New Actinide Hydrogen Transition Metal Compounds. Synthesis of $[K(C_{12}H_{24}O_6)][(\eta\text{-}C_5Me_5)_2(Cl)UH_6Re(PPh_3)_2]$ and the Crystal Structure of its Benzene Solvate

Sophie M. Cendrowski-Guillaume,[a] **Monique Lance,**[b] **Martine Nierlich,**[b] **Julien Vigner**[b] **and Michel Ephritikhine***[a]

[a] *Laboratoire de Chimie de l'Uranium and*
[b] *Laboratoire de Cristallographie, Service de Chimie Moléculaire, CNRS URA 331, CEA-CE Saclay, 91191 Gif sur Yvette, France*

The title compound is isolated from the reaction of $[\{U(C_5Me_5)_2(\mu\text{-}Cl)\}_3]$ with $[K(18\text{-crown-}6)][ReH_6(PPh_3)_2]$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) and is oxidized by $TlBPh_4$ into the neutral derivative $[(C_5Me_5)_2(Cl)UH_6Re(PPh_3)_2]$; the ^1H NMR spectra reveal that in both complexes, the uranium and rhenium atoms are linked by three bridging hydrides.

We report the synthesis of the compound $[K(18\text{-crown-}6)][(C_5Me_5)_2(Cl)UH_6Re(PPh_3)_2]$ **1** and its oxidation into $[(C_5Me_5)_2(Cl)UH_6Re(PPh_3)_2]$ **2**. Complex **1**, which is a unique example of an anionic heterobimetallic polyhydride,[1] is the first compound containing a transition metal and an actinide(III) metal in close proximity. After $[(\eta\text{-}C_5H_5)_3UH_6Re(PAr_3)_2]$ (Ar = C_6H_5 or p-F-C_6H_4),[2] **1** and **2** are new 5*f*-element–hydrogen–transition metal derivatives and **1** is the only one to have been crystallographically characterized, as its benzene solvate.

Complex **1** was isolated in 95% yield from the reaction of $[\{U(C_5Me_5)_2(\mu\text{-}Cl)\}_3]$[3] with 1 equiv. of $[K(18\text{-crown-}6)][ReH_6(PPh_3)_2]$[2] in thf; after 3 h at 20 °C, the solution was filtered and evaporated, leaving the product as a dark-green, microcrystalline powder. The anion $[(C_5Me_5)_2(Cl)UH_6Re(PPh_3)_2]^-$ was also formed by treatment of $[\{U(C_5Me_5)_2(\mu\text{-}Cl)\}_3]$ with $[K(thf)_2][ReH_6(PPh_3)_2]$,[2,4] showing that encapsulation of the potassium ion is not necessary for the stability of the U–Cl bond. This synthesis of **1** is noteworthy because such reactions between a metal halide [M]X and a transition metal polyhydride anion $[M']H_n^-$ invariably gave so far the neutral mixed-metal compounds $[M]H_n[M']$,[2,5] which were also classically prepared by reductive elimination of HX between [M]X and $[M']H_{n+1}$ (X = alkyl or amido group).[6,7] Anionic bimetallic polyhydride complexes are much less common and are, to our knowledge, limited to carbonyl derivatives such as $[NEt_4][W_2H_2(CO)_8]$ and $[NEt_4][Re_2H_3(CO)_6]$.[1]

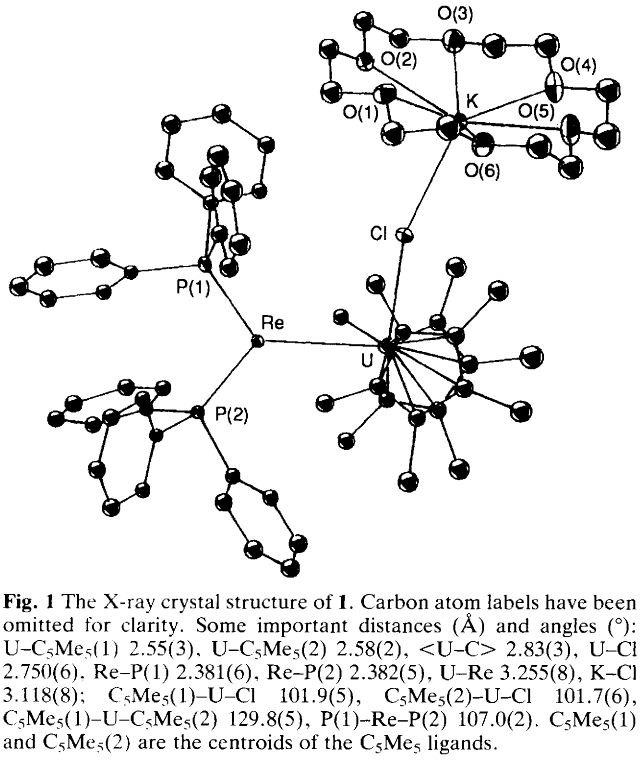

Fig. 1 The X-ray crystal structure of **1**. Carbon atom labels have been omitted for clarity. Some important distances (Å) and angles (°): U–C_5Me_5(1) 2.55(3), U–C_5Me_5(2) 2.58(2), <U–C> 2.83(3), U–Cl 2.750(6), Re–P(1) 2.381(6), Re–P(2) 2.382(5), U–Re 3.255(8), K–Cl 3.118(8); C_5Me_5(1)–U–Cl 101.9(5), C_5Me_5(2)–U–Cl 101.7(6), C_5Me_5(1)–U–C_5Me_5(2) 129.8(5), P(1)–Re–P(2) 107.0(2). C_5Me_5(1) and C_5Me_5(2) are the centroids of the C_5Me_5 ligands.

Crystals of a benzene solvate of **1** suitable for X-ray diffraction[†] were obtained from benzene; the structure is shown in Fig. 1 together with selected data. The geometry of the anionic fragment resembles that of the neutral complex $[(\eta\text{-}C_5H_5)_2(Cl)ZrH_6Re(PPh_3)_2]$,[7] with the cyclopentadienyl ligands on each side of the mean-plane (within ± 0.2 Å) defined by the U, Re, P(1), P(2) and Cl atoms; the C_5Me_5 and PPh_3 groups are thus in a staggered rotational conformation about the U–Re vector. The distance between the uranium and rhenium atoms [3.255(8) Å] is longer than the sum of the metallic radii of these elements, 2.9 Å,[8] precluding a direct U–Re bonding. The hydride ligands could not be located. The chlorine atom interacts with the potassium ion which is out of the mean-plane (within ± 0.2 Å) of the six oxygen atoms of the crown ether by 0.8(1) Å; the U–Cl bond length is similar to that determined in $[U(\eta\text{-}C_5H_3\{SiMe_3\}_2\text{-}1,3)_2(\mu\text{-}Cl)_2Li(thf)_2]$ [2.730(7) Å] and is longer than in $[PPh_4][U(\eta\text{-}C_5H_3\{SiMe_3\}_2\text{-}1,3)_2(Cl)_2]$ [2.666(8) Å].[9]

The ^1H and ^{31}P NMR spectra[‡] of **1** revealed that the complex was slightly dissociated in thf (*ca.* 20%), being in equilibrium with $[K(18\text{-crown-}6)][ReH_6(PPh_3)_2]$ and $[U(C_5Me_5)_2(Cl)(thf)]$.[3] Despite this dissociation and the possible rotation about the Re–U vector which would facilitate the rapid exchange of the two phosphine ligands, two equivalent C_5Me_5 groups and two distinct PPh_3 ligands were visible at 30 °C, showing that the most stable conformation of **1** in solution is similar to that in the solid state. At 30 °C, the broad band at δ 24.5 could be assigned to the six fluxional hydride ligands; on cooling to −90 °C, this signal was resolved into two separate resonances of equal intensity, indicating the presence of three bridging hydrogens in a $U(\mu\text{-}H)_3Re$ fragment and three terminal rhenium-hydrogens.

Oxidation of **1** by 1 equiv. of $TlBPh_4$ in thf gave immediately a black precipitate of metallic thallium in a red solution; after filtration and evaporation to dryness, the red neutral compound $[(C_5Me_5)_2(Cl)UH_6Re(PPh_3)_2]$ **2** was extracted in toluene and recrystallized from this solvent (89% yield). Complex **2** was also obtained in *ca.* 50% yield with another unidentified product when $[U(C_5Me_5)_2(Cl)_2]$ was treated with $[K(thf)_2][ReH_6(PPh_3)_2]$. Reduction of **2** by sodium amalgam gave back the anion of **1**. The NMR spectra of **2**[‡] showed that the two PPh_3 groups were inequivalent, suggesting that the neutral complex has retained the solid state structure of the corresponding anion; this geometry is not rigid in solution since spin saturation transfer experiments[10] demonstrated that the phosphine ligands were readily exchanging. As in the case of **1**, the six hydrides were fluxional, giving rise at 30 °C to a broad signal which collapsed at −70 °C into two peaks with an intensity ratio 3 : 3, attributed to the terminal and bridging ligands.

Compounds **1** and **2** gave satisfactory elemental analyses (C, H, P).

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Footnotes

† *Crystal data* for **1**·0.5 C_6H_6 : $C_{71}H_{93}P_2O_6ClKReU$, monoclinic, space group $P2_1/n$, a = 23.181(8), b = 12.732(7), c = 24.316(9) Å, β = 102.88(5)°, V = 6996(4) Å^3, Z = 4, D_c = 1.522 g cm^{-3}, μ = 41.33 cm^{-1}. Data were collected using an Enraf-Nonius CAD-4 diffractometer (Mo-Kα radiation, λ = 0.71073 Å) in the range $2 < 2\theta < 40°$, 6513 reflections were collected at 23 °C and 1865 reflections with $I > 3\sigma(I)$ were used after correction of Lorentz polarisation effects, intensity decay (−49% after 87 h, linearly corrected), and absorption (using the empirical DIFABS method). Despite the relatively poor diffraction quality of the crystal which limited the accuracy of the X-ray analysis, the structure was solved by the heavy-atom method and refined by full-matrix least-squares analysis (F). Only the U and Re atoms were refined anisotropically; the hydrogen atoms were introduced in idealized positions and constrained to ride on their parent carbon atoms with fixed thermal parameters (6 Å^2). Analytical scattering factors for neutral atoms were corrected for f' and f''. The final R values were R = 0.034 and R_w = 0.038 (w = 1). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ *NMR spectroscopic data* for **1**: ^{1}H NMR: δ (60 MHz, 30 °C in [$^2H_8$]thf) : 24.5 (6H, br, $w_{1/2}$ 200 Hz, ReH_6), 5.60 (6H, s, p-Ph), 4.45 (12H, s, m-Ph), 3.06 (24H, s, 18-crown-6), 0.17 (12H, s, o-Ph), −0.66 (30H, s, $w_{1/2}$ 30 Hz, C_5Me_5). The spectrum also exhibited signals attributed to [K(18-crown-6)][$ReH_6(PPh_3)_2$] [δ 7.5 and 6.9 (m, Ph), −7.45 (t, J 14 Hz, ReH_6)] and [$U(C_5Me_5)_2(Cl)(thf)$] (δ −5.02), resulting from the reversible dissociation (about 20%) of **1**; this equilibrium was shifted towards the formation of **1** after addition of [$K(thf)_2$][$ReH_6(PPh_3)_2$] or [$\{U(C_5Me_5)_2(\mu\text{-}Cl)\}_3$]. Coalescence of the hydride resonance occured at −10 and at −90 °C, two signals of equal intensity were visible at δ 24.2 ($w_{1/2}$ 100 Hz) and −45.7 ($w_{1/2}$ 200 Hz). ^{31}P {^{1}H}NMR: δ relative to external 85% H_3PO_4 (81 MHz, 30 °C in [$^2H_8$]thf): two signals of equal intensity were visible at δ 112.4 ($w_{1/2}$ 210 Hz) and 59.8 ($w_{1/2}$ 210 Hz); the signal at δ 38.3 was attributed to the anion [$ReH_6(PPh_3)_2$]$^-$.

For **2**: ^{1}H NMR: δ (60 MHz, 10 °C, in [$^2H_8$]thf): 14.98 (30H, s, $w_{1/2}$ 10 Hz, C_5Me_5), 5.76 (3H, t, J 6 Hz, p-Ph), 4.10 (6H, t, J 6 Hz, m-Ph), 2.92 (3H, t, J 6 Hz, p-Ph), 0.99 (6H, t, J 6 Hz, m-Ph), −5.12 (6H, t, J 8 Hz, o-Ph), −7.90 (6H, t, J 8 Hz, o-Ph). The hydride ligands gave rise, at 30 °C, to a broad band at δ −7.5 which was masked by the signal of the ortho hydrogens. Coalescence of the hydride resonance occurred at −10° and at −70 °C, two signals of equal intensity were visible at δ −61.0 ($w_{1/2}$ 110 Hz) and −114.7 ($w_{1/2}$ 130 Hz); bridging and terminal hydrides were exchanging, as demonstrated by spin saturation transfer experiments.

^{31}P {^{1}H}NMR: δ relative to external 85% H_3PO_4 (81 MHz, 30 °C in [$^2H_6$]benzene): two singlets of equal intensity were visible at δ 93.5 ($w_{1/2}$ 35 Hz) and 64.4 ($w_{1/2}$ 35 Hz). In the ^{1}H NMR spectra of **1** and **2**, the chemical shift and half height width of the C_5Me_5 signal are characteristic of [$U^{III}(C_5Me_5)_2X$] and [$U^{IV}(C_5Me_5)_2X_2$] complexes, respectively.[3]

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