) 2.9782(10), P(1)-N(1) 1.681(4), Th(1)-Cl(1) 2.6711(11), N(1)-Th(1)-P(1) 35.51(9), N(1)-Th(1)-Cl(1) 119.45(10), Cl(1)-Th(1)-P(1) 94.55(4).

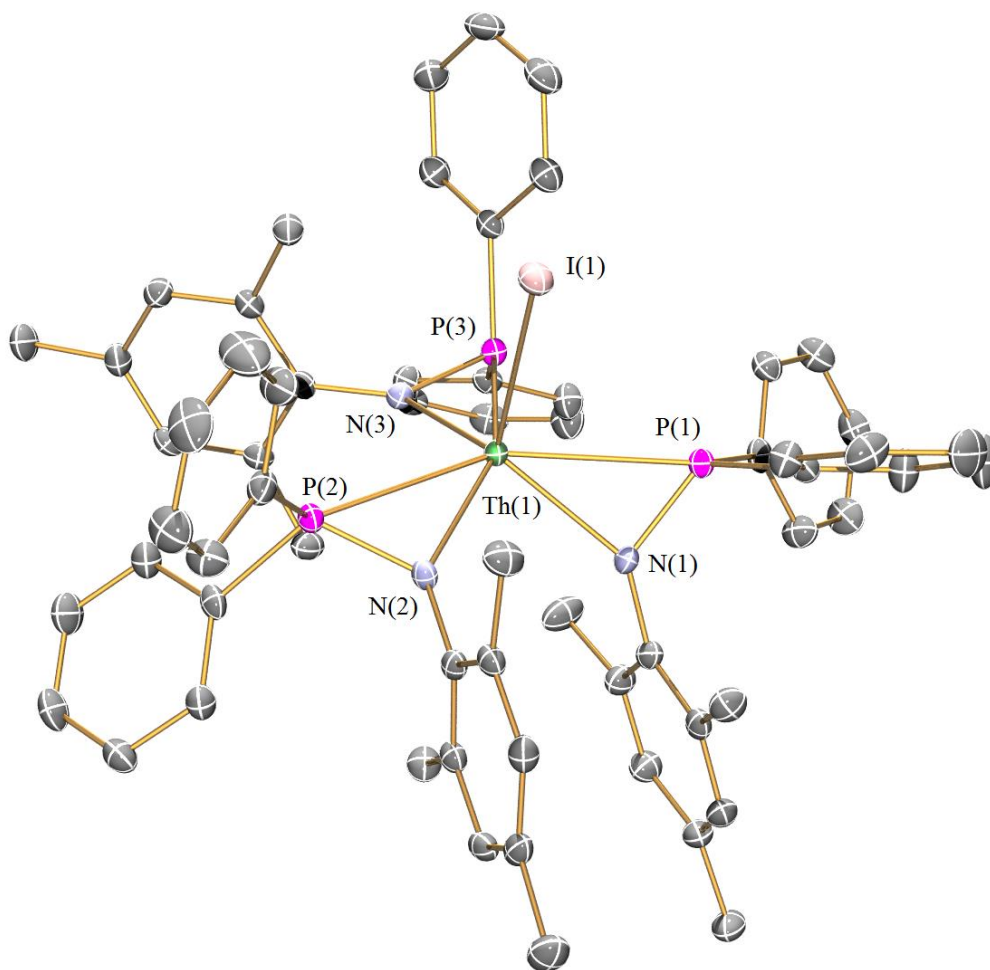
3.5 Tris(phosphinoamide) Thorium Iodide Complexes

In an analogous methodology to the synthesis of the tris(phosphinoamide) uranium iodide complexes **173** and **161**, the tris(phosphinoamide) thorium iodide complexes $[\text{ThI}(\text{MesNPPh}_2)_3]$ (**177**) and $[\text{ThI}(\text{MesNP}^i\text{Pr}_2)_3]$ (**178**) were targeted via the treatment of complexes **175** and **176** with Me_3SiI (**Scheme 42**).



Scheme 42 – Synthesis of $[\text{ThI}(\text{MesNPPh}_2)_3]$ (**177**) and $[\text{ThI}(\text{MesNP}^i\text{Pr}_2)_3]$ (**178**)

Complex **175** was treated with one equivalent of Me_3SiI at room temperature in toluene to form a colourless precipitate which after work up and crystallisation from toluene afforded a colourless crystalline solid in 88% yield (**Scheme 42**). A single crystal X-ray diffraction study was performed which revealed the product to be **177** with the molecular structure illustrated in **Fig. 54** with selected bond lengths and angles. Complex **177** crystallises in the space group $P/2_1n$ as a discrete monomeric species with each phosphinoamide ligand coordinates in a bidentate manner, to afford a 7-coordinate thorium centre that adopts a distorted capped trigonal antiprismatic geometry analogous to **175**.



177

Fig. 54 – Structure of $[ThI(MesNPPH_2)_3]$ (**177**)

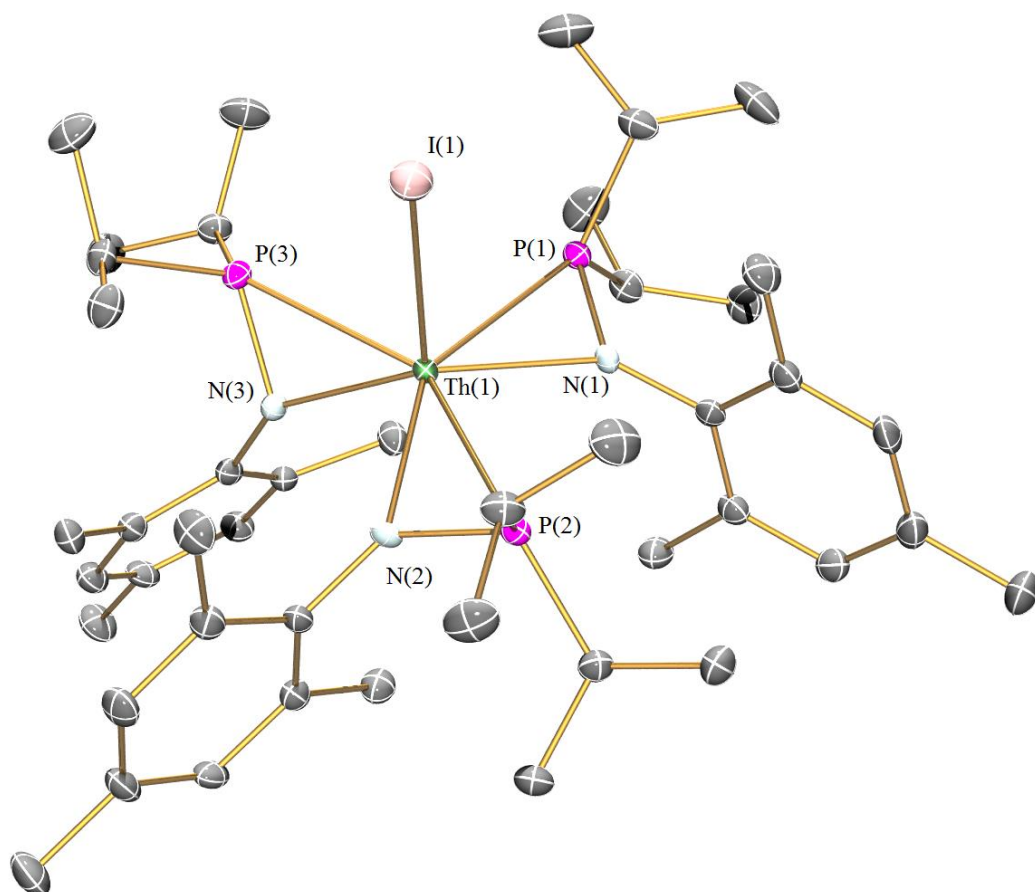
Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) Th(1)-N(1) 2.342(2), Th(1)-N(2) 2.351(2), Th(1)-N(3) 2.332(2), Th(1)-P(1) 2.9618(6), Th(1)-P(2) 2.8612(6), Th(1)-P(3) 2.9454(7), P(1)-N(1) 1.692(2), Th(1)-I(1) 3.08187(19), N(1)-Th(1)-P(1) 34.79(6), N(1)-Th(1)-I(1) 108.64(5), Cl(1)-Th(1)-P(1) 101.748(13).

The Th-N bond distances of 2.342(2), 2.351(2) and 2.332(2) Å are almost statistically identical to the corresponding bond distances present in **175**, as are the Th-P bond distances of 2.9618(6), 2.8612(6) and 2.9454(7) Å. The ^1H NMR spectrum of **177** is suggestive of an approximate C_{3v} symmetry on the NMR timescale and all of the

analytical data is consistent with the formulation of **177** and the assignment of a thorium(IV) centre.

Complex **176** was treated with one equivalent of Me₃SiI at room temperature in toluene to form a colourless precipitate which after work up and crystallisation from dibutyl ether afforded a colourless crystalline solid in an 82 % yield (**Scheme 42**). A single crystal X-ray diffraction study was performed which revealed the product to be **178** with the molecular structure illustrated in **Fig. 55** with selected bond lengths and angles. Complex **178** crystallises in the space group *P*-1 as a discrete monomeric species with each phosphinoamide ligand coordinating in a bidentate manner, to afford a 7-coordinate thorium centre that adopts a distorted capped trigonal antiprismatic geometry analogous to **176**.

As with all previously reported tris(phosphinoamide) metal halide complexes the ¹H NMR spectrum is suggestive of an approximate C_{3v} symmetry on the NMR timescale and all of the other analytical data is consistent with the formulation of **178** and the assignment of a thorium(IV) centre.



178

Fig. 55 – Structure of $[ThI(MesNP^iPr_2)_3]$ (**178**)

Thermal ellipsoids set at 40% probability. Solvent molecules and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) Th(1)-N(1) 2.337(3), Th(1)-N(2) 2.384(3), Th(1)-N(3) 2.325(3), Th(1)-P(1) 2.9517(8), Th(1)-P(2) 2.8900(9), Th(1)-P(3) 2.9126(8), P(1)-N(1) 1.683(3), Th(1)-I(1) 3.0761(3), N(1)-Th(1)-P(1) 34.71(7), N(1)-Th(1)-I(1) 103.36(7), I(1)-Th(1)-P(1) 96.279(18).

3.6 Concluding Remarks

The lithium phosphinoamide ligand transfer reagents [Li(MesNPPh₂)(Et₂O)₂] (**151**), [Li(DippNPPh₂)(Et₂O)₂] (**152**) and [Li(TrippNPPh₂)(Et₂O)₂] (**153**) were reacted with uranium tetrachloride in a molar ratio of 3:1 in an attempt to prepare the tris(phosphinoamide)uranium chloride complexes. The reaction of **151** with UCl₄ afforded [UCl(MesNPPh₂)₃] (**165**) which was structurally characterised. However, reaction of **152** and **153** with UCl₄ resulted in the two solvent separated ion pair complexes [UCl₃(DippNPPh₂)₂][Li(THF)₄] (**166**) and [UCl₃(TrippNPPh₂)₂][Li(THF)₄] (**167**) respectively. The two latter compounds were also characterised with single crystal X-ray diffraction studies.

To allow for systematic modification of the electron donating capacity of the phosphine whilst keeping the amido portions constant the diisopropyl-phosphine analogues were targeted. The lithium phosphinoamide ligand transfer reagents [{LiNMes(PⁱPr₂)(Et₂O)}₂] (**154**) [Li(DippNPⁱPr₂)] (**155**) and [Li(TrippNPⁱPr₂)] (**156**) were reacted with UCl₄ in an analogous manner to the preparation of **165**. Reaction of **154** with UCl₄ afforded [UCl(MesNPⁱPr₂)₃(μ-Cl)Li(THF)₃] (**168**) which was structurally characterised. Extraction of complex **168** in toluene led to the precipitation of LiCl resulting in [UCl(MesNPⁱPr₂)₃] (**169**). Whilst the reaction of **155** with UCl₄ yielded the tris(phosphinoamide)uranium chloride complex [UCl(DippNPⁱPr₂)₃] (**170**), the only product isolated and structurally characterised from the reaction of **156** with UCl₄ was the THF-solvated lithium phosphinoamide THF adduct [Li(TrippNPⁱPr₂)(THF)₂] (**172**). This is potentially a consequence of the increased steric nature of the *tripp* group vs the *dipp* group.

In an attempt to synthesis the tris(phosphinoamide)uranium iodide [UI(MesNPPh₂)₃] (**173**), three molar equivalents of the potassium salt [K(MesNPPh₂)₃] (**157**) was reacted with [UI₄(OEt₂)₂]. Unfortunately this resulted in a mixture of inextractable products and although the desired **173** was later identified, it could not be isolated. Therefore, an alternative halide exchange route was proposed utilising trimethylsilyl iodide (Me₃SiI). The treatment of **165** and **169** with Me₃SiI afforded the tris(phosphinoamide)uranium iodide complexes **173** and [UI(MesNPⁱPr₂)₃] (**161**),

both of which were structurally characterised. The treatment of **170** with Me₃SiI was however less straight forward with the partial conversion of starting material to the bis(phosphinoamide)uranium diiodide complex [UI₂(DippNPⁱPr₂)₂] (**174**) as identified by a single crystal X-ray diffraction study.

To allow for determination of any role that *f*-electrons play in any potential uranium-transition metal interaction, the tris(phosphinoamide)thorium chloride complexes were targeted. The treatment of thorium tetrachloride with three molar equivalents of **151** and **154** afforded the desired products [ThCl(MesNPPPh₂)₃] (**175**) and [ThCl(MesNPⁱPr₂)₃] (**176**), both of which were structurally characterised. As with the uranium analogues the tris(phosphinoamide) thorium iodide complexes were successfully isolated. The reaction of **175** and **176** with Me₃SiI resulted in the isolation of [ThI(MesNPPPh₂)₃] (**177**) and [ThI(MesNPⁱPr₂)₃] (**178**) as determined by single crystal X-ray diffraction studies.

Complexes **161**, **165**, **169**, **170** and **173** are all potential precursors to uranium-transition metal heterobimetallic complexes. Although it is not practical to perform variable temperature NMR studies due to the paramagnetic nature of these complexes to determine the lability of the phosphine centres; the apparent C_{3v} molecular symmetry on the NMR timescale at room temperature is suggestive of a reversible phosphine coordination/dissociation process in solution. These small differences in the solid state structures can be ascribed to a combination of steric ordering effects and crystal packing effects. Complexes **175-178** represent precursors to thorium heterobimetallic complexes for the investigation into the role of the *f*-electrons in the bonding of these species.

3.7 Experimental

Preparation of [UCl(MesNPPPh₂)₃] (**165**)

THF (30 ml) was added slowly to a cold (-78 °C) stirring mixture of UCl₄ (1.90 g, 5.0 mmol) and [Li(MesNPPPh₂)(Et₂O)₂] (**151**) (7.10 g, 15 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. Volatiles were removed in *vacuo* and the resulting pale brown solid was extracted into toluene, concentrated to 15ml and cooled to -30 °C to afford **165** as a brown crystalline solid. Brown crystals of **165** suitable for a single crystal X-ray diffraction study were obtained from storage of a toluene solution at -30 °C for 72 hours. Yield: 4.05 g, 66 %. Anal. Calc'd for C₆₃H₆₃ClN₃P₃U 0.35(C₇H₈): C, 62.35; H, 5.26; N, 3.33 %. Found: C, 62.43; H, 5.30; N, 3.42 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) -11.41 (12H, s, br, Ar-CH), 5.58 (9H, s, Mes-CH₃), 7.44 (6H, s, Ar-CH), 7.89 (18H, s, Mes-CH₃), 11.20 (6H, s, br, Ar-CH), 11.73 (12H, s, br, Ar-CH). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 1973 (br, s). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 507 (s), 539 (s), 567 (w), 589 (m), 619 (w), 658 (s), 698 (s), 729 (m), 744 (s), 765 (s), 854 (m), 897 (m), 934 (m), 958 (m), 978 (m), 1000 (s), 1153 (w), 1188 (w), 1218 (s), 1247(w), 1301 (w), 1318 (m), 1434 (s). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 2.38 \mu_{\text{B}}$. UV-vis (THF): λ_{max} (ε/dm³mol⁻¹cm⁻¹) 685 (180.2) nm, 872 (30.7) nm, 919 (23.7) nm, 1027 (33.8) nm, 1121 (27.5) nm, 1270 (29.4) nm, 1421 (20.6) nm, 1561 (26.0) nm, 1697 (12.9) nm, 1758 (12.4) nm.

Preparation of [UCl₃(DippNPPPh₂)₂][Li(THF)₄] (**166**)

THF (30 ml) was added slowly to a cold (-78 °C) stirring mixture of UCl₄ (0.19 g, 0.5 mmol) and [Li(PPh₂NDipp)(Et₂O)₂] (**152**) (0.76 g, 1.5 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. The resulting brown reaction mixture was concentrated to 5 ml and cooled to -30 °C to afford **166** as a brown crystalline solid suitable for a single crystal X-ray diffraction study. Yield 0.35g, 52 %. Anal. Calc'd for C₆₈H₉₄Cl₃N₂P₂O₅LiU: C, 56.98; H, 6.62; N, 1.96 %. Found: C, 56.72; H, 6.43; N, 1.91 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) -43.57, -31.45, -8.03, 4.23, 6.87, 8.21, 8.82, 10.25, 11.79, 13.47, 17.17, 21.69. FTIR

(Nujol): $\tilde{\nu}$ (cm⁻¹) 646 (m), 698 (m), 744 (m), 771 (m), 890 (w), 923 (w), 1042 (m), 1100 (m), 1156 (m), 1188 (m), 1240 (m), 1321 (w). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 2.05\mu_{\text{B}}$.

Preparation of [UCl₃(TrippNPPPh₂)₂][Li(THF)₄] (**167**)

THF (30 ml) was added slowly to a cold (-78 °C) stirring mixture of UCl₄ (0.19 g, 0.5 mmol) and [Li(PPh₂NTripp)(Et₂O)₂] (**153**) (0.77 g, 1.5 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. The resulting brown reaction mixture was concentrated to 5 ml and cooled to -30 °C to afford **167** as a brown crystalline solid suitable for a single crystal X-ray diffraction study. Yield 0.32g, 44 %. Anal. Calc'd for C₇₀H₉₈Cl₃N₂P₂O₅LiU: C, 58.17; H, 6.84; N, 1.94 %. Found: C, 61.00; H, 7.16; N, 2.22 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) - 43.11, -31.60, -8.03, 4.15, 4.20, 4.27, 6.62, 6.78, 8.26, 8.83, 10.32, 13.65, 17.15, 21.72. FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 635 (w), 644 (w), 659 (w), 698 (s), 733 (m), 747 (s), 793 (s), 835 (w), 874 (m), 886 (m), 913 (m), 942 (m), 1042 (s), 1084 (m), 1098 (m), 1117 (m), 1208 (m), 1314 (m), 1338 (s). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 2.23 \mu_{\text{B}}$.

Preparation of [UCl(MesNP^{*i*}Pr₂)₃] (**169**)

THF (30 ml) was added slowly to a cold (-78 °C) stirring mixture of UCl₄ (0.38 g, 1.0 mmol) and [{LiNMes(P^{*i*}Pr₂)(Et₂O)}₂] (0.77 g, 1.5 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. Volatiles were removed in *vacuo* and the resulting pale brown solid was extracted into hexane to afford **169** as light brown needles. Yield: 0.59 g, 59 %. Anal. Calc'd for C₄₅H₇₅ClN₃P₃U: C, 52.76; H, 7.38; N, 4.10 %. Found: C, 52.72; H, 7.42; N, 3.96 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) -4.42 (12H, s-br, ^{*i*}Pr-CH₃), -2.22 (18H, s, ^{*i*}Pr-CH₃), 4.24 (6H, s, ^{*i*}Pr-CH), 6.75 (9H, s, Mes-CH₃), 7.35 (18H, s, Mes-CH₃), 13.18 (6H, s, Ar-CH). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 1949. FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 529 (w), 568 (w), 590 (w), 655 (w), 666 (w), 759 (w), 853 (w), 880 (w), 902 (w), 927 (w), 961 (w), 1055 (w), 1153 (m), 1213 (m), 1302 (m). Magnetic moment (Evans method,

C₆D₆, 298 K): $\mu_{\text{eff}} = 2.27 \mu_{\text{B}}$. UV-vis (THF): λ_{max} ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) 1019 (46.4) nm, 1083 (41.3) nm, 1252 (29.9) nm, 1406 (19.1) nm, 1549 (22.2) nm, 1769 (16.93) nm.

Preparation of [UCl(DippNPⁱPr₂)₃] (**170**)

THF (30 ml) was added slowly to a cold (-78 °C) stirring mixture of UCl₄ (0.38 g, 1.0 mmol) and [Li(DippNPⁱPr₂)] (**155**) (1.12 g, 3.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. Volatiles were removed in *vacuo* and the resulting pale brown solid was extracted into hexane, concentrated to 15ml and cooled to -30 °C to afford **170** as a light brown crystalline solid. Brown needles of **170** suitable for a single crystal X-ray diffraction study were obtained from storage of a hexane solution at room temperature °C for 72 hours. Yield 0.56 g, 49 %. Anal. Calc'd for C₅₄H₉₃ClN₃P₃U: C, 56.36; H, 8.15; N, 3.65 %. Found: C, 56.15; H, 7.98; N, 3.46 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) -30.33 (6H, s-br, CH), 9.95 (36H, s-br, CH₃), 16.11 (36H, s-br, CH₃), 26.27 (6H, s-br, CH), 35.57 (6H, s-br, CH). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 561 (w), 670 (w), 722 (w), 768 (w), 877 (w), 892 (w), 904 (w), 904 (w), 915 (w), 928 (w), 960 (w), 1019 (w), 1041 (w), 1180 (w), 1232 (w), 1307 (w), 1322 (w), 1336 (w), 1365 (w), 1426 (m). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 2.58 \mu_{\text{B}}$.

Preparation of [UI(MesNPPh₂)₃] (**173**)

A solution of [UCl(MesNPPh₂)₃] (**165**) (3.07 g, 2.5 mmol) in toluene (30 mL) was cooled to 0 °C. To this was added Me₃SiI (0.63 g, 0.45 mL 3.13 mmol). The resulting brown solution was allowed to warm slowly to room temperature and stirred for 18 hours to afford a pale brown solution and a green precipitate. The precipitate was isolated *via* filtration and washed with hexanes (3 x 20 mL) to yield **173** as an analytically pure green powder. Green crystals suitable of **173** suitable for a single crystal X-ray diffraction study were obtained from storage of a toluene solution at -30 °C for 72 hours. Yield: 0.68 g, 72%. Calc'd for C₆₃H₆₃IN₃P₃U: C, 57.30; H, 4.81; N, 3.18 %. Found: C, 57.19; H, 4.80; N, 2.91 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) -10.71 (18H, s-br, Mes-CH₃), 5.82 (9H, s, Mes-CH₃), 8.17 (12H, s, Ar-CH), 11.60 (6H, s, Ar-CH), 12.92 (12H, s, Ar-CH). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 2048.

FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 507 (w), 538 (w), 567 (w), 589 (w), 658 (w), 699 (w), 743 (w), 763 (w), 854 (w), 897 (w), 959 (w), 1153 (w), 1182 (w), 1217 (w), 1303 (w), 1379 (w), 1434 (m). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 2.46 \mu_{\text{B}}$.

Preparation of [UI(MesNPⁱPr₂)₃] (**161**)

To a cooled (0 °C) solution of [UCl(MesNPⁱPr₂)₃] (**169**) (2.56 g, 2.5 mmol) in toluene (30 ml) was added TMSI (0.63 g, 0.45 mL 3.13 mmol). The resulting brown solution was allowed to warm slowly to room temperature and stirred for 18 hours to afford a brown solution. Volatiles were removed in *vacuo* and the resulting pale brown solid was extracted into hexane and cooled (-30 °C) to afford **161** as green blocks. Green crystals of **161** suitable for a single crystal X-ray diffraction study were obtained from storage of a concentrated hexane solution at 9 °C for 24 hours. Yield: 1.56 g, 56%. Anal. Calc'd for C₄₅H₇₅IN₃P₃U 0.2(C₆H₁₄): C, 48.97; H, 6.92; N, 3.71 %. Found: C, 49.24; H, 7.07; N, 3.74 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) -5.98 (18H, s-br, CH₃), 1.96 (18H, s, CH₃), 2.62 (6H, s, ⁱPr-CH), 6.45 (9H, s, CH₃), 9.40 (18H, s, CH₃), 12.77 (6H, s, Ar-CH). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 2106. FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 519 (m), 531 (s), 569 (w), 591 (m), 662 (s), 681 (m), 760 (s), 852 (s), 901 (s), 925 (m), 959 (m), 1037 (m), 1053 (s), 1153 (s), 1205 (s), 1218 (s), 1301 (m), 1366 (m). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 2.40 \mu_{\text{B}}$. UV-vis (THF): λ_{max} ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) 486 (89.1) nm, 525 (85.1) nm, 601 (41.5) nm, 619 (43.2) nm, 683 (74.0) nm, 782 (32.3) nm, 1011 (47.0) nm, 1095 (56.6) nm.

Preparation of [UI₂(DippNPⁱPr₂)₂] (**174**)

To a cooled (0 °C) solution of [UCl(DippNPⁱPr₂)₃] (**170**) (2.87 g, 2.5 mmol) in toluene (30 ml) was added TMSI (0.63 g, 0.45 mL 3.13 mmol). The resulting brown solution was allowed to warm slowly to room temperature and stirred for 18 hours to afford a brown solution. Volatiles were removed in *vacuo* to result in a mixture of products. brown crystals of **174** suitable for a single crystal X-ray diffraction study were obtained from storage of an NMR sample in C₆D₆ at room temperature. ¹H NMR (C₆D₆, 295 K): δ (ppm) -28.49 (6H, s-br, CH), 10.03 (36H, s-br, CH₃), 14.35 (36H, s-br, CH₃), 20.05 (6H, s-br, CH), 36.46 (6H, s-br, CH).

Preparation of [ThCl(MesNPPPh₂)₃] (**175**)

THF (30 ml) was added slowly to a cold (-78 °C) stirring mixture of ThCl₄(DME)₂ (0.55 g, 1.0 mmol) and [Li(MesNPPPh₂)(Et₂O)₂] (**151**) (1.42 g, 3.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. Volatiles were removed in *vacuo* and the resulting pale yellow solid was extracted into toluene and washed with Et₂O (3x10 mL) to afford **175** as a colourless solid. Colourless crystals of **175** suitable for a single crystal X-ray diffraction study were obtained from storage of an Et₂O solution at 25 °C for 24 hours. Yield: 0.81 g, 66 %. Anal. Calc'd for C₆₃H₆₃ClN₃P₃Th: C, 61.89; H, 5.19; N, 3.44 %. Found: C, 61.79; H, 4.98; N, 3.40 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) 1.96 (18H, s, Mes-CH₃), 2.25 (9H, s, Mes-CH₃), 6.72 (6H, s, Mes-CH), 6.97 (18H, m, Ar-CH), 7.47 (12H, m, Ar-CH). ¹³C{¹H} NMR (C₆D₆, 295 K): δ (ppm), 20.65 (Mes-CH₃), 127.66 (Ar-CH), 127.89 (Ar-CH), 129.39 (Ar-CH), 129.61 (Ar-CH), 132.79 (Ar-C), 134.40 (Ar-C), 134.97 (Ar-C), 149.70 (Ar-C). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 20.72 (s). FTIR ν/cm⁻¹ (Nujol): 514 (m), 540 (m), 566 (m), 590 (m), 618 (m), 661 (m), 695 (s), 741 (m), 767 (m), 856 (m), 893 (m), 959 (m), 1153 (m), 1216 (s), 1302 (m), 1435 (s).

Preparation of [ThCl(MesNPⁱPr₂)₃] (**176**)

THF (30 ml) was added slowly to a cold (-78 °C) stirring mixture of ThCl₄(DME)₂ (0.55 g, 1.0 mmol) and [Li(MesNPⁱPr₂)] (**154**) (0.77 g, 3.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. Volatiles were removed in *vacuo* and the resulting pale yellow solid was extracted into hexane to afford **176** as an analytically pure pale yellow solid. Colourless crystals of **176** suitable for a single crystal X-ray diffraction study were obtained from storage of a hexane solution at -30 °C for 72 hours. Yield: 0.93 g, 91 %. Anal. Calc'd for C₄₅H₇₅ClN₃P₃Th: C, 53.07; H, 7.42; N, 4.13 %. Found: C, 52.40; H, 7.35; N, 3.95 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) 0.98 (18H, m, ⁱPr-CH₃), 1.21 (18H, m, ⁱPr-CH₃), 2.20 (9H, s, Mes-CH₃), 2.30 (6H, m, ⁱPr-CH), 2.46 (18H, m, Mes-CH₃), 6.79 (6H, s, Mes-CH). ¹³C{¹H} NMR (C₆D₆, 295 K): δ (ppm) 19.60 (ⁱPr-CH₃), 20.41 (ⁱPr-CH₃), 21.47 (Mes-CH₃), 29.60 (ⁱPr-CH), 129.10 (Ar-CH), 131.08 (Ar-C), 132.00 (Ar-C), 150.12 (Ar-C). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 54.15 (s).

Preparation of [ThI(MesNPPH₂)₃] (177)

To a cooled (0 °C) solution of [ThCl(MesNPPH₂)₃] (0.61 g, 0.5 mmol) in toluene (30 ml) was added Me₃SiI (0.11 g, 0.08 mL 0.55 mmol). The resulting pale yellow solution was allowed to warm slowly to room temperature and stirred for 18 hours to afford a colourless precipitate. The precipitate was isolated by filtration and washed with hexane (3x10 mL) to afford **177** as a colourless solid. Colourless crystals of **177** suitable for a single crystal X-ray diffraction study were obtained from storage of a toluene solution at 0 °C for 48 hours. Yield: 0.57 g, 88 %. Anal. Calc'd for C₆₃H₆₃IN₃P₃Th: C, 57.58; H, 4.83; N, 3.20 %. Found: C, 57.17; H, 4.82; N, 2.94 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) 1.96 (18H, s, Mes-CH₃), 2.22 (9H, s, Mes-CH₃), 6.70 (6H, s, Mes-CH), 6.96 (18H, m, Ar-CH), 7.53 (12H, m, Ar-CH). ¹³C{¹H} NMR (C₆D₆, 295 K): δ (ppm), 20.60 (Mes-CH₃), 20.96 (Mes-CH₃), 127.65 (Ar-CH), 127.95 (Ar-CH), 129.31 (Ar-CH), 129.65 (Ar-CH), 132.68 (Ar-C), 134.44 (Ar-C), 134.70 (Ar-C). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 17.65 (s). FTIR ν/cm⁻¹ (Nujol): 658 (w), 696 (m), 743 (m), 765 (m), 959 (w), 1153 (w), 1184 (w), 1215 (m), 1302 (m), 1434 (m).

Preparation of [ThI(MesNP^{*i*}Pr₂)₃] (178)

To a cooled (0 °C) solution of [ThCl(MesNP^{*i*}Pr₂)₃] (0.51 g, 0.5 mmol) in hexane (30 ml) was added Me₃SiI (0.11 g, 0.08 mL 0.55 mmol). The resulting pale yellow solution was allowed to warm slowly to room temperature and stirred for 18 hours to afford a colourless precipitate. The precipitate was isolated by filtration and washed with hexane (3x10 mL) to afford [ThI(MesNP^{*i*}Pr₂)₃] as a colourless solid. Colourless crystals of [ThI(MesNP^{*i*}Pr₂)₃] suitable for a single crystal X-ray diffraction study were obtained from storage of a ⁿBu₂O solution at 25 °C for 24 hours. Yield: 0.45 g, 82 %. Anal. Calc'd for C₄₅H₇₅IN₃P₃Th: C, 48.70; H, 6.81; N, 3.78 %. Found: C, 48.31; H, 6.75; N, 3.76 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) 1.00 (18H, t, ²J_{HH} = 8.0 Hz, ^{*i*}Pr-CH₃), 1.22 (18H, m, ^{*i*}Pr-CH₃), 2.19 (9H, s, Mes-CH₃), 2.36 (6H, sp, ²J_{HH} = 7.0 Hz, ^{*i*}Pr-CH), 2.44 (18H, m, Mes-CH₃), 6.77 (6H, s, Mes-CH). ¹³C{¹H} NMR (C₆D₆, 295 K): δ (ppm) 19.82 (^{*i*}Pr-CH₃), 20.40 (^{*i*}Pr-CH₃), 21.64 (Mes-CH₃), 30.90 (^{*i*}Pr-CH), 131.30 (Ar-CH), 131.10 (Ar-C), 131.80 (Ar-C), 149.92 (Ar-C). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 50.41 (s). FTIR ν/cm⁻¹ (Nujol): 660 (w), 683 (w), 761 (w), 852 (w), 883 (w), 900 (w), 924 (w), 958 (w), 1036 (w), 1053 (w), 1152 (w), 1216 (m).

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Chapter four

Heterobimetallic Actinide-Cobalt Complexes

Contents

4.1	Background	151
4.2	Heterobimetallic Actinide-Cobalt Complexes	154
4.3	Characterisation of Actinide-Cobalt Complexes	165
4.4	Concluding remarks	173
4.5	Experimental	176
4.6	References	179

4.1 Background

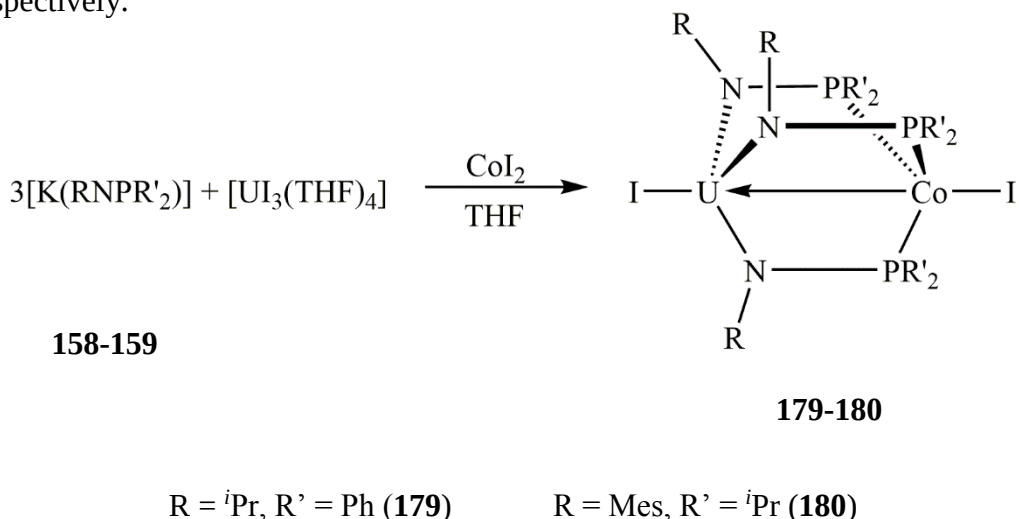
To date, comparatively few examples of metal-metal bonds between an actinide, such as uranium, and transition metals have been reported.¹⁻⁴ The next step towards the synthesis of such linkages is the reaction of the previously described tris(phosphinoamide) actinide halide complexes with suitable transition metal fragments. Nagashima reported a range of zirconium-transition metal complexes utilising the tris(phosphinoamide) zirconium starting materials $[\text{ZrCl}(\text{RNPPH}_2)_3]$ ($\text{R} = \text{tBu}$, **51**; $i\text{Pr}$, **52**) as tripodal-type metalloligands. The heterobimetallic complexes $[\text{ZrCl}(\text{tBuNPPH}_2)_3\text{CuCl}]$ (**54**), $[\text{ZrCl}(i\text{PrNPPH}_2)_3\text{CuCl}]$ (**55**), and $[\text{ZrCl}(i\text{PrNPPH}_2)_3\text{Mo}(\text{CO})_3]$ (**56**) were synthesised from the appropriate zirconium compounds and either CuCl or $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ respectively.⁵ Thomas further developed this work by reaction of $[\text{ZrCl}(\text{RNP}^i\text{Pr}_2)_3]$ ($\text{R} = \text{Mes}$, **62**; $i\text{Pr}$, **63**) with CoI_2 resulting in the reduction of the cobalt metal and the formation of the heterobimetallic complexes $[\text{ZrCl}(\text{RNP}^i\text{Pr}_2)_3\text{CoI}]$ ($\text{R} = \text{Mes}$, **65**; $i\text{Pr}$, **66**).⁶ Chemical reduction of **65** and **66** and subsequent reaction with small molecules has resulted in a plethora of small molecule activations.⁷⁻¹⁶

At the start of this work the only example of an unsupported bonding interaction between uranium and a first row d-block metal was $[\text{U}(\text{Ts}^{\text{Xy}})\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}]$ (**14**) reported by Liddle.¹⁷ More recently, Arnold has reported the supported complexes $[\text{U}(\text{N}(\sigma\text{-}\{\text{NCH}_2\text{P}^i\text{Pr}_2\}\text{C}_6\text{H}_4)_3\text{Co}(\text{CO})_3)]$ (**19**) and $[\text{Th}(\text{N}(\sigma\text{-}\{\text{NCH}_2\text{P}^i\text{Pr}_2\}\text{C}_6\text{H}_4)_3\text{Co}(\text{CO})_3)]$ (**20**) whilst Thomas has reported the tris(phosphinoamide) supported uranium-cobalt complexes $[\text{UI}(i\text{PrNPPH}_2)_3\text{CoI}]$ (**179**), $[\text{UI}(\text{MesNP}^i\text{Pr}_2)_3\text{CoI}]$ (**180**) and $[(i\text{PrNPPH}_2)\text{U}(i\text{PrNPPH}_2)_3\text{CoI}]$ (**181**), $[(\text{MesNP}^i\text{Pr}_2)\text{U}(\text{MesNP}^i\text{Pr}_2)_3\text{CoI}]$ (**182**).^{18, 19} However, compound **180** was not structurally characterised so its structure remains unclear.

At the beginning of this project all examples of uranium-d-block bonds, be they formally polarized covalent or dative, employed closed shell d-block fragments.¹⁻⁴ No open shell d-block-uranium interactions had been reported involving clear-cut metal-metal bonds therefore such systems were considered long-standing targets as they offered the potential for interesting magnetic phenomena including magnetic

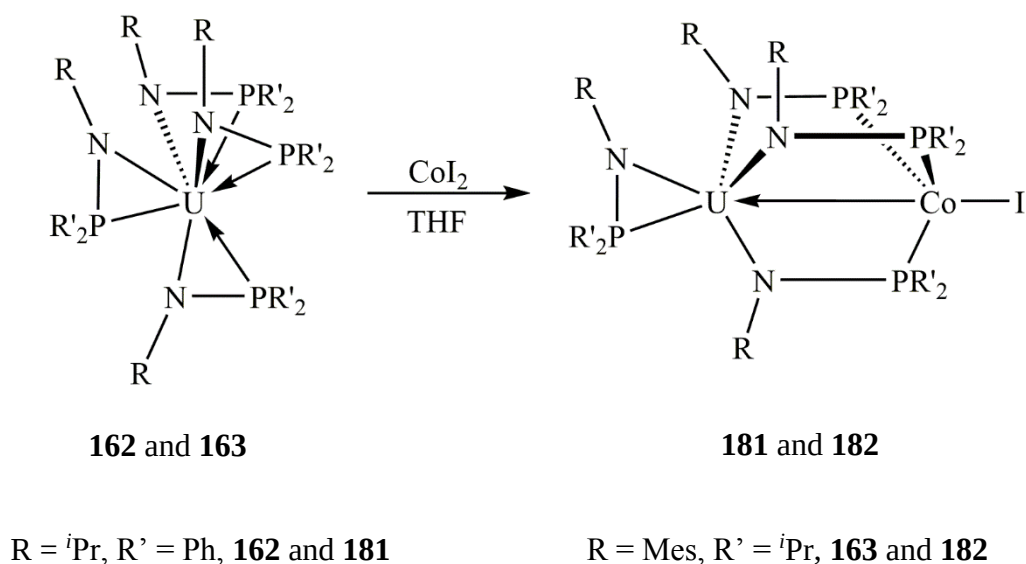
coupling.^{3, 4} It was identified that cobalt would be a suitable d-block metal since it would be possible to compare a dative uranium-cobalt bond with the polarised covalent uranium-cobalt bond reported by Liddle and described previously. Furthermore, it was envisaged that combining an open shell uranium(IV) centre with an open shell cobalt centre, such as tetrahedral cobalt(I), might result in unprecedented magnetic communication. Whilst Thomas published very similar uranium-cobalt systems to the ones described below, that were the original focus of this work, there is fortunately very little overlap in results due to different *N*- and *P*-substituents being almost completely different in both studies. It is, however, prudent to discuss Thomas's results.¹⁹

At the start incorporation of cobalt into the uranium tris(phosphinoamide) derivatives [UCl(*i*PrNPPh₂)₃] (**160**) and [UI(MesNP^{*i*}Pr₂)₃] (**161**) was done by treating both species with CoI₂, generating the heterobimetallic complexes **179** and **180**, this synthetic method did not result in particularly high isolated yields. Therefore, a one pot synthetic route was developed in which [UI₃(THF)₄] was treated with three equivalents of either [K(*i*PrNPPh₂)] (**158**) or [K(MesNP^{*i*}Pr₂)] (**159**) followed by CoI₂ (**Scheme 43**). This produced **179** and **180** cleanly with higher isolated yields of 83% and 91% respectively.



Scheme 43 – Synthesis of [UI(*i*PrNPPh₂)₃CoI] (**179**), [UI(MesNP^{*i*}Pr₂)₃CoI] (**180**)

In a procedure more similar to the synthesis of the zirconium-cobalt heterobimetallic complexes, stirring the uranium(IV) tetra(amides) $[U(^iPrNPPh_2)_4]$ (**162**) and $[U(MesNP^iPr_2)_4]$ (**163**) with one equivalent of CoI_2 , after workup, the products obtained were $[(^iPrNPPh_2)U(^iPrNPPh_2)_3CoI]$ (**181**), $[(MesNP^iPr_2)U(MesNP^iPr_2)_3CoI]$ (**182**) (**Scheme 44**).



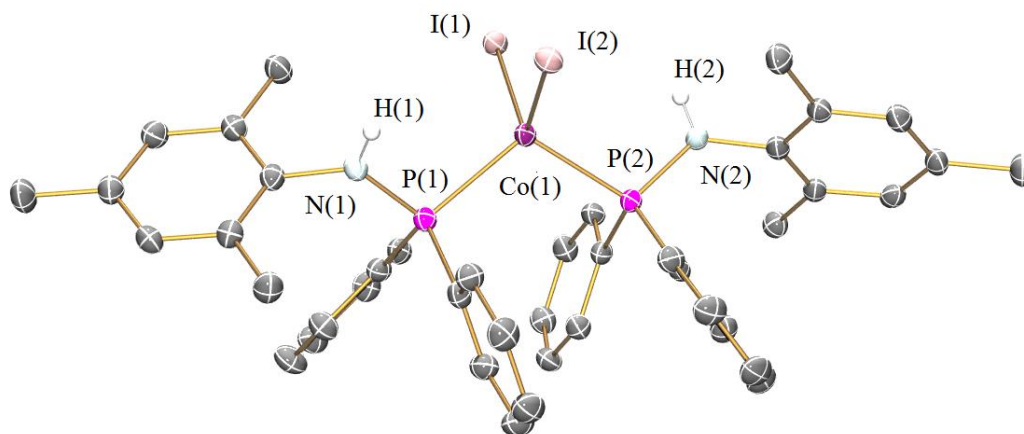
Scheme 44 – Synthesis of $[(^iPrNPPh_2)U(^iPrNPPh_2)_3CoI]$ (**181**),
 $[(MesNP^iPr_2)U(MesNP^iPr_2)_3CoI]$ (**182**)

Single crystal X-ray diffraction studies were used to determine the molecular structures of **179** and **181**. The molecular structure of **181** features a four coordinate cobalt centre in a tetrahedral geometry adjacent to a five coordinate uranium centre ligated by three amido ligands and an additional η^2 -phosphinoamide. The uranium-cobalt distance of 3.0812(7) Å is longer than the sum of the covalent radii for uranium and cobalt (2.81 Å) and longer than the previously reported U-Co distances reported by Liddle (2.94540(9)Å) and Arnold (3.0319(7) Å). The molecular structure of **179** was revealed to be similar to that of **181** with the cobalt atom in the same tetrahedral environment. The uranium centre exhibited similar bonding to the bridging phosphinoamide ligands but with an iodide occupying the apical position. The uranium cobalt distance of 2.874(3) Å is shorter than all previously reported uranium-cobalt distances but still longer than the sum of the covalent radii.

DFT calculations were used to probe the nature of the interaction between uranium and cobalt for **179**. Examination of the natural frontier molecular orbitals reveal U-Co interactions with two doubly occupied molecular orbitals containing a U-Co interaction were present, one with U-amide antibonding character and one with U-amide bonding character. The metal-metal interaction is best thought of as dative, with the more electron rich cobalt(I) centre donating electron density in the direction of the uranium(IV) centre.

4.2 Heterobimetallic Actinide-Cobalt Complexes

With the tris(phosphinoamides) uranium halides in hand, installation of cobalt centres to the coordination sphere of uranium was attempted. The addition of THF to a mixture of cobalt diiodide and $[\text{UCl}(\text{MesNPPH}_2)_3]$ (**165**) resulted in the solution darkening. The mixture was largely intractable except for the isolation of a small crop of the cobalt(II) bis(phosphinoamine)diiodide complex $[\text{CoI}_2\{\text{MesN}(\text{H})\text{PPh}_2\}_2]$ (**183**) as identified by a single crystal X-ray diffraction study with the molecular structure shown in **fig. 56**. Complex **183** crystallises as a discrete monomeric species in the space group *P*-1. The two phosphinoamine ligands are coordinated to the cobalt(II) centre through the two phosphorus atoms. Two iodide centres complete the coordination sphere with Co(1) adopting a pseudo tetrahedral geometry. The angles around the Co(II) centre range from $101.81(2)^\circ$ to $115.73(2)^\circ$. These deviations from the ideal 109.5° can be attributed to the greater steric demands of the phosphinoamine ligands relative to I. The geometries around the P(1) and P(2) centres are also tetrahedral. This geometry is analogous to that in the complex $[\text{CoI}_2\{^i\text{PrN}(\text{H})\text{PPh}_2\}_2]$ (**67**) reported by Thomas.⁶ The Co(1)-P(1) and Co(1)-P(2) bond distances of $2.3458(7)$ Å and $2.3438(7)$ Å respectively are almost identical to the cobalt-phosphorus distances of $2.3505(5)$ Å and $2.3428(5)$ Å in the complex **67**, with the N(1)-P(1) and N(2)-P(2) bond lengths of $1.690(2)$ Å and $1.691(2)$ Å slightly longer than the nitrogen-phosphorus bond lengths of $1.6561(16)$ Å and $1.6554(16)$ Å but still comparable. The paramagnetic ^1H NMR spectrum of **183** exhibits resonances in the range of -8 ppm to +17 ppm.

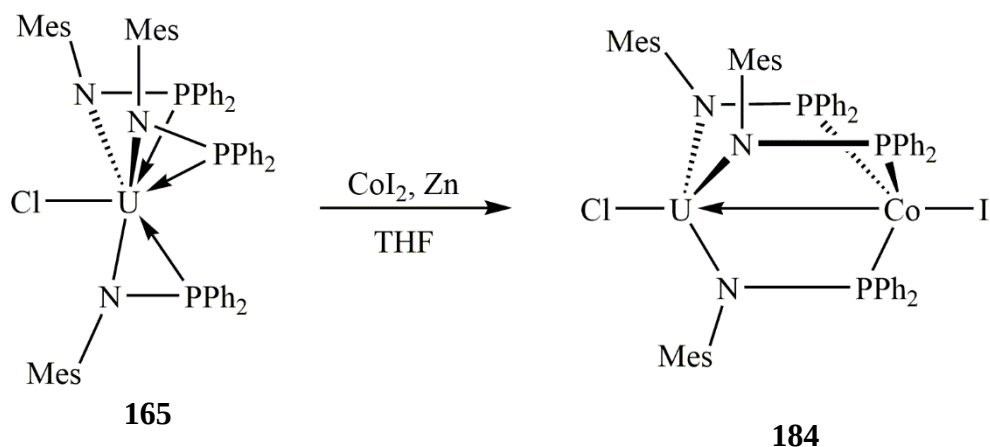


183

Fig. 56 – Structure of $[\text{CoI}_2\{\text{MesN(H)PPh}_2\}_2]$ (**183**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. Co(1)-P(1) 2.3458(7), I(1)-Co(1) 2.5484(4), P(1)-N(1) 1.690(2), Co(1)-P(2) 2.3438(7), I(2)-Co(1) 2.5519(4), P(2)-N(2) 1.691(2), P(1)-Co(1)-I(1) 115.73(2), N(1)-P(1)-Co(1) 107.76(8), P(2)-Co(1)-P(1) 111.54(3), I(1)-Co(1)-I(2) 109.990(15).

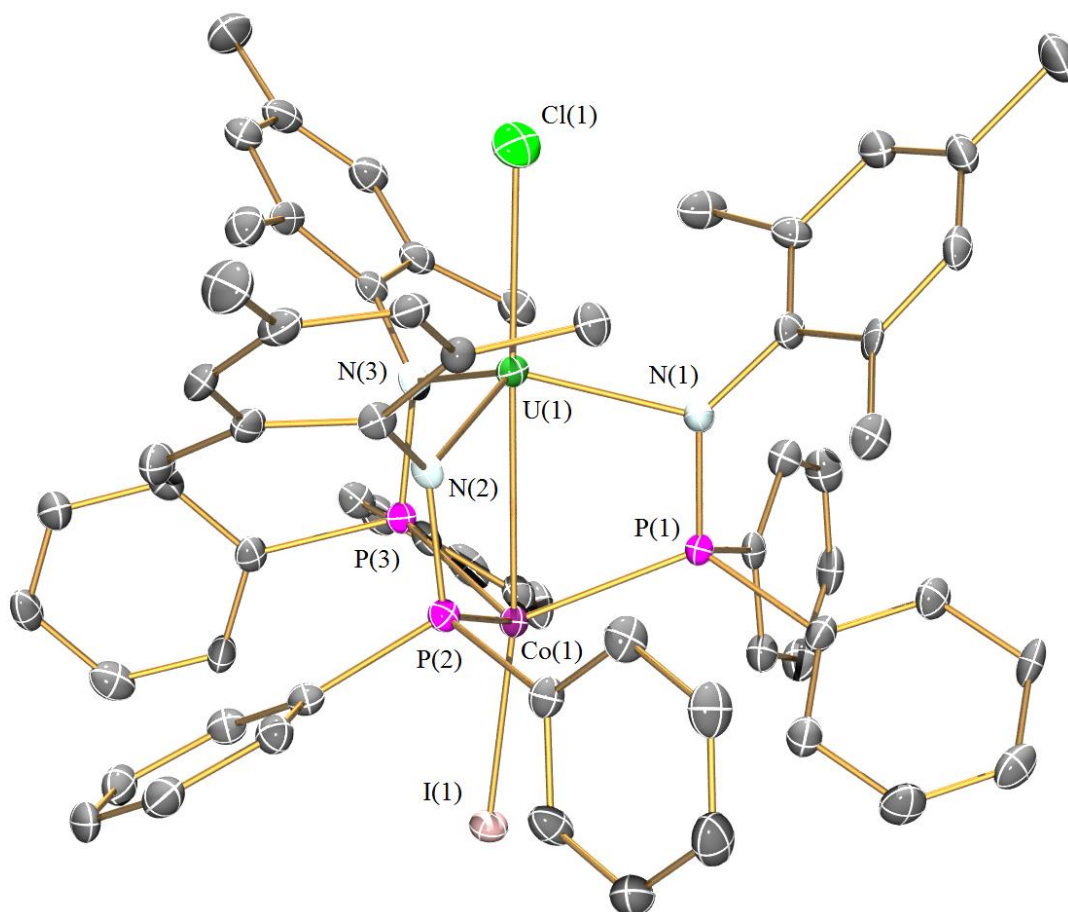
It was reasoned that the tetrahedral geometry and the coordination sites required to accommodate three phosphine centres, would call for a reduction to cobalt(I). Therefore the reaction was repeated in the presence of the mild reductant zinc⁶ resulting in the isolation of the uranium cobalt complex $[\text{UCl}(\text{MesNPPH}_2)_3\text{CoI}]$ (**184**) (Scheme 45). The ^1H NMR spectrum of **184** consists of only six resonances that span the range +13 to -6 ppm, which is consistent with a three-fold symmetric paddle-wheel type structure. In order to confirm the structure of **184** a single crystal X-ray diffraction experiment was performed with the molecular structure shown in fig. 57 with selected bond lengths and angles.



Scheme 45 – Synthesis of $[UCl(MesNPPH_2)_3CoI]$ (**184**)

Consistent with the ^1H NMR spectrum, the solid state structure adopts a three-fold symmetric paddle-wheel structure where the amide centres bond to uranium and the phosphine centres to cobalt, which is in line with hard-soft-acid-base considerations. The coordination sphere of each slightly distorted tetrahedral metal (ignoring any metal-metal bonding) is completed by a halide ligand where the soft iodide binds to cobalt and the hard chloride to uranium. Two unique molecules of **184** are present in the asymmetric unit with the two U-Co bond distances determined to be 2.9159(8) and 3.0350(8) Å. The former value is ~ 0.03 Å shorter than the unsupported U-Co bond length of 2.9450(9) Å in $[U(Ts^{Xy})\{Co(CO)_3(PPh_3)\}]$ (**14**) and lies between the values of 2.874(3) and 3.0812(7) Å for $[UI(^iPrNPPH_2)_3CoI]$ (**179**) and $[(^iPrNPPH_2)U(^iPrNPPH_2)_3CoI]$ (**181**) respectively.^{17, 19} The longer bond distance suggests that these polar uranium-cobalt interactions are easily perturbed as has been observed previously in polarised covalent uranium-gallium bonds.²⁰ The formal shortness ratio (FSR) takes into account differences in atomic size allowing for direct comparison of intermetallic distances regardless of the elements involved. The FSR_{UCo} for **184**, defined as $FSR_{UCo} = D_{UCo}/(R_U + R_{Co})$ (where D_{UCo} is the uranium-cobalt bond length and the R values are the atomic radii of uranium and cobalt) is 1.04, which compares to FSR values of 0.97-1.03 for uranium-ruthenium and -rhenium bonds,²¹⁻²⁴ 1.05 for **14**,¹⁷ 1.02 and 1.09 for **179** and **181** respectively¹⁹ and 1.00 calculated for $[ZrCl(MesNP^iPr_2)_3CoI]$ (**65**) which contains a dative zirconium-cobalt

interaction.⁶ The U-N bond lengths of 2.256(4), 2.263(4) and 2.267(4) Å are comparable to **165** and are suggestive of a uranium(IV) centre. The Co-P bond distances of 2.3199(15), 2.3296(15) and 2.3334(15) Å are as expected when compared to **65** and **66** whilst the metal halide distances are unexceptional.⁶

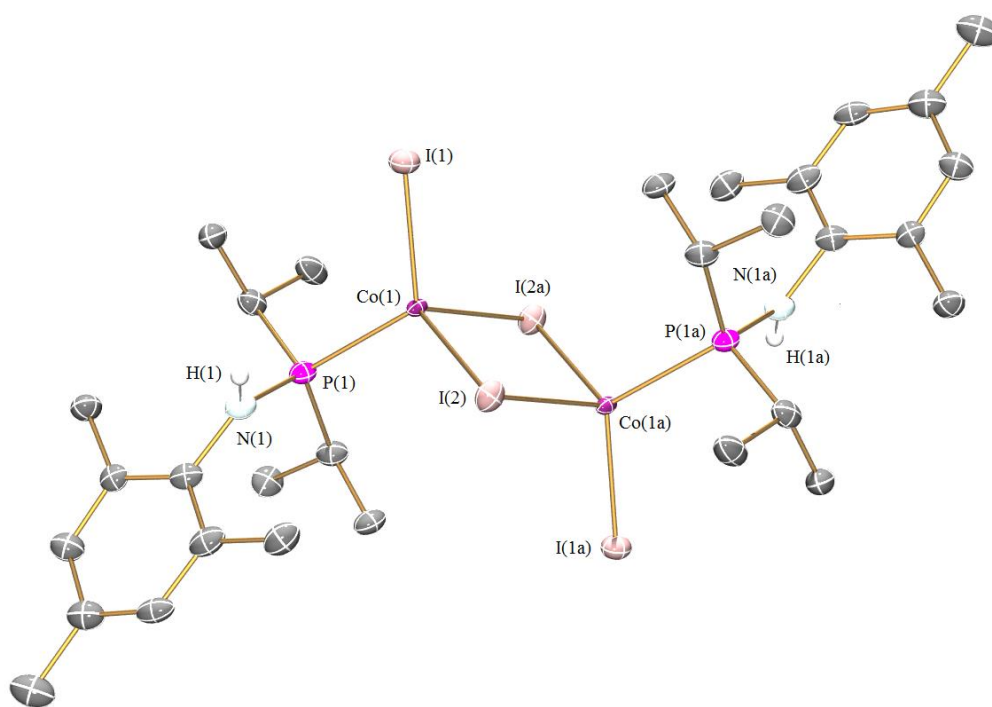


184

Fig. 57 – Structure of $[UCl(MesNPPPh_2)_3CoI]$ (**184**)

Thermal ellipsoids set at 40% probability. Solvent molecules, one of the two crystallographically unique units and H atoms omitted for clarity. U(1)-Co(1) 2.9159(8), U(1)-N(1) 2.256(4), Co(1)-P(1) 2.3334(15), P(1)-N(1) 1.678(5), U(1)-Cl(1) 2.6195(15), I(1)-Co(1) 2.5535(9), N(1)-U(1)-Cl(1) 100.27(12), P(1)-N(1)-U(1) 101.9(2), N(1)-P(1)-Co(1) 108.89(16), P(1)-Co(1)-I(1) 106.37(4).

In an analogous manner to the initial attempts of isolating **184**, the addition of THF to a mixture of cobalt diiodide and $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**168**) resulted in a largely intractable mixture of products with the exception of the decomposition product $[\text{CoI}(\mu\text{-I})\{\text{MesN}(\text{H})\text{P}^i\text{Pr}_2\}]_2$ (**185**) in small yields as identified by single crystal X-ray diffraction with the molecular structure shown in **fig. 58** with selected bond lengths and angles.

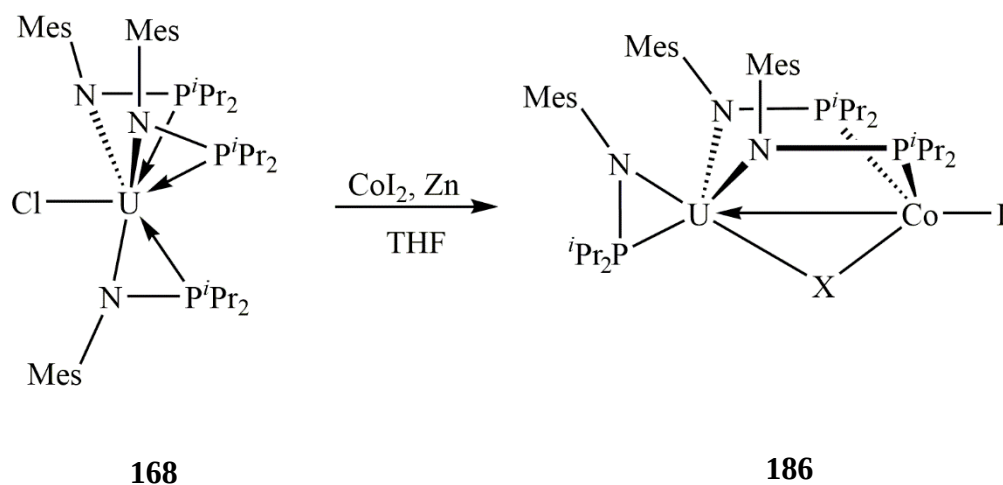


185

Fig. 58 – Structure of $[\text{CoI}(\mu\text{-I})\{\text{MesN}(\text{H})\text{P}^i\text{Pr}_2\}]_2$ (**185**)

Thermal ellipsoids set at 40% probability. Solvent molecules and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) I(1)-Co(1) 2.5327(10), I(2)-Co(1) 2.6784(11), Co(1)-P(1) 2.3862(18), P(1)-N(1) 1.673(5), N(1)-C(1) 1.457(8), Co(1)-I(2)-Co(1a) 82.01(3), I(2)-Co(1)-I(2a) 97.99(3), I(1)-Co(1)-I(2) 109.81(3), P(1)-Co(1)-I(2) 112.69(5), N(1)-P(1)-Co(1) 110.05(19).

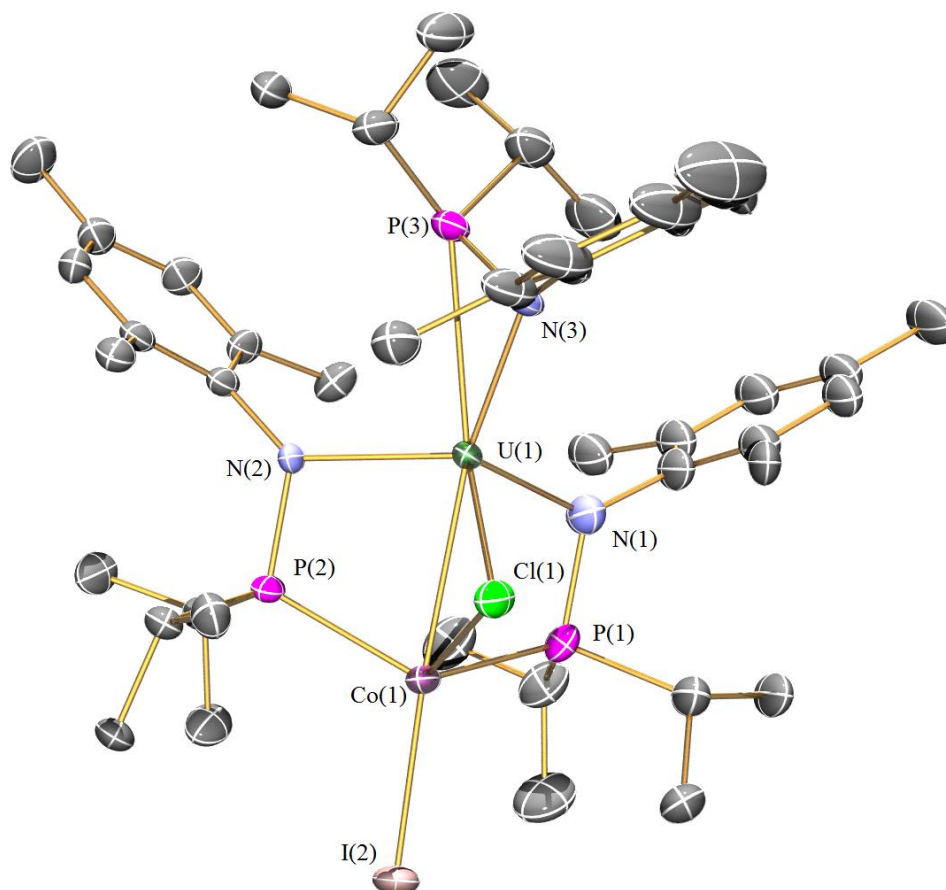
Unlike **183**, complex **185** crystallises as a discrete dimeric species in space group $C2/c$ with the phosphinoamine substituents in a *cis* conformation about the P(1)-N(1) bond. The decreased steric strain of the i Pr groups on the phosphorus compared to **185** allow for the formation of this dimeric species. The two phosphinoamine ligands are coordinated to the cobalt(II) centres through the two phosphorus atoms. Each cobalt centre is bridged by two iodide atoms with a terminal iodide completing the coordination sphere that is best described as adopting a pseudo-tetrahedral geometry. The angles around the two cobalt centres range from $97.99(3)^\circ$ to $119.16(5)^\circ$. These deviations from the ideal 109.5° can be attributed to the greater steric demands of the phosphinoamine ligands relative to I. The Co(1)-P(1) bond distance of $2.3862(18)\text{\AA}$ is almost identical to the Co-P distances of the Co(1)-P(1) and Co(1)-P(2) bond distances of $2.3458(7)\text{\AA}$ and $2.3438(7)\text{\AA}$ in complex **183** respectively. The N(1)-P(1) bond length of $1.673(5)\text{\AA}$ is also comparable to the N(1)-P(1) bond lengths in complex **183**. The ^1H NMR spectrum of **185** exhibits resonances in the range of 0 ppm to +8 ppm.



Scheme 46 – Synthesis of $[(\text{MesNP}^i\text{Pr}_2)\text{U}(\mu\text{-X})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ (**186**, $X = 42\% \text{ I}$, $58\% \text{ Cl}$)

Repeating the reaction, once again, in the presence of zinc powder allowed for the isolation of $[(\text{MesNP}^i\text{Pr}_2)\text{U}(\mu\text{-X})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ (**186**, $X = 42\% \text{ I}$, $58\% \text{ Cl}$) (**Scheme 46**) in a 35 % yield. Unlike the ^1H spectrum of **184** the NMR spectrum of **186** consists of fifteen resonances spanning the large range of +42 to -64 ppm, which

is indicative of a more asymmetric coordination environment in solution. Whilst this ^1H NMR spectrum is almost identical to that reported by Thomas for complex $[\text{UI}(\text{MesNP}^i\text{Pr}_2)_3\text{CoI}]$ (**180**) the mixed halide nature of **186** allowed crystals of a significant quality to be grown for a single crystal X-ray diffraction study. The structure of **186** was revealed to be significantly different to that of **184** with the molecular structure shown in **fig. 59** with selected bond lengths and angles. Like **184**, the cobalt centre in **186** adopts a slightly distorted tetrahedral geometry, but instead of presenting a triphosphine-halide ligand set, the cobalt centre in **186**, setting aside any uranium-cobalt interaction, is coordinated by two phosphines, a terminal iodide and a disordered mixture of chloride and iodide ligands which bridge to the uranium centre. The coordination sphere of the uranium centre is composed of the bridging halide, two amide centres which bridge from the cobalt bound phosphines and a phosphinoamide ligand the is bound through through both amide and phosphine centres. The uranium thus adopts a highly irregular six-coordinate geometry. Although there is one less phosphinoamide to stabilise any uranium-cobalt interaction, it has been replaced by a halide ligand. The U-Co bond distance in **186** was determined to be 2.9078(12) Å which is at least ~ 0.01 Å shorter than the corresponding distance in **184** but within the range of previously reported U-Co bonds.¹⁷⁻¹⁹ The U-N distances of 2.277(6), 2.254(8) and 2.263(6) Å and the U-P distance of 2.932(2) Å in **186** are similar to the corresponding bond lengths in **184** and **168**, respectively, despite the formation of different isomers. The Co-P bond lengths of 2.306(3) and 2.313(2) Å can be considered to be marginally shorter than the Co-P distances in **184** commensurate with their alkyl- rather than phenyl-substituted natures. As expected, the formal shortness ratio for **186** is 1.03, marginally shorter than in **184**.

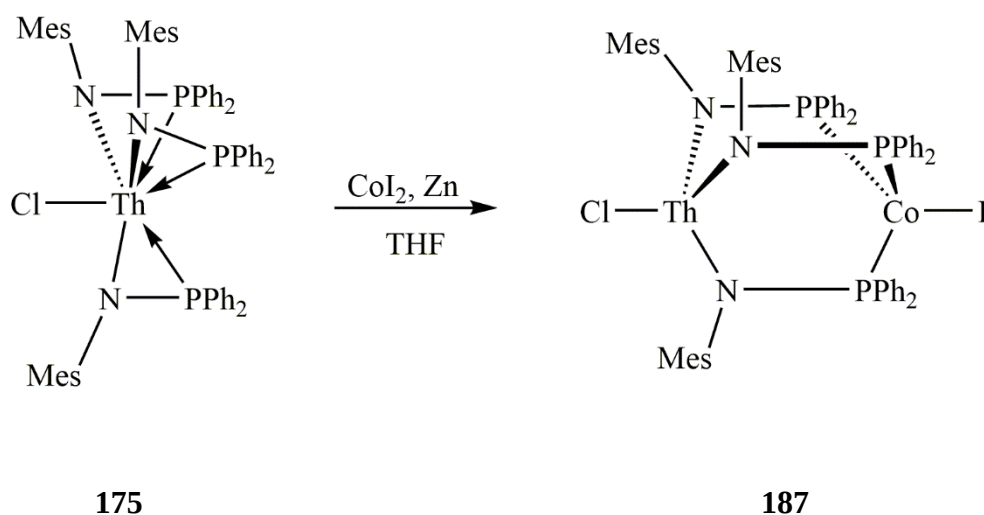


186

Fig. 59 – Structure of $[(\text{MesNP}^i\text{Pr}_2)\text{U}(\mu\text{-X})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ (**186**, $X = 42\% \text{ I}, 58\% \text{ Cl}$)

Thermal ellipsoids set at 40% probability. Solvent molecules, minor disorder components and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°) U(1)-Co(1) 2.9058(11), U(1)-N(1) 2.283(5), Co(1)-P(1) 2.312(2), P(1)-N(1) 1.699(6), U(1)-Cl(1) 2.702(8), Co(1)-Cl(1) 2.507(8), U(1)-N(3) 2.266(6), U(1)-P(3) 2.9309(18), N(3)-U(1)-N(1) 113.1(2), N(3)-U(1)-Cl(1) 101.9(2), N(3)-U(1)-P(3) 35.42(16), N(3)-U(1)-Co(1) 154.82(17), P(1)-Co(1)-I(2) 113.01(6), Cl(1)-Co(1)-I(2) 109.51(18), I(2)-Co(1)-U(1) 168.87(5).

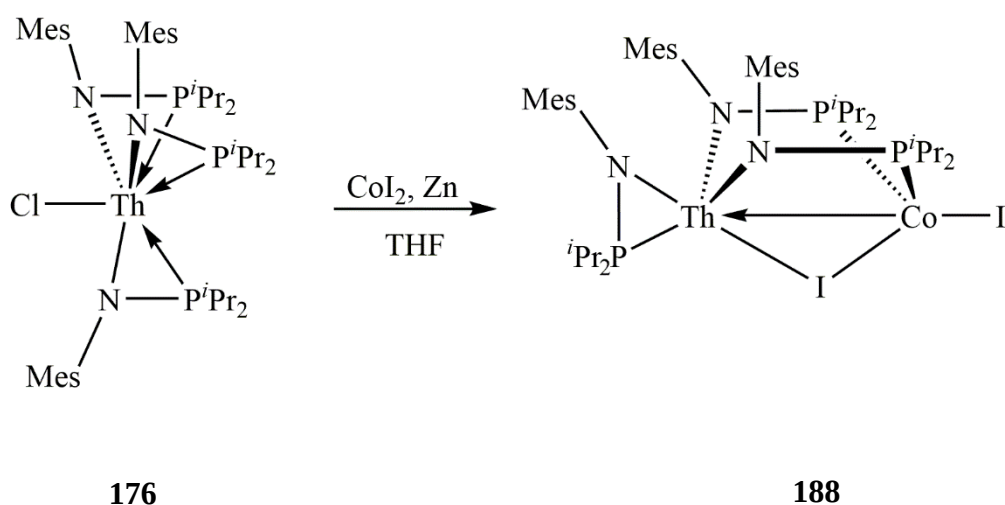
As previously mentioned in Chapter 3 the synthesis of the analogous thorium-metal complexes is of vital importance to determine the role that any 5f-electrons play in any potential actinide-cobalt metal interactions. Unlike the ground electronic state of uranium(IV) which has two 5f-electrons, the ground electron state of thorium(IV) has no *f*-electrons. With this in mind the Th-Co complexes, $[\text{ThCl}(\text{MesNPPh}_2)_3\text{CoI}]$ (**187**) and $[(\text{MesNP}^i\text{Pr}_2)\text{Th}(\mu\text{-X})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ were targeted (**188**). In an analogous methodology to the preparation of **184** Treatment of $[\text{ThCl}(\text{MesNPPh}_2)_3]$ (**175**) with one molar equivalent of CoI_2 in the presence of the mild reductant zinc in THF resulted in a dark green solution (Scheme 47). The resulting green solid was extracted into toluene and concentrated to 5 ml to yield $[\text{ThCl}(\text{MesNPPh}_2)_3\text{CoI}]$ (**187**) as an analytically pure green powder. Yield: 0.59 g, 42 %.



Scheme 47 – Synthesis of $[\text{ThCl}(\text{MesNPPh}_2)_3\text{CoI}]$ (**187**)

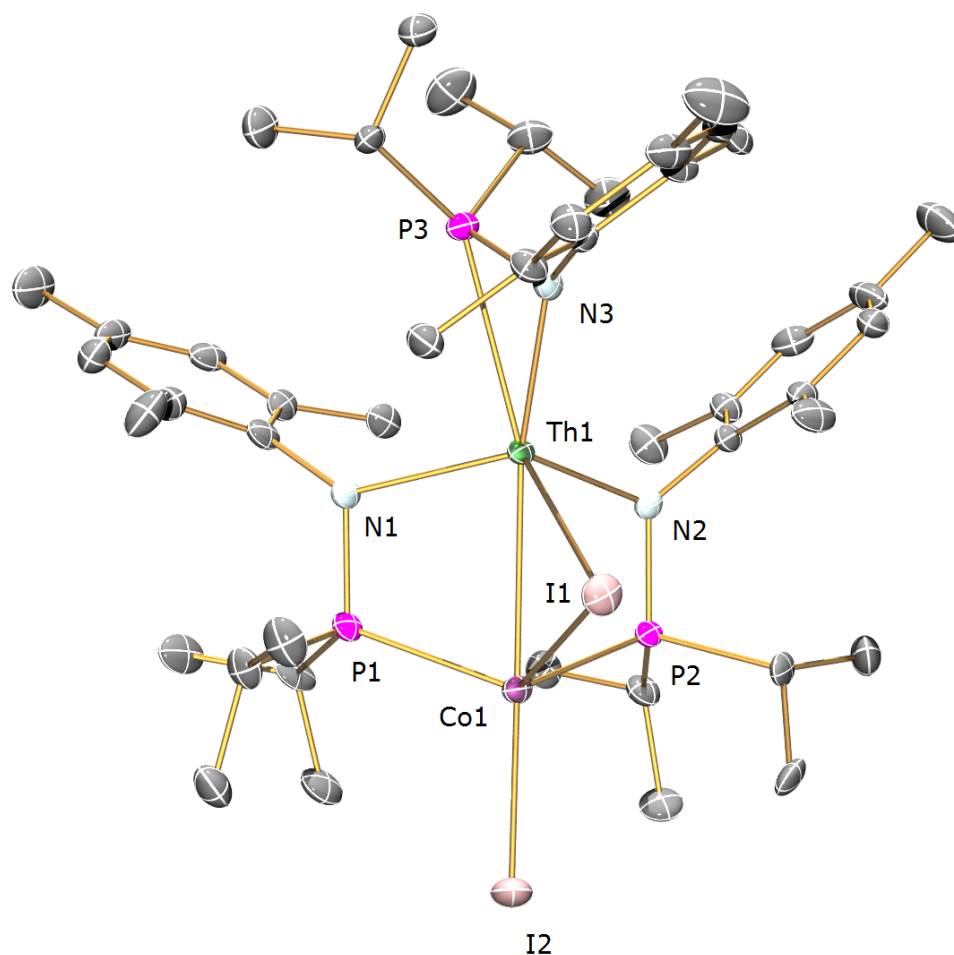
Unfortunately no crystals of significant quality were acquired to perform a single crystal X-ray diffraction study to confirm the proposed structure. The now paramagnetic ^1H NMR spectrum of **187** consists of only six resonances that span the range +13 to -3 ppm, which is consistent with a three-fold symmetric paddle-wheel type structure observed in **184**.

In an attempt to isolate the thorium analogue of $[(\text{MesNP}^i\text{Pr}_2)\text{U}(\mu\text{-X})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ (**186**), $[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**176**) was reacted with one molar equivalent of CoI_2 once again in the presence of the mild reductant zinc resulting in $[(\text{MesNP}^i\text{Pr}_2)\text{Th}(\mu\text{-I})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ (**188**) in a 15% yield (**Scheme 48**). Unlike the ^1H spectrum of **187** but similarly to the ^1H spectrum of **186**, the NMR spectrum of **188** consists of 10 resonances spanning the large range of +18 to -13 ppm, which is indicative of the more asymmetric coordination environment in solution that we would expect.



Scheme 48 – Synthesis of $[(\text{MesNP}^i\text{Pr}_2)\text{Th}(\mu\text{-I})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ (**188**)

The structure of **188** was revealed to be, like its uranium analogue, significantly different to that of **184** with the molecular structure shown in **fig. 60** with selected bond lengths and angles. Compound **188** adopts a slightly distorted tetrahedral geometry about the cobalt centre, but like **186** instead of presenting a triphosphine-halide ligand set, the cobalt centre in **188** is coordinated by two phosphines, a terminal iodide and unlike the disordered mixture of chloride and iodide ligands seen in **186**, an iodide ligand which bridges to the thorium centre. The coordination sphere of the thorium centre is composed of the bridging iodide, two amide centres which bridge from the cobalt bound phosphines and a phosphinoamide ligand that is bound through both amide and phosphine centres.



188

Fig. 60 – Structure of $[(\text{MesNP}^i\text{Pr}_2)\text{Th}(\mu\text{-I})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ (**188**)

Thermal ellipsoids set at 40% probability. Solvent molecules, minor disorder components and H atoms omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$) Th(1)-Co(1) 2.9977(12), Th(1)-N(1) 2.313(6), Co(1)-P(1) 2.319(2), P(1)-N(1) 1.697(6), Th(1)-I(1) 3.0961(6), Co(1)-I(1) 2.7416(13), Th(1)-N(3) 2.335(6), Th(1)-P(3) 2.9574(18), N(3)-Th(1)-N(1) 113.8(2), N(3)-Th(1)-I(1) 97.74(16), N(3)-Th(1)-P(3) 34.85(15), P(1)-Co(1)-I(2) 109.98(6), I(1)-Co(1)-I(2) 104.02(4).

The thorium, like the uranium in **186**, adopts a highly irregular six-coordinate geometry. The Th-Co bond distance in **188** was determined to be 2.9977(12) Å which is at least ~ 0.01 Å longer than the corresponding distance in **186** but shorter than the previously reported bridging Th-Co bond of 3.0771(5) Å in Arnold's complex $[\text{Th}(\text{N}\{\sigma\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4\}_3)\text{Co}(\text{CO})_3]$ (**20**).¹⁸ The slightly longer Th-Co distance

than the respective U-Co distance in **186** is a result of the larger effective ionic radius of Th(IV) (94 pm) compared to U(IV) (89 pm)²⁵ and is also reflected in the slightly larger FSR of 1.05. As to be expected the Th-N distances of 2.313(6), 2.328(6) and 2.335(6) Å in **188** are slightly longer than the corresponding bond lengths in **186**, respectively, but fall within the expected bond lengths for Th-N. The Co-P bond lengths of 2.319(2) and 2.332(2) Å can be considered to be marginally longer than the Co-P distances in **188** but still within the expected range.

4.3 Characterisation of Actinide-Cobalt Complexes

Although the crystal structure data for **184** and **186** are suggestive of uranium-cobalt interactions the cyclic voltograms of **184** and **186** were examined (**Fig. 61**) in order to electrochemically probe any possible interaction. Cyclic voltammetry has been purported in the related zirconium-cobalt systems to be a useful tool since shifts to more positive potential of up to ~ 1 V compared to [CoI{*i*PrN(H)PPh₂}₃] (**68**) were rationalised on the basis of donation of electron density from cobalt to zirconium.⁶ As a reference point, neither **135** or **138** exhibited reduction events in the accessible solvent window of THF, and thus any observed redox events were tentatively assigned as cobalt-based in light of the EPR data (*vide infra*). For both **184** and **186**, irreversible reductions were observed at $E_p^c = -2.51$ and -2.75 V vs [Cp₂Fe]⁺/[Cp₂Fe], respectively. Smaller follow-up oxidation events are observed at $E_p^a = -1.86$ and -1.58 V vs [Cp₂Fe]⁺/[Cp₂Fe], but these cannot be attributed to the same species due to the large differences in potentials.

The observed reductions, assigned as cobalt-based (Co^{1/0}), can be compared, allowing for variations in experimental conditions and ligand substituents, to a reduction potential of a similar magnitude for the benchmark molecule [CoI{*i*PrN(H)PPh₂}₃] (E_p^c Co^{1/0} = -2.49 V), and the related uranium-cobalt complexes **179** and **181** (E_p^c Co^{1/0} = -2.40 and -2.83 V respectively) but which is significantly different to the related zirconium-cobalt complex [ZrCl(*i*PrNPPh₂)₃CoI] (**64**) (E_p^c Co^{1/0} = -1.65 V).^{6, 19} Although it must be recognised that the protonation state of the

phosphinoamide/amine ligand varies in these complexes which might be expected to impact the redox energetics, it can be qualitatively surmised from this data that the uranium-cobalt interactions in **184** and **186**, which may be formulated as dative donor-acceptor interactions from cobalt to uranium, may be weak. This would be consistent with more electron rich, and hence more difficult to reduce, cobalt centres in **184** and **186** compared to **64** since the former pair of complexes contain $5f^2$ uranium that would arguably not induce as much electron donation from cobalt compared to the latter which contains $4d^0$ zirconium.

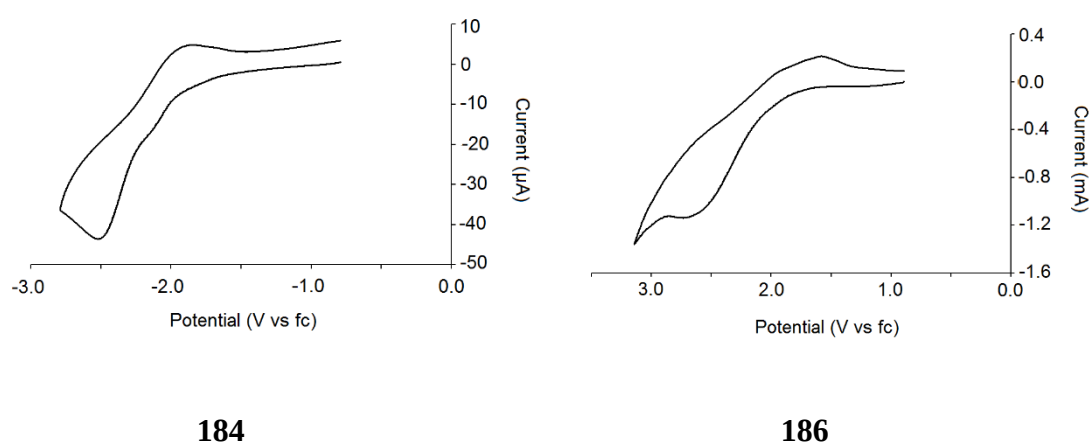


Fig. 61 – Cyclic voltammograms of **184** and **186** referenced to the $[\text{Cp}_2\text{Fe}]^+ / [\text{Cp}_2\text{Fe}]$ couple (1.0 and 0.7 mmol in analyte, 0.5 and 0.32 M $[\text{NBu}_4][\text{BAr}^f_4]$, respectively, in THF) at 100 mV/s scan rate.

Electron paramagnetic resonances (EPR) spectra were recorded on polycrystalline powders using X- and K-band frequencies (9.4 and 24 GHz) at room temperature with the results shown in **fig. 62**. Uranium(IV) is a non-Kramers ion and under the measurement conditions employed, uranium(IV)-based 5f-electrons would not be expected to contribute to the EPR spectrum since f-electrons undergo fast relaxation due to a large contribution of orbital angular momenta under the influence of significant spin-orbit coupling.²⁶ EPR spectra of uranium would normally be expected to require low temperatures (<30 K) to overcome these relaxation effects, even for formally allowed transitions. The cobalt centres in **184** and **186** can be formally described as cobalt(I) and are thus $3d^8$. In a trigonally-distorted tetrahedral crystal field

(for these purposes we ignore the potentially weak uranium-cobalt interaction) cobalt(I) presents two unpaired electrons, which should be observable by EPR spectroscopy. Indeed, the EPR spectra of **184** and **186** obtained at room temperature clearly show asymmetric, broad resonances centred on $g = 2.2$ as expected from d-based electrons. The narrower breadth of **184** versus **186** (i.e. $\Delta B_{p-p} = 870$ and 1250 G at X-band, respectively) is consistent with the presence of the two different ligand fields in crystalline **184** and **186**.

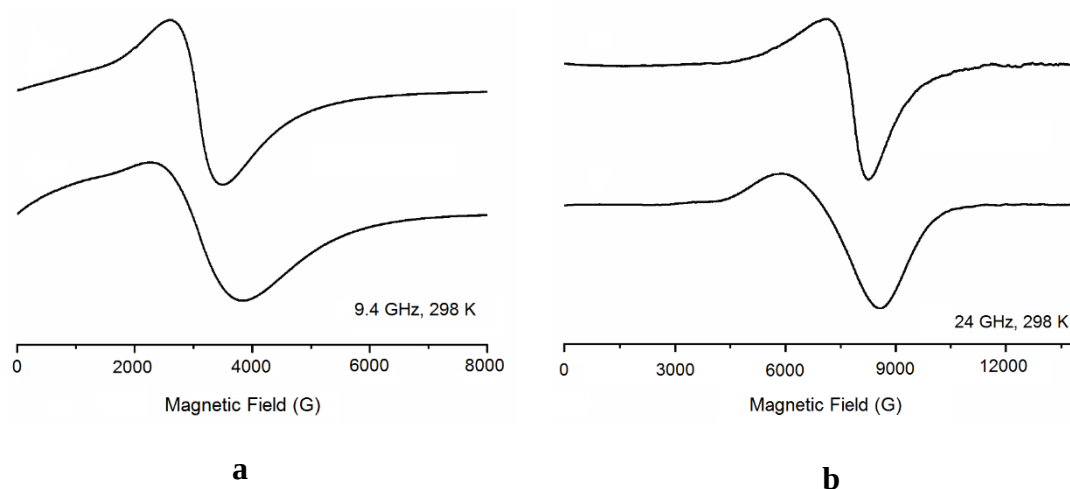


Fig. 62– X- (a) and K-band (b) EPR spectra of polycrystalline spectra samples of **184** and **186**

The room temperature magnetic moments $\mu_{\text{eff}} = 2.38 \mu_{\text{B}}$ (**165**) and $\mu_{\text{eff}} = 2.27 \mu_{\text{B}}$ (**168**) from the Evans method define the contribution of uranium(IV) in these coordination environments, which carry forward to $\mu_{\text{eff}} = 4.08 \mu_{\text{B}}$ (**184**) and $\mu_{\text{eff}} = 3.93 \mu_{\text{B}}$ (**186**), thereby indicating the separate contribution of the proposed cobalt(I) centre. Whilst cobalt(I) is isoelectronic with nickel(II) and the latter ion providing classic examples of magnetic studies of the tetrahedral $3d^8$ electronic configuration,²⁷⁻²⁹ recent examples from Riordan³⁰ and from Power³¹ provide more directly relevant magnetic data on low symmetry cobalt(I). Relevant to this work, Telser³² reported a high frequency-high field EPR study of $[\text{CoX}(\text{PPh}_3)_3]$ ($\text{X} = \text{Cl}$ or Br) following the earlier work of Aresta³³ and of Klein and Karsch,³⁴ along with a detailed analysis of the electronic structure using ligand field theory (LFT), DFT and unrestricted hartree-fock

theory (UHF) methods; this molecule is essentially the Co-containing moieties of **184** and **186**. Readily detectable spectra were found at room temperature and at 10 K, unambiguously assigned to $S = 1$ with large (range +2 to +8 cm^{-1}), well resolved axial zero-field splitting (ZFS), which is exquisitely sensitive to geometry. The three crystallographically distinct sites in the unit cell have appreciably different D values. Significantly, they note that the effect of spin-orbit coupling from the ligands might be opposite in their contribution to ZFS compared to that of cobalt(I) and hence replacement of Cl by Br leads to a lowering of the observed positive D value. Both **184** and **186** with iodide ligand(s) would be expected to have still lower D values, notwithstanding the local presence of the even heavier (larger spin-orbit coupling) uranium on the cobalt-iodide axis, which is entirely consistent with our observations of broad EPR resonances centred on $g = 2.2$. Taking the analogy further, Telser's electronic structural calculations, guided by the experimental D values, gave an isolated electronic ground state in C_{3v} symmetry of $^3A_2[^3T_1(F)]$. Thus, treating the cobalt ion as $S = 1$ and taking $g = 2.2$ from the EPR spectra leads to a high calculated magnetic contribution $\chi T_{Co} = 1.21 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Using $\mu_{eff} = 2.38 \mu_B$ (**165**) gives $\chi T_U = 1.21 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. A combination of these two results gives a $\mu_{eff} = 3.90 \mu_B$, which is in very satisfactory agreement with the observed values for **184** and **186** in view of the assumptions involved.

Uranium(IV) is a magnetic singlet at low temperature, which results in an essentially diamagnetic response with a small temperature-independent paramagnetism (TIP) contribution. Typical values of TIP for uranium(IV) are in the order of $\chi = 25 \times 10^{-4} \text{ emu mol}^{-1}$, as is the case for $[UCl_6]^{2-}$ (emu = electromagnetic units).³⁵ This becomes a more important contribution to the measured magnetic moment at higher temperatures. Additionally, at liquid helium temperatures tetrahedral $3d^8$ can also present a diamagnetic ground state.³⁶ The significant decrease in the observed μ_{eff} values for certain terphenyl cobalt(I) arene complexes below $\sim 30 \text{ K}$,³¹ which would be consistent with large positive zero-field splitting with the spin-Hamiltonian formalism, is itself consistent with the presence of low-lying excited states in the low symmetry four coordinate geometry. However we know that in the case of **184** and **186** the zero-field splitting should be relatively small because of the EPR response observed at the X-band frequency (the energy corresponding to the X-band frequency is $\sim 0.3 \text{ cm}^{-1}$).

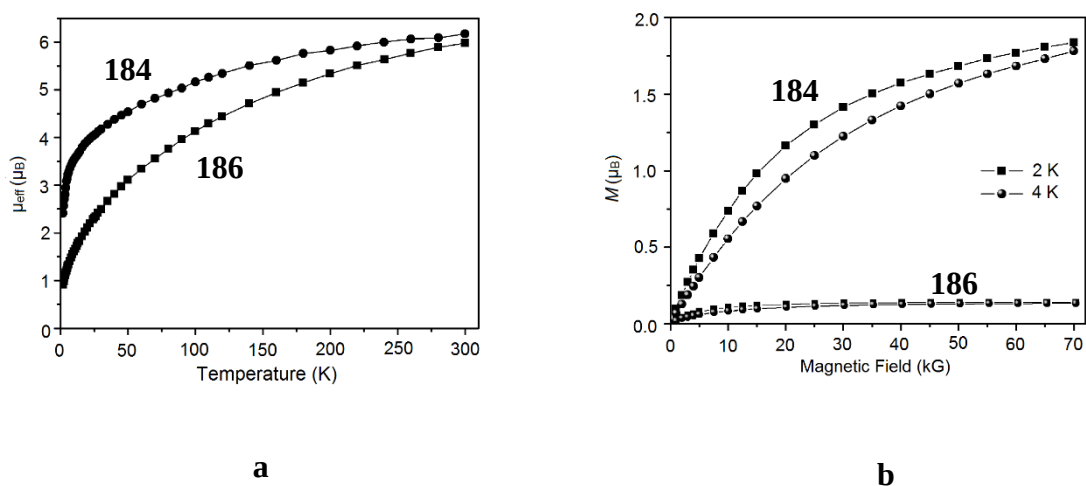


Fig 63 – (a) Temperature dependence of the effective magnetic moment μ_{eff} of powdered samples of **184** (circles) and **186** (squares) in the range 1.8 to 300 K in an applied DC field of 10 kG; (b) Field dependence of the magnetization data at 2 (squares) and 4 K (circles) for **184** and **186**.

The results of the variable temperature squid magnetometry for **184** and **186** dispersed in eicosane are shown in **fig. 63a** as a plot of μ_{eff} (μ_B) versus temperature over the range 300 to 1.8 K. Remarkably, the results are very different for the two compounds. In both cases the magnetic moment falls on cooling from room temperature, but more rapidly for **186** than for **184**, and both moments fall steeply below 30 K. The room temperature moments of $\sim 6 \mu_B$ are each $2 \mu_B$ higher than in the solution phase potentially as a result of a combination of factors; including the different phases of Evans and squid measurements, weighing errors and the effect of the TIP that impacts strongly on high temperature data. It could also be, noting that small changes in geometry are known to significantly affect the magnitude of ZFS at Co(I), that minor fluxional behaviour in solution gives an averaged electronic environment whereas in the solid state a slightly different situation occurs. However, further work will be required to understand this.

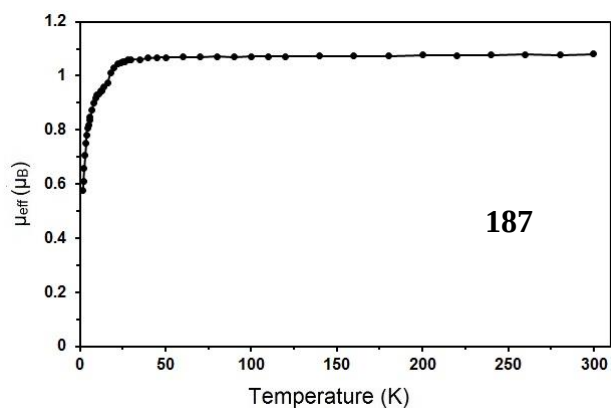
The low temperature magnetisation data at 2 and 4 K are drastically different for the two compounds shown in **fig. 63b**. For **184**, M (μ_B) is approaching a value of $2 \mu_B$ at 7 T ($T = \text{Tesla}$), which is consistent with the dominant contribution of the $S = 1$ cobalt(I) component and the expected near diamagnetism of U(IV), with its small TIP

following thermal depopulation into a nonmagnetic singlet ground state.³⁵ In stark contrast, **186** shows only a very weak magnetic response up to 7 T at both 2 and 4 K. It is already established in **184** and in closely related compounds that the cobalt(I) centre remains magnetic at low temperature responding as a spin triplet because of the relatively small ZFS and hence modest D value. Thus, the non-magnetic $S = 0$ ground state of **186** could potentially arise from antiferromagnetic coupling and/or metal-metal bond formation between uranium(IV) and cobalt(I). The two major structural differences between the uranium(IV) site in **184** and **186** are: (i) the single atom halide bridge and (ii) the η^2 P-N bonding in **186**. The former may encourage the closer approach of the two metals compared to **184** as well as providing a direct pathway for magnetic exchange. However, if the halide bridge provided the mechanism for magnetic exchange from Hund's rule this would be expected to likely be ferromagnetic, which is not experimentally observed, since DFT calculations (see later) show the occupied uranium 5f orbitals to be poorly aligned for σ - or π -bonding to the halide ligand and thus orthogonal orbitals would be involved in the magnetic exchange. The disordered mixture of chloride and iodide bridging ligands is unlikely to significantly impact on the data since the Co-X bond is formally dative in nature; if the Co-X bond was formulated as covalent this would require a Co(II)-U(III) formulation that is completely at odds with all the characterisation data and can hence be dismissed. The latter may ensure that the overall crystal field strength (4 *versus* 5 coordinate, not considering U-Co interactions) and local symmetry (idealized C_{3v} in **184** *versus* at best Cs in **186**) are very different.

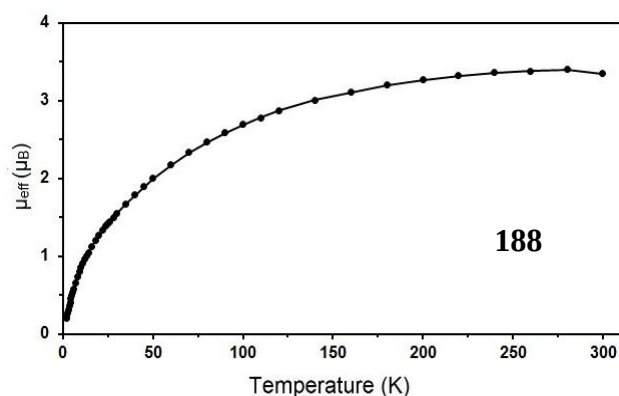
The magnetic behaviour of **186** is potentially notable because directly observable magnetic coupling of uranium(IV) to other metals is an exceptionally rare occurrence that is usually masked by other phenomena requiring diamagnetic surrogate subtraction techniques.³⁷⁻⁴⁸ Furthermore, such coupling is usually mediated by bridging ligands rather than direct metal-metal bonds and **186** could represent the first example of uranium-cobalt antiferromagnetic coupling. Unfortunately, in the absence of a uranium(IV)-metal(d^{10} -diamagnetic) analogue to **186** it is not possible to extract a J_{UCo} value from the data because of the changes in ligand field and uranium angular momentum as a function of temperature. Lastly and importantly, all the above magnetic data are consistent with the assignment of the oxidation states as U(IV) and

Co(I) in both **184** and **186**, which were further confirmed *via* computational methods, and the electronic coupling in **186**.

As already established in the closely related compounds, the cobalt(I) centre remains magnetic at low temperature responding as a spin triplet because of the relatively small ZFS and hence modest D value. So in an attempt to confirm that the non-magnetic $S = 0$ ground state of **186** arises from antiferromagnetic coupling and/or metal-metal bond formation between uranium(IV) and cobalt(I) and not from isolated coupling of the cobalt and uranium electrons respectively variable temperature squid magnetometry for **187** and **188** was performed. The initial results of the variable temperature squid magnetometry for **187** and **188** dispersed in eicosane are shown in **fig. 64** as a plot of μ_{eff} (μ_B) versus temperature over the range 300 to 1.8 K. Once again the results are very different for the two compounds.



A



B

Fig 64 – Temperature dependence of the effective magnetic moment μ_{eff} of powdered samples of **187** (**A**) and **188** (**B**) in the range 1.8 to 300 K in an applied DC field of 10 kG

Whereas the room temperature moments between **184** and **186** were very similar the room temperature magnetic moment for **187** is $1.08 \mu_B$ compared to $3.34 \mu_B$ for **188**. In both cases however, the magnetic moment falls on cooling from room temperature, but more rapidly for **188** than for **187**, and both moments fall steeply below 30 K. The room temperature moments of 3.46 and $2.98 \mu_B$ for **187** and **188** respectively from the Evans method are each comparable to the room temperature moment of the complex $[\text{CoI}\{\text{PrN}(\text{H})\text{PPh}_2\}_3]$ reported by Thomas of $2.89 \mu_B$.⁶ Differences in the solution phase are potentially as a result of a combination of factors; including the different phases of Evans and squid measurements, weighing errors and the effect of the TIP that impacts strongly on high temperature data.

As **Fig. 64B** tends to zero this suggests the asymmetric system **188** becomes non-magnetic. For the uranium complex **186** this is potentially as a result of invoked antiferromagnetic coupling, but for diamagnetic thorium complex **188** this suggests the cobalt becomes $S=0$ without further interaction. This undermines case for antiferromagnetic coupling in **186**. Further analysis of this SQUID data along with the low temperature SQUID and EPR measurements remains ongoing and at this stage it cannot conclusively stated that antiferromagnetic coupling is present but there is sufficient evidence which warrants further investigation that would be expected to be very detailed and that is thus unfortunately beyond the timeframe of this PhD.

4.4 Density Functional Calculations

In order to examine the nature of any potential uranium-cobalt interactions in **184** and **186**, unrestricted density functional calculations on **184** and **186** were carried out, using a chloride bridge in the latter. The geometry optimized structures compare reasonably well to the experimentally derived structures, but although bond lengths and angles are generally computed to within 0.06 Å and 2° the uranium-cobalt bond lengths are underestimated by ca 0.1 – 0.2 Å. DFT calculations for **184** and **186** ($S = 2$) reveal four α -spin orbitals that correspond formally to the two unpaired 5f (HOMO and HOMO-1) and two unpaired 3d (HOMO-2 and HOMO-3) electrons associated with the formal uranium(IV) and cobalt(I) centres, respectively (**Fig. 63**). For **184** and **186** the HOMO-2 and HOMO-3 involve Co 3d orbitals and π -type contributions from the terminal I-donor. Cobalt 3d and terminal I σ -combinations HOMO-7 and HOMO-5 in the α -spin manifolds of **184** and **186**, were also identified respectively, which correspond to formal cobalt-based lone pairs with the potential to donate to the uranium centre.

The Nalewajski-Mrozek bond indices (**Table 1**) suggest an interaction, and the charges and spin densities on the uranium and cobalt centres in **184** and **186** are consistent with charge transfer from cobalt to uranium. The molecular orbitals that comprise the principal uranium-cobalt interactions in **184** and **186** are delocalized across the molecules (**Fig. 63**) and in order to develop a more intuitive description of any potential interactions between the uranium and cobalt centres in **184** and **186** we attempted NBO analyses. However, these did not indicate a formal U-Co bond in either case. Therefore, we turned to QTAIM, to analyse electron density $\rho(\mathbf{r})$ in the U-Co bonds in **184** and **186**. For closed shell interactions the Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$ is typically positive. The electronic energy density $H(\mathbf{r})$ of the charge distribution is defined as $H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r})$ where $G(\mathbf{r})$ is the kinetic energy density and $V(\mathbf{r})$ is the potential energy. For **184** and **186**, uranium-cobalt bond critical points (BCPs) were identified which supporting the notion of formal dative cobalt to uranium interactions. The BCP values for $\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$, $G(\mathbf{r})$, $V(\mathbf{r})$ and $H(\mathbf{r})$ are typical of a predominantly closed-shell interaction in both compounds.²³ QTAIM analyses on

$[(\text{Ts}^{\text{Xy}})\text{UCo}(\text{CO})_3(\text{PPh}_3)](\mathbf{14})$ ¹⁷ that contains formal uranium(IV) and cobalt(-I) centres reveals surprisingly similar BCP parameters.

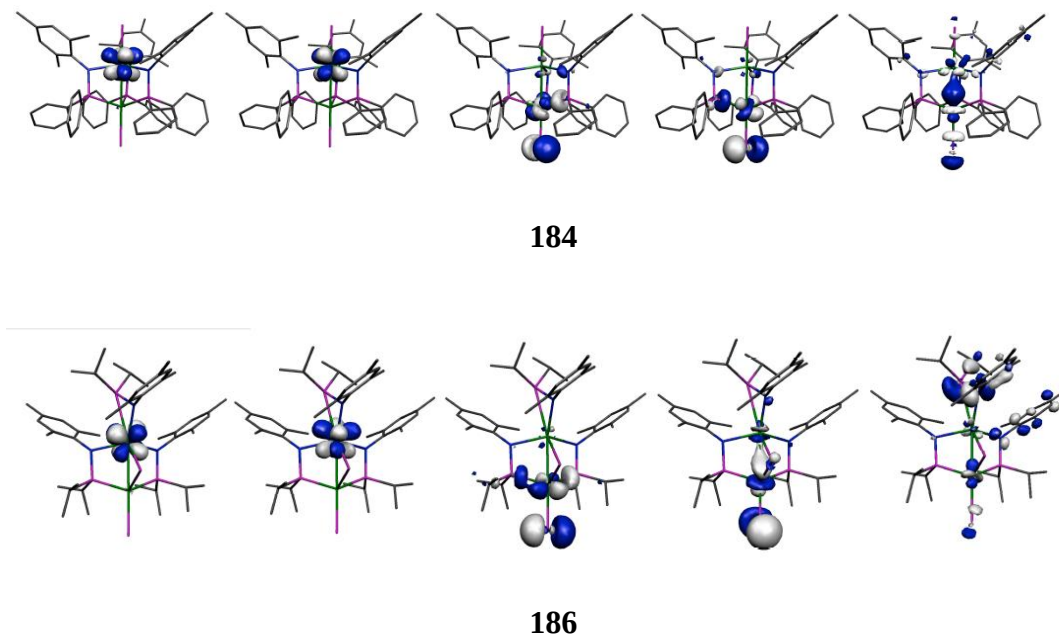


Fig. 63 - α -Spin Kohn–Sham orbital representations of the frontier orbitals of **184** and **186**. For **184** left to right: HOMO (350a, -3.184 eV), HOMO-1 (349a, -3.251 eV), HOMO-2 (348a, -4.490 eV), HOMO-3 (347a, -4.930 eV), HOMO-7 (343a, -3.399 eV). For **186** left to right: HOMO (302a, -3.184 eV), HOMO-1 (301a, -3.267 eV), HOMO-2 (300a, -4.411 eV), HOMO-3 (299a, -4.781 eV), HOMO-5 (297a, -5.038 eV).

In the light of the very different magnetic responses of **184** and **186**, calculations on the $S = 0$ spin forms of these molecules to compare with the $S = 2$ states were conducted. A converged calculation for the $S = 0$ form for **184**, was unable to be obtained, suggesting an inherent instability of this state. However for **186** a converged solution for the $S = 0$ state which lies at 6.7 kJ mol⁻¹ lower in energy relative to the corresponding $S = 2$ state was identified. These results are consistent with an antiferromagnetically coupled system for **186** at low temperature and a different magnetic behaviour. Thus, gas phase calculations on **184** and **186** suggest a greater separation in energy of the $S = 2$ and $S = 0$ states for **184** relative to **186**; this mirrors the differences between **184** and **186** in the experimental magnetization experiments

which suggest $S = 2$ states at room temperature but different $S = 1$ and $S = 0$ states for **184** and **186**, respectively, at low temperature.

In order to further examine any potential interaction in complex **186** unrestricted density functional calculations on **188** were carried out with the geometry optimized structure comparing reasonably well to the experimentally derived structure bond with lengths and angles generally computed to within 0.06 Å and 2°. Computational analysis was not performed on **187** as the absolute structure could not be determined experimentally. DFT calculations on **188** revealed as expected that the thorium centre is more polar than the uranium centre of **186**. The Thorium spin density of 0 is what you expect and results in a very polar and ionic situation so it has been concluded that visualisation of Kohn Sham molecular orbitals is unnecessary.

The Nalewajski-Mrozek bond indices (**Table 1**), like in **186**, is suggestive of an interaction between the thorium and cobalt in **188** so to develop a more detailed description of any potential interactions we attempted NBO analyses this however once again only returned an ionic scenario. Therefore, we turned to QTAIM, to analyse electron density $\rho(\mathbf{r})$ in the Th-Co bond in **188**. For **188** 3,-1 bond critical points (BCPs) were identified which support the notion of formal polar cobalt to thorium interaction. The BCP values for $\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$, $G(\mathbf{r})$, $V(\mathbf{r})$ and $H(\mathbf{r})$ are comparable to the QTAIM analysis performed on **184**, **186** and **14**. A final point is that all ellipticities of the M-Co bonds for **184**, **186** and **188** are all calculated to be <0.1, predicting a cylindrical σ bond, as to be expected.

Entry ^a	M-Co ^b	M-Co ^c	BI ^d	m_M^e	q_M^f	m_{Co}^g	q_{Co}^h	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$G(\mathbf{r})$	$V(\mathbf{r})$	$H(\mathbf{r})$
184	2.9159(8)	2.777	0.86	2.30	2.56	1.60	-0.33	0.053	0.078	0.023	-0.027	-0.004
186	2.9078(12)	2.827	0.87	2.28	2.67	1.70	-0.10	0.049	0.064	0.025	-0.041	-0.013
14	2.9450(9)	3.048	0.45	2.30	1.87	-0.02	0.31	0.033	0.052	0.019	-0.024	-0.013
188	2.9977(12)	2.938	0.57	-0.01	2.61	1.71	-0.24	0.043	0.053	0.024	-0.034	-0.010

Table 1. Bond lengths, indices, spin densities, atomic charges and QTAIM parameters for **184**, **186**, **14** and **188**.¹⁷

^a All molecules geometry optimised without symmetry constraints at the LDA/VWN BP TZP/ZORA level. ^b Exp. M-Co distance (Å). ^c Calc. M-Co distance (Å). ^d Nalewajski-Mrozek bond indices. ^e MDC-m α -spin density on actinide metal. ^f MDC-q charge on actinide metal. ^g MDC-m α -spin density on cobalt. ^h MDC-q charge on cobalt.

4.5 Concluding remarks

The tris(phosphinoamide)uranium chloride complexes $[\text{UCl}(\text{MesNPPH}_2)_3]$ (**165**) and $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**169**) were reacted with cobalt diiodide in the presence of zinc powder to yield the new U-Co complexes $[\text{UCl}(\text{MesNPPH}_2)_3\text{CoI}]$ (**184**) and $[(\text{MesNP}^i\text{Pr}_2)\text{U}(\mu\text{-X})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ (**186**, X = 42% I, 58% Cl) respectively. Both were structurally characterised using single crystal X-ray diffraction experiments to reveal U-Co distances of 2.9159(8) and 2.9058(11) Å respectively. When the reactions were attempted without the presence of zinc powder only the decomposition products $[\text{CoI}_2\{\text{MesN}(\text{H})\text{PPh}_2\}_2]$ (**183**) and $[\text{CoI}(\mu\text{-I})\{\text{MesN}(\text{H})\text{P}^i\text{Pr}_2\}]_2$ (**185**) were isolated.

Complex **184** adopts a paddle-wheel structure with approximate C_{3v} symmetry and three bridging phosphinoamide ligands, **186** exhibits a structure with at best C_{2v} symmetry and two bridging phosphinoamides and one bridging halide ligand. These structural differences confer very different magnetic behavior. Complex **184** can be formulated as a $S = 2$ spin system at room temperature from uranium(IV) and cobalt(I) magnetic triplet contributions, and as a $S = 1$ spin system at low temperature resulting from a combination of a magnetic singlet uranium(IV) and triplet cobalt(I). However, in contrast complex **186** is a $S = 2$ spin system at room temperature but clearly a $S = 0$ spin system at low temperature with antiferromagnetic exchange between uranium and cobalt proposed. Density functional theory calculations and topological bond analyses support the notion of formally dative $\text{Co} \rightarrow \text{U}$ bonds in **184** and **186**.

To further support the claim of antiferromagnetic exchange between uranium and cobalt the thorium analogues $[\text{ThCl}(\text{MesNPPH}_2)_3\text{CoI}]$ (**187**) and $[(\text{MesNP}^i\text{Pr}_2)\text{Th}(\mu\text{-I})(\text{MesNP}^i\text{Pr}_2)_2\text{CoI}]$ (**188**) were synthesised from the reaction of $[\text{ThCl}(\text{MesNPPH}_2)_3]$ (**175**) and $[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**176**) with cobalt diiodide and powdered zinc respectively. Whereas the structure of **188** was able to be authenticated by a single crystal X-ray diffraction study the structure of **187** was inferred from its spectroscopic data. To date, investigations into the electronic structure of **187** and **188** is still on going and conclusions about the nature of the cobalt centre cannot be drawn.

4.6 Experimental

Preparation of [UCl(MesNPPh₂)₃CoI] (184)

THF (30 ml) was added slowly to a cold (-78 °C) stirring mixture of [UCl(MesNPPh₂)₃] (1.24 g, 1.0 mmol), CoI₂ (0.31 g, 1.0 mmol) and Zn (65.44 mg, 1 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. Volatiles were removed in *vacuo* and the resulting pale brown solid was extracted into toluene and concentrated to 5 ml to yield [UCl(MesNPPh₂)₃CoI] as brown/red crystals suitable for a single crystal X-ray diffraction study. Yield 0.48 g, 42 %. Anal. Calc'd for: C₆₃H₆₃ClN₃P₃UCoI: C, 53.48; H, 4.49; N, 2.97 %. Found: C, 52.33; H, 4.79; N, 2.75 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) -5.95 (6H, s, Ar-CH), -5.01 (6H, s, Ar-CH), -2.38 (18H, s, Mes-CH₃), 0.41 (12H, s, Ar-CH), 2.85 (9H, s, Mes-CH₃), 12.32 (12H, s, Ar-CH). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 543, (w) 566 (w), 695 (w), 739 (w), 765 (w), 854 (w), 892 (w), 1147 (w), 1205 (w), 1303 (w). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 4.08 \mu_{\text{B}}$. UV-vis (THF): λ_{max} ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) 711 (299.6) nm, 914 (125.6) nm, 1416 (180.5) nm.

Preparation of [(MesNPⁱPr₂)U(μ -X)(MesNPⁱPr₂)₂CoI] (X = 42% I, 58% Cl) (186)

THF (30 ml) was added slowly to a cold (-78 °C) stirring mixture of [U(Cl)(PⁱPr₂NMes)₃] (1.02 g, 1.0 mmol), CoI₂ (0.31 g, 1.0 mmol) and Zn (65.44 mg, 1 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. Volatiles were removed in *vacuo* and the resulting pale brown solid was extracted into toluene and concentrated to 5 ml to yield [U(η^2 -PⁱPr₂NMes)(μ -X)(PⁱPr₂NMes)₂Co(I)] as green crystals suitable for a single crystal X-ray diffraction study. Yield 0.44 g, 35%. Anal. Calc'd for C₄₅H₇₅Cl_{0.59}I_{1.41}N₃P₃CoU: C, 43.31; H, 6.06; N, 3.37 %. Found: C, 43.11; H, 5.99; N, 3.31 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) -63.75, -56.56, -27.25, -19.37, -16.43, -12.17, -7.93, -4.19, 0.64, 11.71, 15.19, 16.64, 18.24, 24.16, 41.20. FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 528 (m), 568 (w), 590 (w), 676 (m), 742 (w), 764 (m), 799 (s), 855 (m), 908 (w), 933 (w), 961 (w), 1152 (s), 1302 (m), 3349 (w). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 3.93 \mu_{\text{B}}$. UV-vis (THF): λ_{max} ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) 1016 (142.0) nm, 1398 (161.5) nm.

Preparation of [ThCl(MesNPPPh₂)₃CoI] (187)

THF (30 ml) was added slowly to a cold (-78 °C) stirring mixture of [ThCl(MesNPPPh₂)₃] (1.22 g, 1.0 mmol), CoI₂ (0.31 g, 1.0 mmol) and Zn (65 mg, 1.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. Volatiles were removed in vacuo and the resulting green solid was extracted into toluene and concentrated to 5 ml to yield [ThCl(MesNPPPh₂)₃CoI] as a green powder. Yield: 0.59 g, 42 %. Anal. Calc'd for C₆₃H₆₃ClIIN₃P₃ThCo 0.5 C₇H₈: C, 54.91; H, 4.64; N, 2.89 %. Found: C, 54.79; H, 4.70; N, 2.78 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) -2.96 (6H, s, Ar-CH), 0.30 (9H, s, Mes-CH₃), 1.39 (12H, s, Ar-CH), 2.10 (12H, s, Ar-CH), 3.58 (18H, s, Mes-CH₃), 13.11 (6H, s, Ar-CH). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) -236.63 (s) FTIR ν/cm⁻¹ (Nujol): 542, (w) 569 (w), 699 (m), 741 (m), 771 (m), 864 (w), 885 (w), 1147 (w), 1202 (w), 1303 (w). Magnetic moment (Evans method, C₆D₆, 298 K): μ_{eff} = 3.46 μ_B.

Preparation of [(MesNPPrⁱ)₂Th(μ-I)(MesNPPrⁱ)₂CoI] (188)

THF (30 ml) was added slowly to a cold (-78 °C) stirring mixture of [Th(Cl)(MesNPPrⁱ)₃] (1.08 g, 1.0 mmol), CoI₂ (0.33 g, 1.0 mmol) and Zn (65 mg, 1.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. Volatiles were removed in vacuo and the residue was washed with hexane. The resulting green solid was extracted into toluene and concentrated to 5 ml to yield [(MesNPⁱPr₂)Th(μ-I)(MesNPⁱPr₂)₂CoI] as green crystals suitable for a single crystal X-ray diffraction study. Yield 0.21 g, 15 %. Anal. Calc'd for: C₄₅H₇₅N₃P₃ThCoI₂ 0.25(C₇H₈): C, 42.58; H, 5.88; N, 3.19 %. Found: C, 42.43; H, 5.81; N, 2.98 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) -13.05, -2.15, 1.02, 1.52, 2.13, 3.80, 7.12, 12.94, 18.76. ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) -245.23 (s). FTIR ν/cm⁻¹ (Nujol): 1302 (w), 1225 (w), 1207 (s), 1151 (s), 1091 (m) 1038 (m), 955 (w), 925 (w), 881 (m), 869 (m), 855 (s), 775 (w), 763 (m), 693 (w), 676 (s), 656 (m), 604 (w), 594 (w), 528 (m). Magnetic moment (Evans method, C₆D₆, 298 K): μ_{eff} = 2.98 μ_B.

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Chapter five

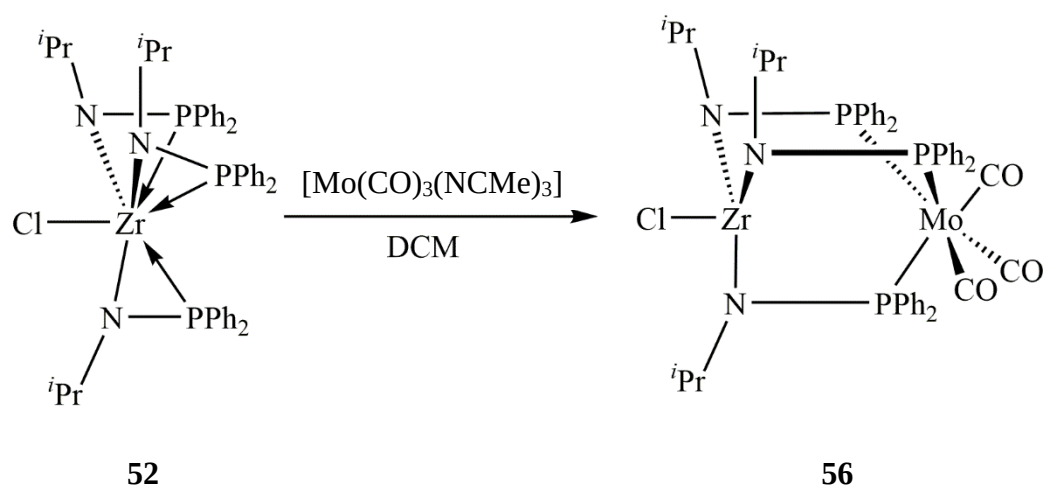
Heterobimetallic Actinide-Molybdenum Complexes

Contents

5.1	Background	183
5.2	Activation of Acetonitrile	184
5.3	Paddlewheel An-Mo Complexes	196
5.4	Concluding remarks	210
5.5	Experimental	211
5.6	References	217

5.1 Background

As previously discussed, comparatively few examples of metal-metal bonds between an actinide, such as uranium, and transition metals have been reported, and to date only include a few actinide-group 7-10 metal complexes. With this in mind accessing a hitherto unknown actinide-group 6 bond would be anticipated to present a synthetic challenge.¹⁻⁴ It was identified that the synthetic methodology employed by Nagashima towards the synthesis of $[\text{ZrCl}(\text{}^i\text{PrNPPH}_2)_3\text{Mo}(\text{CO})_3]$ (**56**) (**Scheme 49**) would be a potential pathway to installing a group 6 metal into the coordination sphere of an actinide metal.⁵



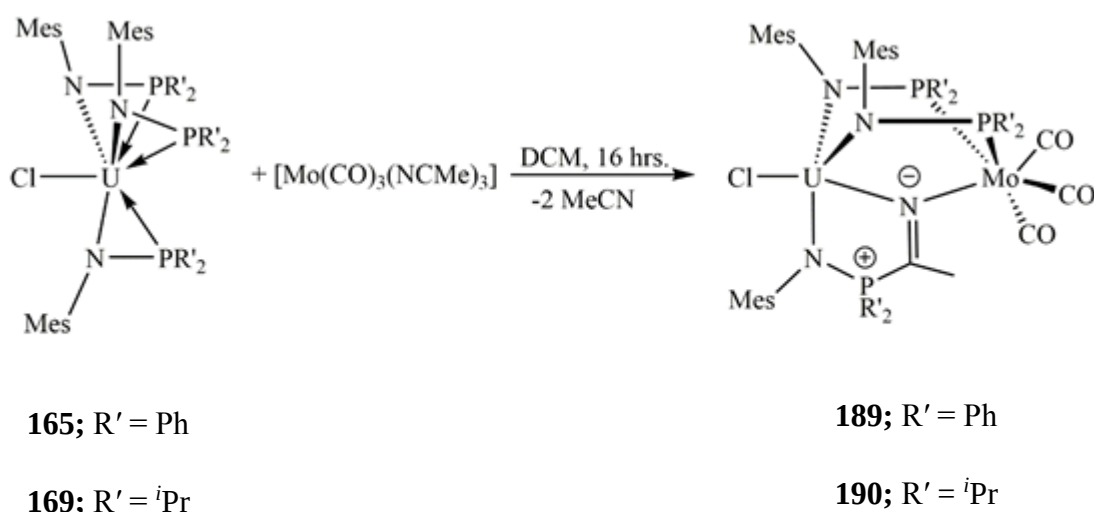
Scheme 49 – Synthesis of $[\text{ZrCl}(\text{}^i\text{PrNPPH}_2)_3\text{Mo}(\text{CO})_3]$ (**56**)

Reaction of $[\text{ZrCl}(\text{}^i\text{PrNPPH}_2)_3]$ (**52**) with the octahedrally-arranged molybdenum precursor $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ resulted in the displacement of the MeCN ligands by the three phosphines in **52** to give the Zr-Mo heterobimetallic complex $[\text{ZrCl}(\text{}^i\text{PrNPPH}_2)_3\text{Mo}(\text{CO})_3]$ (**56**). The IR spectrum shows two characteristic CO stretching bands at 1987 and 1913 cm^{-1} which represents a hypsochromic shift of ca. 60 cm^{-1} relative to $[(\text{trisphos})\text{Mo}(\text{CO})_3]$ (**57**). This weaker back-donation from molybdenum to the π^* orbital of the CO ligands was attributed to either direct through-space interaction between the Lewis acidic zirconium and the molybdenum atoms or by a through-bond interaction *via* the Zr-N-P-Mo bond.

It is with slight modifications of the literature procedures that $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ will be reacted with the tris(phosphinoamide) uranium halides $[\text{UX}(\text{MesNPR}'_2)_3]$ ($\text{X} = \text{Cl}$, $\text{R}' = \text{Ph}$, **165**; $\text{X} = \text{Cl}$, $\text{R}' = i\text{Pr}$, **169**; $\text{X} = \text{I}$, $\text{R}' = \text{Ph}$, **173**; $\text{X} = \text{I}$, $\text{R}' = i\text{Pr}$, **161.**), and the relevant thorium analogues $[\text{ThX}(\text{MesNPR}'_2)_3]$ ($\text{X} = \text{Cl}$, $\text{R}' = \text{Ph}$, **175**; $\text{X} = \text{Cl}$, $\text{R}' = i\text{Pr}$, **176**; $\text{X} = \text{I}$, $\text{R}' = \text{Ph}$, **177**; $\text{X} = \text{I}$, $\text{R}' = i\text{Pr}$, **178.**) in an attempt to synthesise actinide-group 6 metal linkages.

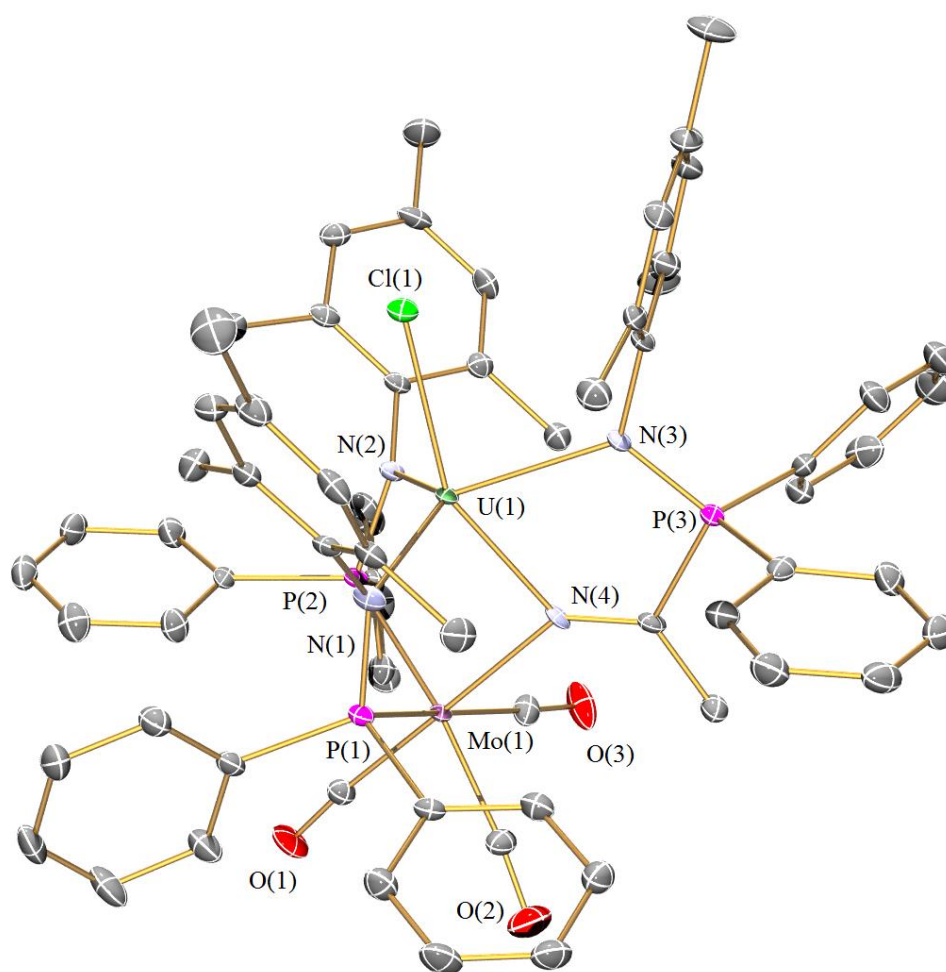
5.2 Activation of Acetonitrile

Treatment of stirring mixtures of the tris(phosphinoamide)uranium chloride precursors $[\text{UCl}(\text{MesNPPH}_2)_3]$ (**165**) and $[\text{UCl}(\text{MesN}^i\text{Pr}_2)_3]$ (**169**) with $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ at -78°C in DCM resulted in the formation of red solutions which were allowed to warm slowly to room temperature over 16 hours, yielding the heterobimetallic complexes $[\text{UCl}(\text{MesNPPH}_2)_2(\text{MesNPPH}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**189**) and $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_2(\text{MesNP}^i\text{Pr}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**190**) (Scheme 50) in respective yields of 52 and 82%.



Scheme 50 – Synthesis of $[\text{UCl}(\text{MesNPPH}_2)_2(\text{MesNPPH}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**189**) and $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_2(\text{MesNP}^i\text{Pr}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**190**)

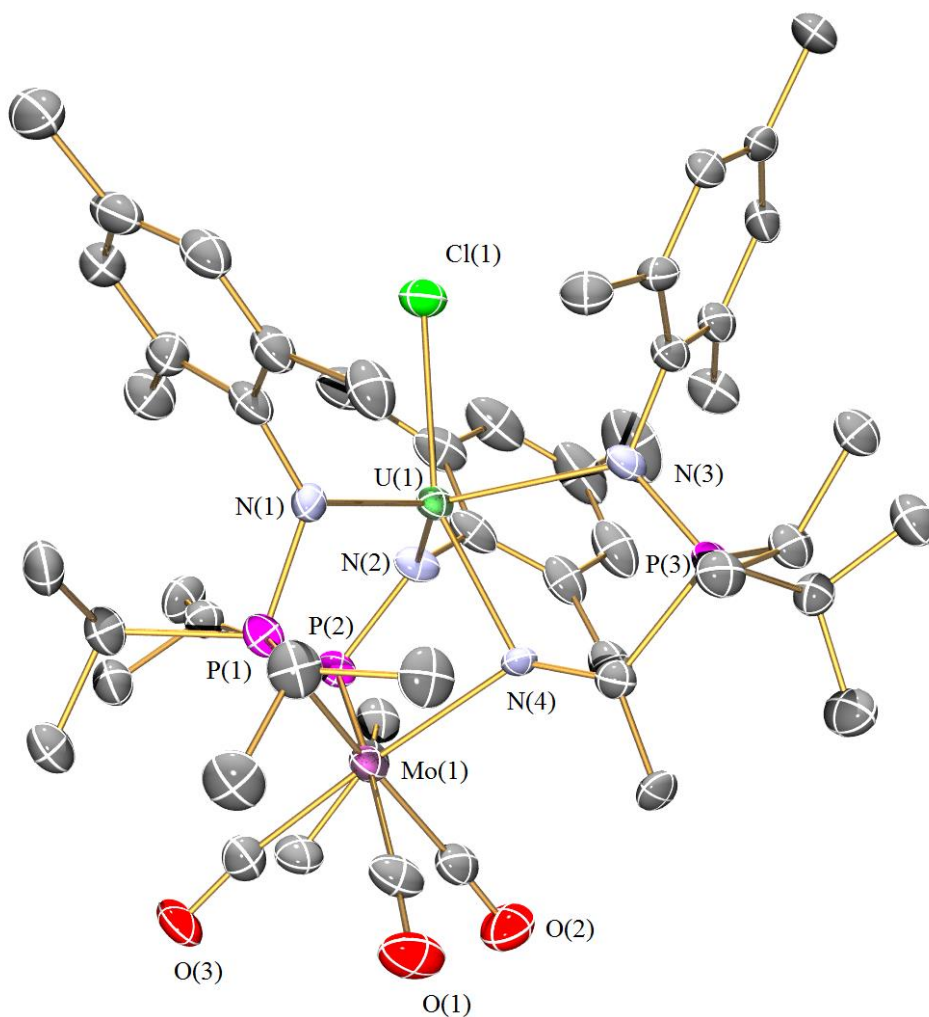
Concentration of the mother liquor afforded red crystals suitable for X-ray diffraction, and in both cases shows the insertion of one acetonitrile ligand of the $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ as a bridging ligand from Mo to the actinide metal. The solid state structures of **189** and **190** are shown in **Fig 66** and **Fig 67** respectively with selected bond lengths and angles.



189

Fig. 66 – Structure of $[\text{UCl}(\text{MesNPPH}_2)_2(\text{MesNPPH}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**189**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. : U(1)-Mo(1) 3.3019(3), U(1)-N(1) 2.307(3), U(1)-N(2) 2.271(3), U(1)-N(3) 2.473(3), U(1)-Cl(1) 2.6260(9), U(1)-N(4) 2.312(3), N(4)-C(64) 1.280(5), Mo(1)-P(1) 2.5956(9), Mo(1)-N(4) 2.227(3), Mo(1)-C(66) 1.995(4), P(1)-N(1) 1.673(3), P(3)-C(64) 1.835(4), Cl(1)-U(1)-Mo(1) 162.85(2).



190

Fig. 67 – Structure of $[UCl(MesNP^iPr_2)_2(MesNP^iPr_2\{\mu\text{-NCMe}\})Mo(CO)_3]$ (**190**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. : U(1)-Mo(1) 3.3150(5), U(1)-N(1) 2.279(4), U(1)-N(2) 2.304(5), U(1)-N(3) 2.437(5), U(1)-Cl(1) 2.6269(15), U(1)-N(4) 2.288(5), N(4)-C(46) 1.263(8), Mo(1)-P(1) 2.6187(15), Mo(1)-N(4) 2.249(4), Mo(1)-C(48) 1.971(6), P(1)-N(1) 1.697(5), P(3)-C(46) 1.855(6), Cl(1)-U(1)-Mo(1) 161.66(3).

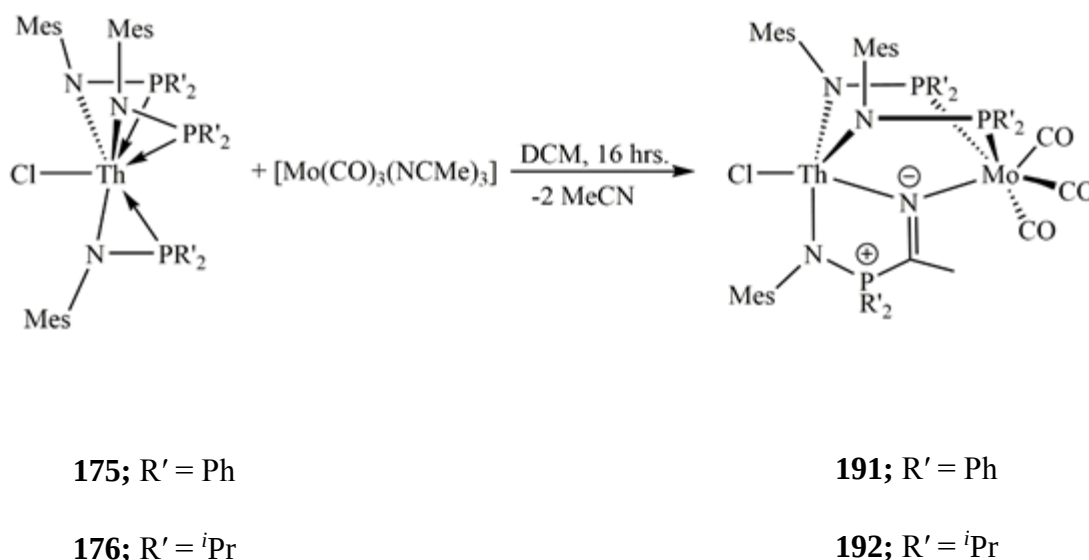
Both in compounds 189 and 190 the U-Mo bond distances of 3.3019(3) Å and 3.3150(5) Å respectively are of comparable length and fall outside the sum of the covalent radii as calculated by Pyykko (3.08 Å)⁶ The U(1)-N(1) and U(1)-N(2) bonds for 189 are within the expected range of uranium(IV) amide bonds [U(1)-N(1)

2.271(3) Å, U1-N2 2.307(3) Å], as verified in other studies.⁷ However, the distance to the third phosphinoamide group is significantly longer [U(1)-N(3) 2.473(3) Å] and the U(1)-N(4) distance of 2.312(3) Å is comparatively short. This suggests a stronger and more covalent interaction of the supposedly dative CH₃CN→U coordination. The interaction with the donor atom N(3) of the MesNPPPh₂ ligand becomes subsequently weaker as evidenced by the elongation of the bond distance. The uranium-amide bonds of the two bridging ligands for complex **190** are once again within the expected range for uranium(IV) [U(1)-N(1) 2.279(4) Å, U(1)-N(2) 2.304(5) Å] and comparable to **189**.⁷ The distance to the N atom of the third, non-bridging ligands is elongated [U(1)-N(3) 2.473(3) Å], whereas the distance to the acetonitrile group is shortened [U(1)-N(4) 2.311(4) Å] as observed for **189**.

The P(3)-C(64) bond length of 1.835(4) in **189** and the corresponding P(3)-C(46) bond length of 1.855(6) in **190** are typical of a single phosphorus-carbon bonds⁸ and is suggestive of a positive phosphonium centre. The activation of the acetonitrile ligand is further evident in the lengthening of the C(64)-N(4) [1.280(5) Å] and C(46)-N(4) bonds [1.263(8) Å], **189** and **190** respectively, compared to the ones reported for the starting material [Mo(CO)₃(NCMe)₃] [1.118(6) Å].⁹ This lengthening is in the typical range for carbon-nitrogen double bonds and allows for an anionic ketimide nitrogen.⁸

The Mo-P bond distances for **189** and **190** are between 2.5454(9) and 2.6187(15) Å and within the normal range. Similarly, the Mo(1)-C bonds (≈1.97 Å) to the three carbonyl groups are within the range normally observed for Mo carbonyl bonds (≈2.005 Å), indicating no significant electronic change within these bonds and the CO ligand.^{5, 9} The bond distances of P(1)-N(1) and P(2)-N(2) are the same in the uranium(IV) molybdenum complexes as in the uranium starting materials **165** and **169** [**189**: P(1)-N(1) 1.673(3) Å, P(2)-N(2) 1.679(3) Å; **190**: P(1)-N(1) 1.697(5) Å, P(2)-N(2) 1.694(5) Å].¹⁶ However, the P(3)-N(3) bond that does not coordinate its phosphorus atom to the molybdenum has a slightly shorter bond distance [**189**: P(3)-N(3) 1.624(3) Å; **190**: P3-N3 1.637(5) Å].

To synthesise the thorium analogues of **189** and **190**, reaction of the tris(phosphino)thorium chloride precursors $[\text{ThCl}(\text{MesNPPh}_2)_3]$ (**175**) or $[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**176**) with $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ at -78°C in DCM resulted in the formation of red solutions which were allowed to warm slowly to room temperature over 16 hours to yield the respective heterobimetallic diamagnetic complexes $[\text{ThCl}(\text{MesNPPh}_2)_2(\text{MesNPPh}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**191**) and $[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_2(\text{MesNP}^i\text{Pr}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**192**), (**Scheme 51**) in respective yields of 51 and 62%.



Scheme 51 – Synthesis of $[\text{ThCl}(\text{MesNPPh}_2)_2(\text{MesNPPh}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**191**) and $[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_2(\text{MesNP}^i\text{Pr}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**192**)

The insertion of one acetonitrile ligand of the $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ as a bridging ligand from Mo to the thorium metal was revealed when the mother liquor was concentrated down to afford red crystals suitable for X-ray diffraction. The solid state structure of **191** is shown in **Fig. 68** with selected bond lengths and angles. A complete discussion of the metrical data acquired for **192** is meaningless due to the poor quality of the data; the overall structure is however identical to that of **189-191** confirming the gross connectivity and chemical identity and is shown in **Fig. 69**.

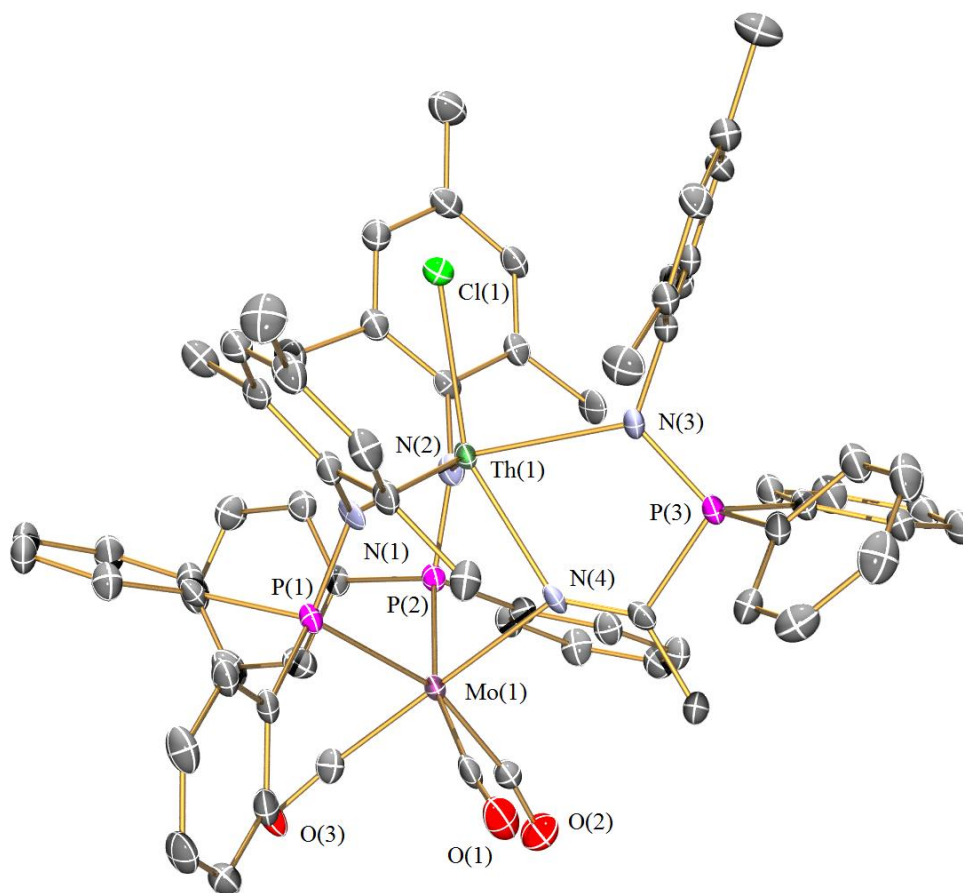
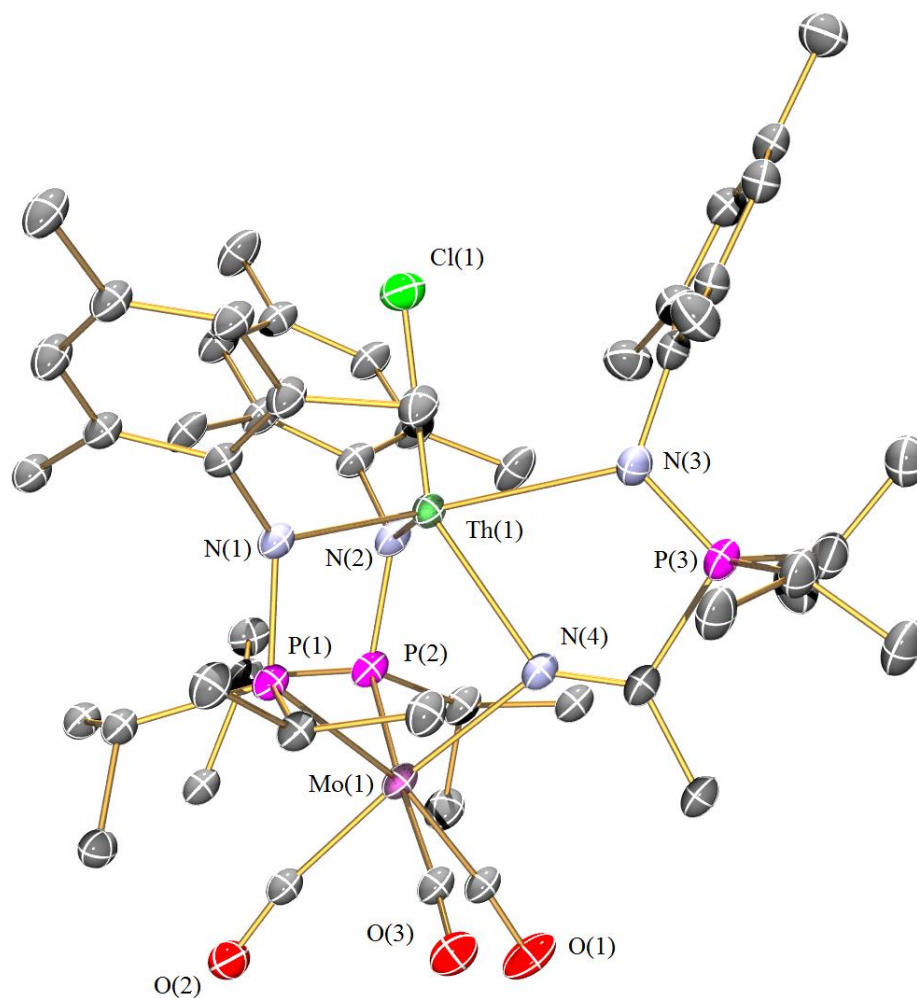


Fig. 68 – Structure of $[ThCl(MesNPPPh_2)_2(MesNPPPh_2\{\mu\text{-}NCMe\})Mo(CO)_3]$ (**191**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity. : Th(1)-Mo(1) 3.4061(3), Th(1)-N(1) 2.344(3), Th(1)-N(2) 2.325(3), Th(1)-N(3) 2.502(3), Th(1)-Cl(1) 2.6959(9), Th(1)-N(4) 2.377(3), N(4)-C(64) 1.269(5), Mo(1)-P(1) 2.5970(10), Mo(1)-N(4) 2.246(3), Mo(1)-C(66) 1.968(4), P(1)-N(1) 1.686(3), P(3)-C(64) 1.848(4), Cl(1)-U(1)-Mo(1) 163.80(2).



192

Fig. 69 – Structure of $[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_2(\text{MesNP}^i\text{Pr}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**192**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity.

The Th-Mo distance of 3.4061(3) is slightly longer than the respective U-Mo distance in **189** resulting from the larger effective ionic radius of Th(IV) (94 pm) compared to U(IV) (89 pm)⁶ The values of the bond distances within the thorium complex **191** are comparable to those of the uranium complexes **189** and **190**. The two ligand bonds Th(1)-N(1) and Th(1)-N(2) have distances of 2.344(3) Å and 2.325(3) Å, respectively. These are within the range of Th-N_{amide} bonds previously observed by us and others.^{10, 11}

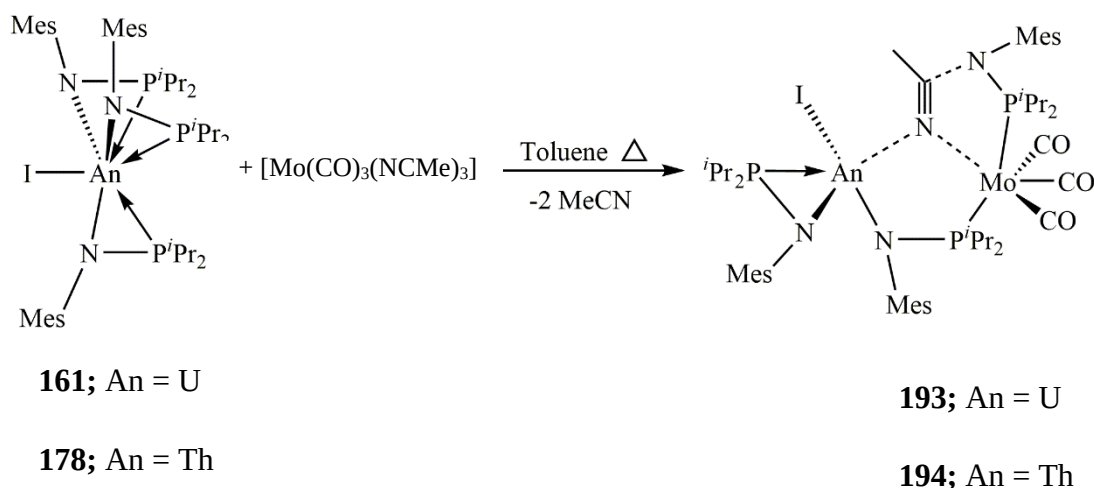
As was found to be the case with **189** and **190**, the third ligand bond Th(1)-N(3) is long at 2.502(3) Å, whereas the Th(1)-N_{acetonitrile} coordination is shortened to 2.377(3) Å. For comparison, only one thorium complex with an isolated dative acetonitrile ligand is known to date, in which the Th-N_{acetonitrile} distance measures 2.802(3) Å.¹² The Mo-P bond distances of 2.5970(10) and 2.5970(10) are again comparable to **189** as are the Mo-C bond distances of 1.968(4) - 1.985(4).

Comparable to the P(3)-C(64) bond length in **189** and P(3)-C(46) bond length in **190** the corresponding bond length in **191** of 1.848(4) is once again typical of a single phosphorus-carbon bond⁸ and a positive phosphonium centre. The activation of the acetonitrile ligand is again further evident in the lengthening of the C(64)-N(4) bond to 1.269(5) Å, this lengthening in to the range of carbon nitrogen double bonds is comparable to the respective bond lengths in **189** and **190**. The activation of the acetonitrile ligand is further reflected in the N≡C-C bond angle, which in complexes **189** – **191** is bent from its linear geometry in free CH₃CN in to 127.0(3)° (**189**), 124.8(5)° (**190**), and 127.9(3)° (**191**). This acetonitrile insertion/activation is as far as we are aware unprecedented in actinide-containing complexes, and has only been observed in a small number of transition metal¹³⁻¹⁵ and main group complexes.^{16, 17}

To further elucidate the characteristics of these complexes experiments were carried out on the two iodide complexes [UI(MesNPⁱPr₂)₃] (**161**) and [ThI(MesNPⁱPr₂)₃] (**178**) with [Mo(NCMe)₃(CO)₃]. In contrast to the aforementioned experiments treatment of an equimolar mixture of **161** and **178** and [Mo(NCMe)₃(CO)₃] in refluxing toluene led to the formation of [(η²-MesNPⁱPr₂)UI(MesNPⁱPr₂)(μ-NCMe)MesNPⁱPr₂)Mo(CO)₃] (**193**) and [(η²-MesNPⁱPr₂)ThI(MesNPⁱPr₂)(μ-NCMe)MesNPⁱPr₂)Mo(CO)₃] (**194**) respectively in yields of 57 and 67%.

Concentration of the mother liquor of **193** yielded red crystals suitable for X-ray diffraction from which the solid state structure could be determined **Fig 70**. Although a complete discussion of the metrical data acquired for **193** is meaningless due to the poor quality of the data the overall structure is beyond

doubt. Despite multiple crystallisation attempts **194** could only be obtained as an analytically pure microcrystalline powder; as a result of its diamagnetic nature the proposed structure is proposed from the relevant spectroscopic data (^1H , ^{31}P , FTIR and CHN, *cf.* Experimental).



Scheme 52 – Synthesis of

$[(\eta^2\text{-MesNP}^i\text{Pr}_2)\text{UI}(\text{MesNP}^i\text{Pr}_2)(\{\mu\text{-NCMe}\}\text{MesNP}^i\text{Pr}_2)\text{Mo}(\text{CO})_3]$ (**193**) and
 $[(\eta^2\text{-MesNP}^i\text{Pr}_2)\text{ThI}(\text{MesNP}^i\text{Pr}_2)(\{\mu\text{-NCMe}\}\text{MesNP}^i\text{Pr}_2)\text{Mo}(\text{CO})_3]$ (**194**)

The solid state structure of **193** is significantly different from compounds **189** – **192**. The three ligand moieties are present in three individual coordination modes. The first ligand moiety remains on the uranium as a phosphinoamide ligand. The second ligand moiety serves as a bridging ligand between the uranium and the molybdenum whilst the third ligand moiety coordinates as an amidophosphine to the molybdenum. As with **189-192**, activation of the acetonitrile ligand is reflected in the $\text{N}\equiv\text{C}-\text{C}$ bond angle, which is bent from its linear geometry in free MeCN .

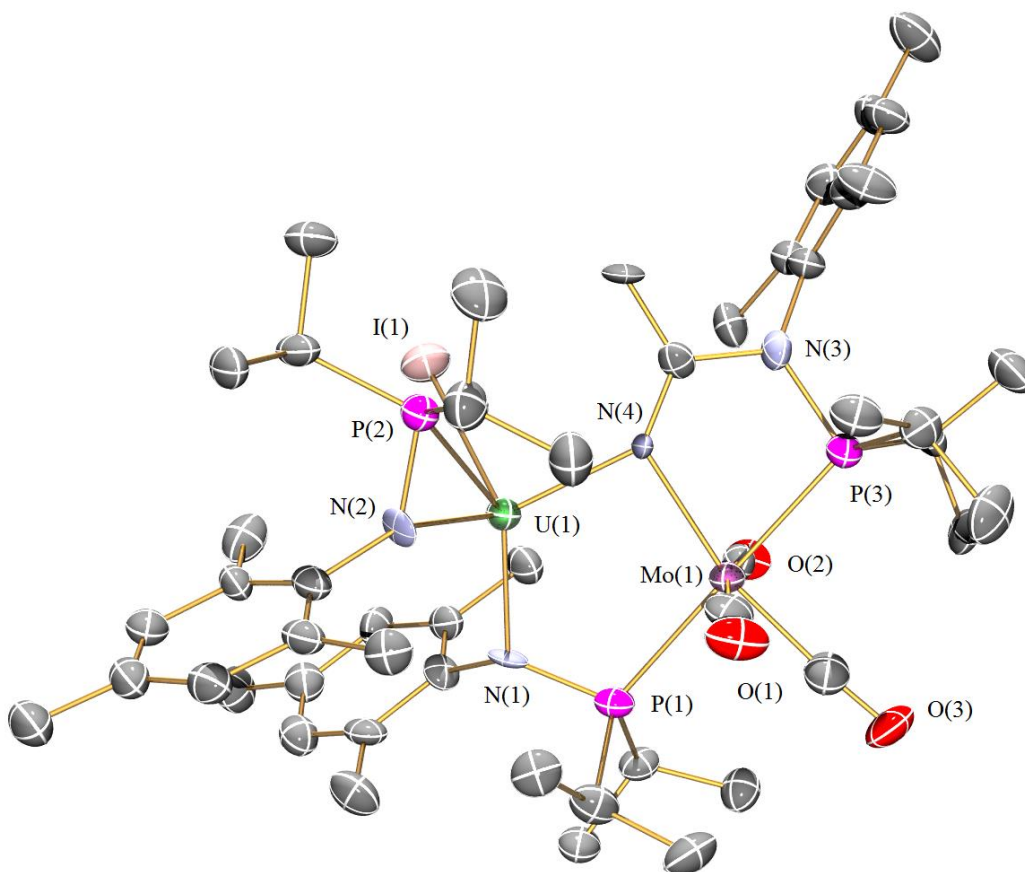


Fig. 70 – Structure of
 $[(\eta^2\text{-MesNP}^i\text{Pr}_2)\text{UI}(\text{MesNP}^i\text{Pr}_2)(\{\mu\text{-NCMe}\}\text{MesNP}^i\text{Pr}_2)\text{Mo}(\text{CO})_3]$ (**193**)

Thermal ellipsoids set at 40% probability and H atoms omitted for clarity.

The asymmetry of compounds **189** – **194** is evidenced by their relevant $^{31}\text{P}\{^1\text{H}\}$ -NMR shifts, which were detected for the Th complexes **191**, **192** and **194**. In complexes **191** and **192** two ^{31}P resonances were observed at 66.27 ppm and 70.67 ppm (**191**) and 44.87 ppm and 47.08 ppm (**194**), which can be attributed to the two bridging phosphorus atoms as well as to the non-bridging phosphinoamide. Complex **194** shows three different ^{31}P resonances at 59.64 ppm, 89.47 ppm and 154.27 ppm which represent the three different ligand environments.

The IR spectra of compounds **1** – **6** (Table 2) show that the C≡O stretches are shifted to higher wavenumbers by about 20-44 cm⁻¹ for $\tilde{\nu}_1$ and about 37-64 cm⁻¹ for $\tilde{\nu}_2$ relative to those reported for *fac*-[Mo(NCMe)₃(CO)₃].¹⁸⁻²⁰ Upon coordination to the actinide the back-donation from molybdenum into the π^* orbital of the CO ligand is slightly weakened, explaining the shift to a higher wave number.⁵

Compound	$\tilde{\nu}_1(\text{C}\equiv\text{O})^{\text{a}}$	$\tilde{\nu}_2(\text{C}\equiv\text{O})^{\text{a}}$
189	1933(s)	1854 (s)
190	1926 (s)	1833 (s)
191	1934 (s)	1854 (s)
192	1925 (s)	1827 (s)
193	1949 (s)	1840 (s)
194	1949 (s)	1838 (s)
	1915 (s) ^b	1783 (s) ^b
[Mo(NCMe) ₃ (CO) ₃]	1905 (s) ^c	1790 (s, br) ^c
	1921 (s) ^d	1793 (vs) ^d

Table 2. IR frequencies for the C≡O stretch for compounds **189** – **194** and [Mo(NCMe)₃(CO)₃]

[a] $\tilde{\nu}$ in (cm⁻¹) [b] nujol mull¹⁸ [c] KBr disk¹⁹ [d] CH₃CN solutions²⁰

The Evans method effective magnetic moment of solutions of **189**, **190** and **193** in benzene at 298 K were found to be 2.49 μ_{B} , 2.41 μ_{B} and 2.91 μ_{B} , respectively, which are within the range for reported uranium(IV) complexes.²¹⁻²⁴ Confirmation of the uranium(IV) assignments was obtained by variable temperature squid magnetometry. The results of the variable temperature squid magnetometry for **189**, **190** and **193** dispersed in eicosane are shown in **Fig. 71** as plots of μ_{eff} (μ_{B}) versus temperature over the range 300 to 1.8 K. The magnetic moment at 300 K was found to be 2.71 μ_{B} , 2.67 μ_{B} and 2.55 μ_{B} for **189**, **190** and **193** respectively, which is within the range for reported

uranium(IV) complexes.²¹⁻²⁴ For all three compounds the value of μ_{eff} decreases smoothly as the temperature is lowered from 300 K to ~30 K, where it begins to decrease more sharply and at 1.8 K the respective magnetic moments for **189**, **190** and **193** are $0.57 \mu_{\text{B}}$, $0.53 \mu_{\text{B}}$ and $0.59 \mu_{\text{B}}$. The magnetisation traces tend to zero at this temperature, which is consistent with the presence of $^3\text{H}_4$ uranium(IV) which is a magnetic singlet at low temperature.

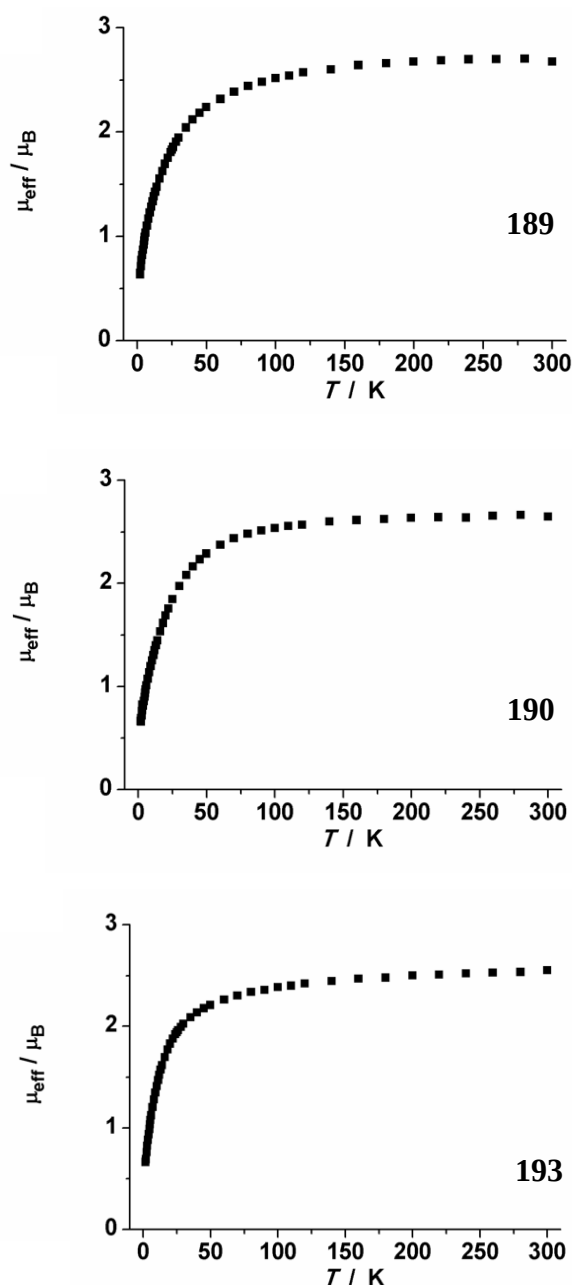
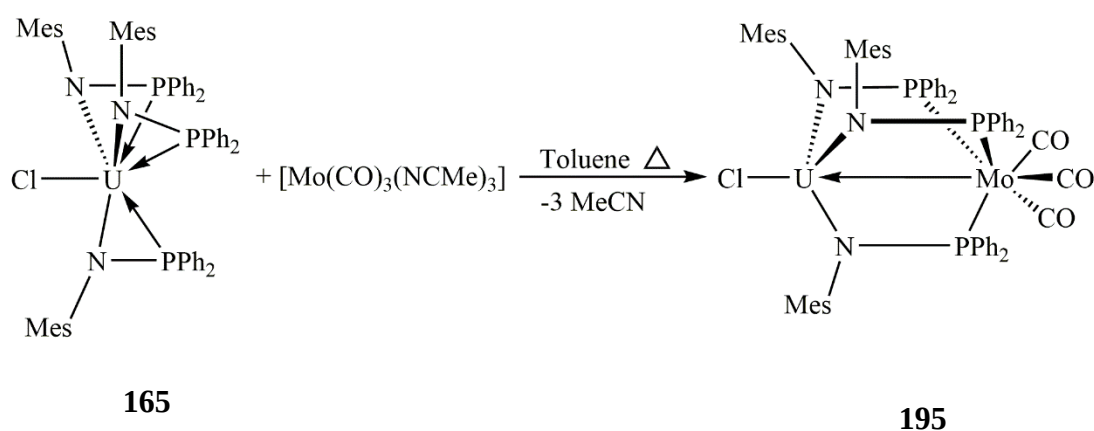


Fig. 71 - Plots of $\mu_{\text{eff}} (\mu_{\text{B}})$ versus temperature (K) for **189**, **190** and **193**

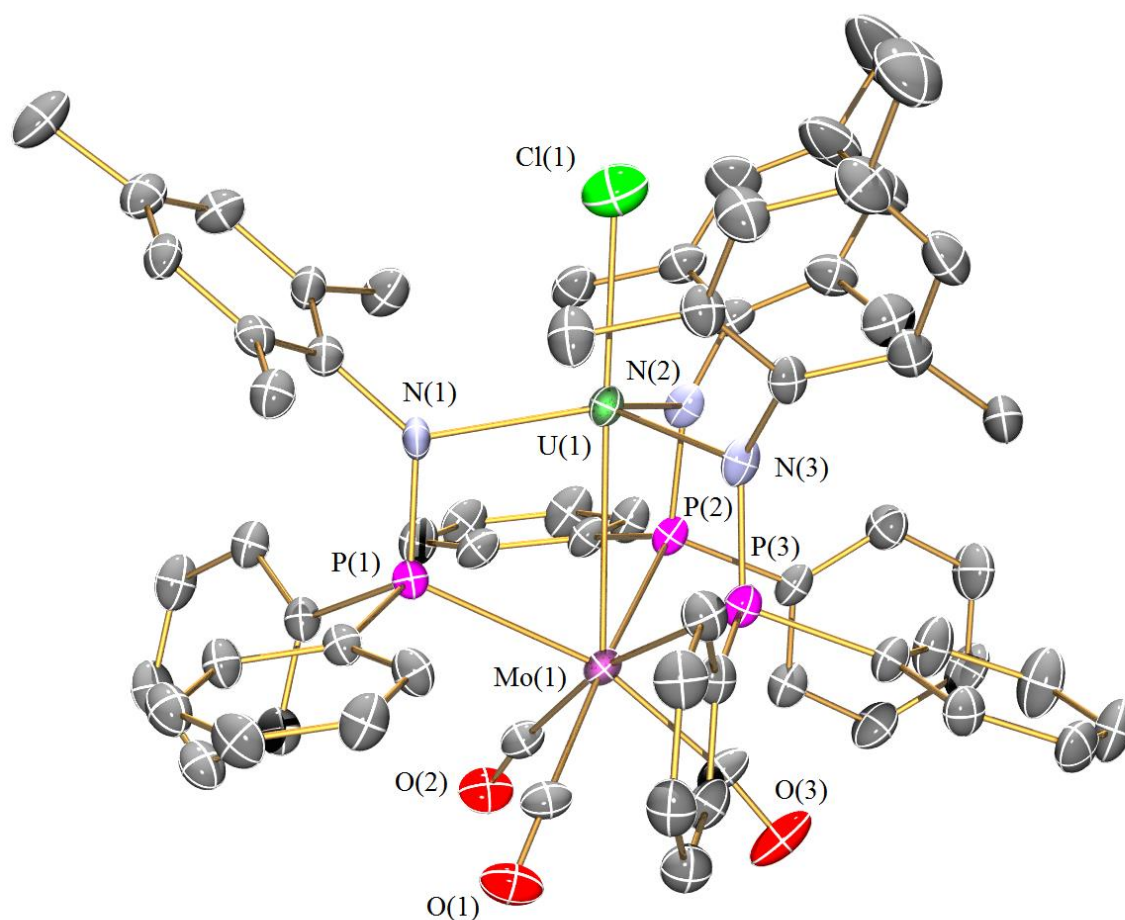
5.3 Paddlewheel An-Mo Complexes

As attempts to synthesise the symmetrical An-Mo complexes in DCM resulted in the acetonitrile inserted products **189-192** and refluxing in toluene of the iso-propyl substituents **161** and **178** resulted in the respective alternative acetonitrile inserted products **193** and **194**, the symmetrical paddlewheel complex $[\text{UCl}(\text{MesNPPH}_2)_3\text{Mo}(\text{CO})_3]$ (**195**) (analogous to the uranium cobalt complex $[\text{UCl}(\text{MesNPPH}_2)_3\text{CoI}]$ (**184**)) was targeted by treatment of $[\text{UCl}(\text{MesNPPH}_2)_3]$ (**165**) with $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ (**Scheme 53**). The heterobimetallic uranium complex (**195**) was isolated in an 88 % yield. The ^1H NMR spectrum of **189** consists of only six broad resonances that span the range +14 to +3 ppm, which is consistent with a three-fold symmetric paddle-wheel type structure seen in **184**. Washing with hexane and recrystallisation from toluene afforded crystals suitable for X-ray diffraction. The solid state structure is presented in **fig. 72** with selected bond lengths and angles.



Scheme 53 – $[\text{UCl}(\text{MesNPPH}_2)_3\text{Mo}(\text{CO})_3]$ (**195**)

The solid state structures of **195** reveals the uranium centre to be in a distorted trigonal-bipyramidal environment, with the apices being occupied by the chloride ion and molybdenum, respectively. The distortion is evident in the Cl(1)-U(1)-Mo(1) angle of $171.80(4)^\circ$. The U(1)-Mo(1) distance measures $3.1683(4)$ Å. The formal shortness ratio (FSR) of 1.03 and compares very well to the FSR value for **184** of 1.04 as well as FSR values of 0.97-1.09 for other uranium-transition metal bonds,^{25-28 29 30}



195

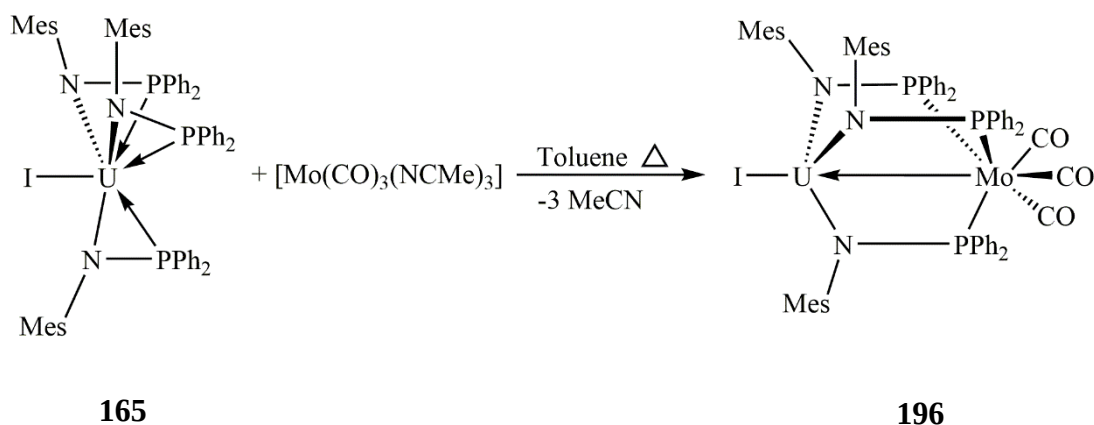
Fig. 72 – Structure of $[UCl(MesNPPH_2)_3Mo(CO)_3]$ (**195**)

Thermal ellipsoids set at 40% probability. Solvent molecules, one of the two crystallographically unique units and H atoms omitted for clarity. U(1)-Mo(1) 3.1683(4), U(1)-N(1) 2.291(4), U(1)-Cl(1) 2.5534(16), Mo(1)-P(1) 2.6396(12), Mo(1)-C(64) 1.997(5), O(1)-C(64) 1.135(6), N(1)-P(1) 1.681(4), Cl(1)-U(1)-Mo(1) 171.78(4).

The U(1)-N_{amide} distances for **195** are within the range of 2.277(3) – 2.291(4) Å and are representative for five-coordinate U(IV)-amide complexes.^{26, 30, 31} The coordination environment around the Mo atom is seven-coordinate and can be described as a distorted octahedron, face-capped by the U atom.³² The Mo-CO distances of 1.997(5) – 2.002(5) Å are only slightly longer than in the molybdenum

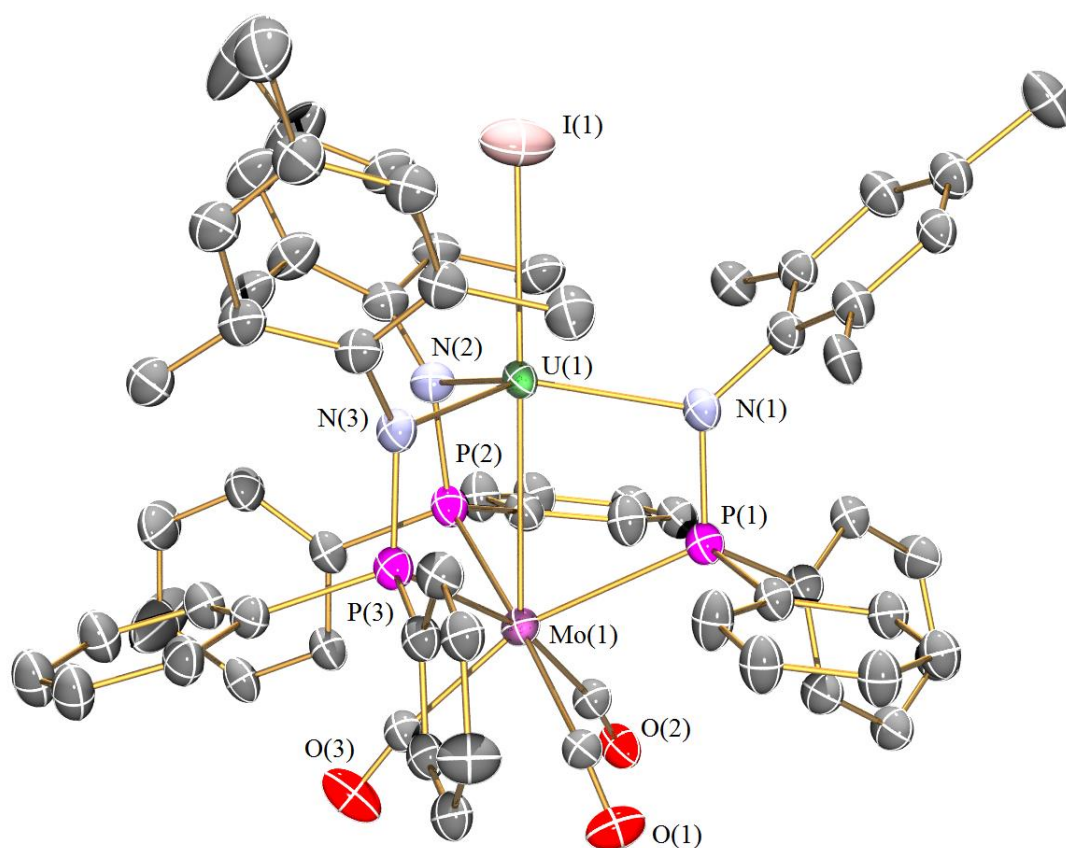
starting material *fac*-Mo(NCMe)₃(CO)₃ (1.923 Å).⁹ This difference may be attributed to the change in coordination number from 6 to 7 upon complexation with U(IV). Similarly, the C≡O bond distances of 1.135(6) – 1.138(6) Å show no significant elongation compared to the starting material (1.167(5) Å).

Using the tris(phosphinoamides) uranium halide [UI(MesNPPh₂)₃] (**173**) in an analogous methodology to the preparation of **195**, **173** was treated with [Mo(NCMe)₃(CO)₃] in refluxing toluene to afford the heterobimetallic uranium-complexes [UI(MesNPPh₂)₃Mo(CO)₃] (**196**) (**Scheme 54**) in an 62% yield. Consistent with the three-fold symmetric paddle-wheel type structure seen in **195** the ¹H NMR spectrum of **196** consists of only six broad resonances characteristically.



Scheme 54 – Synthesis of [UI(MesNPPh₂)₃Mo(CO)₃] (**196**)

In order to confirm the structure of **196** a single crystal X-ray diffraction experiment was performed with the molecular structure shown in **fig. 73**. A complete discussion of the metrical data acquired for **196** is meaningless due to the poor quality of the data; the overall structure is however identical to that of **195**. The uranium centre shows a distorted trigonal-bipyramidal environment, with the apices being occupied by the iodide ion and molybdenum, respectively. The distortion is evident in the I(1)-U(1)-Mo(1) angle with the coordination environment around the Mo atom is seven-coordinate and can be described as a distorted octahedron, face-capped by the U atom analogous to **195**.³²

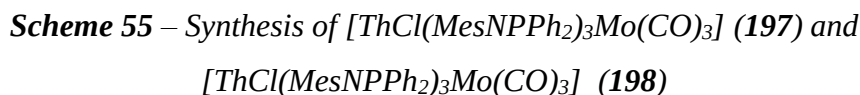


196

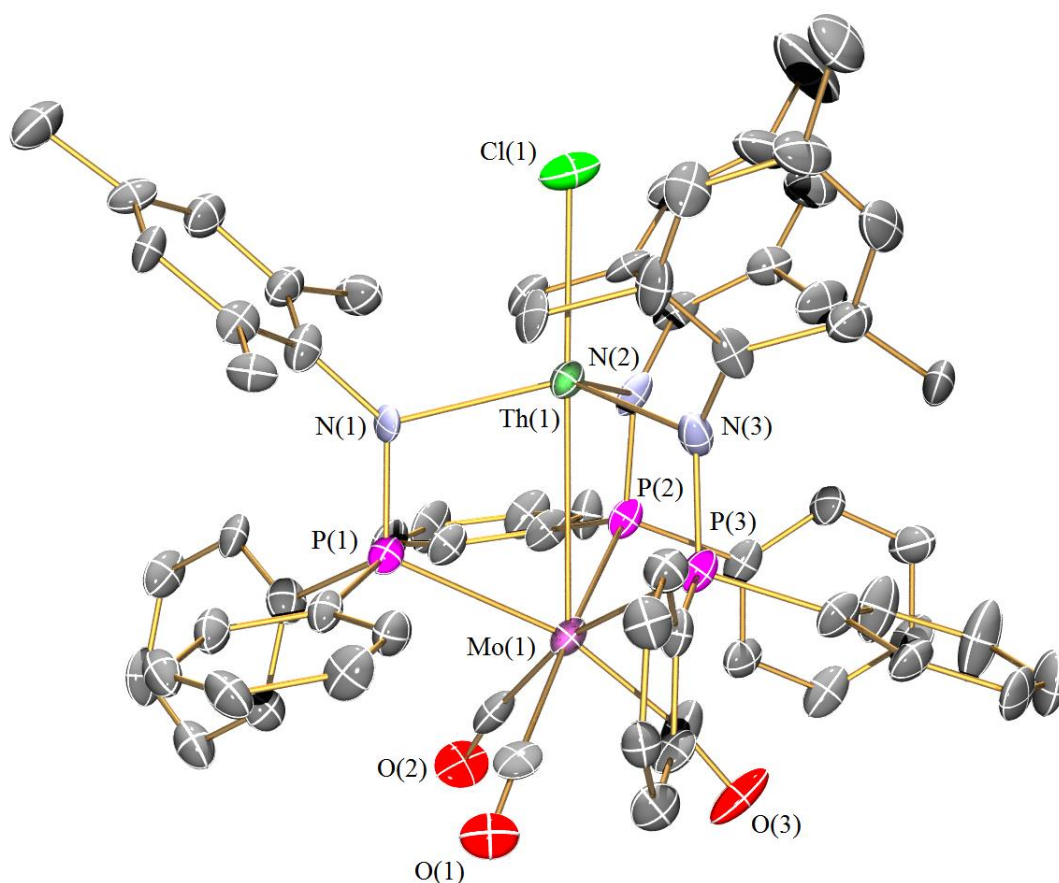
Fig. 73 – Structure of $[UI(MesNPPPh_2)_3Mo(CO)_3]$ (**196**)

Thermal ellipsoids set at 40% probability. Solvent molecules and H atoms omitted for clarity.

To prepare the analogous thorium compounds to **195** and **196** treatment of the tris(phosphinoamide) thorium halides $[ThCl(MesNPPPh_2)_3]$ (**175**) or $[ThI(MesNPPPh_2)_3]$ (**177**) with $[Mo(NCMe)_3(CO)_6]$ in refluxing toluene afforded the respective heterobimetallic thorium-molybdenum complexes $[ThCl(MesNPPPh_2)_3Mo(CO)_3]$ (**197**) and $[ThI(MesNPPPh_2)_3Mo(CO)_3]$ (**198**) (**Scheme 55**) in moderate yields (**197** = 36%, **198** = 48%). As with **195** and **196**, the ^1H NMR spectra of **197** and **198** consist of only six broad resonances in each case which is consistent with the three-fold symmetric paddle-wheel type structure.



The thorium centre of **197** shows a distorted trigonal-bipyramidal environment, with the apices being occupied by the chloride ion and molybdenum, respectively. The distortion is evident in the Cl(1)-Th(1)-Mo1 angle of 172.12(8)°. The Th(1)-Mo(1) separation measures 3.2982(10) Å, and is thus slightly longer than the respective U-Mo distance in **195** of 3.1683(4) Å, resulting from the larger effective ionic radius of Th(IV) (94 pm) compared to U(IV) (89 pm).³³ The formal shortness ratio (FSR) of 1.05 is comparable to the FSR of 1.03 for **195**



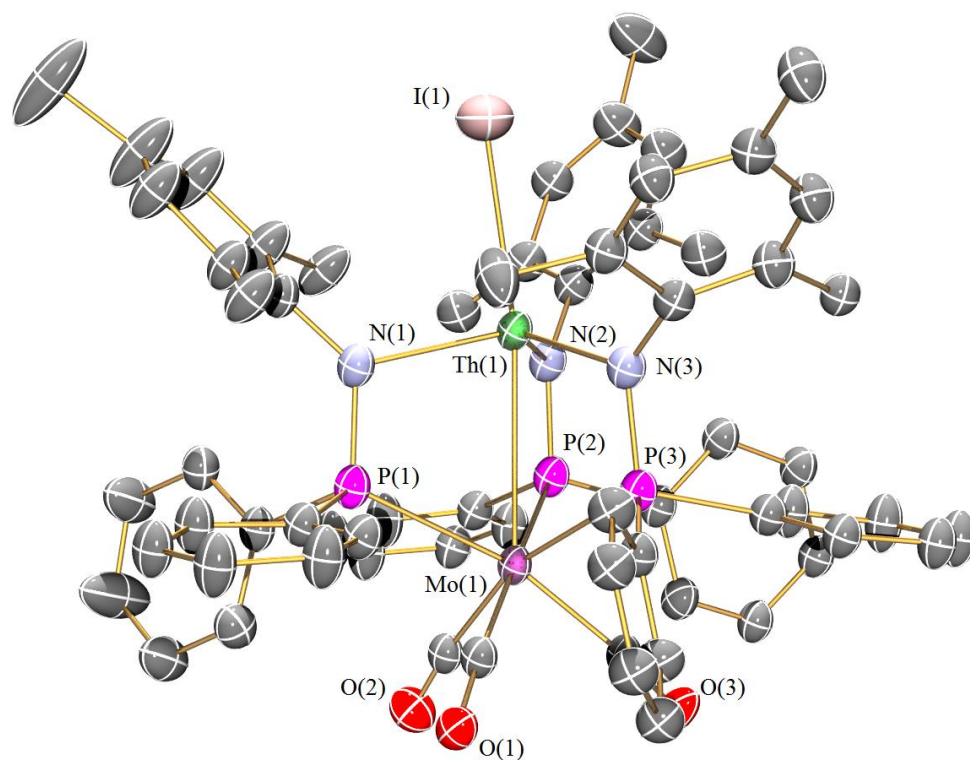
197

Fig. 74 – Structure of $[ThCl(MesNPPPh_2)_3Mo(CO)_3]$ (**197**)

Thermal ellipsoids set at 40% probability. Solvent molecules and H atoms omitted for clarity. Th(1)-Mo(1) 3.298(1), Th(1)-Mo(1) 3.2982(10), Th(1)-N(1) 2.321(9), Th(1)-Cl(1) 2.638(3), Mo(1)-P(1) 2.628(3), Mo(1)-C(64) 1.943(13), O(1)-C(64) 1.194(17), N(1)-P(1) 1.689(11), Cl(1)-Th(1)-Mo(1) 172.12(8).

The Th(1)-N_{amide} distances **197** of are within the range of 2.306(9) – 2.343(9) Å and within the same range as other Th(IV)-amide bonds.^{10, 11, 34} Similarly to the U(IV) complexes the coordination environment around the Mo atom is seven-coordinate and can be described as a distorted octahedron, face-capped by the Th atom.³² The Mo-CO distances in **197** of 1.943(13) – 2.005(15) Å] and are only slightly longer than in the molybdenum starting material *fac*-Mo(NCMe)₃(CO)₃ (1.923 Å).⁹ This difference

can again be attributed to the change in coordination number from 6 to 7 upon complexation with Th(IV). Similarly, the C≡O bond distances of 1.106(17) – 1.194(17) Å show only a slight fluctuation compared to the starting material (1.167(5) Å).⁹



198

Fig. 75 – Structure of $[ThI(MesNPPh_2)_3Mo(CO)_3]$ (**198**)

Thermal ellipsoids set at 40% probability. Solvent molecules and H atoms omitted for clarity.

The thorium centre in complex **198**, in a directly comparable manner to **195-197** shows a distorted trigonal-bipyramidal environment, with the apices being occupied by the iodide ion and molybdenum, respectively. The distortion is evident in the I(1)-Th(1)-Mo(1) angle with the coordination environment around the Mo atom is seven-coordinate and can be described once again as a distorted octahedron, face-capped by the Th atom analogous to **197**.³²

The acetonitrile inserted products **189-192** are potentially a result of solvent effects irrespective of substituent on the phosphorus. In the more polar DCM the phosphorus moiety is often more de-coordinated and hence available to activate the acetonitrile. In comparison refluxing in toluene has resulted in either the acetonitrile inserted products **193** and **194** where the iso-propyl group was utilised, or in the symmetrical paddlewheel complexes **195-198** where the phenyl group was the substituent on the phosphorous. This difference between these two could be that the iso-propyl groups renders the phosphorus centre more electron rich so more likely to attack the acetonitrile.

Due to their paramagnetic nature it was not possible to obtain $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compounds of **195** and **196**, however, the single resonances observed for compounds **197** (46.18 ppm) and **198** (45.07 ppm) indicate the complexes homogeneity in solution compared to the multiple resonances seen in the asymmetric complexes **191,192** and **194**. The resonances are shifted to higher frequencies with respect to the starting materials $\text{ThCl}(\text{MesNPPH}_2)_3$ (**175**) (20.72 ppm) and $\text{ThI}(\text{MesNPPH}_2)_3$ (**177**) (17.65 ppm) and are within the range observed for $\text{Mo}(\text{PPh}_3)(\text{CO})_5$ (37.91 ppm).³⁵ This is consistent with the overall trend of higher frequency ^{31}P shifts upon complexation with Mo.³⁶

Compound	$\tilde{\nu}_1(\text{C}\equiv\text{O})^{\text{a}}$	$\tilde{\nu}_2(\text{C}\equiv\text{O})^{\text{a}}$
195	1969 (s)	1891 (s)
196	1969 (s)	1904 (s)
197	1967 (s)	1896 (s)
198	1967 (s)	1898 (s)
	1915 (s) ^b	1783 (s) ^b
$[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$	1905 (s) ^c	1790 (s, br) ^c
	1921 (s) ^d	1793 (vs) ^d

Table 3. IR frequencies for the $\text{C}\equiv\text{O}$ stretch for compounds **195 – 198** and $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$

[a] $\tilde{\nu}$ in (cm^{-1}) [b] nujol mull¹⁸ [c] KBr disk¹⁹ [d] CH_3CN solution²⁰

The IR spectra of compounds 195 - 198 (Table 3) show that the C≡O stretches are shifted to higher wavenumbers by about 50 cm⁻¹ for $\tilde{\nu}_1$ and about 100 cm⁻¹ for $\tilde{\nu}_2$ relative to those reported for fac-Mo(NCMe)₃(CO)₃.²⁹⁻³¹ This can potentially be attributed to a weaker back-donation from molybdenum into the π^* orbital of the CO ligand upon coordination to the actinide, as observed previously in a similar manner by Nagashima.⁵ These shifts are larger than those reported for 189-194 where C≡O stretches were only shifted to higher wavenumbers by about 20-44 cm⁻¹ for $\tilde{\nu}_1$ and about 37-64 cm⁻¹ for $\tilde{\nu}_2$ for those reported for fac-Mo(NCMe)₃(CO)₃.²⁹⁻³¹ This suggests that the back-donation from molybdenum into the π^* orbital of the CO ligand upon coordination to the actinide is only slightly weakened in 189-194 compared to the symmetric paddlewheel complexes potentially as a result of An-Mo interactions.²¹

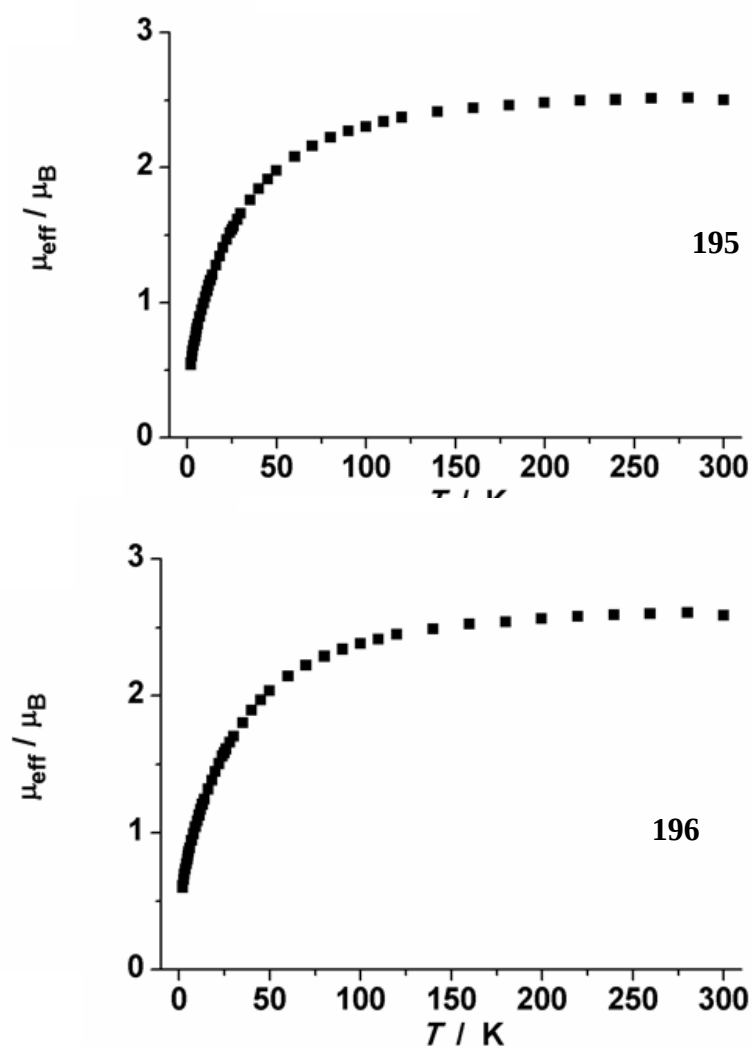


Fig. 76 - Plots of μ_{eff} (μ_B) versus temperature (K) for 195 and 196

The Evans method effective magnetic moments in solution of **195** and **196** in benzene at 298 K were found to be $2.25\mu_B$ and $2.39\mu_B$, respectively which is comparable to the acetonitrile insertion products **189**, **190** and **193** and is within the range for reported uranium(IV) complexes.²¹⁻²⁴ Confirmation of the uranium(IV) assignments found *via* variable temperature squid magnetometry. The results of the variable temperature squid magnetometry for **195** and **196** dispersed in eicosane are shown in **Fig. 76** as plots of μ_{eff} (μ_B) *versus* temperature over the range 300 to 1.8 K. The magnetic moments at 300 K were found to be $2.51\mu_B$, and $2.62\mu_B$ for **195** and **196** respectively, which is within the range for reported uranium(IV) complexes.²¹⁻²⁴ As was the case for **189**, **190** and **193**, for both compounds the value of μ_{eff} decreases smoothly as the temperature is lowered from 300 K to ~ 30 K, where it begins to decrease more sharply and at 1.8 K the respective magnetic moments for **195** and **196** are $0.51\mu_B$, and $0.58\mu_B$. The magnetisation traces tend to zero at this temperature, which is consistent the presence of $^3H_4$ uranium(IV) which is a magnetic singlet at low temperature.

In order to probe the bonding in **195-198** we conducted computational investigations using density functional theory (DFT) on the full structures of these complexes. The calculations were unrestricted for the open-shell uranium complexes but restricted for closed-shell thorium compounds. The geometry optimised gas phase structures compare well to the experimental solid state structures, with bond lengths and angles computed to within 0.05 Å and 2° of experiment. On the basis of these agreeable results we conclude that the calculations represent a qualitative picture of the electronic structure of complexes **195-198**.

The computed MDC-q charges for uranium and thorium, respectively, for **195-198** of 2.20, 2.17, 2.18, and 2.14 and the calculated MDC-m spin densities of -2.24 and -2.27 for **195** and **196**, respectively, are consistent with charges and spin densities typically observed in calculations on uranium(IV) and thorium(IV) complexes and suggest donation of electron density from the ligand to metal ions. The molybdenum charges for **195-198** span a narrow range of 0.62-0.65 and are consistent with the notion of a formally zero valent metal ion that is engaged in synergic back-donation to carbonyl ligands. Interestingly, inspection of the Mayer bond orders reveals U-Mo and Th-Mo bond orders of 0.56, 0.56, 0.38, and 0.40 for **195-198**, respectively. This is indicative

of predominantly electrostatic, dative M-Mo bonds, and it is notable that the U-Mo bond orders are uniformly ca 0.15 higher than the analogous Th-Mo bonds, suggesting that the latter pair are more polarised interactions than the former pair; indeed, this is also suggested by visualisation of Kohn Sham molecular orbitals that represent the principal actinide-molybdenum interactions in **195-198** (see Figure X below).

Inspection of the Kohn Sham molecular orbital manifolds of **195-198** reveals a common electronic structure pattern, once differences between the $5f^2$ uranium and $5f^0$ thorium complexes are accommodated. Specifically, in gross terms this can be classified into three zones comprising a high-lying 5f orbital band, followed by a Mo-CO backbonding manifold, then U/Th-Mo dative bonds. Kohn Sham molecular orbital representations of the M-Mo interactions are illustrated in **fig. 77**. For **195**, five vacant 5f orbitals constitute a LUMO band spanning -2.821 to -3.169 eV. Just below that in the α -spin manifold a vacant 5f band with two quasi-degenerate singly occupied 5f orbitals reside at -3.421 (HOMO) and -3.439 eV (HOMO-1). The HOMO-2 to HOMO-6 represent Mo-CO back-bonding combinations that span -4.957 to -5.192 eV. Underneath that relatively dense block of Mo-CO molecular orbitals that spans only 0.25 eV (ca 24 kJ mol^{-1}) resides HOMO-7 that represent the principal U-Mo dative bond at -5.347 eV. For **196** a very similar picture emerges, where the vacant five 5f orbitals are -2.90 to -3.261 , then in the α -spin manifold the HOMO and HOMO-1 are quasi-degenerate singly occupied 5f orbitals at -3.517 and -3.529 eV, HOMO-2 to HOMO-6 are Mo-CO back-bonding interactions spanning the range -4.945 to -5.188 eV, and the U-Mo dative bond is represented by HOMO-7 at -5.334 eV. Interestingly, since the sole difference between **195** and **196** is the halide ligand, it is germane to note that replacing chloride with iodide results in the uranium 5f orbitals (vacant LUMOs or occupied HOMO/HOMO-1) being stabilised by ca 0.1 eV (ca 10 kJ mol^{-1}), but this has essentially no impact on the Mo-CO or U-Mo molecular orbital energies suggesting that they are reasonably well isolated from the halide. Interestingly, when the HOMO-7 of **195** and **196** is visualised and inspected in detail it can be seen that this molecular orbital is not just a pure σ -donor orbital but is also has modest orbital coefficient overlap with lobes that form part of the π^* orbitals of

the CO ligands. Thus, the notion discussed above that the CO stretching frequency acts as a reporter as to the extent of Mo→U donation appears to be valid.

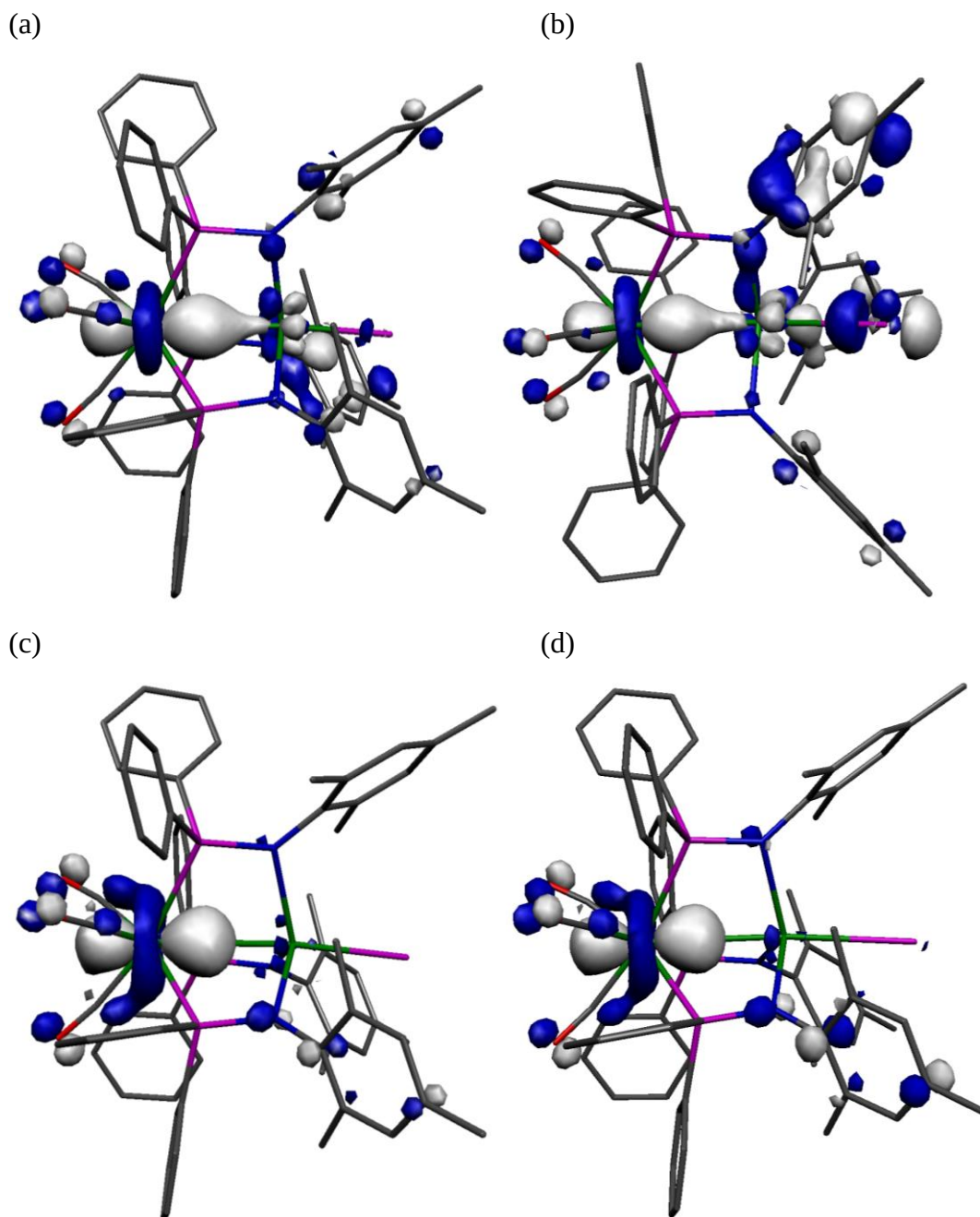


Figure 76. (a) HOMO-7 of **195** (344a, -5.347 eV), (b) HOMO-7 of **196** (362a, -5.334 eV), (c) HOMO-2 of **197** (347, -5.029 eV), (d) HOMO-2 of **198** (365, -5.057 eV). Colour key: gray = carbon; green = metal; magenta = phosphorus; maroon = halide; red = oxygen. Hydrogen atoms are omitted for clarity

The molecular orbital manifolds of **197** and **198** are simpler than for **195** and **196** due to the restricted, closed shell nature of the former. For the former pair the seven vacant 5f orbitals reside at and above -2.032 and -2.090 eV, respectively, lying ca 0.7 eV higher than the analogous LUMOs of the latter, which is consistent with the expected trend that the 5f orbitals lie generally higher for thorium than uranium. For **197** and **198** the Mo-CO bonding interactions are found principally in the quasi-degenerate HOMO and HOMO-1 orbitals in each case, at $-4.874/-4.896$ and $-4.930/-4.941$ eV, respectively. Although it would be tempting to speculate that these orbitals reside overall at slightly higher energy as a group than the analogous orbitals for **195** and **196** a clear-cut reason for this cannot be known for sure because although this may reflect more polarised Mo $\rightarrow$ Th donation than Mo $\rightarrow$ U the Mo-CO orbital manifold is more complicated in the uranium cases due to being unrestricted to they are not a true like-for-like comparison. Again, directly underneath the Mo-CO molecular orbital combinations are Mo-Th dative bond orbitals at -5.029 and -5.057 eV for **197** and **198**, respectively. These two Mo-Th bonds lie ~ 0.3 eV higher than the corresponding Mo-U bonds (ca 30 kJ mol $^{-1}$) destabilised, which may reflect more polar bonding in the former than latter.

In order to probe the nature of the U-Mo and Th-Mo bonds in **195-198** as suggested by the Kohn Sham orbitals we probed them with Natural Bond Orbital (NBO) analyses since in the DFT approach the MOs, being by their nature delocalised, suffer from intrusion of other orbital coefficients. However, NBO returns these bonds as essentially electrostatic and so no orbital breakdown could be determined. Although NBO can be forced to generate a bond by dictating a particular Lewis bonding scheme in the input of the calculation this would skew the analysis and thus be meaningless. Thus, instead we probed the U-Mo and Th-Mo bonds by looking not at orbitals but by density through analysis of the topology of the electron density using the Quantum Theory of Atoms in Molecules (QTAIM) (**Table 4**).

Entry	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$G(\mathbf{r})$	$V(\mathbf{r})$	$H(\mathbf{r})$
195	0.03682	0.04807	0.019424	-0.01242	-0.007
196	0.0372	0.04763	0.019361	-0.01191	-0.00745
197	0.02955	0.03351	0.01344	-0.0185	-0.00506
198	0.03027	0.03316	0.01353	-0.01877	-0.00524

Table 4. QTAIM parameters for **195-198**

In all cases, 3,–1 bond critical points (BCPs) were found between the actinide and molybdenum atoms of **195-198** indicating that indeed U-Mo and Th-Mo bonds are present in these complexes. The $\rho(\mathbf{r})$ values for **195-198** span the narrow range of 0.03-0.04 indicative of dative bonds, in agreement with the Mayer bond orders. Also consistent with this the $H(\mathbf{r})$ energy terms are rather small, which is again consistent with dative metal-metal bonding. The DFT analysis revealed metal-metal σ -bonds that are largely dative in nature, but the Mo-based orbital is in all cases a complex 4d-hybrid and so is not purely symmetrical around the actinide-molybdenum bond vector as, for example, a pure d_{z^2} orbital would be, assuming the z-axis was coincident with the actinide-molybdenum bond vector. This is reflected by the ellipticity of the actinide-molybdenum bonds which span the range 0.09-0.13; a single σ -bond or triple σ - π - π -bond present symmetrical electron density distributions around the internuclear axes with $\mathcal{A}(\mathbf{r})$ values of 0, whereas σ - π -double bonds are asymmetric with $\mathcal{A}(\mathbf{r}) > 0$. For comparison, the calculated $\mathcal{A}(\mathbf{r})_{\text{CC}}$ values for the C-C bonds in ethane ($\text{H}_3\text{C}-\text{CH}_3$), benzene (C_6H_6), ethene ($\text{H}_2\text{C}=\text{CH}_2$), and acetylene ($\text{HC}\equiv\text{CH}$) are 0.0, 0.23, 0.45, and 0.0, respectively.³⁷ On the basis of these data, though not entirely symmetrical the actinide-molybdenum bonds are clearly close to being symmetrical.

5.4 Concluding remarks

The tris(phosphinoamide)actinide chlorides $[\text{UCl}(\text{MesNPPH}_2)_3]$ (**165**), $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**169**), $[\text{ThCl}(\text{MesNPPH}_2)_3]$ (**175**) and $[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**176**) were treated with $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ at $-78\text{ }^\circ\text{C}$ in DCM resulted in the formation of the acetonitrile insertion products $[\text{UCl}(\text{MesNPPH}_2)_2(\text{MesNPPH}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**189**), $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_2(\text{MesNP}^i\text{Pr}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**190**), $[\text{ThCl}(\text{MesNPPH}_2)_2(\text{MesNPPH}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**191**) and $[\text{ThCl}(\text{MesNP}^i\text{Pr}_2)_2(\text{MesNP}^i\text{Pr}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (**192**). Alternatively reaction of $[\text{UI}(\text{MesNP}^i\text{Pr}_2)_3]$ (**161**) and $[\text{ThI}(\text{MesNP}^i\text{Pr}_2)_3]$ (**178**) with $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ in refluxing toluene yielded $[(\eta^2\text{-MesNP}^i\text{Pr}_2)\text{UI}(\text{MesNP}^i\text{Pr}_2)(\{\mu\text{-NCMe}\}\text{MesNP}^i\text{Pr}_2)\text{Mo}(\text{CO})_3]$ (**193**) and $[(\eta^2\text{-MesNP}^i\text{Pr}_2)\text{ThI}(\text{MesNP}^i\text{Pr}_2)(\{\mu\text{-NCMe}\}\text{MesNP}^i\text{Pr}_2)\text{Mo}(\text{CO})_3]$ (**194**) respectively in which the $\text{MesNP}^i\text{Pr}_2$ ligand shows three different binding modes. The compounds **189-194** showed an unprecedented acetonitrile insertion as a bridging ligand between the actinide metal and Mo with structural analysis suggesting an activation of the nitrile group.

Reaction of the tris(phosphinoamide)actinide halides $[\text{UCl}(\text{MesNPPH}_2)_3]$ (**165**), $[\text{UI}(\text{MesNPPH}_2)_3]$ (**173**), $[\text{ThCl}(\text{MesNPPH}_2)_3]$ (**175**) and $[\text{ThI}(\text{MesNPPH}_2)_3]$ (**177**) with $[\text{Mo}(\text{NCMe})_3(\text{CO})_6]$ in refluxing toluene afforded the respective heterobimetallic thorium-molybdenum complexes $[\text{UCl}(\text{MesNPPH}_2)_3\text{Mo}(\text{CO})_3]$ (**195**) and $[\text{UI}(\text{MesNPPH}_2)_3\text{Mo}(\text{CO})_3]$ (**198**), $[\text{ThCl}(\text{MesNPPH}_2)_3\text{Mo}(\text{CO})_3]$ (**197**) and $[\text{ThI}(\text{MesNPPH}_2)_3\text{Mo}(\text{CO})_3]$ (**198**). Orbital- and density-based quantum chemical calculations reveal dative $\text{Mo}\rightarrow\text{M}$ σ -interactions in all cases and so these complexes constitute unprecedented actinide-group 6 metal-metal bonds. In future, although it is outside the scope of this thesis, it will be interesting to see if analogous U-Cr, U-W, Th-Cr, and Th-W bonds can be prepared to enable comparison of the entire group 6 triad to be accomplished.

5.5 Experimental

Preparation of $[\text{UCl}(\text{MesNPPh}_2)_2(\text{MesNPPh}_2\{\mu\text{-CNMe}\})\text{Mo}(\text{CO})_3]$ (**189**)

DCM (30 ml) was added slowly to a cold (-78°C) stirring mixture of $[\text{UCl}(\text{MesNPPh}_2)_3]$ (**165**) (1.24 g, 1.0 mmol) and $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ (0.30 g, 1.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. The resulting red solution was concentrated to 10 ml and stored at -30°C for 24 hours to yield **189** as red crystals suitable for a single crystal X-ray diffraction study. Yield: 0.76 g, 52%. Anal. Calc'd for: $\text{C}_{68}\text{H}_{66}\text{ClMoN}_4\text{O}_3\text{P}_3\text{U}$: C, 56.34; H, 4.59; N, 3.86%. Found: C, 57.13; H, 4.78; N, 3.32%. ^1H NMR (C_6D_6 , 295 K): δ (ppm) -31.07 (6H, s, Mes- CH_3), -17.34 (4H, s, Ar-CH), -5.35 (6H, s, Mes- CH_3), -2.36 (4H, s, Ar-CH), -1.94 (2H, s, Ar-CH), -0.55 (2H, s, Ar-CH), -0.40 (3H, s, Mes- CH_3) 0.84 (3H, s, Mes- CH_3), 2.35 (4H, s, Ar-CH), 2.49 (2H, s, Ar-CH), 3.48 (4H, s, Ar-CH), 3.53 (3H, s, CH_3CN), 4.13 (2H, s, Ar-CH), 6.40 (6H, s, Mes- CH_3), 8.08 (4H, s, Ar-CH), 12.80 (2H, s, Ar-CH), 13.39 (4H, s, Ar-CH), 18.89 (3H, s, Mes- CH_3). FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}) 597 (m), 625 (m), 658 (w), 667 (w), 696 (m), 728 (m), 748 (w), 767 (m), 853 (m), 893 (m), 938 (w), 970 (w), 1027 (w), 1089 (m), 1151 (m), 1208 (m), 1434 (s), 1823 (s), 1854 (s), 1933 (s). Magnetic moment (Evans method, C_6D_6 , 298 K): $\mu_{\text{eff}} = 2.49\mu_{\text{B}}$.

Preparation of $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_2(\text{MesNP}^i\text{Pr}_2\{\mu\text{-CNMe}\})\text{Mo}(\text{CO})_3]$ (**190**)

DCM (30 ml) was added slowly to a cold (-78°C) stirring mixture of $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_3]$ (**169**) (1.02 g, 1.0 mmol) and $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ (0.30 g, 1.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. The resulting red solution was concentrated to 5 ml and stored at 9°C for 24 hours to yield **190** as red crystals suitable for a single crystal X-ray diffraction study. Yield: 1.02 g, 82%. Anal. Calc'd for: $\text{C}_{50}\text{H}_{78}\text{ClMoN}_4\text{O}_3\text{P}_3\text{U}$: C, 48.22; H, 6.31; N, 4.50%. Found: C, 48.17; H, 6.45; N, 4.30%. ^1H NMR (C_6D_6 , 295 K): δ (ppm) -27.64 (6H, s-br, $^i\text{Pr-CH}_3$), -16.17 (6H, s-br, $^i\text{Pr-CH}_3$), -12.29 (12H, s-br, $^i\text{Pr-CH}_3$), -5.80 (12H, s-br, $^i\text{Pr-CH}_3$), -2.16 (6H, s-br, Mes- CH_3), -0.97 (12H, s-br,

Mes-CH₃), -0.05 (6H, s, Mes-CH₃), 0.27 (3H, s, Mes-CH₃), 4.61 (6H, s-br, ⁱPr-CH), 4.77 (3H, s-br, CH₃CN) 13.57 (2H, s, Ar-CH) 18.66 (4H, s, Ar-CH). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 500 (w), 539 (w), 588 (w), 647 (w), 671 (w), 765 (w), 854 (m), 878 (w), 934 (w), 965 (w), 1142 (m), 1198 (m), 1261 (w), 1303 (w), 1833 (s), 1926 (s). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 2.41 \mu_{\text{B}}$

Preparation of [ThCl(MesNPPPh₂)₂(MesNPPPh₂{ μ -CNMe})Mo(CO)₃] (191)

DCM (30 ml) was added slowly to a cold (-78 °C) stirring mixture of [ThCl(MesNPPPh₂)₃] (**175**) (1.24 g, 1.0 mmol) and [Mo(NCMe)₃(CO)₃] (0.30 g, 1.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. The resulting red solution was concentrated to 10 ml and stored at -30 °C for 24 hours to yield **191** as red crystals suitable for a single crystal X-ray diffraction study. Yield: 0.82 g, 57%. Anal. Calc'd for: C₆₈H₆₆ClMoN₄O₃P₃Th: C, 55.84; H, 4.42; N, 3.61%. Found: C, 52.43; H, 4.42; N, 3.61%. ¹H NMR (C₆D₆, 295 K): δ (ppm) 1.48 (6H, s, Mes-CH₃), 1.87 (3H, S, CH₃CN), 1.98 (6H, s, Mes-CH₃), 2.10 (6H, s, Mes-CH₃), 2.59 (6H, s, Mes-CH₃), 2.77 (3H, s, Mes-CH₃), 6.26 (2H, s, Mes-CH), 6.62 (2H, s, Mes-CH), 6.76 (2H, s, Mes-CH), 6.97 (8H, s, Ar-CH), 7.01 (2H, m, Ar-CH), 7.05 (8H, m, Ar-CH), 7.48 (4H, m, Ar-CH), 7.83 (H, m, Ar-CH), 7.90 (4H, m, Ar-CH) ¹³C{¹H} NMR (C₆D₆, 295 K): δ (ppm) 20.21 (Mes-CH₃), 20.50 (Mes-CH₃), 23.12 (d, ³J_{PC} = 68.0 Hz, CH₃CN), 29.32 (Mes-CH₃), 29.82 (Mes-CH₃), 127.06 (Ar-CH) 127.25 (Ar-CH), 127.69 (Ar-CH), 128.85 (Ar-CH), 129.56 (Ar-CH), 129.85 (Ar-CH), 130.22 (Ar-CH), 132.95 (Ar-C), 133.31 (Ar-C), 133.31 (Ar-C), 133.65 (Ar-C), 134.22 (Ar-C), 134.72, (Ar-C) 140.98 (Ar-C), 141.27 (Ar-C), 143.15 (Ar-C), 143.48 (Ar-C). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 44.87 (s), 47.08 (s). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 596 (m), 624 (m), 658 (w), 667 (w), 695 (m), 728 (m), 748 (w), 768 (m), 853 (m), 895 (m), 938 (w), 970 (w), 1027 (w), 1092 (m), 1152 (m), 1208 (m), 1434 (s), 1822 (s), 1854 (s), 1934 (s).

Preparation of [ThCl(MesNPⁱPr₂)₂(MesNPⁱPr₂{ μ -CNMe})Mo(CO)₃] (192)

DCM (30 ml) was added slowly to a cold (-78 °C) stirring mixture of [ThCl(MesNPⁱPr₂)₃] (**176**) (1.01 g, 1.0 mmol) and [Mo(NCMe)₃(CO)₃] (0.30 g, 1.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and

stirred over 16 hours. The resulting red solution was concentrated to 5 ml and stored at 9 °C for 24 hours to yield **192** as red crystals suitable for a single crystal X-ray diffraction study. Yield: 0.75 g, 61%. Anal. Calc'd for: C₅₀H₇₈ClMoN₄O₃P₃Th: C, 48.45; H, 6.34; N, 4.52%. Found: C, 47.67; H, 6.30; N, 3.95%. ¹H NMR (C₆D₆, 295 K): δ (ppm) 0.73 (6H, q, ²J_H = 6 Hz, ⁱPr-CH₃), 0.83 (6H, q, ²J_H = 6 Hz, ⁱPr-CH₃), 1.17 (6H, m, ⁱPr-CH₃), 1.31 (6H, q, ²J_H = 6 Hz, ⁱPr-CH₃), 1.35 (12H, m, ⁱPr-CH₃), 1.68 (6H, q, ²J_H = 6 Hz, ⁱPr-CH₃), 1.97 (3H, s, CH₃CN), 2.04 (2H, m, ⁱPr-CH), 2.14 (6H, s, Mes-CH₃), 2.20 (6H, s, Mes-CH₃), 2.41 (6H, s, Mes-CH₃), 2.60 (3H, d, ²J_H = 6 Hz, Mes-CH₃), 2.72 (6H, s, Mes-CH₃), 6.43 (2H, s, Ar-CH), 6.83 (H, s, Ar-CH). ¹³C{¹H} NMR (C₆D₆, 295 K): δ (ppm) 17.32 (ⁱPr-CH₃), 17.81 (ⁱPr-CH₃), 19.96 (Mes-CH₃), 20.21 (Mes-CH₃), 20.44 (Mes-CH₃), 21.59 (Mes-CH₃), 22.92 (CNCH₃), 32.04 (ⁱPr-CH), 32.68 (ⁱPr-CH₃), 127.69 (Ar-C), 129.51 (Ar-CH), 129.99 (Ar-CH), 132.51 (Ar-C), 133.23 (Ar-C), 133.98 (Ar-C), 141.84 (Ar-C), 141.93 (Ar-C). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 66.27 (s), 70.67 (s). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 647 (w), 682 (w), 718 (w), 766 (w), 855 (m), 933 (w), 964 (w), 1143 (m), 1199 (m), 1261 (w), 1303 (w), 1827 (s), 1925 (s).

Preparation of [(η²-MesNPⁱPr₂)UI(MesNPⁱPr₂)(μ-CNMe)MesNPⁱPr₂)Mo(CO)₃] (**193**)

Toluene (30 ml) was added to a stirring mixture of [UI(MesNPⁱPr₂)₃] (**161**) (1.12 g, 1.0 mmol) and [Mo(NCMe)₃(CO)₃] (0.30 g, 1.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Volatiles were removed *in vacuo* and the resulting red solid was washed with hexanes (3 x 10 ml) to yield **193** as an analytically pure powder. Red crystals suitable for a single crystal X-ray diffraction study were grown from the storage of a concentrated toluene solution of **193** at room temperature over 24 hours. Yield: 0.77 g, 57%. C₅₀H₇₈IMoN₄O₃P₃U: C, 44.92; H, 5.88; N, 4.19%. Found: C, 44.68; H, 5.56; N, 4.09%. ¹H NMR (C₆D₆, 295 K): δ (ppm) -9.44 (6H, m-br, CH₃), -8.81 (6H, m-br, CH₃), -3.31 (12H, m-br, CH₃), -1.11 (6H, s, CH₃), 0.44 (6H, s, CH₃), 0.80 (3H, s, CH₃), 1.84 (3H, sr, CH₃), 1.97 (3H, s-br, CH₃), 2.04 (3H, s, CH₃), 2.11 (6H, s, CH₃), 12.11 (6H, s, CH₃), 12.81 (2H, s, Ar-CH), 13.82 (6H, s-br, CH₃), 17.70 (2H, s-br, Ar-CH), 1.46 (2H, s-br, Ar-CH). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 500 (w), 529 (w), 560 (m), 615 (w), 675 (m), 729 (w), 763 (w), 850 (m), 878

(m), 1038 (m), 1153 (m), 1205 (m), 1304 (w), 1542 (m), 1840 (s), 1949 (m). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 2.91\mu_{\text{B}}$.

Preparation of $[(\eta^2\text{-MesNP}^i\text{Pr}_2)\text{ThI}(\text{MesNP}^i\text{Pr}_2)(\{\mu\text{-CNMe}\}\text{MesNP}^i\text{Pr}_2)\text{Mo}(\text{CO})_3]$ (**194**)

Toluene (30 ml) was added to a stirring mixture of $[\text{ThI}(\text{MesNP}^i\text{Pr}_2)_3]$ (**178**) (1.11 g, 1.0 mmol) and $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ (0.30 g, 1.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Volatiles were removed *in vacuo* and the resulting yellow solid was washed with hexanes (3 x 10 ml) to yield **194** as an analytically pure powder. Yield: 0.89 g, 67%. C₅₀H₇₈IMoN₄O₃P₃Th 0.4(C₇H₈): C, 46.36; H, 5.98; N, 4.10%. Found: C, 46.28; H, 5.92; N, 3.97%. ¹H NMR (C₆D₆, 295 K): δ (ppm) 0.54 (3H, m, ⁱPr-CH₃), 0.73 (3H, m, ⁱPr-CH₃), 0.93 (6H, m, ⁱPr-CH₃), 1.16 (6H, m, ⁱPr-CH₃), 1.47 (12H, m, ⁱPr-CH₃), 1.73 (6H, m, ⁱPr-CH₃), 1.87 (3H, s, CH₃CN), 2.22 (12H, m, Mes-CH₃), 2.44 (6H, s, Mes-CH₃), 2.46 (3H, s, Mes-CH₃), 2.52 (6H, s, Mes-CH₃), 2.67 (2H, m, ⁱPr-CH), 2.85 (2H, m, ⁱPr-CH), 3.07 (3H, s, Mes-CH), 6.70–7.00 (6H, m, Mes-CH). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 59.64 (s), 89.47 (s), 154.27 (s). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 595 (m), 615 (m), 671 (m), 685 (m), 729 (m), 764 (m), 851 (m), 860 (w), 883 (m), 1036 (m), 1156 (m), 1206 (m), 1213 (w) 1304 (w), 1549 (m), 1838 (s), 1949 (s).

Preparation of $[\text{UCl}(\text{MesNPPh}_2)_3\text{Mo}(\text{CO})_3]$ (**195**)

Toluene (30 ml) was added to a stirring mixture of $[\text{UCl}(\text{MesNPPh}_2)_3]$ (**165**) (1.24 g, 1.0 mmol) and $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ (0.30 g, 1.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Volatiles were removed *in vacuo* and the resulting orange solid was washed with hexanes (3 x 10 ml) to yield **195** as an analytically pure powder. Orange crystals suitable for a single crystal X-ray diffraction study were grown from the storage of a concentrated toluene solution of **195** at room temperature over 24 hours. Yield: 1.24 g, 88%. Anal. Calc'd for: C₆₆H₆₃ClMoN₃O₃P₃U 0.4(C₇H₈): C, 57.03; H, 4.63; N, 2.92%. Found: C, 57.00; H, 4.72; N, 2.92%. ¹H NMR (C₆D₆, 295 K): δ (ppm) 3.22 (12H, s, Ar-CH), 7.59 (6H, s, Ar-CH), 7.79 (12H, s, Ar-CH), 8.84 (9H, s, Mes-CH₃), 9.70 (6H, s, Ar-CH), 14.32 (18H, s, Mes-CH₃). FTIR

ν/cm^{-1} (Nujol): 519 (m), 542 (m), 579 (w), 601 (w), 661 (w), 697 (m), 722 (m), 745 (m), 762 (m), 800 (w), 854 (w), 897 (w), 959 (w), 1088 (m), 1144 (m), 1203 (m), 1307 (m), 1434 (m), 1891 (s), 1969 (s). Magnetic moment (Evans method, C_6D_6 , 298 K): $\mu_{\text{eff}} = 2.25 \mu_{\text{B}}$.

Preparation of [UI(MesNPPPh₂)₃Mo(CO)₃] (**196**)

Toluene (40 ml) was added to a stirring mixture of [UI(MesNPPPh₂)₃] (**173**) (2.64 g, 2.0 mmol) and [Mo(NCMe)₃(CO)₃] (0.60 g, 2.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Upon cooling an orange microcrystalline solid precipitated from the reaction mixture which was isolated *via* filtration and washed with hexanes (3 x 10 ml) to yield **196** as an analytically pure powder. Orange crystals suitable for a single crystal X-ray diffraction study were grown from the storage of a concentrated toluene solution of **196** at room temperature over 24 hours. Yield: 1.86g, 62%. Anal. Calc'd for: $\text{C}_{66}\text{H}_{63}\text{IMoN}_3\text{O}_3\text{P}_3\text{U} \cdot 0.65(\text{C}_7\text{H}_8)$: C, 54.32; H, 4.66; N, 2.69%. Found: C, 54.11; H, 4.66; N, 2.56%. ^1H NMR (C_6D_6 295 K): δ (ppm) 3.54 (12H, s, Ar-CH), 7.94 (6H, s, Ar-CH), 8.25 (12H, s, Ar-CH), 9.28 (9H, s, Mes-CH₃), 11.32 (6H, s, Ar-CH), 22.54 (18H, s, Mes-CH₃). FTIR ν/cm^{-1} (Nujol): 518 (m), 541 (m), 578 (w), 600 (w), 660 (w), 696 (m), 724 (m), 745 (m), 761 (m), 800 (w), 854 (w), 895 (w), 959 (w), 1088 (m), 1142 (m), 1203 (m), 1307 (m), 1434 (m), 1893 (s), 1904 (s), 1969 (s). Magnetic moment (Evans method, C_6D_6 , 298 K): $\mu_{\text{eff}} = 2.39 \mu_{\text{B}}$.

Preparation of [ThCl(MesNPPPh₂)₃Mo(CO)₃] (**197**)

Toluene (40 ml) was added to a stirring mixture of [ThCl(MesNPPPh₂)₃] (**175**) (1.22 g, 1.0 mmol) and [Mo(NCMe)₃(CO)₃] (0.30 g, 1.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Upon cooling a yellow microcrystalline solid precipitated from the reaction mixture which was isolated *via* filtration and washed with hexanes (3 x 10 ml) to yield **197** as an analytically pure powder. Yellow crystals suitable for a single crystal X-ray diffraction study were grown from the storage of a concentrated toluene solution of **197** at room temperature over 24 hours. Yield: 0.51 g, 36%. Anal. Calc'd for: $\text{C}_{66}\text{H}_{63}\text{ClMoN}_3\text{O}_3\text{P}_3\text{Th}$: C, 56.52; H, 4.53; N, 3.00%. Found: C, 55.84; H, 4.68; N, 2.82%. ^1H NMR (C_6D_6 295 K): δ (ppm) 2.03 (9H, s, Mes-CH₃)

2.14, (18H, s, Mes-CH₃), 6.66 (6H, s, Ar-CH), 6.95 (18H, m, Ar-CH), 7.81 (4H, m, Ar-CH). ¹³C{¹H} NMR (C₆D₆, 295 K): δ (ppm) 20.23 (Mes-CH₃), 21.28 (Mes-CH₃), 127.48 (Ar-CH), 127.8 (Ar-CH), 129.07 (Ar-CH), 129.47 (Ar-CH), 131.06 (Ar-C), 134.08 (Ar-C), 142.41 (Ar-C), 142.84 (Ar-C). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 46.18 (s). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹): 522 (m), 542 (m), 581 (w), 606 (w), 665 (w), 697 (m), 744 (m), 765 (m), 854 (w), 899 (w), 959 (w), 1090 (m), 1144 (m), 1206 (m), 1305 (m), 1884 (s), 1896 (s), 1967 (s).

Preparation of [ThI(MesNPPH₂)₃Mo(CO)₃] (**198**)

Toluene (40 ml) was added to a stirring mixture of [ThI(MesNPPH₂)₃] (**176**) (1.31 g, 1.0 mmol) and [Mo(NCMe)₃(CO)₃] (0.30 g, 1.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Upon cooling a yellow microcrystalline solid precipitated from the reaction mixture which was isolated *via* filtration and washed with hexanes (3 x 10 ml) to yield **198** as an analytically pure powder. Yellow crystals suitable for a single crystal X-ray diffraction study were grown from the storage of a concentrated toluene solution of **198** at room temperature over 24 hours. Yield: 0.62 g, 41%. Anal. Calc'd for: C₆₆H₆₃IMoN₃O₃P₃Th 0.55(C₇H₈): C, 54.31; H, 4.40; N, 2.72%. Found: C, 54.09; H, 4.70; N, 2.72%. ¹H NMR (C₆D₆ 295 K): δ (ppm) ¹H NMR (C₆D₆ 295 K): δ (ppm) 2.02 (9H, s, Mes-CH₃) 2.17, (18H, s, Mes-CH₃), 6.71 (6H, s, Ar-CH), 6.93 (18H, m, Ar-CH), 7.82 (4H, m, Ar-CH). ¹³C{¹H} NMR (C₆D₆, 295 K): δ (ppm) 20.29 (Mes-CH₃), 21.58 (Mes-CH₃), 127.48 (Ar-CH), 127.8 (Ar-CH), 129.09 (Ar-CH), 129.54 (Ar-CH), 131.48 (Ar-C), 134.23 (Ar-C), 142.13 (Ar-C), 142.57 (Ar-C). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 45.07 (s). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹): 579 (w), 604(w), 663 (w), 696 (m), 745 (m), 763 (m), 854 (w), 902 (w), 960 (w), 1092 (m), 1144 (m), 1206 (m), 1305 (m), 1884 (s), 1898 (s), 1967 (s).

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Supplementary Information

General

All manipulations described in this thesis were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques, or an MBraun UniLab glovebox operating under an atmosphere of dry nitrogen with H_2O and $\text{O}_2 < 0.1$ ppm. All glassware was dried either by overnight storage in an oven at $150\text{ }^\circ\text{C}$ or by flame-drying with subsequent cooling under 10^{-3} mm Hg vacuum followed by repeated alternate evacuation and purging with nitrogen. Oxygen-free nitrogen gas cylinders were supplied by BOC Gases UK. The solvents THF, diethyl ether, toluene, hexanes and pentane were dried by passage through activated alumina towers and degassed before use. 1,2-dimethoxyethane (DME) and benzene were distilled from potassium. Dichloromethane (DCM) was distilled calcium hydride. All solvents were stored over potassium mirrors except for DCM, and ethers which were stored over activated 4 Å sieves. Deuterated NMR solvents (d^6 -benzene, d^8 -toluene, d^6 -dimethylsiloxane) were purchased from Goss Scientific Ltd and were distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under nitrogen prior to use. Nujol was purchased from Sigma-Aldrich and used as received.

Instrumentation

^1H , ^7Li , ^{13}C , ^{29}Si , and ^{31}P NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2, 155.5, 100.6, 79.5, and 162.0 MHz respectively; chemical shifts are quoted in ppm and are relative to TMS (^1H , ^{13}C , ^{29}Si), LiCl (^7Li) and external 85% H_3PO_4 (^{31}P). FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. UV/Vis/NIR spectra were recorded on a Perkin Elmer Lambda 750 spectrometer. Data were collected in 1mm path length cuvettes loaded in an MBraun UniLab glovebox and were run versus the appropriate reference solvent. Variable-temperature magnetic moment data were recorded in an applied dc field of 0.1 T on a Quantum Design MPMS XL7 superconducting quantum interference device (SQUID) magnetometer using doubly recrystallized powdered samples. Samples were carefully checked for

purity and data reproducibility between several independently prepared batches for each compound examined. Care was taken to ensure complete thermalization of the sample before each data point was measured and samples were immobilized in an eicosane matrix to prevent sample reorientation during measurements. Solution magnetic moments were recorded at room temperature using the Evans method. EPR spectra were measured at X- and K-band (*ca.* 9.4 and 24 GHz) on a Bruker Elexsys E500 spectrometer with an ER4118SMS5 or ER5106QT resonator, respectively. Polycrystalline samples were sealed under vacuum in 1mm i.d. silica tubing, and double-contained for EPR by insertion into an X-band silica tube or PTFE sleeve. Measurements were made on several independently prepared batches, which were also analyzed by SQUID and CHN microanalyses, to ensure reproducibility. Spectra were background corrected against blank sample holders measured under identical conditions. Cyclic voltammetry was carried out in THF solution containing [NBuⁿ₄][BAR^f₄] as supporting electrolyte in a sealed, single compartment cell under a nitrogen atmosphere using a three-electrode arrangement. A Pt-wire working electrode, a Pt-wire secondary electrode and an unbridged AgCl/Ag-wire, acting as a pseudo-reference electrode, were used in the cell. The redox potentials are quoted versus the [Cp₂Fe]⁺/[Cp₂Fe] couple used as an internal reference: E_{1/2} ([Cp₂Fe]⁺/[Cp₂Fe]) was 0.56 V vs. AgCl/Ag under these conditions. CHN microanalyses were carried out by Tong Liu at the University of Nottingham.

X-Ray Crystallography

Crystals were examined variously on a Bruker APEX CCD area detector diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å), or on an Oxford Diffraction SuperNova Atlas CCD diffractometer using mirror-monochromated Cu K α radiation ($\lambda = 1.5418$ Å). Intensities were integrated from data recorded on 0.3° (APEX) or 1° (SuperNova) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semi-empirical absorption correction based on symmetry equivalent and repeat reflections (APEX) or Gaussian grid face-indexed absorption correction with a beam profile correction (Supernova) were applied. The structures were solved variously by direct and heavy atom methods and were refined by full-matrix least-squares on all

unique F^2 values, with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; $U_{iso}(H)$ was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. Programs were Bruker AXS SMART and CrysAlisPro (control), Bruker AXS SAINT and CrysAlisPro (integration), and SHELXTL and Olex2 were employed for structure solution and refinement and for molecular graphics.