DALTON

Synthesis and reactivity of hydrogen-rich uranium–rhenium compounds; an unsuspected detrimental effect of alkali-metal halide on chemical metathesis

Sophie M. Cendrowski-Guillaume and Michel Ephritikhine

Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, CEA CE Saclay,
91191 Gif sur Yvette, France

Reaction of $[U(\eta\text{-}C_5Me_5)_2Cl(thf)]$ and $[K(thf)_2][ReH_6(PPh_3)_2]$ did not afford the metathesis product with elimination of KCl but gave the anionic addition compound $[K(thf)_2][Cl(\eta\text{-}C_5Me_5 \quad H_6Re(PPh_3)_2]$ (thf = tetrahydrofuran); the borohydride analogue was similarly prepared. The bimetallic complexes $[(\eta\text{-}C_5H_4R)_3UH_6Re(PPh_3)_2]$ (R = Bu^t or $SiMe_3$) could not be isolated from $[U(\eta\text{-}C_5H_4R)_3Cl]$ and $[K(thf)_2][ReH_6(PPh_3)_2]$ because of their reverse cleavage by KCl which led to an equilibrium mixture; these hexahydrides were cleanly synthesized by reaction of $[U(\eta\text{-}C_5H_4R)_3][BPh_4]$ and $[K(thf)_2][ReH_6(PPh_3)_2]$.

In contrast to the variety of alumino- and boro-hydride compounds of the lanthanides and actinides,[1] heterometallic complexes containing f element–hydrogen–d transition metal bonds, $M^f–H_n–M^d$, are relatively scarce. Special attention has recently been paid to the synthesis of such mixed-metal polyhydrides, which are expected to exhibit some interesting structure and reactivity patterns, as a result of the co-operative effects between the distinct metallic centres. Among the different approaches considered,[2,3] it is not surprising to find the metathesis reaction (1) which has been widely used for

$$M^f–X + K[M^dH_n] \longrightarrow M^f–H_n–M^d + KX \qquad (1)$$

the preparation of a number of hetero-d transition-metal polyhydrides.[4] This method has been successful in the synthesis of some trinuclear complexes associating 4f and d elements: $[Sm\{H_5W(PMe_3)_3\}_2]$, $[Yb\{H_5W(PMe_3)_3\}_2L_3]$ and $[Yb\{H_2Nb(\eta\text{-}C_5H_5)_2\}_2L_3]$ [$L_3 = (MeOCH_2CH_2)_2O$].[5] The first actinide–hydrogen–transition metal compounds, $[(\eta\text{-}C_5H_5)_3UH_6Re\{P(C_6H_4R)_3\}_2]$ (R = H or F), were also obtained in this way.[6] However, it was noted that, in certain cases, reaction (1) failed to produce the neutral species $M^f–H_n–M^d$; for instance, $[(\eta\text{-}C_5H_5)_2(thf)MH_6Re(PPh_3)_2]$ could not be synthesized by treating $[M(\eta\text{-}C_5H_5)_2Cl(thf)]$ (M = Y or Lu; thf = tetrahydrofuran) with $[K(thf)_2][ReH_6(PPh_3)_2]$.[7] In our search for polymetallic complexes associating 5f and d elements, we studied the hydrogen-rich uranium–rhenium derivatives containing the $ReH_6(PPh_3)_2$ fragment. We found that some compounds of uranium and $H_6Re(PPh_3)_2$ could not be readily prepared from the actinide halide and $[K(thf)_2][ReH_6(PPh_3)_2]$ because of either formation of an adduct without elimination of KCl, or cleavage of the expected bimetallic product by the KCl salt which is concomitantly formed. This negative effect of the alkali-metal halide in the metathetical exchange (1) is highlighted in this paper by the synthesis of the uranium–rhenium hexahydrides $[K(thf)_2][Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$ and $[(\eta\text{-}C_5H_4R)_3UH_6Re(PPh_3)_2]$ (R = H, Bu^t or $SiMe_3$). The reactivity of these new complexes was also investigated.[8]

Results

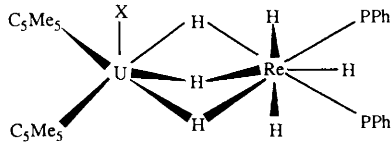
Synthesis of the anions $[X(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]^-$ (X = Cl or BH_4)

Treatment of $[U(\eta\text{-}C_5Me_5)_2Cl(thf)]$ with 1 equivalent of $[K(thf)_2][ReH_6(PPh_3)_2]$ in tetrahydrofuran did not yield the neutral product $[(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$ resulting from halide substitution [equation (1)], but instead afforded the anionic compound $[K(thf)_2][Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$ **1**, according to equation (2).[8] The same reaction in the presence

$$[U(\eta\text{-}C_5Me_5)_2Cl(thf)] + [K(thf)_2][ReH_6(PPh_3)_2] \rightleftharpoons \underset{\mathbf{1}}{[K(thf)_2][Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]} \qquad (2)$$

of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) or with $[K(18\text{-crown-}6)][ReH_6(PPh_3)_2]$ gave $[K(18\text{-crown-}6)][Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$, which was isolated as dark green microcrystals in 95% yield. Complex **1** did not show any tendency to eliminate KCl; attempts to obtain the neutral derivative $[(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$ by performing reaction (2) in toluene were unsuccessful, indicating the great stability of the U–Cl bond. The ^1H and ^{31}P NMR spectra revealed that **1** was reversibly dissociated in thf (*ca.* 20%) into $[U(\eta\text{-}C_5Me_5)_2Cl(thf)]$ and $[K(thf)_2][ReH_6(PPh_3)_2]$; addition of either of these two species caused the equilibrium to be shifted towards the formation of **1**. The borohydride derivative $K[(BH_4)(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$ **2** was similarly synthesized in 97% yield from $[U(\eta\text{-}C_5Me_5)_2(BH_4)]$ and the anionic rhenium hydride. In contrast to the chloride analogue, **2** was not dissociated in solution; we cannot provide an explanation for this difference.

Complexes **1** and **2** are unique examples of anionic heterobimetallic polyhydrides; these are also the first compounds in which a transition metal and a trivalent actinide are maintained in close proximity. Their NMR spectra (Table 1) are in agreement with the structure represented in Scheme 1. The two equivalent C_5Me_5 groups and the two distinct PPh_3 ligands of **1** in its staggered rotational conformation around the U–Re vector were detected at 30 °C; this geometry is also that adopted by $[K(18\text{-crown-}6)][Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$ in its crystalline form.[8] The borohydride analogue **2** was found to be less rigid; while the cyclopentadienyl groups were chemically equivalent, the phosphine ligands gave rise, at 30 °C, to a broad ^{31}P resonance which was split, below −35 °C, into two peaks of equal intensity. For both **1** and **2** the six fluxional



Scheme 1 Preferred conformation of the anions $[X(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]^-$

Table 1 The NMR data for complexes **1**–**5**[a]

	^{1}H NMR			
Compound	Uranium ligands	Hydride ligands[b]	Rhenium PPh_3 ligands	^{31}P-{^{1}H} NMR
1 $[K(thf)_2][Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$	0.95 (C_5Me_5)[c]	21.7 ($w_{\frac{1}{2}}$ 215) At −80 °C: 23.0 (3 H, $w_{\frac{1}{2}}$ 95) −36.5 (3 H, $w_{\frac{1}{2}}$ 170)	1.35 (*o*-H of Ph)[c] 4.79 (12 H, t, *J* 7, *m*-H of Ph) 5.33 (6 H, t, *J* 7, *p*-H of Ph)	112.4 (1 PPh_3, $w_{\frac{1}{2}}$ 210)[d] 59.8 (1 PPh_3, $w_{\frac{1}{2}}$ 210)
2 $K[(BH_4)(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$	1.41 (30 H, C_5Me_5) 47.7 (4 H, $w_{\frac{1}{2}}$ 240, BH_4)	13.3 (3 H, $w_{\frac{1}{2}}$ 180)	1.8 (*o*-H of Ph)[e] 4.79 (12 H, t, *J* 6, *m*-H of Ph) 5.43 (6 H, t, *J* 6, *p*-H of Ph)	88.8 ($w_{\frac{1}{2}}$ 300) At −37 °C: 141.72 (1 PPh_3, $w_{\frac{1}{2}}$ 35) 34.57 (1 PPh_3, $w_{\frac{1}{2}}$ 35)
3a $[(\eta\text{-}C_5H_5)_3UH_6Re(PPh_3)_2]$	−7.04 (15 H, C_5H_5)	−30.89 (t, *J* 13)	2.20 (12 H, t, *J* 8, *o*-H of Ph) 6.88 (12 H, t, *J* 8, *m*-H of Ph) 7.03 (6 H, *p*-H of Ph)	61.70
3b $[(\eta\text{-}C_5H_4Bu^t)_3UH_6Re(PPh_3)_2]$	0.47 and −9.04 (6 H × 2, CH) −3.97 (27 H, Me)	−25.65 (t, *J* 12)	3.12 (12 H, t, *J* 9, *o*-H of Ph) 7.27 (12 H, t, *J* 7, *m*-H of Ph) 7.50 (6 H, t, *J* 7, *p*-H of Ph)	69.84
3c $[(\eta\text{-}C_5H_4SiMe_3)_3UH_6Re(PPh_3)_2]$	0.00 and −7.95 (6 H × 2, CH) −3.23 (27 H, Me)	−24.40 (t, *J* 14)	2.87 (12 H, t, *J* 8, *o*-H of Ph) 7.21 (12 H, t, *J* 7, *m*-H of Ph) 7.56 (6 H, t, *J* 7, *p*-H of Ph)	74.10
4 $[Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$	14.98 (30 H, C_5Me_5)	−7.5[f] At −70 °C: −61.0 (3 H, $w_{\frac{1}{2}}$ 110) −114.7 (3 H, $w_{\frac{1}{2}}$ 130)	−5.12 and −7.90 (6 H × 2, t, *J* 8, *o*-H of Ph) 4.10 and 0.99 (6 H × 2, t, *J* 6, *m*-H of Ph) 5.76 and 2.92 (3 H × 2, t, *J* 6, *p*-H of Ph)	93.52 (1 PPh_3, $w_{\frac{1}{2}}$ 35) 64.41 (1 PPh_3, $w_{\frac{1}{2}}$ 35)
5 $[(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)_2UH_6Re(PPh_3)_2]$	−9.54 (10 H, C_5H_5) 10.33 (15 H, C_5Me_5)	−35.6 (t, *J* 14, $w_{\frac{1}{2}}$ 65)	1.43 (12 H, t, *J* 8, *o*-H of Ph) 6.27 (12 H, t, *J* 7, *m*-H of Ph) 6.65 (6 H, t, *J* 7, *p*-H of Ph)	61.19

[a] At 30 °C (except the ^{1}H NMR spectrum of complex **4** at 10 °C) in [$^2H_8$]thf (except the ^{31}P-{^{1}H} NMR spectrum of **4** in [$^2H_6$]benzene). Data are given as chemical shift δ (relative intensity, multiplicity, coupling constant *J* or width at half-height $w_{\frac{1}{2}}$ in Hz, assignment); when not specified, the signal is a singlet with $w_{\frac{1}{2}}$ 10–30 Hz. [b] The signal integrates for 6 H when not specified. [c] The C_5Me_5, *o*-H of Ph and thf signals overlap. [d] Spectrum of $[K(18\text{-crown-}6)]\ [Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$. [e] This resonance and the [$^2H_8$]thf signal overlap. [f] The signal is masked by the *o*-H of Ph resonance.

hydrides appeared at 30 °C as a broad low-field signal. The slow-limit spectrum of **1** could be obtained and revealed the presence of three bridging hydrogens in a $\mathrm{U(\mu\text{-}H)_3Re}$ fragment and three terminal rhenium hydrogens; spin-saturation-transfer experiments[9] indicated that the bridging and terminal hydrides were still exchanging at low temperature. It has been noted that bimetallic compounds with three bridging hydride ligands are common; this situation was explained by the most classical geometry of the metal complexes, polyhedra with triangular faces, which would not be much distorted by forming an $\mathrm{M(\mu\text{-}H)_3M'}$ arrangement.[10]

Synthesis of the complexes $[(\eta\text{-}C_5H_4R)_3UH_6Re(PPh_3)_2]$ ($R = H$, $\mathrm{Bu^t}$ or $SiMe_3$)

We have previously reported that treatment of $[U(\eta\text{-}C_5H_5)_3Cl]$ with $[K(thf)_2][ReH_6(PPh_3)_2]$ readily gave the bimetallic hexahydride $[(\eta\text{-}C_5H_5)_3UH_6Re(PPh_3)_2]$ **3a**, according to equation (1), but was contaminated by 10% of an unidentified uranium(IV) species.[6] In contrast, reactions of the ring-substituted analogues $[U(\eta\text{-}C_5H_4R)_3Cl]$ ($R = \mathrm{Bu^t}$ or $SiMe_3$) with 1 equivalent of $[K(thf)_2][ReH_6(PPh_3)_2]$ remained incomplete, leading to equilibrium (3); 10% of $[U(\eta\text{-}C_5H_4\mathrm{Bu^t})_3Cl]$ and 50% of $[U(\eta\text{-}C_5H_4SiMe_3)_3Cl]$ were converted into **3b** ($R = \mathrm{Bu^t}$) and **3c** ($R = SiMe_3$) respectively, while the equilibria were shifted to the left upon addition of chloride ions. Nevertheless, the hexahydride compounds **3a**–**3c** could be isolated from the reaction of the cationic derivatives $[U(\eta\text{-}C_5H_4R)_3][BPh_4]$ with $[K(thf)_2][ReH_6(PPh_3)_2]$, according to equation (4); the compound $[(thf)(\eta\text{-}C_5H_5)_2YH_6Re(PPh_3)_2]$ had been similarly prepared from $[Y(\eta\text{-}C_5H_5)_2(thf)_2][BPh_4]$.[3,7] This method appeared most practical and efficient since complexes **3** were easily separated from the insoluble and inert salt $KBPh_4$ and were isolated in good yield (50–90%) as microcrystalline powders. It also has the advantage of selectivity, no side reaction having ever been observed.

$$[U(\eta\text{-}C_5H_4R)_3Cl] + [K(thf)_2][ReH_6(PPh_3)_2] \rightleftharpoons [(\eta\text{-}C_5H_4R)_3UH_6Re(PPh_3)_2] + KCl \quad (3)$$

$$[U(\eta\text{-}C_5H_4R)_3][BPh_4] + [K(thf)_2][ReH_6(PPh_3)_2] \longrightarrow [(\eta\text{-}C_5H_4R)_3UH_6Re(PPh_3)_2] + KBPh_4 \quad (4)$$

Complexes **3**, once isolated pure, were transformed in the presence of chloride ions into a mixture of $[U(\eta\text{-}C_5H_4R)_3Cl]$ and $[ReH_6(PPh_3)_2]^-$, thus confirming the occurrence of equilibrium (3). Addition of 1 equivalent of KCl to a solution of **3c** gave the same equilibrating mixture as that obtained from $[U(\eta\text{-}C_5H_4SiMe_3)_3Cl]$ and $[K(thf)_2][ReH_6(PPh_3)_2]$; this equilibrium was more displaced towards these species (90%) when LiCl was used in place of KCl, a difference which certainly reflects the higher solubility of the lithium salt.

The hexahydrides **3** were characterized by elemental analyses, ^1H and ^{31}P NMR spectroscopy (Table 1). Whatever the temperature, the three cyclopentadienyl, as well as the two phosphine ligands, were chemically equivalent. The six hydride ligands were equivalent at 30 °C, indicating a rapid fluxional process; below −60 °C the triplet signal broadened into the baseline but the slow-limit spectrum could not be observed. Although it was not possible to determine the exact structure of these hexahydrides, it seems likely, in view of the tridentate configuration of the borohydride ligand in $[U(\eta\text{-}C_5H_5)_3(BH_4)]$[11] and the structure of several rhenium–transition metal polyhydrides,[4,10] that at least three hydrogens are bridging the metals in products **3**.

Some reactions of compounds 1–3

Many heterobimetallic complexes have previously been synthesized with the hope of gaining the enhanced reactivity which would result from the synergic effects of the two distinct metals.[3,12] In this context, reactions of the present hexahydride complexes were rather limited and disappointing. The anionic uranium(III) compound **1** was oxidized by $TlBPh_4$ or $[NEt_3H][BPh_4]$ to the neutral derivative $[Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$ **4**, which was isolated as a red microcrystalline powder in 89% yield. Oxidation of the borohydride analogue **2** was not as clean and $[(BH_4)(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$ could not be obtained pure. According to the NMR spectra, **4** adopts the same structure as that of **1** in solution (Scheme 1). Not surprisingly, **4** was reduced back to the anion of **1** in the presence of sodium amalgam. Treatment of complexes **3** with reducing agents (Na–Hg, KH or LiMe), as well as the addition of $[ReH_6(PPh_3)_2]^-$ to $[U(\eta\text{-}C_5H_4R)_3]$ ($R = H$, $\mathrm{Bu^t}$ or $SiMe_3$), led to immediate elimination of a cyclopentadiene molecule C_5H_5R and formation of unidentified and unstable hydride species. The neutral hexahydrides gave no clean reaction with $[NEt_3H][BPh_4]$. The hexahydrides **3** were inert towards hex-1-ene, phenylacetylene, acetone or carbon dioxide; this lack of reactivity, also observed with some rhenium–d transition metal polyhydrides,[13] may be due to the steric and electronic saturation of the metal centres. Reactions with $CDCl_3$, EtOH or water caused complete cleavage or decomposition of the dinuclear unit. Treatment of **4** with 2 equivalents of $K[C_5H_5]$ led to the formation of $[(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)_2UH_6Re(PPh_3)_2]$ **5**, isolated as red microcrystals in 83% yield. Complexes **1**–**5** were thermally and photochemically stable, being recovered unchanged after several hours in refluxing $[^2H_8]$thf or under UV light irradiation; no hydrogen–deuterium exchange was observed.

Discussion

We have demonstrated that preparation of the hydrogen-rich uranium–rhenium compounds by metathetical exchange between actinide halide and $[K(thf)_2][ReH_6(PPh_3)_2]$ may be impeded by two reactions. One is formation of an anionic adduct without elimination of KCl, as illustrated here by the synthesis of $[K(thf)_2][Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$ **1**, according to equation (2). Although such an approach to anionic bimetallic polyhydrides has no precedent in transition-metal chemistry, this formation of **1** and the borohydride analogue **2** may seem not too surprising. Indeed, it has often been mentioned that reaction of an f-element halide with the alkali-metal salt of an anionic ligand does not systematically yield the metathesis product but gives instead an anionic addition compound; this retention of the alkali metal and formation of 'ate' complexes is a pervasive problem in the chemistry of the lanthanides and actinides.[14]

Even more frustrating, the other obstacle to the metathesis reaction (1) is the reverse cleavage of the expected bimetallic product by KCl, giving rise to an equilibrium. This was observed in the attempted preparation of the hexahydrides $[(\eta\text{-}C_5H_4R)_3UH_6Re(PPh_3)_2]$ ($R = \mathrm{Bu^t}$ **3b** or $SiMe_3$ **3c**) from $[U(\eta\text{-}C_5H_4R)_3Cl]$ and $[K(thf)_2][ReH_6(PPh_3)_2]$, but not in the similar synthesis of **3a** ($R = H$).[6] It is possible that reaction (3) proceeds by an associative mechanism involving the anionic species $[Cl(\eta\text{-}C_5H_4R)_3UH_6Re(PPh_3)_2]^-$ as an intermediate; this latter, in contrast to **1** and **2**, would be unstable because of greater steric crowding and/or electron richness. The different proportions of **3b** and **3c** in equilibrium (3) and the absence of equilibrium with **3a** revealed that both steric and electronic parameters of the R substituents have an influence on the course of the reaction. The steric repulsions induced by the bulky R groups would destabilize a dinuclear species but it is clear that electronic factors also play an important role since the more electron-rich complex **3b** is less stable than its isosteric counterpart **3c**. It is interesting that the aptitude of complexes **3** for cleavage by Cl^- parallels the relative stability of the anionic hydrides $Na[(\eta\text{-}C_5H_4R)_3UHU(C_5H_4R)_3]$, also governed by both steric and electronic factors. These are stable for R = H or Me but the anion $[(\eta\text{-}C_5H_4Bu^t)_3UHU(C_5H_4Bu^t)_3]^-$ could not be isolated, being totally dissociated into $[UH(\eta\text{-}C_5H_4Bu^t)_3]^-$ and $[U(\eta\text{-}C_5H_4Bu^t)_3]$, and the trimethylsilyl analogue is only partially cleaved in solution.[15]

The results reported here suggest that equilibria such as (3) might play an important role in the failed isolation of some bimetallic polyhydrides *via* the classical metathesis reaction.[7] From a more general point of view, the metathesis reaction between a transition-metal halide and an alkali-metal salt of an organic or inorganic anion is one of the most common synthetic routes in co-ordination chemistry. It has been often observed that this method is more straightforward when potassium rather than lithium salts are formed, a fact that is generally accounted for by the lower solubility of the former; the use of non-polar solvents was sometimes recommended. However, we are not aware of any report where the reverse reaction, *i.e.* cleavage of the expected product by the alkali-metal halide, is clearly established.* It seems very likely that this reaction might have occurred in some cases but was overlooked. As an illustration in organouranium chemistry, we found that $[U(\eta\text{-}C_5H_5)_4]$ reacted with 4 equivalents of KCl in thf to give $[U(\eta\text{-}C_5H_5)_3Cl]$ and $K[C_5H_5]$.[17] This experiment permits one to explain why tetracyclopentadienyluranium was prepared in low yield from UCl_4 and an excess of $K[C_5H_5]$,[18] whereas it was quantitatively obtained by treating the cationic derivative $[U(\eta\text{-}C_5H_5)_3(thf)][BPh_4]$ with 1 equivalent of the cyclopentadienyl anion.[16]

The difficulties encountered with the metathesis reaction (1) should be effectively avoided by replacing the halide substrate with the corresponding cationic derivative. Indeed, the hexahydrides **3** could be isolated by reaction (4) which provides a new example of the utility of cationic precursors for the synthesis of actinide derivatives.[19]

Experimental

All preparations and reactions were carried out under argon (< 5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove-box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Deuteriated solvents were dried over Na–K alloy. Elemental analyses were performed by Analytische Laboratorien at Gummersbach (Germany). The ^1H NMR spectra were recorded on either a Bruker WP 60 (FT) or AC 200 instrument and referenced internally using the residual protiosolvent resonances relative to tetramethylsilane (δ 0); the low-temperature spectra were recorded on the 60 MHz apparatus. The ^{31}P NMR spectra were recorded on a Bruker AC 200 instrument, the external reference being 85% H_3PO_4. The compound 18-crown-6 (Janssen) was dried under vacuum after evaporation from toluene; $TlBPh_4$ precipitated in water upon mixing $TlNO_3$ and $NaBPh_4$. The compounds $[K(thf)_2][ReH_6(PPh_3)_2]$,[6] $[K(18\text{-crown-}6)][ReH_6(PPh_3)_2]$,[6] $[\{U(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)\}_3]$,[20] $[U(\eta\text{-}C_5Me_5)_2(BH_4)]$,[21] $[U(\eta\text{-}C_5H_4R)_3Cl]$ (R = H,[22] Bu^t[23] or $SiMe_3$,[24]) $[U(\eta\text{-}C_5H_5)_3(thf)][BPh_4]$[25] and $[U(\eta\text{-}C_5H_4R)_3][BPh_4]$ (R = Bu^t or $SiMe_3$[26]) were prepared by published methods.

Preparations

$[K(thf)_2][Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$ 1. A round-bottom flask (50 cm^3) was charged with $[\{U(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)\}_3]$ (106 mg, 0.065 mmol) and $[K(thf)_2][ReH_6(PPh_3)_2]$ (176 mg, 0.195 mmol) and thf (25 cm^3) were condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 3 h at 20 °C, filtered, evaporated to dryness, and the residue quickly washed with pentane (15 cm^3). After filtration and drying, complex 1 was isolated as a dark green microcrystalline powder (84 mg, 30%).

$[K(18\text{-crown-}6)][Cl(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$. A round-bottom flask (100 cm^3) was charged with $[\{U(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)\}_3]$ (277 mg, 0.170 mmol) and $[K(18\text{-crown-}6)][ReH_6(PPh_3)_2]$ (519 mg, 0.509 mmol) and thf (50 cm^3) were condensed into it at −78 °C under vacuum. After 3 h at 20 °C the solution was filtered and evaporated, leaving dark green microcrystals of the product (756 mg, 95%). A benzene solvate of this complex was obtained after crystallization from this solvent and was characterized by X-ray crystallography[8] (Found: C, 54.05; H, 5.6; P, 3.85. $C_{74}H_{96}ClKO_6P_2ReU$ requires C, 54.1; H, 5.9; P, 3.75%). ^1H NMR (25 °C in $[^2H_8]$thf): δ 24.5 (6 H, $w_{\frac{1}{2}}$ 200 Hz, ReH_6), 5.60 (6 H, s, *p*-H of Ph), 4.45 (12 H, s, *m*-H of Ph), 3.06 (24 H, s, 18-crown-6), 0.17 (12 H, s, *o*-H of Ph) and −0.66 (30 H, s, C_5Me_5).

$K[(BH_4)(\eta\text{-}C_5Me_5)_2UH_6Re(PPh_3)_2]$ 2. A round-bottom flask (50 cm^3) was charged with $[U(\eta\text{-}C_5Me_5)_2(BH_4)]$ (167 mg, 0.280 mmol) and $[K(thf)_2][ReH_6(PPh_3)_2]$ (212 mg, 0.280 mmol) and thf (25 cm^3) were condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 3 h at 20 °C and after filtration and evaporation to dryness, complex **2** was isolated as a green powder (347 mg, 97%) (Found: C, 52.45; H, 5.35; P, 5.0. $C_{56}H_{70}BKP_2ReU$ requires C, 52.6; H, 5.5; P, 4.85%).

Reactions of $[U(\eta\text{-}C_5H_4R)_3Cl]$ (R = Bu^t or $SiMe_3$) with $[K(thf)_2][ReH_6(PPh_3)_2]$. An NMR tube was charged with $[U(\eta\text{-}C_5H_4R)_3Cl]$ (*ca.* 10 μmol) and 1 equivalent of $[K(thf)_2][ReH_6(PPh_3)_2]$ in $[^2H_8]$thf (0.3 cm^3). After 18 h at 20 °C the NMR spectra showed that the reactions had not gone to completion; 10% of $[U(\eta\text{-}C_5H_4Bu^t)_3Cl]$ and 50% of $[U(\eta\text{-}C_5H_4SiMe_3)_3Cl]$ were converted into **3b** and **3c** respectively; these proportions were lowered upon addition of chloride ions.

$[(\eta\text{-}C_5H_5)_3UH_6Re(PPh_3)_2]$ 3a. A round-bottom flask (50 cm^3) was charged with $[U(\eta\text{-}C_5H_5)_3(thf)][BPh_4]$ (195 mg, 0.231 mmol) and $[K(thf)_2][ReH_6(PPh_3)_2]$ (208 mg, 0.231 mmol) and thf (35 cm^3) were condensed into it at −78 °C under vacuum. The mixture was stirred for 1.5 h at 20 °C, evaporated to dryness and the residue extracted in benzene (15 cm^3). After filtration and evaporation, complex **3a** was quickly recrystallized from benzene–pentane; the red microcrystals were filtered off and dried under vacuum (135 mg, 51%) (Found: C, 53.5; H, 4.6; P, 5.15. $C_{51}H_{51}P_2ReU$ requires C, 53.25; H, 4.5; P, 5.4%).

$[(\eta\text{-}C_5H_4Bu^t)_3UH_6Re(PPh_3)_2]$ 3b. A round-bottom flask (50 cm^3) was charged with $[U(\eta\text{-}C_5H_4Bu^t)_3][BPh_4]$ (284 mg, 0.308 mmol) and $[K(thf)_2][ReH_6(PPh_3)_2]$ (277 mg, 0.308 mmol) and thf (40 cm^3) were condensed into it at −78 °C under vacuum. The mixture was stirred for 1 h at 20 °C, evaporated to dryness and the residue extracted in pentane (15 cm^3). After filtration and evaporation, complex **3b** was recrystallized from thf–pentane; the red microcrystals were filtered off and dried under vacuum (203 mg, 50%) (Found: C, 57.2; H, 5.75; P, 4.6. $C_{63}H_{75}P_2ReU$ requires C, 57.4; H, 5.75; P, 4.7%).

$[(\eta\text{-}C_5H_4SiMe_3)_3UH_6Re(PPh_3)_2]$ 3c. The compound was prepared similarly to **3b**, from $[U(\eta\text{-}C_5H_4SiMe_3)_3][BPh_4]$ (575 mg, 0.593 mmol) and $[K(thf)_2][ReH_6(PPh_3)_2]$ (534 mg, 0.593 mmol). Green microcrystals were obtained in 89% yield (721 mg) (Found: C, 52.45; H, 5.5; P, 4.7. $C_{60}H_{75}P_2ReSi_3U$ requires C, 52.75; H, 5.55; P, 4.55%).

Reactions of complex 3c with KCl and LiCl. An NMR tube was charged with complex **3c** (12.3 mg, 0.009 mmol) and KCl

---

* *Note added in proof.* A paper describing the equilibrium $2[Ce(\eta\text{-}C_5H_3Bu^t_2)_3] + 2KCl \rightleftharpoons [\{Ce(\eta\text{-}C_5H_3Bu^t_2)_2Cl\}_2] + 2K[C_5H_3Bu^t_2]$ was published after submission of this article.[16]

(0.7 mg, 0.009 mmol) in [$^2H_8$]thf (0.3 cm^3). After 15 min at 20 °C the NMR spectrum showed the same equilibrating mixture as that obtained from [U(η-$C_5H_4SiMe_3)_3Cl$] and [K(thf)$_2$][$ReH_6(PPh_3)_2$]. The equilibrium was more displaced towards these complexes (90%) when LiCl was used instead of KCl.

[Cl(η-$C_5Me_5)_2UH_6Re(PPh_3)_2$] 4. (*a*) A round-bottom flask (50 cm^3) was charged with [K(18-crown-6)][Cl(η-$C_5Me_5)_2$-$UH_6Re(PPh_3)_2$] (615 mg, 0.393 mmol) and $TlBPh_4$ (206 mg, 0.393 mmol) and thf (15 cm^3) were condensed into it at −78 °C under vacuum. Upon warming to 20 °C, precipitation of black metallic thallium quickly occurred; the red suspension was decanted, filtered and evaporated to dryness. The residue was extracted in toluene (15 cm^3) and complex **4** was isolated after evaporation as a red powder (441 mg, 89%) (Found: C, 53.15; H, 5.2; Cl, 2.7; P, 5.0. $C_{56}H_{66}ClP_2ReU$ requires C, 53.35; H, 5.3; Cl, 2.8; P, 4.9%).

(*b*) An NMR tube was charged with complex **1** (14.5 mg, 0.01 mmol) and [NEt_3H][BPh_4] (4.2 mg, 0.01 mmol) in [$^2H_8$]thf (0.3 cm^3). A gas immediately evolved and the spectrum showed that **1** was completely transformed into **4**.

Reaction of complex 2 with $TlBPh_4$. Compound **2** was oxidized in a manner similar to that of **1** and thus transformed into a mixture of an unidentified uranium(IV) species (*ca.* 30%) and [(BH_4)(η-$C_5Me_5)_2UH_6Re(PPh_3)_2$]. NMR (25 °C in [$^2H_8$]thf): ^1H, δ 14.2 (30 H, s, C_5Me_5), 5.0 and 2.1 (9 H + 9 H, m, *m*- and *p*-H of Ph), −1.60 and −5.77 (6 H + 6 H, s, *o*-H of Ph), −13.4 (6 H, br, $w_{\frac{1}{2}}$ 600 Hz, ReH_6) and −76.8 (4 H, br, $w_{\frac{1}{2}}$ 275 Hz, BH_4); ^1H-{^{31}P}, two signals of equal intensities at δ 91.83 and 83.40 ($w_{\frac{1}{2}}$ 35 Hz). This compound was reduced back to **2** by addition of sodium amalgam.

[(η-C_5Me_5)(η-$C_5H_5)_2UH_6Re(PPh_3)_2$] 5. A round-bottom flask (50 cm^3) was charged with complex **4** (159 mg, 0.126 mmol) and K[C_5H_5] (27 mg, 0.255 mmol) and thf (15 cm^3) were condensed into it at −78 °C under vacuum. The reaction mixture was refluxed for 3 h, evaporated to dryness and the residue extracted in benzene (10 cm^3). After evaporation, complex **5** was obtained as a dark red powder (128 mg, 83%) (Found: C, 54.85; H, 4.9; P, 4.95. $C_{56}H_{61}P_2ReU$ requires C, 55.1; H, 5.05; P, 5.1%).

References

1 G. L. Soloveichik, *New J. Chem.*, 1995, **19**, 597; T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263.

2 D. J. Schwartz, G. E. Ball and R. A. Andersen, *J. Am. Chem. Soc.*, 1995, **117**, 6027; N. S. Radu, P. K. Gantzel and T. D. Tilley, *J. Chem. Soc., Chem. Commun.*, 1994, 1175; W. J. Evans, J. H. Meadows and T. P. Hanusa, *J. Am. Chem. Soc.*, 1984, **106**, 4454.

3 D. Alvarez, K. G. Caulton, W. J. Evans and J. W. Ziller, *Inorg. Chem.*, 1992, **31**, 5500.

4 I. Moldes, S. Nefedov, N. Lugan and R. Mathieu, *J. Organomet. Chem.*, 1995, **490**, 11; I. Moldes, B. Delavaux-Nicot, N. Lugan and R. Mathieu, *Inorg. Chem.*, 1994, **33**, 3510; Z. He, D. Neibecker and R. Mathieu, *J. Organomet. Chem.*, 1993, **460**, 213; J. W. Bruno, J. C. Huffman, M. A. Green and K. G. Caulton, *J. Am. Chem. Soc.*, 1984, **106**, 8310.

5 D. M. Michaelidou, M. L. H. Green, A. K. Hughes, P. Mountford and A. N. Chernega, *Polyhedron*, 1995, **14**, 2663; M. L. H. Green, A. K. Hughes, D. M. Michaelidou and P. Mountford, *J. Chem. Soc., Chem. Commun.*, 1993, 591.

6 D. Baudry and M. Ephritikhine, *J. Organomet. Chem.*, 1986, **311**, 189.

7 K. G. Caulton, personal communication.

8 S. M. Cendrowski-Guillaume, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1994, 1655.

9 S. Forsen and R. A. Hoffman, *J. Chem. Phys.*, 1963, **39**, 2892.

10 D. Michos, X. L. Luo and R. H. Crabtree, *Inorg. Chem.*, 1993, **32**, 2118.

11 T. J. Marks and J. R. Kolb, *J. Am. Chem. Soc.*, 1975, **97**, 27.

12 Z. He, L. Plasseraud, I. Moldes, F. Dahan, D. Neibecker, M. Etienne and R. Mathieu, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 916; Z. He, D. Neibecker, N. Lugan and R. Mathieu, *Organometallics*, 1992, **11**, 817.

13 Z. He, S. Nefedov, N. Lugan, D. Neibecker and R. Mathieu, *Organometallics*, 1993, **12**, 3837.

14 T. J. Marks and R. D. Ernst, *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, ch. 21; D. L. Clark and J. G. Watkin, *Inorg. Chem.*, 1993, **32**, 1766.

15 J. C. Berthet, C. Villiers, J. F. Le Maréchal, B. Delavaux-Nicot, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Organomet. Chem.*, 1992, **440**, 53.

16 C. D. Sofield and R. A. Anderson, *J. Organomet. Chem.*, 1995, **501**, 271.

17 J. C. Berthet and M. Ephritikhine, unpublished work.

18 E. O. Fischer and Y. Hristidu, *Z. Naturforsch., Teil B*, 1962, **17**, 275; M. L. Anderson and L. R. Crisler, *J. Organomet. Chem.*, 1969, **17**, 345.

19 J. C. Berthet, C. Boisson, M. Lance, J. Vigner, M. Nierlich and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, 1995, 3019, 3027; J. C. Berthet, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Organomet. Chem.*, 1991, **420**, C9.

20 P. J. Fagan, J. M. Manriquez, T. J. Marks, C. S. Day, S. H. Vollmer and V. W. Day, *Organometallics*, 1982, **1**, 170.

21 P. Gradoz, D. Baudry, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, *J. Organomet. Chem.*, 1994, **466**, 107.

22 L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **2**, 246.

23 A. Dormond, C. Duval Huet and J. Tirouflet, *J. Organomet. Chem.*, 1981, **209**, 341.

24 J. G. Brennan, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1986, **25**, 1756.

25 J. C. Berthet and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1993, 1566.

26 J. C. Berthet, J. F. Le Maréchal, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, 1992, 1573.

Received 23rd *October* 1995; *Paper* 5/06987D