

SYNTHESIS OF A HYDRIDE-RICH URANIUM–RHENIUM DIMER: $[(p\text{-F-C}_6\text{H}_4)_3\text{P}]_2\text{ReH}_6\text{U}(\eta\text{-C}_5\text{H}_5)_3$

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Summary

Reaction of $\text{L}_2\text{ReH}_6\text{K}$ with Cp_3UCl gives the complexes $\text{L}_2\text{ReH}_6\text{UCp}_3$ ($\text{L} = \text{Ph}_3\text{P}$ or $(p\text{-F-C}_6\text{H}_4)_3\text{P}$).

Introduction

Deprotonation of the transition metal polyhydrides L_2ReH_7 ($\text{L} =$ tertiary phosphine), $(\text{PMe}_3)\text{WH}_6$ and $(\text{PMe}_2\text{Ph})_3\text{OsH}_4$ gives the compounds $\text{L}_2\text{ReH}_6\text{K}$ [1,2], $(\text{PMe}_3)_3\text{WH}_5\text{M}$ ($\text{M} = \text{Na}, \text{K}$) [3] and $(\text{PMe}_2\text{Ph})_3\text{OsH}_3\text{K}$ [2], respectively. A few reactions of these complexes are known. Thus the rhenium hexahydrides were used for activation of cyclopentane CH bonds [4] and synthesis of trihydrido(η -diene) and tetrahydrido(η -allyl) complexes [1]. The polyhydride salts were also found to be useful intermediates in the synthesis of heterobimetallic complexes [2,3].

Hydrogen rich and/or bimetallic compounds with a 5f-element are uncommon [5], and we thought that it would be of interest to synthesize such a complex containing rhenium and uranium. We describe here the complexes $\text{L}_2\text{ReH}_6\text{U}(\eta\text{-C}_5\text{H}_5)_3$, prepared from the reaction of $\text{L}_2\text{ReH}_6\text{K}$ ($\text{L} = \text{Ph}_3\text{P}$ or $(p\text{-F-C}_6\text{H}_4)_3\text{P}$) with $(\eta\text{-C}_5\text{H}_5)_3\text{UCl}$.

Results and discussion

Reaction of the rhenium heptahydrides L_2ReH_7 ($\text{L} = \text{Ph}_3\text{P}$ (Ia); $\text{L} = (p\text{-F-C}_6\text{H}_4)_3\text{P}$ (Ib)) with KH in tetrahydrofuran (THF) proceeds with evolution of H_2 to give yellow solutions of the compounds $\text{L}_2\text{ReH}_6\text{K}$ (II). These complexes are formed in quantitative yields and can be used in situ after filtration to remove the excess of KH. Solutions of the lithium derivatives $\text{L}_2\text{ReH}_6\text{Li}$, which may be oligomeric [3], are obtained by treatment of I with BuLi in toluene or benzene. Addition of 18 crown 6 to THF solutions of II gives $\text{L}_2\text{ReH}_6\text{K}$ (18 crown 6), isolated as moderately

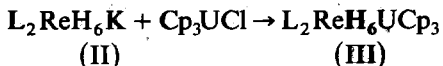
TABLE 1
ELEMENTAL ANALYSIS, IR AND ¹H NMR SPECTRA

Compound	Analysis (Found (calcd.)(%))			ν(Re-H) (cm ⁻¹) ^a	¹ H NMR ^b
	C	H	P		
Ib	53.11 (52.36)	3.99 (3.76)	7.35 (7.51)	1890	7.5 and 6.7 (m, ArH and C ₆ D ₆), -4.43 (t, 18, ReH)
IIa (18 crown 6) ·THF	56.96 (57.14)	6.09 (6.23)	5.79 (5.68)	1850, 1880	8.0 and 7.0 (m,30H,Ph) 3.57(m,4H,THF), 3.19 (s,24H,18 crown6), 1.41 (m,4H,THF), -6.80(t, 14.5,6H,ReH)
IIb (18 crown 6) ·toluene	53.91 (54.10)	5.11 (5.08)	5.20 (5.08)	1790, 1820	7.8 (m,12H, <i>m</i> -ArH), 7.20(5H, toluene) 6.74 (t,8.5, 12 H, <i>o</i> -ArH), 3.14 (s, 24H, 18 crown 6), 2.10(3H, toluene) -6.97 (t, 14.5, 6H, ReH)
IIIa ^c				1810sh, 1860	7.7 and 6.95 (m, <i>m-p</i> -ArH and C ₆ D ₆) 2.58(t, 8, 12H, <i>o</i> -ArH) -6.84(s, 15H, Cp), -29.34(t, 14, 6H, ReH)
IIIb ^d	48.64 (48.69)	3.76 (3.60)	4.74 (4.92)	1810sh, 1860	6.39(t, 8.5, 12 H, <i>m</i> -ArH), 1.97(dd, 15 and 8.5, 12 H, <i>o</i> -ArH) -6.76 (s, 15H,Cp), -36.72 (t, 13.5,6H,ReH)

^a Nujol mull. ^b 30°C, in C₆D₆; reported as δ in ppm from TMS (multiplicity; *J* in Hz, intensity, assignment). ^c 80% in a mixture. ^d Analysis: Re: 14.70 (14.80); U: 19.20% (18.92%).

air stable yellow crystals (see Table 1). The hexahydride anions revert to their colourless neutral precursors I in the presence of traces of water.

The method developed by Caulton et al. [2], which involves treatment of compounds II with equimolecular amounts of Cp₃UCl (Cp = η-C₅H₅) gave the complexes L₂ReH₆UCp₃ (III). These first examples of U/Re heterobimetallic complexes are very sensitive to air and moisture; traces of water convert III into I and insoluble uranium products.



(a, L = Ph₃P;

b, L = (*p*-F-C₆H₄)₃P)

The fluorotriphenylphosphine derivative IIIb was obtained pure (see Experimental) and isolated as bright red microcrystals. In the ¹H NMR spectra of III (see Table 1), the signal from the phenyl *ortho*-hydrogens, which are the closest to the paramagnetic uranium centre, is shifted upfield; the cyclopentadienyl signal is that expected for a Cp₃U^{IV} derivative [6]. The 6 hydride ligands of IIIb are apparently equivalent at 30°C; coalescence of the triplet signal occurs at -80°C and the slow limit spectrum could not be observed. However, in view of the fact that in the

borohydride complex Cp_3UBH_4 , the BH_4 ligand is tridentate [7], we can be confident that not less than three hydrogens are bridging in complexes III.

It seemed possible that hydrogen rich complexes III would provide appropriate models for catalysts in hydrogenation of unsaturated molecules by bimetallic systems [2], but no interaction was detected between compounds III and CO or 1-pentene. Complexes III are readily cleaved; their reaction with H_2O was mentioned above, and another example is provided by the reaction of III with Bu^nLi , which gives $\text{L}_2\text{ReH}_6\text{Li}$ and Cp_3UBu^n [8].

Experimental

Microanalyses were carried out by the Service Central d'analyse du CNRS and the Analytical Laboratories at Engelskirchen (F.R.G.). The infrared spectra were recorded on a Perkin-Elmer 782 instrument, the ^1H NMR spectra on a Bruker W 60 instrument with TMS as internal reference. Analyses, and IR and ^1H NMR spectral data for compounds Ib, II-(18 crown 6) and III are listed in Table 1.

All experiments were carried out under argon using standard Schlenk techniques; evaporation was under reduced pressure. THF and toluene were distilled from sodium-benzophenone before use; n-pentane was dried on molecular sieves (4 Å). KH in mineral oil (Aldrich) was washed with THF before use; 18 crown 6 (Fluka) was used without purification. Cp_3UCl [9] and $(\text{Ph}_3\text{P})_2\text{ReH}_7$ [10] were prepared by published methods.

$[(p\text{-F-C}_6\text{H}_4)_3\text{P}]_2\text{ReOCl}_3$. This was prepared as described for $(\text{Ph}_3\text{P})_2\text{ReOCl}_3$ [11], using $(p\text{-F-C}_6\text{H}_4)_3\text{P}$ [12] instead of Ph_3P . IR: 830 cm^{-1} ($\nu(\text{Re} = \text{O})$). Analysis: Found: C, 46.10; H, 2.72; P, 6.68; Cl, 11.40. $\text{C}_{36}\text{H}_{24}\text{Cl}_3\text{F}_6\text{OP}_2\text{Re}$ calcd.: C, 45.88; H, 2.54; P, 6.58; Cl, 11.31%.

$[(p\text{-F-C}_6\text{H}_4)_3\text{P}]_2\text{ReH}_7$ (Ib). This was prepared as described for Ia [10], using $[(p\text{-F-C}_6\text{H}_4)_3\text{P}]_2\text{ReOCl}_3$ instead of $(\text{Ph}_3\text{P})_2\text{ReOCl}_3$. The product was recrystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (yield 60%).

$(\text{Ph}_3\text{P})_2\text{ReH}_6\text{K}$ (IIa). Ia (150 mg) was added to a magnetically stirred suspension of KH (~ 100 mg) in THF (30 ml). When gas evolution had ceased (~ 30 min) the suspension was decanted. The ^1H NMR spectrum of the yellow solution showed that the hydride signal of Ia at -4.9 ppm was no longer present and that IIa had been formed quantitatively. ^1H NMR, 30°C , $\delta(\text{THF})$: $-7.50(\text{t}, J 14\text{ Hz}, \text{ReH})$. Subsequently 18 crown 6 (55 mg) was added to the solution; upon cooling to -10°C , yellow crystals of IIa (18 crown 6), THF were obtained, and these were filtered off and dried under vacuum (148 mg, 65%).

$[(p\text{-F-C}_6\text{H}_4)_3\text{P}]_2\text{ReH}_6\text{K}$ (IIb). The preparation of IIb was similar to that of IIa, but using Ib instead of Ia. ^1H NMR, 30°C , $\delta(\text{THF})$: $-7.68(\text{t}, J 14.5\text{ Hz}, \text{ReH})$. Crystals of IIb (18 crown 6) were obtained from THF in 60% yield. An analytical sample of IIb (18 crown 6) · toluene was prepared by recrystallisation from toluene.

Reactions of I with Bu^nLi . BuLi (1.6 M in hexane, 20 μl) was added to a solution of Ia (20 mg) in C_6D_6 (0.4 ml) in an NMR tube. The hydride signal of Ia at -4.20 ppm (t, $J 18$ Hz) was replaced by a broad triplet at -7.4 ppm. A similar experiment was conducted with Ib; the triplet at -4.43 ppm ($J 18$ Hz) was replaced by a broad triplet at -7.6 ppm.

$(\text{Ph}_3\text{P})_2\text{ReH}_6\text{UCp}_3$ (IIIa). A yellow solution of IIa, prepared from 365 mg of Ia, in THF (30 ml) was added to solid Cp_3UCl (238 mg); a red solution and a white

precipitate were immediately formed. Evaporation gave a red-brown residue which was extracted with hot pentane (2×30 ml); the red extract obtained was reduced to 20 ml and cooled to -10°C , to give a red violet powder which was filtered off and dried under vacuum (330 mg). This powder was a mixture of Ia (11%), an unidentified $\text{Cp}_3\text{U}^{\text{IV}}$ product (10%) which gives a singlet signal at -6.6 and a broad triplet at -27.8 ppm, and IIIa. Further recrystallisation did not give pure crystals of IIIa. The ^1H NMR spectrum of IIIa was deduced from the spectra of the mixtures.

[(p-F-C₆H₄)₃P]₂ReH₆UCp₃ (IIIb). A yellow solution of Ib, prepared from 257 mg of Ib, in THF (30 ml) was added to solid Cp_3UCl (146 mg); a red solution and a white precipitate were immediately formed. Evaporation gave a red-brown residue, which was washed with pentane (30 ml) to remove Ib (30 mg), then extracted with toluene (10 ml). The red extract was evaporated to 1 ml, n-pentane (10 ml) was added, and the resulting solution was cooled to -20°C . Red crystals of IIIb were filtered off, washed with cold pentane, and dried under vacuum (228 mg, 58%).

Reaction of IIIb with BuLi. A 1.6 M solution of BuLi in hexane (35 μl) was added to a solution of IIIb (8 mg) in C_6D_6 (0.4 ml) in an NMR tube. The NMR spectrum of the resulting red solution showed the absence of IIIb and formation of $[(p\text{-F-C}_6\text{H}_4)_3\text{P}]_2\text{ReH}_6\text{Li}$ and Cp_3UBu [8] (65%).

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