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CYCLOPENTADIENYLURANIUM(IV) COMPLEXES CONTAINING PHOSPHIDO AND/OR AMIDO LIGANDS: ACCESS TO THE NEW COMPLEX $(C_5H_5)_3UP(C_6H_5)_2$ *

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Summary

The first organoactinide complex involving a phosphido ligand, Cp_3UPPh_2 ($Cp = \eta^5\text{-}C_5H_5$, $Ph = C_6H_5$), has been prepared by several routes, the best of which involves the reaction of equimolar quantities of $Cp_2U(NEt_2)_2$ and $HPPh_2$. The complex Cp_3UPPh_2 is also formed on treatment of the new compounds $(NEt_2)_3UPPh_2$ and $CpU(NEt_2)_3$ with HCp and PPh_2, respectively. The by-products containing both amido and phosphido ligands, e.g. $(NEt_2)_2U(PPh_2)_2$, $CpU(NEt_2)_2PPh_2$ and $Cp_2U(NEt_2)(PPh_2)$, are very unstable. The direct U–P bond in Cp_3UPPh_2 is very reactive towards all types of chemically unsaturated or (proton) acidic molecules. The MS-, NIR/VIS- and ^1H NMR-spectroscopic data show that the virtually free electron pair of the P atom is notably less involved in the U–P bonding than, e.g., the corresponding electron pair of the related amido complexes Cp_3UNEt_2 and Cp_3UNPh_2.

Introduction

The U–X bond length in organouranium(IV) complexes of the general type Cp_3UX is known to display significant variability; e.g. when X is bonded via one carbon atom in a η^1-fashion, the crystallographically determined U–C bond distances range from 229 to 254 pm [2]. The U–N distances in η^1-N-bonded Cp_3U derivatives show an even larger variation (206 to ca. 267 pm [3]). Moreover, another aspect of variability is revealed by the fact that the (almost certain) η^1-coordination of $X = NC_4H_4$ = pyrrolyl [4a] is in contrast to the η^2-coordination of $X = N_2C_3H_3$

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= pyrazolyl [4b]. In view of the U–N bond length of 229 pm for $X = N(C_6H_5)_2$ [5], it is not unreasonable to expect an even shorter U–N bond length for $X = N(C_2H_5)_2$ [6], and, consequently, some multiple bonding character [7]. There are some data for compounds with X = Cl, Br and I, and some unpublished results for X = SR (R = alkyl or phenyl [8]), but there is no information on the behaviour of ligands involving other third- or fourth-row elements. In the present paper we concentrate on the preparation and general properties of the new complex Cp_3UPPh_2 (**1**). In contrast to some lanthanide complexes [9], no 5*f*-element complexes involving the potentially bridging and frequently rather reductive [10] phosphido ligand PR_2 have so far been reported [11]. Very few complexes involving direct U–P bonds are known; recent examples are mainly phosphine adducts [12,40] and a unique phosphinidene complex [13].

Preparation of Cp_3UPPh_2 (1)

As indicated by Table 1, the preparation of analytically pure **1** is less straightforward than the synthesis of most other Cp_3UX-systems. Thus for reaction nr. 1, for which the yield of crude **1** is largest, there are problems in separating the product from the starting material and the formed LiCl, as well as from some decomposition products of **1**. In reaction 2, in which, on the other hand, consumption of the reactants is complete, the yield of crude **1** does not exceed 40% because of increased thermal decomposition. Similar difficulties were encountered in reactions 3–9, involving incomplete reaction and/or unwanted subsequent processes. Reactions 5 and 6, for instance, lead almost exclusively to products involving uranium(III). Since complex **4** ($X = C_6H_5$) reacts with the phosphine $HPPh_2$ to give about 10–20% of **1** (reaction 9), it seemed likely that **4** could be replaced by the similarly reactive [7,14] amide **5** ($X = NEt_2$). Complex **5** was previously mentioned only briefly as a

TABLE 1

SUMMARY OF EXPERIMENTS AIMED AT OPTIMIZING THE PREPARATION OF THE COMPLEX Cp_3UPPh_2, **1**: Cp_3UPPh_2; **2**: Cp_3UCl; **3**: Cp_3UMe; **4**: Cp_3UPh; **5**: Cp_3UNEt_2; **6**: $Cp_2U(NEt_2)_2$.

Reaction	Reactants	Solvent	Conditions	Production of crude 1 (%)	Consumption of reactants
1	**2**, $LiPPh_2$, 1/1	benzene, toluene	room temp., 3–4 h	60	in part
2	**2**, $LiPPh_2$, 1/1	benzene	reflux, 3 h	40	complete
3	**2**, $LiPPh_2$, 1/2	benzene, toluene	room temp., 3–4 h	24	in part [a]
4	**2**, $LiPPh_2 \cdot$dioxane 1/1	THF	room temp., 3 d	–	complete [b]
5	**2**, $KPPh_2 \cdot 2$ dioxane	benzene	room temp., 20 h	–	complete [c]
6	**2**, $KPPh_2 \cdot 2$ dioxane	THF	room temp., 20 h	–	complete [d]
7	**3**, $HPPh_2$, 1/1	benzene, toluene	room temp., 4 h		none
8	**3**, $HPPh_2$, 1/1	benzene, toluene	reflux, 2 h	traces	in part
9	**4**, $HPPh_2$, 1/1	toluene	reflux, 1.5 h	10–20	in part [a]
10	**5**, $HPPh_2$, excess 1/3	THF	room temp., 5–6 d room temp., 4 d	–	in part [e]
11	**6**, $HPPh_2$, 1/1; 1/2	n-hexane		45 [f]	in part

[a] Unidentified decomposition products. [b] Formation of Cp_3UOR derivatives from THF and dioxane. [c] Presence of Cp_3U^{III} derivatives. [d] Presence of Cp_3U^{III} derivatives (confirmed by NIR-VIS-spectra). [e] Formation of one unidentified product. [f] Analytically pure.

by-product of the preparation of $Cp_2U(NEt_2)_2$ (**6**) [4], but we recently made it in excellent yields during studies of the reaction of $U(NEt_2)_4$ with HCp [14]. Unexpectedly, however, complex **1** was not observed as a product of reaction 10, although **5** does react with $HPPh_2$ to give another unidentified product.

As a modification of reaction 10, the preparation of **1** was also approached by the proposed two-step route indicated in eq. 1 and 2.

$$Cp_2U(NEt_2)_2 + HPPh_2 \xrightarrow[-HNEt_2]{(1/1)} Cp_2U(NEt_2)(PPh_2) \text{ (assumed first step)} \qquad (1)$$

$$Cp_2U(NEt_2)(PPh_2) + HCp \xrightarrow[-HNEt_2]{(1/1)} Cp_3UPPh_2 \text{ (assumed second step)} \qquad (2)$$

Surprisingly, however, **1** was obtained as a red-brown precipitate in the first step during 5–6 days (cf. reaction 11 of Table 1). As **1** turns out to be the only component insoluble in n-hexane, reaction 11 provides optimal conditions for access to analytically pure **1**. The ^1H NMR spectrum of the mother liquor from reaction 11 showed six resonances with relative intensities and multiplet structures compatible with the assumed intermediate $Cp_2U(NEt_2)(PPh_2)$ (**7**), along with the similarly intense resonances of the two reactants (Table 4). Relative to those of the other diethylamidouranium complexes listed in Table 4, the two ethyl proton resonances of the anticipated (amido-)(phosphido-)uranium complex **7** are shifted strongly towards lower fields. Pure **7** has not so far been obtained.

In view of the rather facile formation of **1** from **6** and $HPPh_2$ without use of HCp (eq. 2), the assumed intermediate **7** must either undergo ligand redistribution more readily than **5** (eq. 3) or react with additional $HPPh_2$ to give the corresponding bis-phosphido complex before a similar ligand redistribution step ("dismutation") takes place (eq. 4):

$$2Cp_2U(NEt_2)(PPh_2) \rightarrow \mathbf{1}\downarrow + \underset{(\mathbf{8})}{CpU(NEt_2)_2(PPh_2)} \qquad (3)$$

$$2Cp_2U(NEt_2)(PPh_2) \xrightarrow[-2HNEt_2]{2HPPh_2} \{2Cp_2U(PPh_2)_2\} \rightarrow \mathbf{1}\downarrow + CpU(PPh_2)_3 \qquad (4)$$

To distinguish between these alternative pathways, attempts were made to prepare compound **8** of eq. 3 by the reactions shown in eq. 5 and 6:

$$(NEt_2)_3UPPh_2 + HCp \xrightarrow[-HNEt_2]{(1/1)} \mathbf{8}\ (?) \qquad (5)$$

$$CpU(NEt_2)_3 + HPPh_2 \xrightarrow[-HNEt_2]{(1/1)} \mathbf{8}\ (?) \qquad (6)$$

In both experiments, however, instead of **8** complex **6** was obtained in good yield (together with smaller quantities of **7**), suggesting that the mixed-ligand system **8** itself readily undergoes "dismutation" (eq. 7):

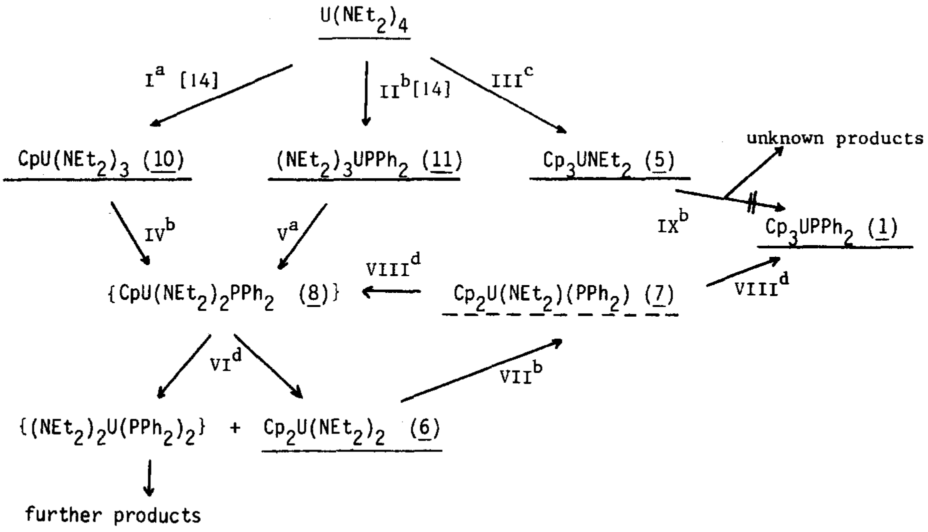
$$2CpU(NEt_2)_2PPh_2 \rightarrow \mathbf{6} + \underset{(\mathbf{9})}{(NEt_2)_2U(PPh_2)_2} \qquad (7)$$

For confirmation of this latter assumption independent synthesis of the unknown complex $(NEt_2)_2U(PPh_2)_2$ would be desirable, but reaction of $(NEt_2)_3UPPh_2$ (**11**) with additional $HPPh_2$ did not give any well-defined single product. The starting complexes of eq. 5 and 6 (**11** and **10**) are readily accessible from $U(NEt_2)_4$ and $HPPh_2$ and HCp, respectively [14].

Scheme 1 depicts the available information on the formation of **1** from other uranium complexes containing NEt_2 and/or PPh_2 ligands. It should be pointed out that the formation of **1** by the routes depicted in Scheme 1 represent one of the relatively rare cases in which the build-up of a Cp_3UX moiety occurs spontaneously by "dismutation" of a $CpUX_3$ or Cp_2UXY species [15]. It is noteworthy that complex **6** reacts with alcohols (ROH) to give essentially Cp_3UOR and $Cp_nU(OR)_{4-n}$ ($n \leqslant 2$) unless R is rather bulky [16]. The driving force of all the steps of Scheme 1 except VI and VIII is probably associated with the rather high proton acidities of both HCp ($pK_a \approx 18.0$ [17] and $HPPh_2$ ($pK_a \approx 21.7$ [18]) which exceed that of $HNEt_2$ by several orders of magnitude ($pK_a \approx\ \geqslant 27$ [19]). In view of the similarly much weaker acidity of the aliphatic phosphine $HPEt_2$, ($pK_a \approx 33.7$ [18]) realization of the reactions depicted in Scheme 1 after replacement of $HPPh_2$ by $HPEt_2$ seems unlikely. The proton acidity of pentamethylcyclopentadiene, $HCp^{\star}$ ($pK_a \approx 26.1$ [17]), is notably reduced relative to that of HCp, and $U(NEt_2)_4$ has been reported to be transformed exclusively into $Cp^{\star}U(NEt_2)_3$ even by excess $HCp^{\star}$ [20]. On the other hand, **6** has been reported to react in benzene with $HMoCp(CO)_3$ to give $UCp_2[MoCp(CO)_3]_2$ [21].

General and spectroscopic properties of Cp_3UPPh_2

Complex **1** is a light brown, very sensitive powder (pyrophoric at the air), non-volatile in vacuo, and thermally unstable above ca. 70°C, yielding P_2Ph_4 as one decomposition product. **1** is sufficiently soluble for NMR spectroscopic purposes and the solutions are stable (at least in the absence of light) in aromatic hydro-



SCHEME 1. The various reaction steps relevant to formation of **1**, and their potential interrelation. (a) reaction with HCp (1/1); (b) reaction with $HPPh_2$ (1/1); (c) reaction with HCp (1/3); (d) "dismutation"; fully underlined formulae indicate isolated compounds, broken underlining denotes probably metastable species, so far only detected spectroscopically; formulae in { } denote postulated intermediates.

carbons and THF, but almost insoluble e.g. in n-hexane. Reaction takes place immediately with water, alcohols, acetone, acetonitrile (vide infra), and probably many other proton acidic or chemically unsaturated solvents. The moderate solubility of **1** in C_6H_6 has so far precluded the determination of the molecular weight. However, in view of recent conclusions drawn for Cp_3UX systems on the basis of the "SAS-rule" [7] it seems likely that formation of dimers or oligomers of **1** involving a PPh_2 bridge would be sterically inhibited.

The mass spectrum (MS) of **1** (Table 2) clearly reflects the weakness of the U–P bond both in the neutral molecule and in its molecular ion M^+, neither the cationic fragment containing the PPh_2 group being notably intense. In Table 2 the MS results for various different Cp_3UX systems ($X = I$, NEt_2 and OPh) are compared with those of **1**. In particular, by comparison of the relative abundances of the "key fragments" Cp_3UX^+, Cp_2UX^+ and Cp_3U^+, which are extremely low for Cp_3UX^+ and Cp_2UX^+ and high for Cp_3U^+, for $X = PPh_2$ and alkyl, but not for X = halide, OR and NR_2, some similarity between the U–C and the U–P bond may be inferred. Morss et al. have recently confirmed by calorimetric studies that for the series $Cp^\star_2ThX_2$ ($Cp^\star = C_5Me_5$) the Th–X bond strength increases in the order X = alkyl $< NR_2 <$ OR [22].

The vibrational spectrum between 400 and 3500 cm^{-1} of a Nujol mull of **1** is dominated by the usual absorption bands of phenyl and η^5-cyclopentadienyl groups, but an absorption at 1435 cm^{-1} is consistent with the expected $\nu(PC)$ vibration [23].

The electronic absorption spectrum of **1** (between ca. 6000 and 20000 cm^{-1} $\hat{=}$ NIR/VIS-range) is quite similar to those of e.g., the complexes Cp_3UNEt_2 and Cp_3UOPh (the latter was obtained from equimolar amounts of **5** and phenol [14]), and so seems to be in good accordance with the NIR/VIS spectra of pseudotetrahedral Cp_3UX systems (Fig. 1). However, the spectrum of **1** uniquely displays a relatively broad moderately intense extra absorption around 12500 cm^{-1}, which is tentatively assigned to an intramolecular charge transfer, and may account for the light sensitivity of dissolved **1**. It should be recalled that phosphorus is one of the least electronegative elements [24] which have so far been coordinated to the uranium atom of Cp_3UX systems and this feature would also favour the appearance of a rather low-lying charge transfer band [11]. The main products obtained from the reactions 5 and 6 of Table 1, on the other hand, have NIR/VIS spectra more reminiscent of those reported for Cp_3U^{III} derivatives [25]. In Table 3 the individual absorption maxima obtained after reduction of Cp_3UCl in two different ways are compared. Reaction of **1** with carbon monoxide (vide infra [7]) also seems to generate a U^{III} species, while exposure to traces of dioxygen leads to a slightly modified $Cp_3U^{IV}X$ type spectrum devoid of the relatively broad specific absorption of **1** around 12500 cm^{-1}.

In the ^1H NMR spectrum of **1** only the four expected resonances of the Cp and C_6H_5 groups are apparent (Table 4). The pronounced deviations of the observed shifts from positions typical of diamagnetic compounds confirm that **1** is strongly paramagnetic. Probably as a result of the direct attachment of the P atom to the paramagnetic centre, any coupling of the Cp and C_6H_5 protons with the ^{31}P nucleus is quenched. A corresponding result has been reported for the (probably monomeric) complex Cp_2SmPPh_2 [9d], although the influence of the paramagnetic Sm^{III} ion on the magnitude of both the contact and the dipolar contribution of the isotropic shift Δ^{iso} is usually weaker than that of the U^{IV} ion. On the other hand, in case of the

TABLE 2

MASS SPECTRA OF FIVE Cp_3UX-SYSTEMS (COMPARISON OF MOST CHARACTERISTIC FRAGMENTS CONTAINING URANIUM)

Fragment	Cp_3UCH_3		Cp_3UPPh_2		Cp_3UNEt_2		Cp_3UI [a]		Cp_3UOPh	
	m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
Cp_3UX^+	448	2	618	9.5	505	60	560	86.4	526	33.3
Cp_2UX^+	–	–			440	15	495	≡100.0	461	77.8
Cp_3UH^+			434		434	70	–	–	–	–
Cp_3U^+	433	≡100	433	≡100	433	80	433	67.8	433	60.4
$Cp_2UC_3H^+$			405	18	405	6	405	–	–	–
Cp_2UH^+			369		369	80	–	–	–	–
Cp_2U^+	368	80	368	59	358	≡100	368	80.1	368	75.4
$CpUX^+$	–		–	–	–	–	–	–	396	2.5
$CpUC_3H_3^+$			342	4	342	26	342	1.7	–	–
$CpUC_3H^+$			340	16	340	38	340	7.1	–	–
CpU^+	303	8	303	4	303	60	303	18.1	–	–
Cp_2UO^+	–	–	–	–	–	–	–	–	384	3.2
$CpUO^+$	–	–	–	–	–	–	–	–	319	15.4

[a] Data from ref. 41.

similarly paramagnetic complexes $\mathrm{Cp_3UCHP(Ph)}_n\mathrm{(CH_3)}_m$ ($n + m = 3$), which do not have a direct U–P bond, *J*(HCP) 12 Hz for the *o*-phenyl protons [26]. No $^{31}\mathrm{P}$ NMR signal was observed for **1**, in contrast to $\mathrm{Cp_3UCHPPh}_n\mathrm{(CH_3)}_m$, despite numerous attempts. Again, this result matches that for $[\mathrm{Cp_2^*U(OCH_3)}]_2\mathrm{PH}$ [13] and

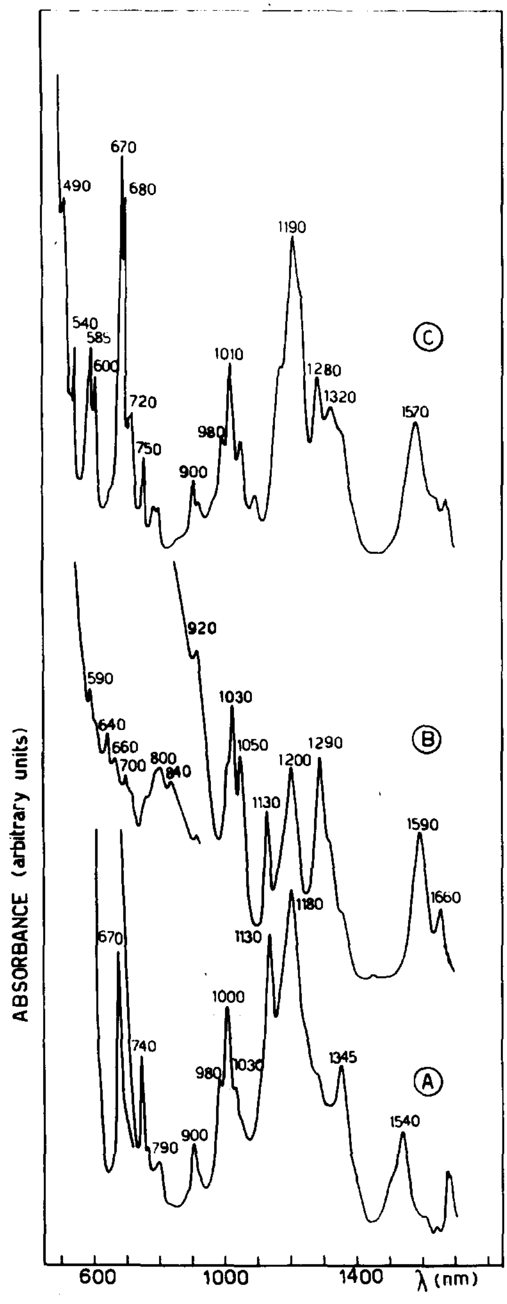


Fig. 1. Comparison of the absorption spectra of three related $\mathrm{Cp_3UX}$ systems (A : X = $\mathrm{NEt_2}$, B : X = $\mathrm{PPh_2}$, C : X = OPh) in the near infrared and visible (NIR-VIS) range.

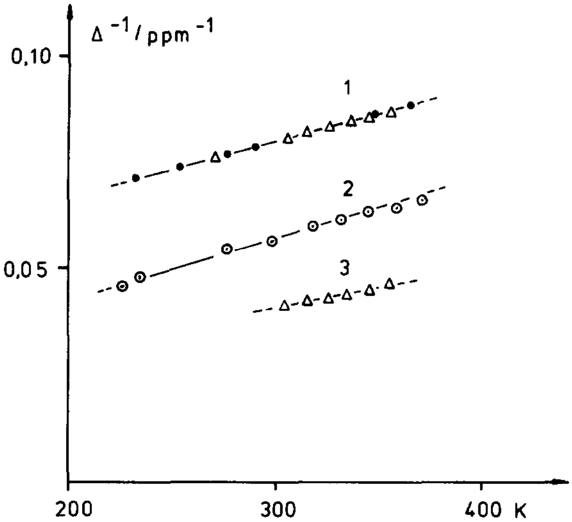


Fig. 2. Temperature dependence of the reciprocal isotropic shifts Δ of pure Cp_3UPPh_2 (curve 1: resonance of C_5H_5, curve 3: resonance of *ortho*-phenyl protons) and Cp_3PPh_2 in the presence of little CH_3CN (curve 2: resonance of C_5H_5). Values of Δ are relative to C_6H_6. Solvents used: ● toluene-d_8; Δ benzene-d_6; ⊙ toluene-d_8/benzene-d_6.

even for the lanthanoid complex, Cp_2SmPPh_2 [9d]. The temperature dependence of the Cp and *o*-phenyl proton resonances of **1** is presented in Fig. 2.

Addition of ca. one drop of deuterated acetonitrile to **1** in a toluene-d_8/benzene-d_6 solution causes a colour change towards yellow-green, and all the ^1H NMR signals of **1** change their positions (Table 4). The Cp proton resonance not only shows a considerable upfield shift, but also displays a clean "Curie–Weiss-like" temperature dependence (i.e. Δ^{-1} increases linearly with T). Formation of an adduct $Cp_3UPPh_2 \cdot NCMe$ of trigonal bipyramidal coordination is therefore less likely than the

TABLE 3

NIR-VIS ABSORPTIONS (in cm^{-1}) OF TWO REDUCTION PRODUCTS FROM $Cp_3U^{IV}Cl$

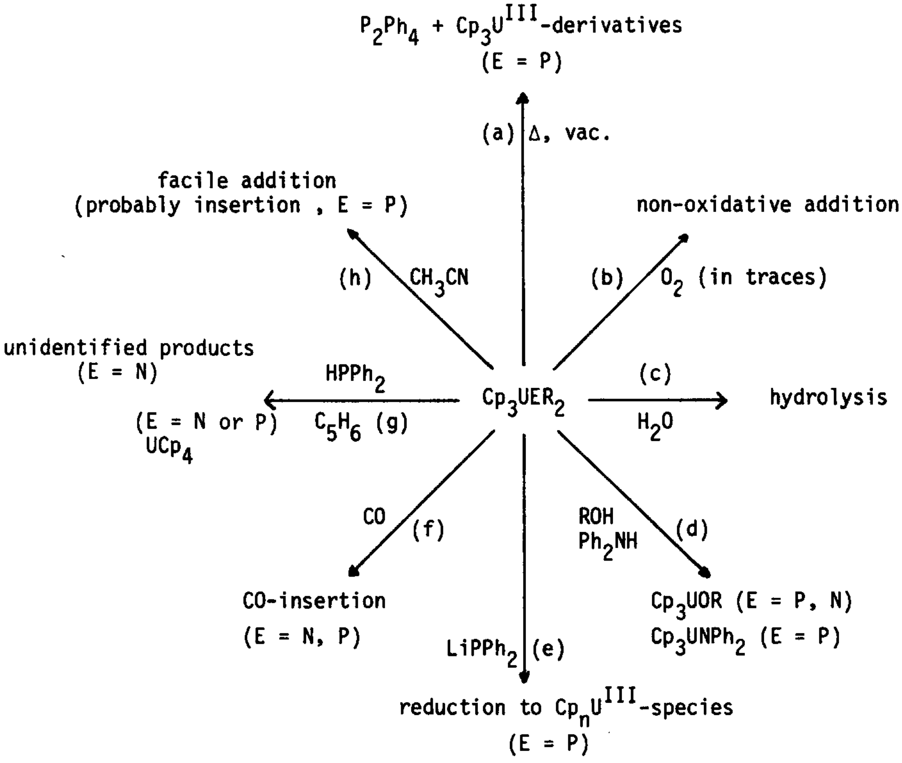
$Cp_3UCl + (LiCH_3)$ exc. in THF [a]	$Cp_3UCl + KPPh_2$ in THF [b]
5306	
	6053, 6667 sh
7236	7296
8117	8118, 8333 sh
9009	9115
	9659 sh
10331	10272 sh
10661	10794
11236	11386
	12160
13386	13600
15129	15350

[a] From ref. 15. [b] This work.

sterically less favourable side-on (*cis*-)coordination of PPh_2 and $NCCH_3$ [7,27], probably via an insertion-type reaction. One possible reaction path might parallel the well-understood insertion of $NCCH_3$ into Cp_3UCHPR_3 [3a]. Addition of CH_3CN to a solution of complex **5** did not cause corresponding changes in the NMR spectrum.

Chemistry of Cp_3UPPh_2 and Cp_3UNEt_2

Scheme 2 depicts the various chemical reactions to which the two complexes Cp_3UER_2 **1** and **5** (i.e. E = P, R = Ph, and E = N, R = Et, respectively) have been subjected. Thermal decomposition (a) probably depends both on the U–E bond strength and the reductive power of the ER_2 ligand, and the complexes mainly give different products. Exposure of solutions of **1** or **5** in C_6H_6 to traces of air (b) results in clear solutions, the ^1H NMR spectra of which show (at 27°C) only one rather intense singlet, at 10.33 ppm, and no resonances indicative of paramagnetically shifted PPh_2 or NEt_2 protons, respectively. Attempts to hydrolyze **1** (c) by oxygen-free D_2O led only to partial dissolution, leaving a green precipitate; the solution had a yellow-green colour and showed one strong ^1H NMR singlet at 20.81 ppm (relative to C_6D_6), ruling out the presence of the expected (deep green) $[Cp_3U(OD_2)_2]^+$ cation ($\sim$ 9.4 ppm [28]). Aliphatic or aromatic alcohols (d) convert **1** and **5** almost quantitatively into the corresponding Cp_3UOR systems, which were identified from their reported ^1H NMR spectra [16]. Phenol gave the new complex Cp_3UOPh [14].



SCHEME 2. Outline of the known reactions of Cp_3UER_2 systems (E = P or N).

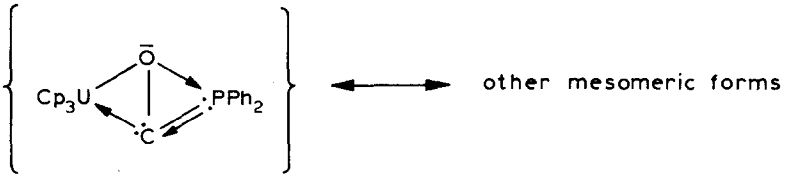
The sufficiently acidic amine $HNPh_2$ (d) converts **1**, but not **5**, into Cp_3UNPh_2 [5]. Free $HPPh_2$ was detected by ^1H NMR after all reactions of the types (a)–(d).

$LiPPh_2$ reduces complex **1** (solvent: C_6D_6 plus a few drops of THF) to at least one Cp_nU^{III} derivative ($n \leqslant 3$), as indicated by a strong Cp proton resonance at 22.63 ppm [25] (solvent-free sample: 20.5 ppm). The resonances of the coordinated PPh_2 group are replaced by the two multiplets characteristic of free Ph_2P–PPh_2. Surprisingly, the similarly rather labile complex Cp_3UCH_3(**3**) remains unchanged on addition of $LiPPh_2$. The stronger reductant $KPPh_2$ reduces even Cp_3UCl (**2**) to Cp_3U^{III} species, without any evidence of intermediately formed **1**. Reduction of **2** by $KPPh_2$ in the presence of either THF or dioxane gives rise to ^1H NMR spectra displaying additional resonances indicative of Cp_3UOR systems (THF: δ(Cp) 25.09 ppm; THF/dioxane: δ(Cp) 24.33 and 24.88 ppm; $\delta(H_\alpha$ of R) -49.64 and -44.64 ppm, respectively). The formation of $Cp_3U^{IV}OR$ compounds via U^{III} species has been reported previously [29].

Migratory insertion of CO (f) into the U–N bond of **5** has been described in detail [7], but the corresponding reaction of **1** with CO has still to be discussed. The ultimately detectable Cp_3U^{III} species could be formed from **1** by a route which also leads to formation of Ph_2P–PPh_2, e.g.

$$2Cp_3U^{IV}PPh_2 \xrightarrow{2CO} Ph_2P\text{–}PPh_2 + \text{so far unspecified } Cp_3U^{III} \text{ species} + \text{other products}$$

Another route might involve the hypothetical intermediate



which could formally rearrange in a number of ways, e.g. by formation of a binuclear phosphine oxide complex, $Cp_3U^{III} \leftarrow \underline{\overline{O}}\text{–}P(Ph_2)C{\equiv}C\text{–}P(Ph)_2\text{–}\underline{\overline{O}} \rightarrow U^{III}Cp_3$ [44]. Complex **5** reacts with $HPPh_2$ (f) (rather surprisingly it does not give **1** (see Scheme 1)), but complex **1** is apparently inert towards this phosphine.

A somewhat unexpected feature is that both **1** and **5** react with traces (i.e., almost equimolar amounts) or dioxygen without any evidence of an immediate increase of the oxidation number of the central metal ((b), vide infra). Attempts to isolate and characterize the primary product(s) of oxygenation, presumably either $(Cp_3U^{IV})_2O$ or $(Cp_3U^{IV})_2O_2$, confirmed that the IR spectra of samples prepared very rapidly and carefully did not show the usual ν(UO) absorption(s) (around 900 cm^{-1}) of uranyl derivatives. However, within less than one hour, the expected ν(UO)-bands emerge progressively from the base line, suggesting that a stepwise oxygenation/oxidation process is occurring. The latter step is apparently promoted by traces of H_2O; the ^1H NMR spectrum of a solution of **1** in "wet" C_6D_6 solution immediately shows two resonances of similar intensity at 10.33 and 10.57 ppm. Very few cases of the oxygenation of organouranium compounds which avoid immediate formation of uranyl species are known: thus, Cp_3U^{III} reacts with O_2 to give $(Cp_3U^{IV})_2O$ [30], and

TABLE 4

^{1}H NMR DATA FOR VARIOUS U^{IV}-COMPLEXES CONTAINING METAL-BONDED NR_2 OR/AND PR_2 GROUPS (solvent: all shifts are relative to C_6D_5H which was used as internal standard and a positive sign indicates a high-field shift; temperature 27°C)

Complex	Resonances		
	C_5H_5	C_2H_5	C_6H_5
Cp_3U-PPh_2 (**1**)	12.36 (s. 15H)		24.45 (d, 4H, *ortho*, *J* 7.4 Hz) 5.60 (t, 4H, *meta*, *J* 7.5 Hz) 7.49 (t, 2H, *para*, *J* 7.4 Hz)
Cp_3U-NPh_2 (**12**)	14.82 (s. 15H)		21.24 (d, 4H, *ortho*, *J* 7.9 Hz) [a]
Cp_3U-PPh_2 + CD_3CN	17.00 (s. 15H)		7.57 (t, 4H, *meta*, *J* 7.9 Hz) 2.19 (t, 2H, *para*, *J* 7.9 Hz) 3.89 (d, 4H, *ortho*, *J* 7.9 Hz)
Cp_3U-NEt_2 (**5**)	19.37 (s, 15H)	6.61 (q, 4H, α-CH_2, *J* 6.0 Hz) 8.54 (t, 6H, β-CH_3, *J* 6.1 Hz)	
$Cp_2U(NEt_2)_2$ (**6**)	21.18 (s, 10H)	−1.40 (q, 8H, α-CH_2, *J* 6.4 Hz) 5.70 (t, 12H, β-CH_3, *J* 6.4 Hz)	
"$Cp_2U(NEt_2)(PPh_2)$" [b] (**7**)	28.90 (s. 10H)	−45.62 (bq, 6H, α-CH_2) *J* 7.5 Hz) −15.85 (bt, 6H, β-CH_3)	12.75 (d, 4H, *ortho*, 2.36 (t, 4H, *meta*, *J* 7.5 Hz) 4.91 (t, 2H, *para*, *J* 7.4 Hz)

[a] Other phenyl resonances undetectable because of signal overlapping. [b] Data from an in-situ reaction mixture.

$[(Me_3Si)_2N]_3U^{III}$ with O_2 to give $[(Me_3Si)_2N]_3U^{V}O$ [31], while in CH_3CN solution Cp_3UCl yields the salt $[Cp_3U^{IV}(NCCH_3)_2]_2[U^{VI}O_2Cl_4]$ [28].

Discussion

To our knowledge, compound **1** is the first representative of the $Cp_3U^{IV}X$ series in which X is bonded to the metal atom via an element less electronegative than carbon (and even hydrogen [24]). While various complexes involving bridging hydride groups such as $Cp_3U(\eta^3$-$H_3BR)$ are known, the simple hydride Cp_3UH has so far not been described in the literature. Since **1** is obtained by steps 1–3 of Table 1 although early *d*-transition metal complexes related to **2** (e.g. $Cp_2Zr^{IV}Cl_2$) are known to be easily reduced by $LiPPh_2$ at ambient temperature [32], our results

TABLE 5

SURVEY OF THE VARIATION OF THE Cp PROTON RESONANCE POSITION OF VARIOUS Cp_3UX SYSTEMS AS A FUNCTION OF THE LIGAND X

Ligand X	Δ(Cp) [a]	Ref.
CH_2Ph	9.9	35
$n\text{-}C_4H_9$	10.3	34
Cl	10.7	
Br	10.9	
SEt	11.8	8b
SPh	11.9	
PPh_2	12.4	this work
$(\eta^3\text{-})H_3BEt$	13.8	36
NPh_2	14.8	this work
OPh	16.0	this work
$CHPPh_2Me$	19.3	37
NEt_2	19.4	this work
OEt	25.6	34
$NCMeCHPPh_2Me$	27.9	3a

[a] Reference C_6H_6, the positive sign indicating upfield shifts.

increase the prospect of devicing preparative routes to Cp_3UX systems with X = PEt_2, $SbPh_2$, $SiPh_3$ etc. Mixed-ligand organolanthanoid complexes involving not only Ln–P bonds [38], but also in one case a well-defined Ln–Si bond, as well as Ln-to-metal bonds, have already been described [39].

Another point of interest concerns the role of the virtually free electron pair of the P-atom of 1. The U–N distance for the homologous complex Cp_3UNPh_2 [5] suggests that its N atom forms a partial N → U π-donor bond by using its electron pair; a still more pronounced π-interaction may be assumed for complex **5** on the basis of extensive ^1H NMR-based findings for the related $(C_5Me_5)_2U(NR_2)_2$ systems [33]. Baker et al. have most recently demonstrated that in early 5*d*-element compounds such as $Cp_2Hf^{IV}(PEt_2)_2$ the PR_2 ligands (R = alkyl and aryl) can generate both M–P single and $M \Leftarrow P$ double bonds [34]. As the total number of metal-shared valence electrons of organoactinide complexes is expected not to be governed by the usual "18-electron rule" of *d*-transition metal complexes, the U–P bond of 1 is expected to match the shorter $Hf \Leftarrow P'$-bond in $Cp_2Hf(PEt_2)(PEt_2)'$ [34], as well as the $U \Leftarrow N$ bonds in $(C_5Me_5)_2U(NR_2)Cl$ systems [33], and the $U \Leftarrow C$ bond in Cp_3UCHPR_3 [2]. Marks et al. have deduced from the U–P bond length of 274.3 pm for the novel complex $[(C_5Me_5)_2U(OMe)_2PH$ [13] that P → U π-donation must take place.

Another criterion for the relative π-donor strength of a η^1-coordinated ligand X is provided by the value of the chemical (or isotropic) ^1H NMR shift Δ of the 15 equivalent Cp ring protons of various Cp_3UX systems. Table 5 documents that Δ(Cp) varies over a rather wide range from ca. 9 to 28 ppm, established π-donating ligands X like OR, $CHPPh_2Me$ and $NCMeCHPPh_2Me$ causing pronounced high-field shifts, while X = alkyl or aryl which have no "free" electron pairs, give rise to the lowest Δ(Cp) values. Comparably low Δ(Cp) values as for the latter group of ligands are, however, also found for X = Cl, Br, SR and PPh_2. On the assumption that an increase of the effective π-donor strength of X is reflected in a concomitant increase of the Δ(Cp) value, it might be concluded that, somewhat surprisingly, only elements of the second row of the periodic table display a pronounced tendency for π-donor bonding with the actinide ion. This hypothesis requires further confirmation, but one encouraging feature is the notable reduction of Δ(Cp) when for, $X = OR$ or NR_2 at least, alkyl groups are replaced by the more π-electron-withdrawing phenyl groups. An almost negligible π-donating ability similarly indicated the heavier halide ligands by the results of a recent crystallographic X-ray study of the two complexes Cp_3UCl and Cp_3UBr (U–Cl 261.4 and U–Br 281.9 pm, respectively [42]).

Experimental

All manipulations of organouranium species were carried out, with rigorous exclusion of oxygen and moisture, in a dinitrogen-filled recirculating glove box (Jahan, France). Dinitrogen (SIAD; prepurified) was passed through a series of columns filled with MnO (supported on vermiculite [43]), and Davison 4 Å sieves (BDH) activated before use. All solvents were purified by standard procedures.

^1H NMR spectra were recorded on a Varian FT 80 A spectrometer. All proton shifts are in ppm relative to C_6D_5H, which was used as internal standard, a positive sign denoting shifts towards higher fields. Infrared spectra (vibrational) were run on a Perkin–Elmer 580 B spectrometer, mostly of Nujol mulls sandwiched between KBr plates in an air-tight sample holder; The UV, VIS and NIR spectra of solutions (10 mm cells) were studied on a Cary 17D spectrophotometer. Mass spectra (E.I. 70 eV) were obtained with a V.G. Organic Ltd. ZAB 2F mass spectrometer. Glass capillaries filled with the sample material inside the glove box were closed off with one drop of an inert, low-boiling solvent (usually n-hexane), and quickly transferred into the spectrometer under a N_2 flow.

Diphenylphosphine, $(C_6H_5)_2PH$, was redistilled in vacuo immediately before use. The complexes, $(C_5H_5)_3UCl$, $(C_5H_5)_3UCH_3$ [7], $(C_5H_5)_3UC_6H_5$ [35] and $(C_5H_5)_2U[N(C_2H_5)_2]_2$ [4a,14] were prepared by published procedures. $(C_5H_5)_3UN(C_2H_5)_2$ was made in much improved yield (up to 76%) starting from UCl_4, $LiN(C_2H_5)_2$ and C_5H_6 [14].

$LiPPh_2 \cdot$ dioxane and $KPPh_2 \cdot 2$dioxane were prepared as previously described [45]. Solvent-free $LiPPh_2$ was obtained from $Li(n\text{-}C_4H_9)$ in n-hexane by adding a dilute equimolar solution of $HPPh_2$ with stirring during 2 h at room temperature. The precipitate was filtered off and washed with several small portions of n-hexane, and dried in vacuo, to give $LiPPh_2$ as a yellow powder. Analytical data: found: C, 74.8; H, 4.9. $C_{12}H_{10}LiP$ calcd.: C, 75.0; H, 5.2%.

Reaction 1 (Table 1). $LiPPh_2$ (1.5 m*M*) was added in portions with rapid stirring during 3–4 h at room temperature to a solution of $(C_5H_5)_3UCl$ (1.5 m*M*) in 20 ml C_6H_6. The brown precipitate was separated from the dark brown solution and washed with several portions of C_6H_6 until the washings were colourless. The volume of the combined brown solutions was reduced to ca. 10 ml and ca. 20 ml of hexane was added. The light brown precipitate was filtered off, washed with n-hexane, and vacuum-dried to give 0.68 g of a solid, which was identified (by ^1H NMR) as a mixture of $(C_5H_5)_3UPPh_2$ (80%) and $(C_5H_5)_3UCl$ (20%).

Reaction 2 (Table 1). Following the above procedure, a suspension of $(C_5H_5)_3UCl$ (1.5 m*M*) and $LiPPh_2$ (1.5 m*M*) in C_6H_6 (20 ml) was refluxed over 3 h. The dark brown solution was filtered, concentrated to ca. 10 ml, and diluted with 35 ml of n-hexane. The precipitate obtained (ca. 0.4 g after drying) contained less $(C_5H_5)_3UPPh_2$ and $(C_5H_5)_3UCl$ than the main product of reaction 1 (The yield of this mixture was $\leqslant$ 10% of that of reaction 1.)

Reaction 3 (Table 1). $(C_5H_5)_3UCl$ (1.5 m*M*) and $LiPPh_2$ (3 m*M*) were stirred in C_6H_6 (20 ml) at room temperature for 3–4 h. Only 25% of the theoretically expected quantity of $(C_5H_5)_3UPPh_2$ was present after the usual work-up as indicated by ^1H NMR spectroscopy, the solid finally isolated appeared to be composed of a $(C_5H_5)_3U^{III}$ species on the basis of the ^1H NMR and NIR/VIS spectroscopic data.

Reaction 4 (Table 1). A solution of $(C_5H_5)_3UCl$ (0.8 m*M*) and $LiPPh_2 \cdot$ dioxane (0.8 m*M*) in 20 ml of THF was stirred at room temperature for 3 days, then the solvent was evaporated and the residue was dissolved in toluene, the toluene solution was filtered and an excess of n-pentane was added. Some $(C_5H_5)_3UCl$ (identified by ^1H NMR in C_6D_6) (0.05 g) precipitated out and was filtered off. The remaining solution was evaporated off to give a solid residue (0.49 g) which had an ^1H NMR spectrum indicative of the presence of two different $(C_5H_5)_3UOR$ species, probably produced by a ring cleavage of THF and/or dioxane molecules (C_6D_6; −49.64 br; −44.64 br; −9.29; −8.90; −7.59; −2.24; −1.44; 24.13 and 24.82 ppm).

Reactions 5 and 6 (Table 1). $(C_5H_5)_3UCl$ (1.15 m*M*) and $KPPh_2 \cdot$ 2dioxane (1.15 m*M*) were stirred at room temperature for 20 h in C_6H_6 (reaction 5) and THF (reaction 6), respectively. In the former solvent, a brown precipitate (0.55 g) was the main product. The washed (C_6H_6) and vacuum-dried material was only sparingly soluble in C_6H_6 and THF, and the ^1H NMR spectrum showed no resonances from $(C_5H_5)_3U^{IV}X$ species, but two highfield resonances (20.5 s; 22.6 s) were indicative of $(C_5H_5)_3U^{III}$ species [25]. A brown solid (0.05 g) was isolated from the remaining solution; its NMR spectrum was essentially identical to that of the main product.

Reaction in THF (reaction 6) gave a dark brown solution; filtration and concentration gave 0.525 g of a brown solid. Its ^1H NMR spectrum was similar to that of the main product of reaction 5 (C_6D_6: 20.5 and 22.6 ppm). The NIR/VIS spectra of all the products of reactions 5 and 6 are similarly in agreement with the formation of organouranium(III) species.

Reaction 7 (Table 1). Solutions of $(C_5H_5)_3UCH_3$ (1 m*M*) in C_6H_6 or $CH_3C_6H_5$ (20 ml) and a 2–3 fold excess of $HPPh_2$ were rapidly stirred at room temperature for 4 days. Portions were taken at different times, and evaporated to dryness and the residues were dissolved in C_6D_6, and the solutions were examined by ^1H NMR spectroscopy. Only the resonances of the starting compounds were observed throughout.

Reaction 8 (Table 1). After refluxing of the reaction mixture in C_6H_6 as described for the preceding experiment for 2 h, the usual work-up gave a product, the ^1H NMR spectrum (C_6D_6) of which displayed signals from traces of $(C_5H_5)_3UPPh_2$ together with some unassigned resonances.

Reaction 9 (Table 1). A mixture of $(C_5H_5)_3UC_6H_5$ (1 m*M*) and $HPPh_2$ (3 m*M*) was refluxed in toluene (30 ml) for 1.5 h. The solution was filtered and evaporated and the residue gave an ^1H NMR spectrum (C_6D_6) showing the resonances of $(C_5H_5)_3UPPh_2$ and $(C_5H_5)_3UC_6H_5$ (approximate ratio 1/4).

Reaction 10 (Table 1). Concentrated solutions of $(C_5H_5)_3UNEt_2$ (1 m*M*) and $HPPh_2$ (3 m*M*) in THF were combined and the mixture was stirred at room temperature for 20 h. The brown solution product (0.320 g) was filtered and then evaporated. This solid was poorly soluble in C_6D_6, but the ^1H NMR spectrum unequivocally revealed the absence of $(C_5H_5)_3UPPh_2$. The appearance of several unassigned resonances in addition to the signals from the starting materials indicated that a major portion of the starting material had reacted.

Reaction 11 (Table 1). In three separate experiments $(C_5H_5)_2U(NEt_2)_2$ (2 mM) dissolved in 20 ml of n-hexane was treated with $HPPh_2$ in the molar ratios 1/1, 1/2 and 1/4, respectively. After stirring at room temperature over 4 days, a brown precipitate was obtained in all cases and this was filtered off, washed with several small portions of n-hexane, and dried in vacuo. When the 1/2 ratio was used, 0.550 g (44.5% relative to $(C_5H_5)_2U(NEt_2)_2$) of pure $(C_5H_5)_3UPPh_2$ were obtained. Analytical data: Found: C, 51.79; H, 4.00; P, 5.13. $C_{27}H_{25}PU$ calcd.: C, 52.43; H, 4.04; P, 5.02%.

The residual solution was evaporated to give a solid, the ^1H NMR spectrum of which was dominated by resonances of the starting compounds. Additional weaker resonances were ascribed to complex 7 and to some additional unidentified species (with resonances between -40 and 35 ppm).

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References

1 Presented in part (a) P. Zanella, G. Paolucci, G. Rossetto and O. Traverso, 10th Intern. Conf. Organomet. Chem., Toronto, Canada, August 9–14, 1981, Abstr. 4CO3, p. 132; (b) G. Paolucci, R.D. Fischer, P. Zanella, G. Rossetto, O. Traverso and W. Jahn, XIIth Intern. Conf. Coord. Chem., ICCC Budapest, Hungary, August 23–27, 1982, p. 173.

2 See: R.E. Cramer, R.B. Maynard, J.C. Paw and J.W. Gilje, J. Am. Chem. Soc., 103 (1981) 3589, and further references cited therein (e.g. $X = CHP(CH_3)(C_6H_5)_2$: d(U–C) 229 pm; $X = p\text{-}CH_2C_6H_5CH_3$: d(U–C) 254 pm).

3 (a) R.E. Cramer, K. Panchanatheswaran and J.W. Gilje, J. Am. Chem. Soc., 106 (1984) 1853 ($X = NC(CH_3)CH(C_6H_5)_2(CH_3)$: d(U–N) 206 pm); (b) R.D. Fischer, E. Klähne and J. Kopf, Z. Naturforsch. B, 33 (1978) 1939 ($X = NCS$: d(U–N) 240.7 pm; $X' = NCCH_3$: d(U–N) 267.8 pm).

4 (a) A.L. Arduini, N.M. Edelstein, J.D. Jamerson, J.G. Reynolds, K. Schmid and J. Takats, Inorg. Chem., 20 (1981) 2470; (b) C.W. Eigenbrot and K.N. Raymond, ibid., 20 (1981) 1553 ($X = \eta^2\text{-}N_2C_3H_3$: $d(U\text{–}N)_{ave}$ 238 pm).

5 R.E. Cramer, K.T. Higa, U. Engelhardt and J.W. Gilje, quoted in ref. 3a.

6 E.g. d(U–N) in monomeric $(ArO)_3U^{IV}NEt_2$ 216.2 pm, cf. P.B. Hitchcock, M.F. Lappert, A. Singh, R.G. Taylor and D. Brown, J. Chem. Soc., Chem. Commun., (1983) 561.

7 G. Paolucci, G. Rossetto, P. Zanella, K. Yünlü and R.D. Fischer, J. Organomet. Chem., 272 (1984) 363, and further references therein.

8 (a) J.D. Jamerson and J. Takats, J. Organomet. Chem., 78 (1974) C23; (b) J. Takats, University of Edmonton (Canada), personal communication.

9 (a) H. Schumann and H. Jarosch, Z. Anorg. Allgem. Chem., 426 (1976) 127; (b) G. Bielang and R.D. Fischer, J. Organomet. Chem., 161 (1978) 335; (c) H. Schumann and G.-M. Frisch, Z. Naturforsch. B, 34 (1979) 748; (d) W.J. Evans, I. Bloom, W.E. Hunter and J.L. Atwood, Organometallics, 2 (1983) 709; (e) R.T. Baker, J.F. Whitney, T.H. Tulip and S.S. Wreford, 11th Int. Conf. Organomet. Chem., Callaway Gardens, Ga., U.S.A., Oct. 1983, Abstr. Nr 81.

10 K. Issleib and H. Hackert, Z. Naturforsch. B, 21 (1966) 519.

11 Most recently some unexpectedly coloured examples of the new series $(C_5Me_5)_2{}^fM(PR_2)_2$ with ${}^fM$ = Th and R = C_6H_5, c-C_6H_{11} and C_2H_5 were obtained: D.A. Wroblewski, K.V. Salazar, R.R. Ryan and D.C. Moody, Abstr. Nr. INOR 272, 188th ACS National Meeting, Philadelphia, Pennsylvania, U.S.A., August 26–31, 1984.

12 (a) J.M. Manriquez, P.J. Fagan, T.J. Marks, S.H. Vollmer, C.S. Day and V.W. Day, J. Am. Chem. Soc., 101, (1979) 5075; (b) S.J. Simpson and R.A. Andersen, ibid., 103 (1981) 7792; (c) P.J. Fagan, J.M. Manriquez, T.J. Marks, C.S. Day, S.H. Vollmer and V.W. Day, Organometallics, 1 (1982) 170; (d) M.R. Duttera, P.J. Fagan, T.J. Marks and V.W. Day, J. Am. Chem. Soc., 104 (1982) 865.

13 M.R. Duttera, V.W. Day and T.J. Marks, J. Am. Chem. Soc., 106 (1984) 2907, and J.W. Bruno, M.R. Duttera, C.M. Fendrick, G.M. Smith and T.J. Marks, Inorg. Chim. Acta, 94 (1984) 271.

14 G. Rossetto, P. Zanella, G. Paolucci and R.D. Fischer, Inorg. Chim. Acta, in press.

15 Bagnall et al. first pointed out that in the presence of specific steric constraints monocyclopentadienyluranium(IV) derivatives disproportionate into $Cp_3U^{IV}X$ species and complexes without a Cp ligand, cf. K.W. Bagnall in T.J. Marks and R.D. Fischer (Eds.), Organometallics of the *f*-Elements, D. Reidel Publ., Dordrecht, 1979, p. 221.

16 G. Paolucci, G. Rossetto, P. Zanella and A. Berton, Abstr. XXIIIrd Int. Conf. Coord. Chem., ICCC, Boulder, Col., U.S.A., July 29–Aug. 3, 1984, THp 55-6, p. 551.

17 F.G. Bordwell and M.J. Bausch, J. Am. Chem. Soc., 105 (1983) 6188.

18 K. Issleib and R. Kümmel, J. Organomet. Chem., 3(1965) 84.

19 D.C. Cram, Fundamentals of Carbanion Chemistry, Academic Press, New York, London, 1965.

20 P.J. Fagan, J.M. Manriquez, E.A. Maatta, A.M. Seyam and T.J. Marks, J. Am. Chem. Soc., 103 (1981) 6650.

21 P.J. Fagan, E.A. Mintz and T.J. Marks, Quotated by T.J. Marks and R.D. Ernst in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 3, Chap. 21, p. 173 (Eq. 277).

22 J.W. Bruno, T.J. Marks and L.R. Morss, J. Am. Chem. Soc., 105 (1983) 6824.

23 L.C. Thomas, Identification of Functional Groups in Organophosphorous Compounds, Academic Press, New York, 1974, p. 56.

24 See: J.H. Huheey, Inorganic Chemistry, Harper and Row, Publ. Comp., New York, 1978, p. 160.

25 See: L. Arnaudet, G. Folcher, H. Marquet-Ellis, E. Klähne, K. Yünlü and R.D. Fischer, Organometallics, 2 (1983) 344, and further literature cited therein.

26 R.E. Cramer, R.B. Maynard and J.W. Gilje, Inorg. Chem., 20 (1981) 2466.

27 W. Jahn, K. Yünlü, W. Oroschin, H.-D. Amberger and R.D. Fischer, Inorg. Chim. Acta, 95(1984) 85.

28 See: G. Bombieri, F. Benetollo, E. Klähne and R.D. Fischer, J. Chem. Soc., Dalton Trans., (1983) 1115, and further literature therein.

29 A.B. McLaren, B. Kanellakopulos and E. Dornberger, Inorg. Nucl. Chem. Lett., 16 (1980) 223.

30 B. Kanellakopulos, Habilitationsschrift, Universität Heidelberg, 1972.

31 R.A. Andersen, Inorg. Chem., 18 (1979) 1507.

32 K. Issleib and H. Hackert, Z. Naturforsch. B, 21 (1966) 519; R.T. Baker, J.F. Whitney and S.S. Wreford, Organometallics, 2 (1983) 1049.

33 P.J. Fagan, J.M. Manriquez, S.H. Vollmer, V.W. Day, S.H. Day and T.J. Marks, J. Am. Chem. Soc., 103 (1981) 2206.

34 From: W.D. Luke and A. Streitwieser, Jr., in N.M. Edelstein (Ed.), ACS Symp. Ser. 131, Washington, D.C., 1980, p. 93.

35 E. Cernia and A. Mazzei, Inorg. Chim. Acta, 10 (1974) 239.

36 T.J. Marks, A.M. Seyman and J.R. Kolb, J. Am. Chem. Soc., 95 (1973) 5529.

37 R.B. Maynard, Ph.D. Dissertation, University of Hawaii, 1972 (footnote 4 of ref. 2).

38 H. Schumann and G.M. Frisch, Z. Naturforsch. B, 36 (1981) 1244.

39 H. Schumann, Angew. Chem., 96 (1984) 475; Int. Ed., 23 (1984) 474.

40 P.G. Edwards, R.A. Andersen and A. Zalkin, Organometallics, 3 (1984) 293; and further ref. therein.

41 J. Müller, Chem. Ber., 102 (1969) 152.

42 J. Rebizant, G.D. Andreetti, M.R. Spirlet, B. Kanellakopulos and E. Dornberger, 14èmes Journées des Actinides, April 2–3, 1984, Davos, Switzerland, Abstr. Nr. IX 10, p. 93.

43 C.R. McIlwrick and C.S.G. Phillips, J. Phys. E, 6 (1973) 1208.

44 The unexpected formation of a new C≡C triple bond was recently observed by Cramer et al. in the reaction of Cp_3UCHPR_3 and $CpMn(CO)_3$ via the intermediate $Cp(CO)_2MnC{=}C(OUCp_3)(H)PR_3$. See: R.E. Cramer, K. Higa, K. Panchanatheswaran and J.W. Gilje, Abstr. XXIIIrd Int. Conf. Coord. Chem., ICCC, Boulder, Col., U.S.A., July 29–Aug. 3, 1984, THp 55-4, p. 549.