# Phospholyluranium Complexes

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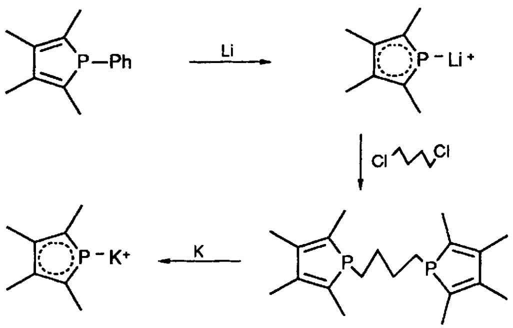
Reaction of $U(BH_4)_4$ with K[tmp] (tmp = 2,3,4,5-tetramethylphospholyl) afforded the uranium(IV) complexes $[U(tmp)(BH_4)_3]$ and $[U(tmp)_2(BH_4)_2]$. Sodium amalgam reduction of these complexes in tetrahydrofuran gave the uranate(III) anions $[U(tmp)(BH_4)_3]^-$ and $[U(tmp)_2(BH_4)_2]^-$ which were alternatively obtained by treating $[U(C_6H_3Me_3\text{-}1,3,5)(BH_4)_3]$ with K[tmp]. Similar reactions in toluene led to the formation of the neutral compound $[\{U(tmp)_2(BH_4)\}_2]$. The fluxionality and the stability of the complexes are described.

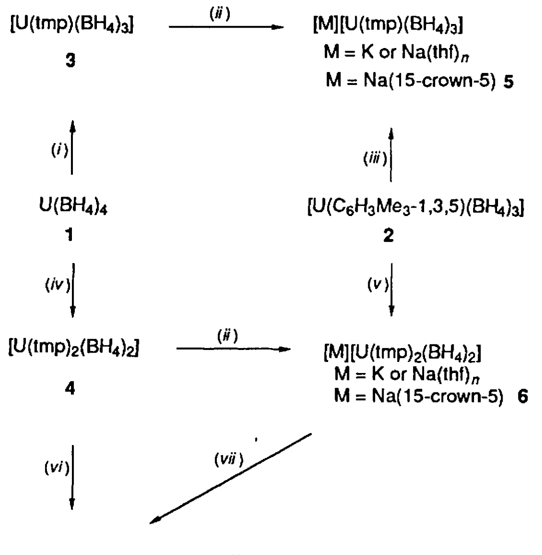
The cyclopentadienyl ligand is most currently employed in organouranium chemistry and, by varying the substitution of the cp ring (cp = $\eta^5$-$C_5H_5$), it is possible to modify strongly the structure and the reactivity of the complexes.[1] Special attention was recently paid to the open pentadienyl[2] and cyclohexadienyl[3] groups which represent an alternative to the ubiquitous cyclopentadienyl fragment. We prepared the first examples of complexes of $U^{IV}$ and $U^{III}$ with these dienyl ligands[4,5] and noted that their properties were quite different from those of the corresponding cp derivatives; in particular, we could isolate sterically and co-ordinatively unsaturated compounds which have no equivalent in the cyclopentadienyl series. Then it seemed to us of interest to examine the behaviour of the phospholyl analogues of these complexes. The phospholyl ligand is capable of π co-ordination to main-group and early transition metals, as well as to lanthanides, to give $\eta^5$-phosphacyclopentadienyl derivatives,[6] in which the phosphorus lone pair is not engaged in bonding and should be available to stabilize unsaturated species. Here we describe the synthesis, characterization and dynamic behaviour of phospholyluranium tetrahydroborate compounds;[7] the stabilities of these complexes are compared with those of their dienyl analogues.

## Results and Discussion

*Syntheses.*—As in the case of the preparation of the pentadienyl and cyclohexadienyl uranium compounds,[4,5] the phospholyl compounds were synthesised from the uranium-(IV) and -(III) tetrahydroborates $U(BH_4)_4$ **1** and $[U(C_6H_3Me_3\text{-}1,3,5)(BH_4)_3]$ **2**, by substitution of a $BH_4$ group by a phospholyl ligand. We wanted to utilize the 2,3,4,5-tetramethylphospholyl anion (hereafter abbreviated as tmp) since this peralkylphospholide gave much more stable and more easily tractable derivatives with other metals.[6] Treatment of **1** or **2** with the known crystalline salt [K(18-crown-6)][tmp][8] (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) led to the formation of insoluble and unidentified products; these difficulties could be avoided by using the donor-free potassium salt K[tmp] which was prepared as shown in Scheme 1 and isolated as colourless needles, after crystallization from tetrahydrofuran (thf).



**Scheme 1** Preparation of K[tmp]



**Scheme 2** Preparation of the phospholyluranium complexes. (*i*) K[tmp] (1 equivalent), toluene; (*ii*) Na/Hg, thf, 15-crown-5; (*iii*) K[tmp] (1 equivalent), thf; (*iv*) K[tmp] (2 equivalents), toluene; (*v*) K[tmp] (2 equivalents), thf; (*vi*) Na/Hg, toluene; (*vii*) toluene; (*viii*) $OPPh_3$

The mono- and bis-phospholyluranium(IV) complexes **3** and **4** were obtained in *ca.* 80% yield from the reactions of **1** with 1 or 2 equivalents of K[tmp] in toluene (Scheme 2). The red compound $[U(tmp)(BH_4)_3]$ **3** could easily be purified by sublimation, its vapour pressure being of the same order of magnitude as that of **1**, $[U(cp)(BH_4)_3]$, $[U(dmpd)(BH_4)_3]$ and $[U(dmch)(BH_4)_3]$[4,5] (dmpd = 2,4-dimethylpentadienyl

**Table 1** NMR spectral data for the complexes *

| | $^1$H NMR | | |
|---|---|---|---|
| Compound | tmp | $BH_4$ and other ligands | $^{31}$P-{$^1$H} NMR |
| **3** $[U(tmp)(BH_4)_3]$ | 6.84 and −4.69 (6 H + 6 H) | 58.74 (12 H, q, *J* 81) | 923 ($w_{\frac{1}{2}}$ 44) |
| **4** $[U(tmp)_2(BH_4)_2]$ | 35.13 and −13.01 (12 H + 12 H) | −36.73 (8 H, q, *J* 86) | 960 ($w_{\frac{1}{2}}$ 200) |
| **5** $[Na(15\text{-crown-}5)][U(tmp)(BH_4)_3]$ | −6.08 and −13.47 (6 H + 6 H) | −109.0 (12 H, br, $w_{\frac{1}{2}}$ 540)<br>3.50 (20 H, s, 15-crown-5) | 419 ($w_{\frac{1}{2}}$ 200) |
| **6** $[Na(15\text{-crown-}5)][U(tmp)_2(BH_4)_2]$ | 3.52 and −13.24 (12 H + 12 H) | 68.81 (8 H, br, $w_{\frac{1}{2}}$ 320) | 618 ($w_{\frac{1}{2}}$ 227) |
| **7** $[\{U(tmp)_2(BH_4)\}_2]$ | 13.45, 8.33, 5.57, −12.45, −20.08, −35.59 −40.95, −46.80 (3 H × 8) | 165 (4 H, br, $w_{\frac{1}{2}}$ 300) | 727 ($w_{\frac{1}{2}}$ 150)<br>3471 ($w_{\frac{1}{2}}$ 1000) |
| **8** $[U(tmp)_2(BH_4)(OPPh_3)]$ | 3.49, −1.45, −8.76, −18.99 (6 H × 4) | 86.9 (4 H, br, $w_{\frac{1}{2}}$ 300)<br>5.85 (3 H, t, *J* 7, *p*-H of $OPPh_3$)<br>5.05 (6 H, t, *J* 7, *m*-H of $OPPh_3$)<br>0.16 (6 H, dd, *J* 7 and 11, *o*-H of $OPPh_3$) | 86 (s, $OPPh_3$)<br>650 (br, $w_{\frac{1}{2}}$ 200, tmp) |

* At 30 °C in [$^2H_8$]toluene, except for complexes **5** and **6** in [$^2H_8$]tetrahydrofuran. Data are given as chemical shift δ (relative integral, multiplicity, coupling constant *J* or half-height width $w_{\frac{1}{2}}$ in Hz). When not specified, the signal is a singlet with $w_{\frac{1}{2}}$ = 10–30 Hz.

dmch = 6,6-dimethylcyclohexadienyl). Complex **3** readily disproportionated in thf, yielding an equimolar mixture of $[U(tmp)_2(BH_4)_2]$ **4** and $[U(BH_4)_4(thf)_2]$; this behaviour is identical to that of $[U(cp)(BH_4)_3]$ but is different from that of the dmpd and dmch analogues which are reduced in co-ordinative solvents.[5,6] The dark brown bis(phospholyl) complex **4** reacted with the stoichiometric amount of **1** in toluene to give **3** in quantitative yield.

Reduction of complex **3** by sodium amalgam in thf afforded the uranium(III) anion $[U(tmp)(BH_4)_3]^-$ which was alternatively formed by treating the uranium(III) tetrahydroborate **2** with 1 equivalent of K[tmp]. In the presence of 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane), the red crystalline complex $[Na(15\text{-crown-}5)][U(tmp)(BH_4)_3]$ **5** was isolated in 94% yield. The bis(phospholyl) anion $[U(tmp)_2(BH_4)_2]^-$ was similarly synthesised in thf either by treatment of **2** with 2 equivalents of K[tmp] or by Na/Hg reduction of **4**. However, the same reaction in toluene led to the neutral compound $[\{U(tmp)_2(BH_4)\}_2]$ **7** which was also obtained by extracting the red powder of $[Na(thf)_n][U(tmp)_2(BH_4)_2]$ with toluene. Whatever its preparation, **7** was isolated as a brown powder after crystallization from toluene–pentane. By treatment with $TlBH_4$, **7** was reoxidized back to **4** and its reaction with $OPPh_3$ gave the Lewis-base adduct $[U(tmp)_2(BH_4)(OPPh_3)]$ **8**.

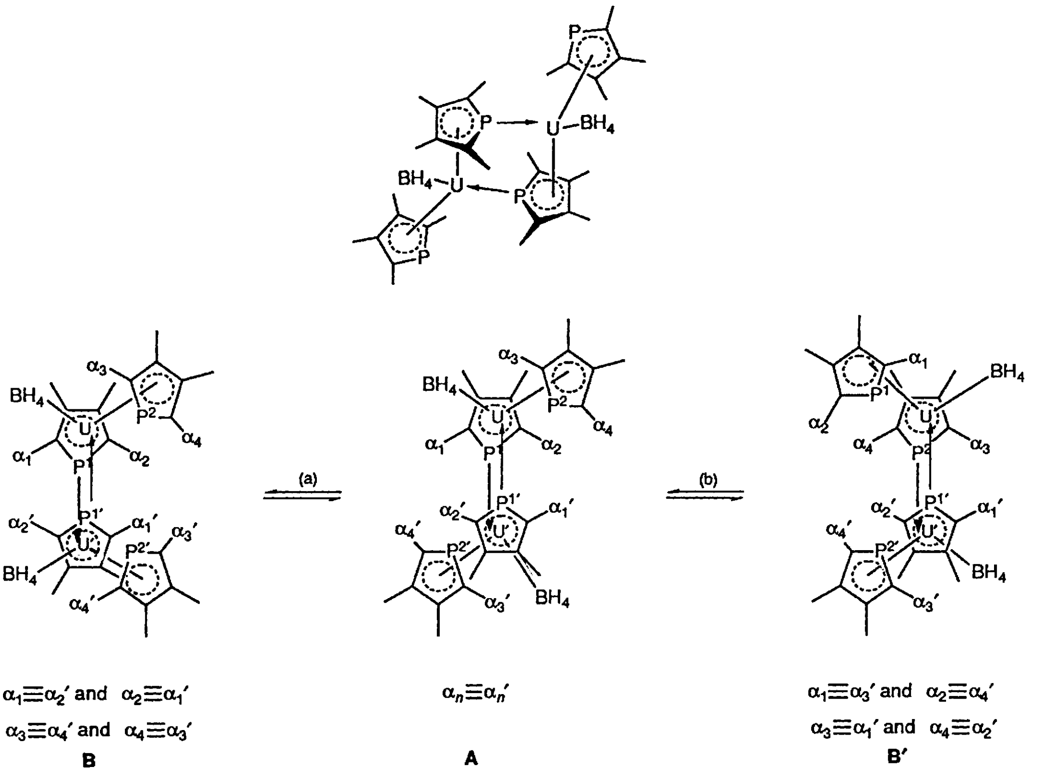
Complexes **3**–**8** have been characterized by their elemental analyses, $^1$H and $^{31}$P-{$^1$H} NMR spectra (Table 1) and, in the case of **4**, by the crystal structure.

*Structure and Dynamic Behaviour in Solution.*—The uranium atom in the phospholyl complexes **3**–**8** has a tetrahedral environment, if the tmp and $BH_4$ ligands are considered to occupy a single co-ordination site. The crystal structure of **4** revealed the pentahapto ligation of the phospholyl ligands and the tridentate bonding of the tetrahydroborate groups.[7]

The $^{31}$P-{$^1$H} NMR spectrum of **7** exhibited two resonances at δ +727 and +3471, indicating that this neutral complex should adopt the dimeric structure shown in Scheme 3, with the two bridging phosphorus atoms giving rise to the strongly shifted paramagnetic signal. Such a dimer can exist in the form of two geometrical isomers **A** and **B** in which the two $BH_4$ ligands are in relative *cis* and *trans* positions with respect to the UPU′P′ ring. It is not possible to determine the most stable configuration of **7** in solution but, in any case, the eight methyl groups of the monomeric unit $U(tmp)_2(BH_4)$ are not equivalent, as was observed in the $^1$H NMR spectra in toluene which exhibited eight signals of equal intensity.

Spin-saturation transfer experiments[9] revealed that the four α-methyl groups, as well as the four β-methyl groups, were exchanging at 50 °C; above 80 °C, the signals were very broad but the fast-limit spectrum could not be obtained. Scheme 3 describes a mechanism that can account for the observed fluxional behaviour. Dissociation of $P^1$ from U′ in isomer **A**, followed by rotation around the bridging tmp centroid–U′ axis and recombination will equivalence the $\alpha_1$ and $\alpha_2{}',\alpha_1{}'$ and $\alpha_2,\alpha_3$ and $\alpha_4{}',\alpha_4$ and $\alpha_3{}'$ positions in isomer **B**. If the dissociation of $P^1$ from U′ is followed by a rotation around $UP^{1\prime}$ the isomer **B′** will be obtained after co-ordination of $P^2$ to U′ and $\alpha_2$ will be equivalent to $\alpha_4{}'$ and also equivalent will be $\alpha_2{}'$ and $\alpha_4,\alpha_1$ and $\alpha_3{}',\alpha_1{}'$ and $\alpha_3$. These two rotation processes, after breaking of a U–P bridge, are sufficient to explain the exchange between the methyl groups. The bis(phospholyl)uranium tetrahydroborate should adopt a monomeric form in tetrahydrofuran, presumably $[U(tmp)_2(BH_4)(thf)]$, resulting from a bridge-splitting reaction involving the co-ordinating solvent. The NMR spectrum of this adduct in [$^2H_8$]tetrahydrofuran exhibited, in addition to the tetrahydroborate resonance at δ 104 ($w_{\frac{1}{2}}$ 350 Hz), two singlets at δ 1.80 and −12.57 corresponding to the α- and β-methyl groups of the equivalent tmp ligands. This equivalence is caused by the permutation of the thf and $BH_4$ ligands in the tetrahedral structure and the rapid equilibrium between the forms **C** and **D** (Scheme 4). This equilibrium could be slowed down and coalescence of the signals corresponding to the α-, α′-, β- and β′-methyl groups occurred at −80 °C, but the slow-limit spectrum could not be reached. The triphenylphosphine oxide ligand is much less easily dissociated than thf and the non-equivalent α-, α′-, β- and β′-methyl groups in compound **8** gave rise to four signals on the NMR spectrum; however, spin-saturation transfer was observed at 30 °C between the α-and α′-, as well as between the β- and β′-methyl, substituents, thus revealing the occurrence of the equilibrium shown in Scheme 4. The fluxionality of the $[U(tmp)_2(BH_4)L]$ complexes (L = thf or $OPPh_3$) is similar to that encountered with the cyclohexadienyl derivatives.[5]

*Stability of the Complexes.*—The stability of the phospholyl complexes **3**–**8** and those of their cyclopentadienyl (cp), dimethylpentadienyl (dmpd) and dimethylcyclohexadienyl (dmch) analogues is summarized in Table 2. We have already seen that the solution behaviour of the phospholyluranium(IV) compounds **3** and **4** is similar to that of the cyclopentadienyl derivatives, but is distinct from that of the dmpd and dmch complexes which are reduced in thf. All the anionic compounds



**Scheme 3** Fluxionality of $[\{U(tmp)_2(BH_4)\}_2]$. (a) Breaking of U′–P[1] followed by rotation around the bridging tmp centroid–U′ axis and recombination. (b) Breaking of U′–P[1] followed by rotation around U–P[1′] and co-ordination of P[2] to U′

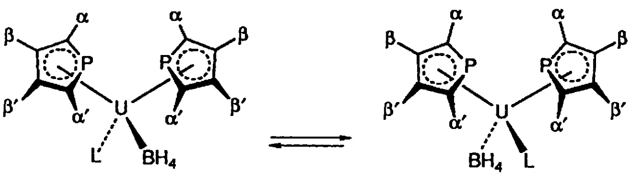
**Table 2** Relative stabilities of analogous cyclopentadienyl, pentadienyl, cyclohexadienyl and phospholyl uranium complexes

| | L | | | |
|---|---|---|---|---|
| Compound | cp | dmpd | dmch | tmp |
| $[UL(BH_4)_3]$ | | | | |
| in toluene | Stable | Stable | Stable | Stable |
| in thf | Disproportionation | Reduction | Reduction | Disproportionation |
| $[UL_2(BH_4)_2]$ | | | | |
| in toluene | Stable | Stable | Stable | Stable |
| in thf | Stable | Reduction | Reduction | Stable |
| [Na(crown ether)]$[UL(BH_4)_3]$ | | | | |
| in thf | Disproportionation | Disproportionation | Disproportionation | Stable |
| [Na(crown ether)]$[UL_2(BH_4)_2]$ | | | | |
| in thf | Stable | Slow Decomposition | Stable | Stable |
| $[\{UL_2(BH_4)\}_2]$ | | | | |
| in toluene | Not observed | Not observed | Stable | Stable |
| $[UL_2(BH_4)(thf)]$ or $[UL_2(BH_4)(OPPh_3)]$ | | | | |
| in thf | Not observed | Not observed | Stable | Stable |

[Na(crown ether)]$[UL_2(BH_4)_2]$ were obtained pure even if [Na(18-crown-6)]$[U(dmpd)_2(BH_4)_2]$ was found to decompose slowly in solution. In contrast to **5**, none of the complexes [Na(crown ether)]$[UL(BH_4)_3]$ (L = cp, dmpd or dmch) could be isolated,[5,6] because of the ready transformation $2[UL(BH_4)_3]^- \longrightarrow [UL_2(BH_4)_2]^- + [U(BH_4)_4]^-$. The cyclohexadienyl ligand was useful to prepare the analogues of **7** and **8**,[6] but such neutral uranium(III) species could not be formed with the other dienyl fragments. In conclusion, if we consider the four series of complexes, it is noteworthy that only the phospholyl ligand gave a complete family of stable derivatives. In order to determine if this superiority of the tmp ligand is due to steric or electronic effects, we are examining the synthesis and properties of the isosteric analogues of complexes **3**–**8** with the pentamethylcyclopentadienyl ligand.

## 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



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**Scheme 4** Fluxionality of the [U(tmp)$_2$(BH$_4$)L] complexes

distilled immediately before use. Deuteriated solvents were dried over Na–K alloy. Elemental analyses were performed by Analytische Laboratorien at Engelskirchen (Germany). The $^1$H NMR spectra were recorded on Bruker WP 60 and AC 200 instruments and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The $^{31}$P NMR spectra were recorded on Bruker WP 80 and AM 400 spectrometers, the external reference being 85% $H_3PO_4$. 2,3,4,5-Tetramethyl-1-phenylphosphole,[10] U(BH$_4$)$_4$[11] and [U(C$_6$H$_3$Me$_3$-1,3,5)(BH$_4$)$_3$][12] were prepared according to published methods.

K[tmp].—In a round-bottomed flask (250 cm$^3$), lithium wires (1.3 g, 0.185 mol) were added to a magnetically stirred solution of 2,3,4,5-tetramethyl-1-phenylphosphole (10 g, 0.046 mol) in thf (150 cm$^3$). After a brief induction period the mixture was yellow, then became red. It was stirred for 1.5 h and the unreacted lithium discarded. After dropwise addition (2 min) of 1,4-dichlorobutane (2.6 cm$^3$, 0.023 mol), the yellow or pale red solution was cooled at 0 °C and was carefully neutralized with 3 mol dm$^{-3}$ HCl. Usual extraction with CH$_2$Cl$_2$ and evaporation of the solvent gave an off-white solid which was extracted in boiling pentane (2 × 100 cm$^3$); the filtrate was evaporated to dryness, yielding colourless crystals (4.5 to 5.5 g, 60–70%) of 1,4-bis(2,3,4,5-tetramethylphospholyl)butane. $^{31}$P-{$^1$H} NMR (30 °C, [$^2$H$_8$]tetrahydrofuran): δ +12. These crystals (5.16 g, 0.015 mol) were dissolved in 1,2-dimethoxyethane (100 cm$^3$) in a round-bottomed flask (250 cm$^3$) and small pieces of potassium (1.8 g, 0.046 mol) were introduced. The reaction mixture was stirred for 2 h at 65 °C and after cooling at 0 °C the unreacted potassium was removed. The solution was filtered, the solvent evaporated off and the residue recrystallized from thf (40 cm$^3$). The colourless crystals of K[tmp] were filtered off, washed with thf (20 cm$^3$), then pentane (20 cm$^3$) and dried under vacuum (3.2 g, 62%). $^{31}$P-{$^1$H} NMR (30 °C, [$^2$H$_8$]tetrahydrofuran): δ +73.

[U(tmp)(BH$_4$)$_3$] **3**.—(*a*) A round-bottomed flask (50 cm$^3$) was charged with U(BH$_4$)$_4$ (510.4 mg, 1.71 mmol) and K[tmp] (305.4 mg, 1.71 mmol), and toluene (20 cm$^3$) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred at 20 °C for 10 min, the solvent evaporated off and the residue extracted with pentane (2 × 15 cm$^3$). The red filtrate was evaporated to dryness below 20 °C, leaving a red microcrystalline powder of complex **3** (593.4 mg, 82%) which was pure enough for further utilization. The analytical sample was obtained by sublimation [10$^{-2}$ mmHg (*ca.* 1.33 Pa), 40–90 °C] (Found: C, 22.8; H, 5.55; B, 7.5; P, 7.4. C$_8$H$_{24}$B$_3$PU requires C, 22.75; H, 5.7; B, 7.8; P, 7.35%).

(*b*) An NMR tube was charged with complexes **4** (15 mg, 0.027 mmol) and **1** (8 mg, 0.027 mmol) in [$^2$H$_8$]toluene (0.5 cm$^3$). After 15 min at 20 °C the spectrum showed the quantitative formation of **3**.

[U(tmp)$_2$(BH$_4$)$_2$] **4**.—A round-bottomed flask (50 cm$^3$) was charged with U(BH$_4$)$_4$ (407.2 mg, 1.37 mmol) and K[tmp] (492.8 mg, 2.77 mmol) and toluene (20 cm$^3$) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred at 20 °C for 15 min; the solvent was removed and the residue extracted with pentane (2 × 20 cm$^3$). After evaporation to dryness, the dark brown microcrystalline powder of complex **4** (588.4 mg, 79%) was pure enough for further utilization. The product could be recrystallized from cold pentane (Found: C, 34.95; H, 5.8; B, 3.8; P, 11.4. C$_{16}$H$_{32}$B$_2$P$_2$U requires C, 35.15; H, 5.85; B, 4.0; P, 11.35%).

[Na(15-crown-5)][U(tmp)(BH$_4$)$_3$] **5**.—A round-bottomed flask (50 cm$^3$) was charged with complex **3** (213.4 mg, 0.50 mmol), 2% Na/Hg (850 mg, 0.74 mmol Na) and 15-crown-5 (111.5 mg, 0.50 mmol) and thf (20 cm$^3$) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred at 20 °C for 4 h. The solution was filtered and evaporated to dryness, leaving a red microcrystalline powder of complex **5** (316.2 mg, 94%) (Found: C, 32.7; H, 6.5; B, 5.05; P, 4.7. C$_{18}$H$_{44}$B$_3$NaO$_5$PU requires C, 32.5; H, 6.6; B, 4.95; P, 4.65%). Similar reaction without the crown ether gave a red powder of [Na(thf)$_n$][U(tmp)(BH$_4$)$_3$].

[Na(15-crown-5)][U(tmp)$_2$(BH$_4$)$_2$] **6**.—A round-bottomed flask (50 cm$^3$) was charged with complex **4** (338.4 mg, 0.62 mmol), 2% Na/Hg (1400 mg, 1.22 mmol Na) and 15-crown-5 (134.2 mg, 0.61 mmol) and thf (20 cm$^3$) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred for 15 min at 20 °C. The solution was filtered and evaporated to dryness, leaving a red microcrystalline powder of complex **6** (357.0 mg, 73%) (Found: C, 39.75; H, 6.5; B, 2.6; Na, 2.8; P, 7.6. C$_{26}$H$_{52}$B$_2$NaO$_5$P$_2$U requires C, 39.55; H, 6.6; B, 2.8; Na, 2.9; P, 7.85%). Similar reaction in the absence of the crown ether gave a red powder of [Na(thf)$_n$][U(tmp)$_2$(BH$_4$)$_2$].

*Reactions of* [U(C$_6$H$_3$Me$_3$-1,3,5)(BH$_4$)$_3$] *with* K[tmp].—An NMR tube was charged with complex **2** (15 mg, 0.037 mmol) and K[tmp] (6.5 mg, 0.037 mmol) in [$^2$H$_8$]tetrahydrofuran (0.3 cm$^3$). Formation of [K(thf)$_n$][U(tmp)(BH$_4$)$_3$] was immediately observed; the NMR spectrum was identical to that of **5**, without the resonance corresponding to the crown ether. Similar reaction with 2 equivalents of K[tmp] gave [K(thf)$_n$][U(tmp)$_2$(BH$_4$)$_2$].

[{U(tmp)$_2$(BH$_4$)}$_2$] **7**.—(*a*) A round-bottomed flask (50 cm$^3$) was charged with [U(C$_6$H$_3$Me$_3$-1,3,5)(BH$_4$)$_3$] (277 mg, 0.69 mmol) and K[tmp] (245 mg, 1.38 mmol) and thf (20 cm$^3$) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred at 20 °C for 20 min and the solvent was evaporated off. The residue was extracted with toluene (25 cm$^3$) and after evaporation of the solvent the crude product **7** was obtained as a brown powder (336 mg, 92%). The latter was recrystallized from toluene–pentane (2.5:10 cm$^3$) and the dark brown crystals of **7** were filtered off, washed with pentane (5 cm$^3$) and dried under vacuum (118 mg, 32%) (Found: C, 36.15; H, 5.25; B, 2.05. C$_{16}$H$_{28}$BP$_2$U requires C, 34.8; H, 5.1; B, 2.0%).

(*b*) A round-bottomed flask (50 cm$^3$) was charged with complex **4** (331 mg, 0.61 mmol) and 2% Na/Hg (1120 mg, 0.97 mmol Na) and toluene (25 cm$^3$) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred at 20 °C for 8 h, filtered and after evaporation of the solvent a brown powder of complex **7** was obtained (267 mg, 82%).

(*c*) An NMR tube was charged with [Na(thf)$_n$][U(tmp)$_2$(BH$_4$)$_2$] (*ca.* 15 mg) in [$^2$H$_8$]toluene (0.3 cm$^3$). The spectrum of the brown solution was identical to that of complex **7**.

The $^1$H NMR spectrum of complex **7** in [$^2$H$_8$]toluene was recorded at 50 °C; δ −44.42, −39.04, −33.16, −19.15, −11.76, 5.24, 8.25 and 12.75 (6 H × 8, $w_{\frac{1}{2}}$ *ca.* 50 Hz, Me), 161 (8 H, $w_{\frac{1}{2}}$ 350 Hz, BH$_4$). Irradiation of the resonance at δ −11.76 caused a decrease in the intensity of the signals at δ −44.42, −33.16 and 5.24 (*ca.* 50% of its original value); irradiation of the resonance at δ −19.15 caused a similar decrease in the intensity of the signals at δ −39.04, 8.25 and 12.75.

[U(tmp)$_2$(BH$_4$)(OPPh$_3$)] **8**.—A round-bottomed flask (50 cm$^3$) was charged with complex **7** (150 mg, 0.14 mmol) and OPPh$_3$ (78 mg, 0.28 mmol) and toluene (20 cm$^3$) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred at 20 °C for 10 min, then filtered. The volume of the solution was reduced to 5 $cm^3$ and upon cooling at −78 °C red microcrystals of complex **8** deposited; these were filtered off, washed with cold (−78 °C) toluene (5 $cm^3$) and pentane (5 $cm^3$) and dried under vacuum (84 mg, 37%) (Found: C, 50.25; H, 5.2; B, 1.25; P, 11.45. $C_{34}H_{43}BOP_3U$ requires C, 50.45; H, 5.3; B, 1.35; P, 11.5%). The $^1H$ NMR data at 30 °C are in Table 1. Irradiation of the resonance at $\delta$ −8.76 caused a decrease in the intensity of the signal at $\delta$ −18.99 (60% of its original value) and the intensity of the signal at $\delta$ −1.45 was similarly reduced when the resonance at $\delta$ 3.49 was irradiated.

*Reaction of Complex* **7** *with* $TlBH_4$.—An NMR tube was charged with complex **7** (*ca.* 10 mg) and $TlBH_4$ (*ca.* 3 mg) in [$^2H_8$]tetrahydrofuran (0.3 $cm^3$). The tube was immersed in an ultrasound bath (60 W, 40 kHz) and after 30 min the spectrum showed the formation of **4** in almost quantitative yield.

## References

1 T. J. Marks and R. D. Ernst, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 3, p. 21; T. J. Marks and V. W. Day, in *Fundamental and Technological Aspects of Organo-f-Element Chemistry*, eds. T. J. Marks and I. L. Fragala, Reidel, Dordrecht, 1985; I. Santos, A. Pires de Matos and A. G. Maddock, *Adv. Organomet. Chem.*, 1989, **34**, 65
2 R. D. Ernst, *Chem. Rev.*, 1988, **88**, 1255.
3 P. T. Di Mauro and P. T. Wolczanski, *Organometallics*, 1987, **6**, 1947; P. T. Di Mauro, P. T. Wolczanski, L. Parkanyi and M. H. Petach, *Organometallics*, 1990, **9**, 1097.
4 D. Baudry, E. Bulot and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1989, 1316; D. Baudry, E. Bulot, P. Charpin, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, *J. Organomet. Chem.*, 1989, **371**, 163.
5 D. Baudry, E. Bulot and M. Ephritikhine, *J. Organomet. Chem.*, 1990, **397**, 169
6 F. Mathey, *J. Organomet. Chem.*, 1990, **400**, 149.
7 D. Baudry, M. Ephritikhine, F. Nief, L. Ricard and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1485.
8 K. Theopold and H. Douglas, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1367.
9 S. Forsen and R. A. Hoffman, *J. Chem. Phys.*, 1963, **39**, 2892.
10 F. Nief, F. Mathey, L. Ricard and F. Robert, *Organometallics*, 1988, **7**, 921.
11 V. V. Volkov and K. G. Myakishev, *Radiokhimiya*, 1980, **22**, 745.
12 D. Baudry, E. Bulot, P. Charpin, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, *J. Organomet. Chem.*, 1989, **371**,155.

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