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Bispentamethylcyclopentadienyl uranium diphenylphosphide compounds

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Abstract

Reaction of $[U(Cp^*)_2(Me)_2]$ with $HPPh_2$ was the best route to the uranium(IV) diphenylphosphide compounds $[U(Cp^*)_2(PPh_2)_2]$ **1** and $[U(Cp^*)_2(PPh_2)(Me)]$ **2**. Thermolysis of **2** afforded the *ortho*-metallated complex $[U(Cp^*)_2(PPh\{o\text{-}C_6H_4\})]$ **3**. Reduction of **1** with KH gave the first U(III) phosphide $K[U(Cp^*)_2(PPh_2)_2]$ **4**. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Phosphide and thiolate compounds of the f-elements have received an increasing attention during the past decade, because of their fundamental interest and industrial applications [1]. It is now well established that such complexes are much more stable than previously expected from considerations on the bonding between 'hard' metals and 'soft' second row atoms. Both lanthanides [2] and actinides [3] were shown to possess a rich coordination chemistry with the SR ligand; in contrast, it seems that phosphide complexes of uranium and thorium have been neglected when compared with the variety of the rare earth counterparts [4]. The only inorganic derivatives are the diphosphinophosphides $[An(\{Me_2PCH_2CH_2\}_2P)_4]$ (An = Th or U) [5] while the few organometallic compounds are $[U(Cp)_3(PPh_2)]$ ($Cp = \eta\text{-}C_5H_5$) [6], $[Th(Cp^*)_2(PR_2)_2]$ ($Cp^* = \eta\text{-}C_5Me_5$, R = Et, Cy, Ph) [7] and $[An(Cp^*)_2(P\{SiMe_3\}_2)(X)]$ (X = Cl or Me) [8]; the latter (X = Me) gave the phosphasilametallacyclobutane $[An(Cp^*)_2(\eta^2\text{-}CH_2SiMe_2P\{SiMe_3\})]$ by thermolysis while the bisphosphide $[Th(Cp^*)_2(PPh_2)_2]$ was converted into the heterobimetallic compounds $[Th(Cp^*)_2(\mu\text{-}PPh_2)_2M]$ ($M = Ni(CO)_2$ or $Pt(PMe_3)$) [9]. Difficulties in preparing the uranium phosphide complexes were underlined, and explained by the easy reduction of the U(IV) centre; however, no phosphide compound of uranium(III) has been so far described. We wish to report here the different routes that we had to envisage for a clean preparation of a series of bispentamethylcyclopentadienyl uranium diphenylphosphides, including the trivalent derivative $K[U(Cp^*)_2(PPh_2)_2]$; we also isolated and characterized the amidophosphide $[U(NEt_2)_3(PPh_2)]$.

2. Results and discussion

2.1. Synthesis from chloride precursors

Actinide phosphide complexes were all prepared by metathetical exchange between actinide halide and alkali metal salt of the phosphide ligand. Thus were synthesized the thorium compounds $[Th(Cp^*)_2(PR_2)_2]$ (R = Et, Cy, Ph) by treatment of $[Th(Cp^*)_2Cl_2]$ with $LiPR_2$ in toluene [7]. Our attempts to prepare the uranium analogue $[U(Cp^*)_2(PPh_2)_2]$ **1** by following the same procedure remained unsuccessful. Complex **1** was

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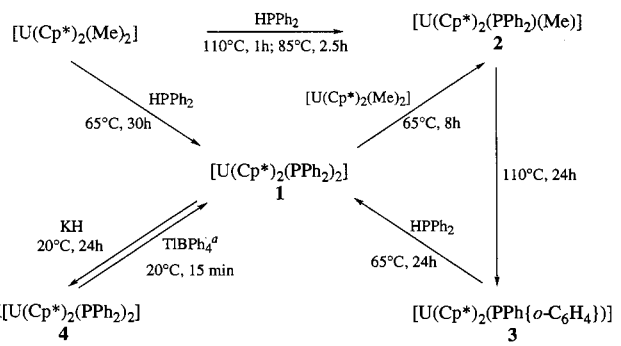
in fact obtained in ca. 60% yield by treating $[U(Cp^*)_2Cl_2]$ with two equivalents of $LiPPh_2$ in benzene but could not be isolated in a pure form from other unidentified products (NMR experiments). In the presence of one equivalent of $LiPPh_2$, $[U(Cp^*)_2Cl_2]$ was transformed into a complex mixture containing **1** (20%) and the chlorophosphide $[U(Cp^*)_2(PPh_2)Cl]$ (60%); the latter was an intermediate in the synthesis of **1**. The same reactions in THF did not afford compound **1**; the NMR spectra exhibited broad resonances, suggesting the formation of some uranium(III) species. The capacity of alkali metal phosphides to act as reducing agents towards uranium has been shown previously in the reactions of $LiP(SiMe_3)_2$ with $[U(Cp^*)_2Cl_2]$ [8] or $[U(C_5H_3\{SiMe_3\}_2)_2Cl_2]$ in THF [10], leading, respectively to $[U(Cp^*)_2Cl(THF)_x]$ and $[U(C_5H_3\{SiMe_3\}_2)_2(\mu\text{-}Cl)_2Li(THF)_2]$, and also in the attempted synthesis of $[U(Cp)_3(PPh_2)]$ from $[U(Cp)_3Cl]$ and $KPPh_2$ in THF [6]. The triscyclopentadienyl compound $[U(Cp)_3(PPh_2)]$ was obtained in a 60% yield by treatment of $[U(Cp)_3Cl]$ with the less reducing $LiPPh_2$ in benzene, but it could not be isolated in pure form, free from LiCl and some decomposition products [6].

2.2. Synthesis from alkyl precursors

In the search of a straightforward route to bispentamethylcyclopentadienyl uranium diphenylphosphide compounds, and in order to avoid the problems encountered with $LiPPh_2$, we considered the reactions of alkyl precursors with $HPPh_2$ (Scheme 1). The reaction of $[U(Cp^*)_2(Me)_2]$ with two equivalents of $HPPh_2$ in toluene cleanly afforded the first uranium bisphosphide $[U(Cp^*)_2(PPh_2)_2]$ **1** in almost quantitative yield; after 30 h at 65°C, the solution was evaporated to dryness and the dark brown powder of **1** extracted in pentane. The synthesis of **1** occurred via the phosphidomethyl intermediate $[U(Cp^*)_2(PPh_2)(Me)]$ **2** which was isolated as an orange powder in a 96% yield from the reaction of $[U(Cp^*)_2(Me)_2]$ with one equivalent of $HPPh_2$. Complex **2** was also obtained by comproportionation of **1**



Scheme 1. Synthesis of complexes **1**–**4**. All reactions in toluene ([a]in THF-d^8).

and $[U(Cp^*)_2(Me)_2]$. Strictly controlled temperature and reaction times were necessary for the selective formation of **2** (see Section 4) because of its easy conversion into the metallacycle $[U(Cp^*)_2(PPh\{o\text{-}C_6H_4\})]$ **3** with elimination of methane. Thermolysis of **2** was a very clean reaction which gave **3** in an 81% yield, after 24 h in refluxing toluene; **3** was isolated as a dark orange powder after extraction in pentane. Such intramolecular alkanolysis reactions have been previously encountered in actinide chemistry, in particular with the synthesis of $[An(Cp^*)_2(\eta^2\text{-}CH_2SiMe_2P\{SiMe_3\})]$ by thermal decomposition of $[An(Cp^*)_2(Me)(P\{SiMe_3\}_2)]$ [8]. Treatment of **3** with $HPPh_2$ in benzene gave **1** in a quantitative yield (NMR experiment).

2.3. Synthesis from amide precursors

Although protonolysis of U–C bonds with $HPPh_2$ was successful for the preparation of complexes **1** and **2**, this method did not allow the isolation of $[U(Cp)_3(PPh_2)]$ from $[U(Cp)_3R]$ (R = Me, Ph) and Zanella et al. examined the reactions of $HPPh_2$ with amide precursors [6]. Treatment of $[U(Cp)_3(NEt_2)]$ with diphenylphosphine in THF gave a non identified compound, but $[U(Cp)_3(PPh_2)]$ was isolated pure, in a 45% yield, from $[U(Cp)_2(NEt_2)_2]$; the mechanism of this reaction was not elucidated. In contrast, we found that $[U(Cp^*)_2(NMe_2)_2]$ was inert towards $HPPh_2$ in THF at 20°C or in refluxing benzene; uncharacterized compounds were obtained after 3 days in refluxing THF.

Zanella et al. also reported that $[U(NEt_2)_4]$ reacted with $HPPh_2$ to give $[U(NEt_2)_3(PPh_2)]$, without giving any details [6]; we confirm this result and present the synthesis and characterization of this unique amidophosphide complex of uranium in the Section 4. It is noteworthy that $[U(NEt_2)_3(PPh_2)]$ was stable in the presence of an excess of $HPPh_2$; this feature, as well as the distinct reactivity of $[U(Cp)_2(NEt_2)_2]$ and $[U(Cp^*)_2(NMe_2)_2]$, indicate that reaction of a uranium amide with diphenylphosphine is strongly influenced by steric and electronic factors.

Reactions of $[U(NEt_2)_3(PPh_2)]$ with C_5Me_5H and $[NEt_3H][BPh_4]$ gave, respectively $[U(Cp^*)(NEt_2)_3]$ [11] and $[U(NEt_2)_3][BPh_4]$ [12] in an almost quantitative yield (NMR experiments), indicating that the U–P bond is more reactive than the U–N bond.

2.4. Reduction reactions of $[U(Cp^*)_2(PPh_2)_2]$

Complex **1** reacted with $LiPPh_2$ in toluene to give unidentified products, resulting presumably from reduction of the U(IV) centre. In the presence of an excess of LiCl, **1** was completely transformed in THF into the U(III) compound $[U(Cp^*)_2Cl(THF)_x]$ [13]. This reaction likely proceeded by substitution of the phosphide

ligands of **1**, giving $[U(Cp^*)_2Cl_2]$, followed by reduction with $LiPPh_2$. Such a detrimental effect of the alkali metal halide on chemical metathesis has already been noted [14]. These results would account for the difficulties encountered during the preparation of **1** by treatment of $[U(Cp^*)_2Cl_2]$ with $LiPPh_2$. It is also noteworthy that the complexes $[U(\{Me_2PCH_2CH_2\}_2P)_4]$ [5] and $[U(Cp^*)_2(P\{SiMe_3\}_2)(Cl)]$ [8] could be prepared by treatment of chloride precursors with the potassium salt, but not the lithium salt of the phosphide ligand, as already mentioned in Section 2.1; reduction and/or lower yields were observed with the lithium reagent. This difference would be related with the lower solubility of KCl versus that of LiCl, favouring a cleaner and more complete reaction.

Unexpectedly, **1** reacted with $TlBPh_4$ in THF to give the U(III) cation $[U(Cp^*)_2(THF)_2]^+$ [15] (quantitative yield by NMR). Similar treatment of $[U(NEt_2)_3(PPh_2)]$ led to the quantitative formation of $[U(NEt_2)_3][BPh_4]$ [12]. It is possible that these reactions occurred by initial oxidation of the neutral complexes, giving the corresponding U(V) cations which were not stable towards reductive elimination of $Ph_2P–PPh_2$. Similar behaviour of uranium(V) amide complexes was previously observed [16].

Reduction of **1** with KH in toluene smoothly afforded the corresponding uranium(III) anionic compound $K[U(Cp^*)_2(PPh_2)_2]$ **4**; after stirring for 24 h at room temperature, the excess KH was filtered off and the solution was evaporated, leaving the dark orange powder of **4** in a 96% yield. Reduction of **1** by means of Na(Hg) in THF also gave **4** which was converted back into **1** by treatment with $TlBPh_4$ (NMR experiments). Compound **4** was quite stable, showing no sign of decomposition after 2 days at 20°C in solution or in the solid state.

3. Conclusion

The results reported here confirm the observations of other authors on the problems encountered during the synthesis of uranium phosphide complexes. The difficulties in isolating such compounds arise from the methods of preparation rather than from an inherent instability. In particular, the classical metathetical exchange between a uranium halide and a alkali metal phosphide would often suffer from further reduction reactions of the expected product. A better route to uranium diphenylphosphide derivatives is the reaction of alkyl or amide precursors with $HPPh_2$. In the series of the bispentamethylcyclopentadienyl compounds, $[U(Cp^*)_2(PPh_2)_2]$ **1** and $[U(Cp^*)_2(PPh_2)(Me)]$ **2** were thus prepared in almost quantitative yields from $[U(Cp^*)_2(Me)_2]$; one electron reduction of **1** cleanly afforded $K[U(Cp^*)_2(Me)_2]$ **4**, the first uranium(III) phosphide complex.

4. Experimental details

4.1. General methods

All preparations and reactions were carried out under argon (less than 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. Deuterated solvents were dried over Na–K alloy.

Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The ^{1}H-NMR spectra were recorded on a Bruker DPX 200 instrument and were referenced internally using the residual protio solvent resonances relative to TMS (δ 0). Analytical and NMR data are given in Table 1.

The compound $HPPh_2$ (Fluka) was used without purification. The compounds $LiPPh_2$ [5], $[U(Cp^*)_2Cl_2]$, $[U(Cp^*)_2(Me)_2]$ [17] and $[U(NEt_2)_4]$ [18] were synthesized by published methods.

4.2. Reactions of $[U(Cp^*)_2Cl_2]$ with $LiPPh_2$

(a) An NMR tube was charged with $[U(Cp^*)_2Cl_2]$ (7.5 mg, 12.9 μmol) and $LiPPh_2$ (2.5 mg, 12.9 μmol) in benzene-d_6 (0.3 ml). After 1.5 h at 20°C, the spectrum revealed the formation of $[U(Cp^*)_2(PPh_2)Cl]$ (60%), **1** (20%) and other unidentified compounds. The chlorophosphide compound was characterized by NMR; δ 13.54 (30 H, Cp*), −4.93 (4 H, t, $J = 7$ Hz, *m*-Ph), −5.86 (2 H, t, $J = 7$ Hz, *p*-Ph), −46.43 (4 H, d, $J = 7$ Hz, *o*-Ph).

(b) An NMR tube was charged with $[U(Cp^*)_2Cl_2]$ (6.3 mg, 10.9 μmol) and $LiPPh_2$ (4.2 mg, 21.8 μmol) in benzene-d_6 (0.3 ml). After 1.5 h at 20°C, the spectrum revealed the formation of **1** in ca. 60% yield with 3% of $[U(Cp^*)_2Cl_2]$ and other unidentified compounds.

4.3. Synthesis of $[U(Cp^*)_2(PPh_2)_2]$ *1*

A round-bottomed flask was charged with $[U(Cp^*)_2(Me)_2]$ (156 mg, 0.29 mmol) and $HPPh_2$ (0.1 ml, 0.58 mmol) in toluene (25 ml). The reaction mixture was heated at 65°C for 30 h and the orange solution turned dark brown. The solvent was evaporated off and **1** was extracted in pentane (20 ml) and isolated as a brown powder after drying under vacuum (252 mg, 99%). The reaction was monitored by NMR and **2** was found to be an intermediate.

Another experiment was carried out with a sample of $[U(Cp^*)_2(Me)_2]$ containing traces of LiCl; in that case, a mixture of **1** and $[U(Cp^*)_2(PPh_2)Cl]$ was obtained.

Table 1
Analytical and ^{1}H-NMR data for the complexes

Compound	Analyses (%)[a]	NMR data[b]
1 $[U(Cp^*)_2(PPh_2)_2]$	C 59.85 (60.15), H 5.6 (5.75), P 7.2 (7.05)	12.17 (30 H, Cp*), 1.39 (8 H, t, *m*-Ph), −0.52 (4 H, t, *p*-Ph), −28.29 (8 H, d, *o*-Ph)
2 $[U(Cp^*)_2(PPh_2)(Me)]$	C 55.7 (55.95), H 6.1 (6.1), P 4.2 (4.35)	11.08 (30 H, Cp*), −3.86 (2 H, t, *p*-Ph), −4.08 (4 H, t, *m*-Ph), −41.04 (4 H, d, *o*-Ph), −160.3 (3 H, Me)
3 $[U(Cp^*)_2(PPh\{o\text{-}C_6H_4\})]$	C 55.2 (55.5), H 5.8 (5.7), P 4.5 (4.45)	4.58 (30 H, Cp*), 8.93 (1 H, t, *m*- or *p*-C_6H_4), 4.22 (1 H, t, *m*- or *p*-C_6H_4), 2.99 (1 H, d, *o*- or *m′*-C_6H_4), 2.81 (2 H, t, *m*-Ph), 0.50 (1 H, t, *p*-Ph), −6.56 (1 H, d, *o*- or *m′*-C_6H_4), −16.11 (2 H, d, *o*-Ph).
4 $K[U(Cp^*)_2(PPh_2)_2]$	C 57.4 (57.6), H 5.6 (5.5), P 6.9 (6.75)	0.07 (30 H, Cp*), 3.60 (8 H, *m*-Ph), 2.81 (4 H, t, *p*-Ph), −10.46 (8 H, *o*-Ph)
$[U(NEt_2)_3(PPh_2)]$	C 45.0 (45.05), H 6.35 (6.3), P 4.75 (4.85)	10.94 (4 H, d, *o*-Ph), 6.59 (4 H, t, *m*-Ph), 5.66 (12 H, CH_2), 4.15 (2 H, t, *p*-Ph), −5.34 (18 H, CH_3)

[a] Analytical data given as found (calc.) (%).

[b] At 23°C in benzene-d_6. Data given as chemical shift δ (relative integral, multiplicity, assignment); the coupling constants J are equal to 6–7 Hz and when not specified, the signal is a singlet with half-height width between 10 and 30 Hz.

4.4. Synthesis of $[U(Cp^*)_2(PPh_2)(Me)]$ **2**

(a) A round-bottomed flask was charged with $[U(Cp^*)_2(Me)_2]$ (312 mg, 0.58 mmol) and $HPPh_2$ (0.1 ml, 0.58 mmol) in toluene (25 ml). The reaction mixture was heated at 110°C for 1 h and then at 85°C for 2.5 h; the orange solution turned dark orange. The solvent was evaporated off and the product was extracted in pentane (20 ml); after drying under vacuum, **2** was isolated as a dark orange crystalline powder (395 mg, 96%).

(b) An NMR tube was charged with **1** (5.9 mg, 6.8 μmol) and $[U(Cp^*)_2(Me)_2]$ (3.7 mg, 6.8 μmol) in benzene-d_6 (0.3 ml). After 8 h at 65°C, the spectrum showed the presence of **2** (77%), **1** (9%), $[U(Cp^*)_2(Me)_2]$ (9%) and **3** (5%).

4.5. Synthesis of $[U(Cp^*)_2(PPh\{o\text{-}C_6H_4\})]$ **3** and its reaction with $HPPh_2$

(a) A round-bottomed flask was charged with **2** (389 mg, 0.55 mmol) in toluene (20 ml). The orange solution was heated at 110°C for 24 h and turned dark brown. The solvent was evaporated off and the product was extracted in pentane (20 ml). After evaporation to dryness, **3** was isolated as a dark brown powder (308 mg, 81%).

(b) Complex **3** was obtained directly from $[U(Cp^*)_2(Me)_2]$ (310 mg, 0.57 mmol) in an almost quantitative yield (394 mg), by treatment with one equivalent of $HPPh_2$ (0.1 ml) in toluene (25 ml) at 110°C for 24 h.

(c) An NMR tube was charged with **3** (14.3 mg, 20.7 μmol) in benzene-d_6 (0.3 ml) and $HPPh_2$ (3.6 μl, 20.7 μmol) was added via a microsyringe. After 24 h at 65°C, the spectrum showed that **3** was completely transformed into **1**.

4.6. Reactions of **1** with LiCl and $TlBPh_4$

(a) An NMR tube was charged with **1** (4.2 mg, 4.8 μmol) and LiCl (0.5 mg, 12 μmol) in THF-d_8 (0.3 ml). After 15 min at 20°C, the spectrum showed that **1** was completely transformed into $[U(Cp^*)_2Cl(THF)_x]$.

(b) An NMR tube was charged with **1** (5.9 mg, 6.7 μmol) and $TlBPh_4$ (3.5 mg, 6.7 μmol) in THF-d_8 (0.3 ml). After 40 min at 20°C, the spectrum showed that **1** was completely transformed into $[U(Cp^*)_2(THF)_2][BPh_4]$.

4.7. Synthesis of $K[U(Cp^*)_2(PPh_2)_2]$ **4** and its reaction with $TlBPh_4$

(a) A round-bottomed flask was charged with **1** (448.2 mg, 0.51 mmol) and KH (53 mg, 1.32 mmol) in toluene (35 ml). The mixture was stirred for 24 h at 20°C. The dark orange solution was filtered and evaporated, leaving **4** as a dark orange microcrystalline powder (449 mg, 96%).

(b) An NMR tube was charged with **1** (5.0 mg, 5.7 μmol) and 1% Na(Hg) (10.9 mg, 9.1 μmol of Na) in THF-d_8 (0.3 ml). After 30 min at 20°C, the spectrum showed that **1** was completely transformed into **4**.

(c) An NMR tube was charged with **4** (4.8 mg, 5.2 μmol) and $TlBPh_4$ (2.7 mg, 5.2 μmol) in THF-d_8 (0.3 ml). After 15 min at 20°C, the spectrum showed that **4** was completely transformed into **1**.

4.8. Synthesis of $[U(NEt_2)_3(PPh_2)]$

A round-bottomed flask was charged with $[U(NEt_2)_4]$ (1959 mg, 3.72 mmol) in pentane (35 ml) and $HPPh_2$ (647 μl, 3.72 mmol) was added via a syringe. After 2 h at 20°C, the dark orange solution was filtered, evaporated to dryness, and $[U(NEt_2)_3(PPh_2)]$ was isolated as a dark orange microcrystalline powder (2308 mg, 97%).

4.9. Reactions of $[U(NEt_2)_3(PPh_2)]$ with $TlBPh_4$, $[NEt_3H][BPh_4]$ and C_5Me_5H

(a) An NMR tube was charged with $[U(NEt_2)_3(PPh_2)]$ (7.1 mg, 11.1 μmol) and $TlBPh_4$ (5.8 mg, 11.1 μmol) or $[NEt_3H][BPh_4]$ (4.7 mg, 11.1 μmol) in THF-d_8 (0.3 ml). After 15 min at 20°C, the spectra showed that $[U(NEt_2)_3(PPh_2)]$ was completely transformed into $[U(NEt_2)_3][BPh_4]$.

(b) An NMR tube was charged with $[U(NEt_2)_3(PPh_2)]$ (15.73 mg, 24.6 μmol) and C_5Me_5H (7.7 μl, 49.2 μmol) in benzene-d_6 (0.3 ml). After 2.5 h at 80°C, the spectrum showed that $[U(NEt_2)_3(PPh_2)]$ was completely transformed into $[U(Cp^*)(NEt_2)_3]$.

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