

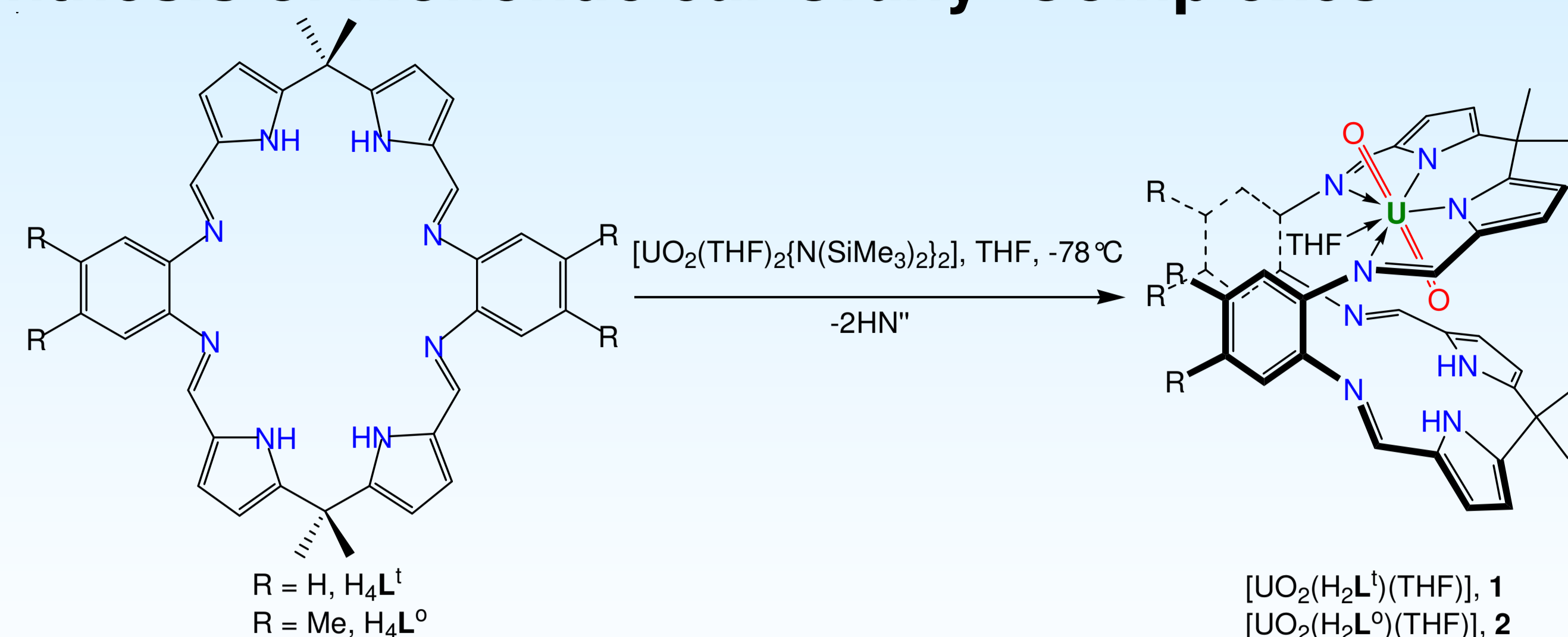
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Introduction

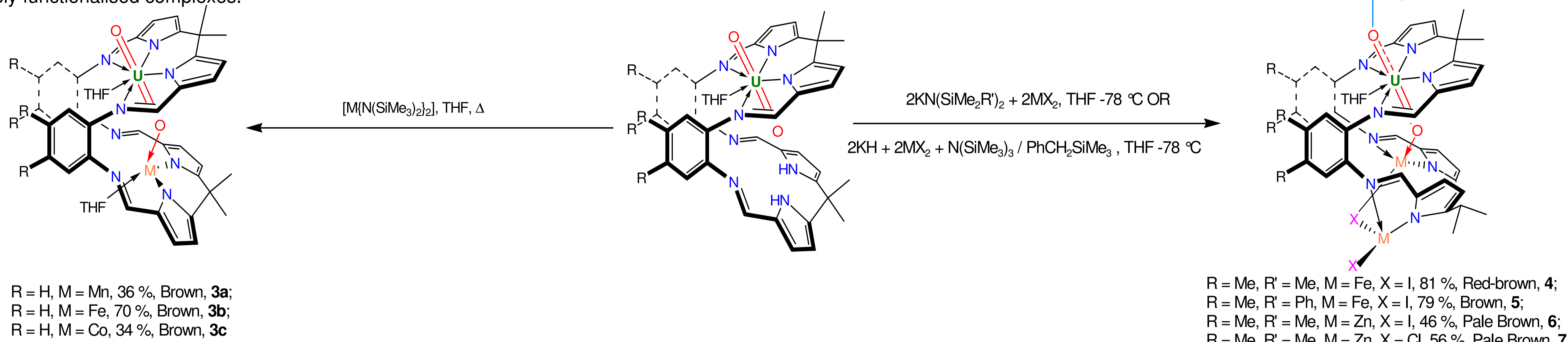
The uranyl ion, $[\text{UO}_2]^{2+}$ is ubiquitous in geology and the nuclear fuel cycle. It is rigorously linear, with a U-O bond order of about 2.5, and is regarded by synthetic chemists as completely inert. However, in the ground and in waste storage, the reduction and deoxygenation of the uranyl ion does occur, and has significant environmental consequences. Understanding and predicting the chemistry of uranyl ions is a strategically important target, yet investigations into chemical reduction and deoxygenation of the uranyl ion are extremely rare. We have recently developed a new strategy in uranyl chemistry that uses the structural rigidity of a Schiff-base pyrrole macrocycle (H_4L) to form uranyl complexes in which the U=O groups reside in different chemical environments. This allows us to explore the reaction chemistry of the tightly bound uranyl oxo atoms in the search for new bonding modes and reactivity of the uranyl group.¹

Synthesis of Mononuclear Uranyl Complexes



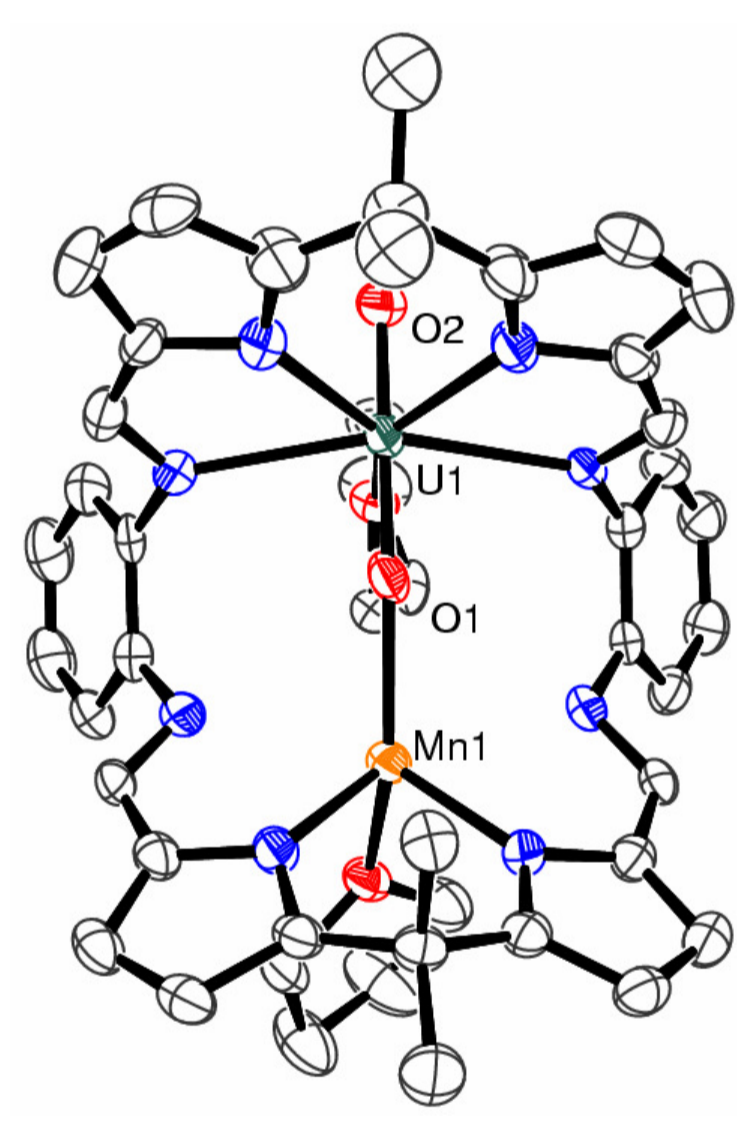
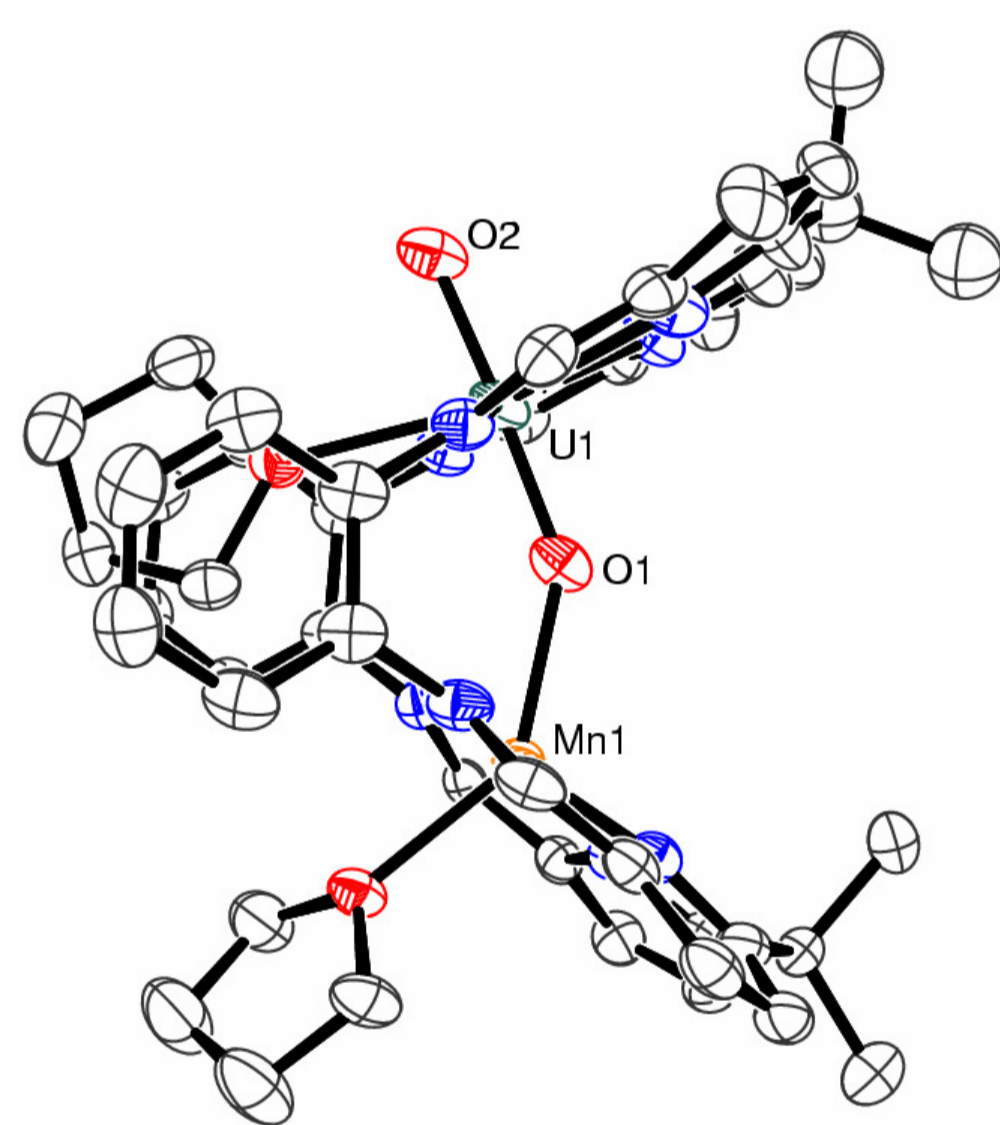
Bimetallic Systems

The pyrrolic macrocycle has two binding compartments and upon metallation folds to form a Pac-Man shaped complex. In both **1** and **2**, only one compartment is occupied due to the large size and linearity of the uranyl fragment and no di-uranyl complex, $[(\text{UO}_2)_2(\text{L})]$, is observed. The transamination reaction between **1** and a divalent transition metal silyl amide results in the formation of a bimetallic complex.² In contrast, the deprotonation of **2** with potassium reagents to generate a potassium salt, followed by salt elimination with a transition metal halide results in the formation of reductively functionalised complexes.³



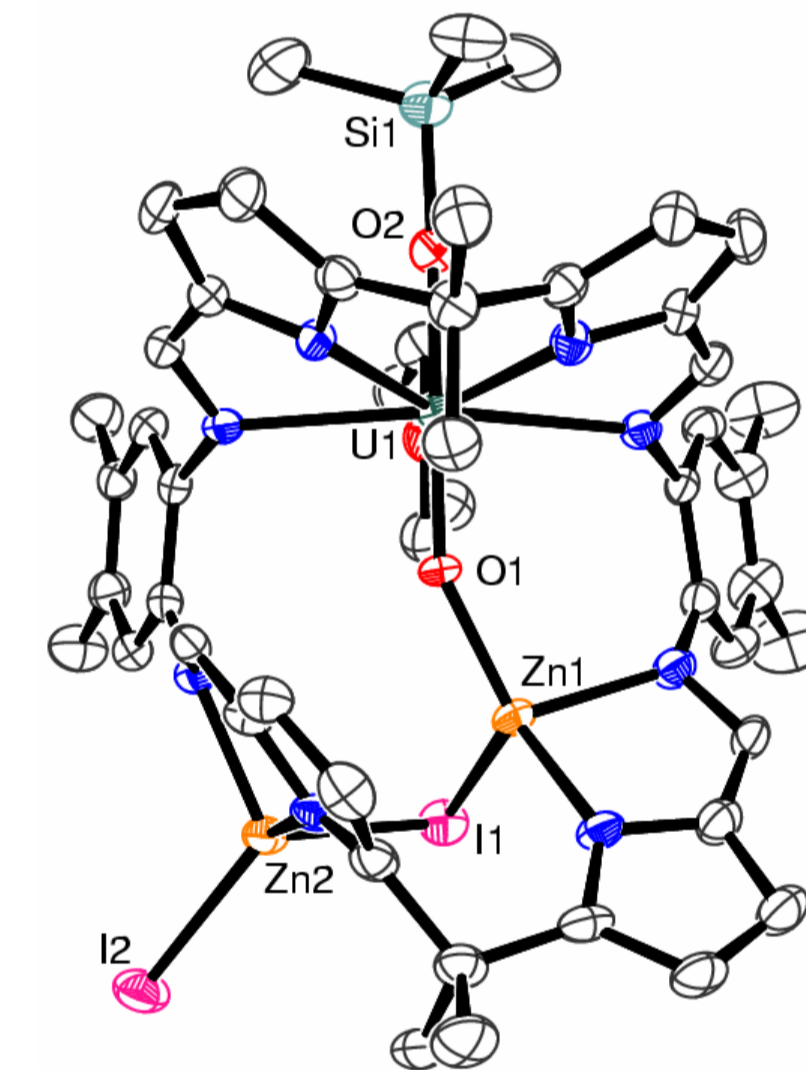
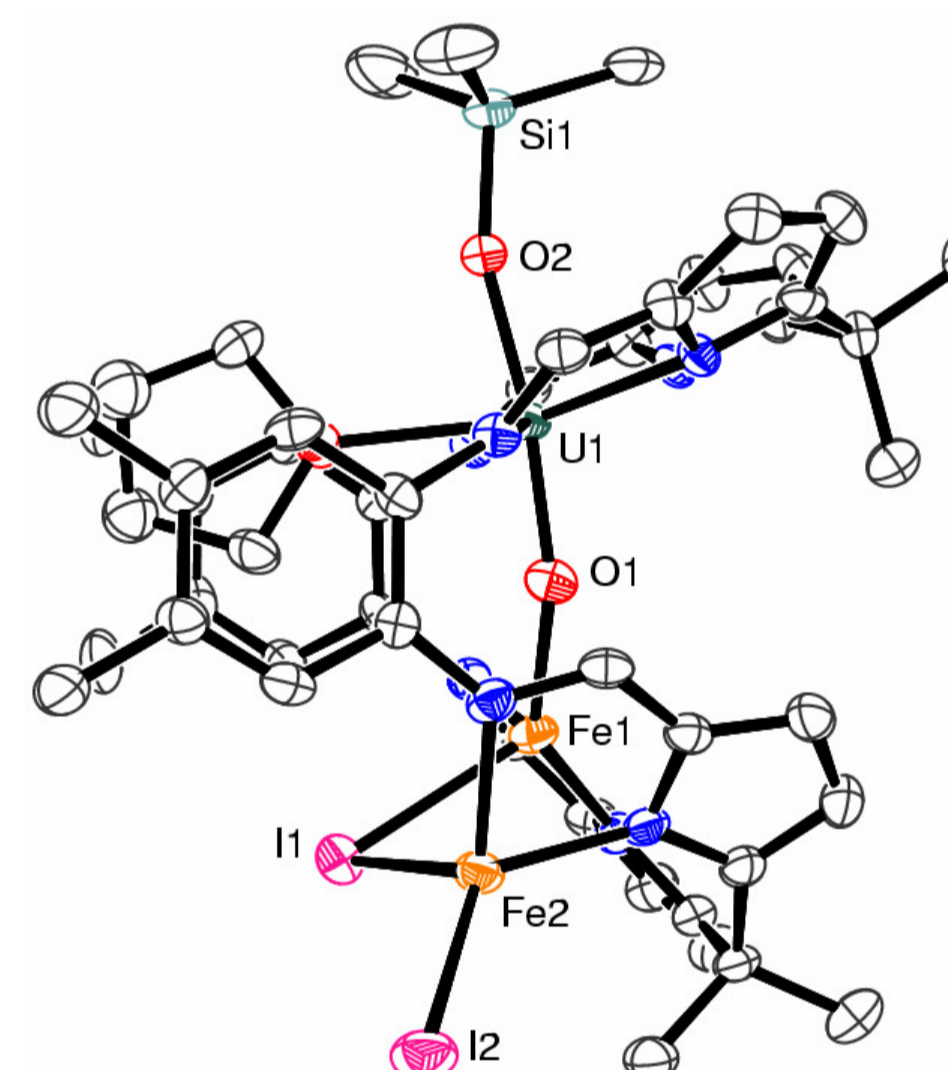
1) Uranyl (VI) Transition Metal Adducts

The transamination reactions between the uranyl complex **1** and the transition metal silylamides results in the formation of **3a** to **3c**. The complexes **3a** and **3c**, were characterised in the solid state by X-ray crystallography, and both complexes are essentially isostructural. The transition metal binds in the second compartment and there is a direct donor bond from the *endo*-oxo ligand to the metal resulting in the selective functionalisation of the uranyl fragment. Vibrational spectroscopy of the complexes (Infra-Red and Raman) indicates the strength of the bonding in the uranyl fragment. The observed values are at the lower end of the range previously reported,⁴ suggesting that the bonding has been weakened. Magnetic susceptibility measurements for **3a** to **3c** were recorded in the solid state by SQUID magnetometry over the temperature range 2 to 300 K and suggest that the metal oxidation states are unchanged. The data for all three are fitted very well by models that assume $\text{U}^{\text{VI}}\text{M}^{\text{II}}$ oxidation states with high-spin configurations for the transition metal cations and Curie-Weiss paramagnetic behaviour. These complexes are the first cation-cation complexes between transition metals and the uranyl cation.



2) Uranyl (V) Transition Metal Complexes

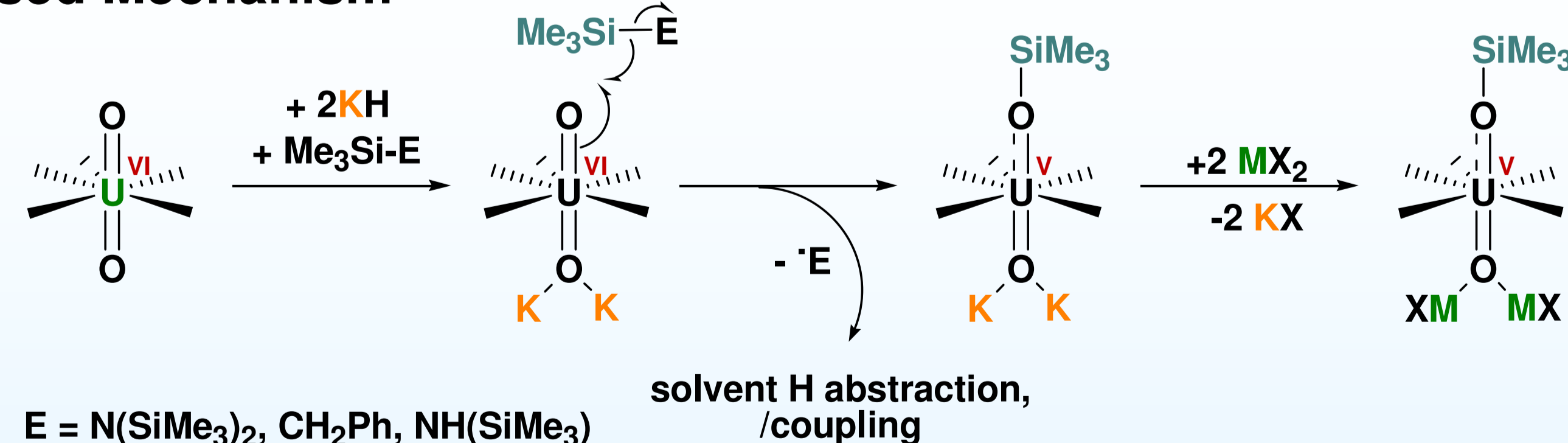
Salt elimination reactions between the uranyl complex **2**, $\text{KN}(\text{SiMe}_2\text{R}')_2$ and divalent transition metal halides resulted in the formation of **4** to **7**. X-ray crystallography revealed two divalent transition metal cations (Fe or Zn) in the second compartment, one of which is bound to the *endo*-oxo ligand of the uranyl, and a SiMe_3 group bound to the *exo*-oxo ligand. The uranium oxo bond distances are lengthened to the long end of the range previously reported for uranyl (V) complexes.⁵ This reaction was further generalised by deprotonation with KH in the presence of a source of SiMe_3 such as $\text{N}(\text{SiMe}_3)_3$ or $\text{PhCH}_2\text{SiMe}_3$; in these cases the desired reductively-silylated complexes were formed. The use of a variety of silylated substrates, and the isolation of the Zn_2 complex **6** confirms that the single reducing equivalent does not originate from the transition metal. It is therefore likely that on deprotonation of the empty cavity of **2**, a highly oxidising uranyl complex is formed that can cleave N-Si and C-Si bonds to form the silylated pentavalent uranyl intermediates $[\text{U}(\text{OSiMe}_3)(\text{O})(\text{K}_2\text{L})]$ that are conveniently isolated as transition metal cation-cation complexes.



Complex	Bond Distances (Å)			Infra-red (cm^{-1})		Magnetic Behaviour	
	M-O _{endo}	U-O _{endo}	U-O _{exo}	U=O _{sym} ν_3	Si-(CH ₃) ₃	μ_B (5 K)	μ_B (300 K)
4	1.946(4)	1.869(4)	1.993(4)	877	846 and 755	4.44, 4.45	7.74, 8.40
6	1.952(3)	1.867(3)	1.975(3)	898	846 and 755	0.48	2.38
Range				797-853 ⁴			

Complex	Bond Distances (Å)			Raman	Infra-Red	Magnetic Behaviour	
	M-O _{endo}	U-O _{endo}	U-O _{exo}	ν_1 (cm^{-1})	ν_3 (cm^{-1})	μ_B (5 K)	μ_B (300 K)
1	-	1.790(4)	1.766(4)	817	910	-	-
3a	2.162(4)	1.806(4)	1.764(4)	811	897	4.97	5.40
3b	-	-	-	804	906	4.25	5.24
3c	2.086(6)	1.783(5)	1.775(5)	807	900	3.41	4.27
Range				790-900 ⁴	900-960 ⁴		

Proposed Mechanism



Conclusions

The rigid aryl hinge in the ligand results in the exclusive formation of a mono-uranyl adduct that uses only one N4 donor set, and provides a pyrrolic, NH-governed, substrate-binding pocket directly underneath one oxo atom. This pocket allows the incorporation of first row transition metal cations that interact selectively with the oxo group within the cleft leading to the formation of the first uranyl transition metal cation-cation complexes. These uranyl transition metal adducts exhibit significant desymmetrisation and weakening of the bonding in the uranyl fragment. We have also demonstrated the first example of the reduction and selective silylation of the uranyl dication to form the new cation-cation complexes, **4** to **7**. It appears that manipulation of the oxo group within the cleft results in disruption of the strongly covalent O=U=O bonding and promotes enhanced reactivity of the oxo group outside the cleft (inverse *trans*-effect); this enables the uranyl dication $[\text{UO}_2]^{2+}$ to undergo oxo-based reactions that are more typical of its transition metal congeners such as $[\text{CrO}_2]^{2+}$ and $[\text{MoO}_2]^{2+}$.

References

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