ruled out by elemental analysis for N). This reduction is expected to cause increased metal center lability and hence metal aggregation.

Catalysis with the supported Wilkinson's catalyst, [P]-$PPh_2Rh(PPh_3)_2Cl$ (2% cross-linked gel resin, 200–400 mesh, 0.03 mmol of Rh/g of beads) under conditions similar to those used for the [P]-bpyRh samples was investigated (80 psi H_2, 100 °C, 24-h reaction time). A small amount of cyclohexane was produced from the H_2 reduction of benzene solvent, again suggesting the formation of a small amount of rhodium metal. No detectable benzene hydrogenation products resulted from a hydrogenation of benzene with the homogeneous complex $Rh((C_6H_5)_3P)_3Cl$ at 100 psi H_2 and 100 °C for 72 h.

We obtained turnovers in the 1-hexane hydrogenation with [P]-bpyRhXCl as great as 300 in first runs, without the attendant formation of detectable benzene hydrogenation products. This demonstrates an important point: the absence of aromatic hydrogenation products is not necessarily a valid criterion for ruling out catalysis by small metal particles. This is of course a result of the much greater reactivity of 1-hexene than benzene toward hydrogenation.

These results also illustrate another point. With the exception of cases in which effective site isolation on a polymer has been achieved, it should be considered that for many polymer-supported transition-metal systems there is considerable potential for metal aggregation. The [P]-$P(C_6H_5)_2Rh((C_6H_5)_3P)_2Cl$ comparison to the homogeneous $Rh((C_6H_5)_3P)_3Cl$ system above is a good example.

Acknowledgment. The authors gratefully acknowledge the support of this research by the Office of Naval Research through Grant NR 356-675.

Registry No. Diethylbenzene, polymer with ethenylbenzene, 9003-70-7; bpy, 366-18-7; 4-ethylpyridine, homopolymer, 25232-41-1; $(C_6H_5CN)_2PtCl_2$, 14873-63-3; $(C_6H_5CN)_2PdCl_2$, 14220-64-5; $[Rh(CO)_2Cl]_2$, 14404-25-2; $[Rh((tol)_3P)(CO)Cl]_2$, 77507-81-4; $[Rh((C_6H_5)_3P)(CO)Cl]_2$, 34676-63-6; $Rh(py)(CO)_2Cl$, 14024-06-7; $Rh(py)((tol)_3P)(CO)Cl$, 77507-82-5; Rh(bpy)(CO)Cl, 52659-24-2; 1-hexene, 592-41-6; *cis*-2-hexene, 7688-21-3; *trans*-2-hexene, 4050-45-7; 1-heptyne, 628-71-7; cyclohexene, 110-83-8; 1,3-COD, 1700-10-3; 1,5-COD, 111-78-4; benzyl chloride, 100-44-7.

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Reaction of $(\eta^5\text{-}C_5H_5)_3UCl$ with Lithiated Phosphoylides. Preparation of Some Mono-, Bis-, and Tris(cyclopentadiene)uranium(IV) Phosphoylide Complexes

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The reaction between $(\eta^5\text{-}C_5H_5)_3UCl$ and $Li(CH_2)(CH_2)P(C_6H_5)_2$ or $Li(CH_2)(CH_2)P(CH_3)(C_6H_5)$ in 1:1 molar ratio produces $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ or $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$, respectively. When $Li(CH_2)(CH_2)P(C_6H_5)_2$ is allowed to react with $(\eta^5\text{-}C_5H_5)_3UCl$ in 2:1 ratio or with $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ in 1:1 ratio the novel metallacycle $(\eta^5\text{-}C_5H_5)_2U[CHP(C_6H_5)_2CH_2]_2U(\eta^5\text{-}C_5H_5)_2$ can be isolated. Finally when the ratio of $(\eta^5\text{-}C_5H_5)_3UCl$ to $Li(CH_2)(CH_2)P(C_6H_5)_2$ or $Li(CH_2)(CH_2)P(CH_3)(C_6H_5)$ is 1:3, the respective complexes $(\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(C_6H_5)_2]_3$ and $(\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(CH_3)(C_6H_5)]_3$ are formed. These are the first phosphoylide complexes of an actinide. They are stable at room temperature under an inert atmosphere and demonstrate that organouranium complexes which are rich in metal–carbon σ bonds can be formed with phosphoylide ligands.

Complexes containing actinide–carbon σ bonds have attributed growing interest during the last few years,[1-3] and it is now well established that such bonds are often stable at and above room temperature. A good deal of recent study has focused on the preparation of compounds in which the actinide's coordination number is less than the most common value of 10.[4-6] Usually this has involved the use of bulky coligands, with the most notable examples being the bis(pentamethylcyclopentadienyl)uranium and -thorium complexes recently reported by Marks and co-workers.[6] Even though these investigations have demonstrated the existence of numerous compounds containing two actinide–carbon σ bonds, prior to this study, there was no thermally stable, neutral actinide complex with three or more such bonds.

Since phosphorus ylides are known to form very stable σ bonds with transition metals[7] and a few uncharged lanthanide ylide complexes are known,[8,9] we have begun an investigation of phosphorus ylides as ligands toward actinides. In this paper we report the reactions of some lithiated phosphoylides, $Li(CH_2)(CH_2)P(R)(C_6H_5)$, R = CH_3 and C_6H_5, with $(\eta^5\text{-}C_5H_5)_3UCl$ and $(\eta^5\text{-}C_5H_5)UCl_3\cdot 2THF$.

Experimental Section

All manipulations were carried out under high-purity dinitrogen in a Vacuum Atmospheres glovebox equipped with an HE-493 Dri-Train, with use of standard Schlenk tube techniques or in a high-vacuum line. Reagents and solvents were of the highest commercially available purity and were dried and deoxygenated by appropriate means before use. Due to the extreme sensitivity of some of the compounds prepared in this study, care must be exercised to exclude oxygen, moisture, or protonic solvents.

Published procedures were used to prepare $(\eta^5\text{-}C_5H_5)_3UCl$,[10] $(\eta^5\text{-}C_5H_5)UCl_3\cdot 2THF$,[11] $Li(CH_2)(CH_2)P(C_6H_5)_2$,[9] $Li(CH_2)(CH_2)$-

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$P(CH_3)(C_6H_5)$,[9] and $Li(CH_2)(CH_2)P(C_2H_5)(C_6H_5)$.[12]

NMR spectra were obtained on a Varian XL-100-15 spectrometer with use of samples prepared in benzene-d_6, toluene-d_8, or THF-d_8. ^1H spectra are referenced to internal benzene and ^{31}P spectra to external 85% H_3PO_4. IR spectra were run with use of a Perkin-Elmer 467 spectrometer. A Cary 14 spectrometer was used to obtain the near IR-visible spectra, and a Beckman Acta III spectrometer was employed in the UV range. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of Tricyclopentadienyluranium(IV) Phosphoylide Complexes. $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ (I). Allowing 0.950 g (2.03 mmol) of $(\eta^5\text{-}C_5H_5)_3UCl$ to react with 0.321 g (2.03 mmol) of $Li(CH_2)(CH_2)P(CH_3)(C_6H_5)$ in a fashion analogous to that described for the preparation of II produced 0.729 g (62% yield) of dark green, pyrophoric crystals of $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ after recrystallization from a 1:1 toluene–heptane mixture. Anal. Calcd for $UPC_{24}H_{27}$: C, 49.31; H, 4.67; P, 5.30. Found: C, 49.53; H, 4.91; P, 5.22. IR spectrum: 3070 w, 1480 m, sh, 1438 s, 1418 w, 1310 w, 1290 w, 1262 w, 1100 s, 1069 m, 1030 m, sh, 1005 vs, 994 s, 950 s, 878 w, 791 vs, 772 vs, 742 s, 731 s, 695 m, 690 m, 500 w, 480 m, 415 w cm^{-1}. Vis–near-IR spectrum: 19.9 (1150), 17.3 (980), 16.6 (1000), 14.9 (660), 14.2 (390), 13.5 (200), 12.5 (52), 12.3 (38), 12.1 (30), 10.9 (16), 9.91 (43), 8.90 (45), 8.38 (59), 7.59 (44), 7.30 (44), 6.67 (27), 6.07 (16), 5.68 (25), 5.38 (12) cm^{-1} × 10^{-3} (extinction coefficients in L mol^{-1} cm^{-1} shown parenthetically).

$(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ (II). A solution containing 0.528 g (2.40 mmol) of $Li(CH_2)(CH_2)P(C_6H_5)_2$ dissolved in 30 mL of THF was slowly added to 1.123 g (2.40 mmol) of $(\eta^5\text{-}C_5H_5)_3UCl$ in 40 mL of THF which was maintained at -40 °C. The solution was stirred for several hours at -50 °C and allowed to warm to -10 °C, and the solvent was immediately evaporated under vacuum. The residue was recrystallized from a 1:2 toluene–heptane solution to give 0.885 g (57% yield) of dark green, microcrystalline $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$. This compound is extremely reactive toward even traces of O_2 or H_2O and spontaneously flames in air. Anal. Calcd for $UPC_{29}H_{29}$: C, 53.87; H, 4.53; P, 4.79. Found: C, 51.03; H, 4.94; P, 4.87. IR spectrum: 3080 w, 1480 m, sh, 1440 s, 1419 w, 1314 m, 1229 m, 1288 m, 1252 w, 1088 m, 1070 m, 1011 vs, 997 s, 959 vs, 920 m, 852 m, 794 s, 770 vs, 750 s, 738 s, 708 m, 699 m, 480 w, 427 m cm^{-1}. Vis–near-IR spectrum: 19.8 (890), 17.2 (760), 16.7 (770), 14.9 (460), 14.0 (255), 13.4 (160), 12.6 (52), 12.3 (40), 12.1 (30), 11.0 (22), 10.7 (18), 9.87 (43), 9.02 (34), 8.48 (55), 8.28 (68), 7.43 (53), 6.58 (26), 6.07 (13), 5.98 (16), 5.66 (21), 5.38 (12) cm^{-1} × 10^{-3} (extinction coefficients in L mol^{-1} cm^{-1} shown parenthetically).

Preparation of $(\eta^5\text{-}C_5H_5)_2U[CHP(C_6H_5)_2CH_2]_2U(\eta^5\text{-}C_5H_5)_2$ (III). A solution containing 1.34 g (6.08 mmol) of $Li(CH_2)(CH_2)P(C_6H_5)_2$ dissolved in 50 mL of THF was slowly added to a solution of 1.42 g (3.03 mmol) of $(\eta^5\text{-}C_5H_5)_3UCl$ in 50 mL of THF. The solution was maintained at room temperature during this addition, after which it was heated to reflux for 2 h. The dark red solution was allowed to cool to room temperature, and the solvent was evaporated under vacuum. The residue was recrystallized from a 1:1 THF–hexane mixture to yield 0.775 g (44% on the basis of starting $(\eta^5\text{-}C_5H_5)_3UCl$) of red $(\eta^5\text{-}C_5H_5)_2U[CHP(C_6H_5)_2CH_2]_2U(\eta^5\text{-}C_5H_5)_2$. Anal. Calcd for $U_2P_2C_{48}H_{46}$: C, 49.65; H, 3.99; P, 5.34. Found: C, 48.02; H, 4.36; P, 4.76. IR spectrum: 3070 w, 3050 w, 1965 w, 1894 w, 1806 w, 1760 w, 1480 m, sh, 1439 s, sh, 1304 w, 1262 w, 1157 w, 1112 m, 1097 m, 1010 s, 985 m, 898 s, 822 w, 791 s, m sh, 776 vs, 744 s, 735 m, 689 s, 518 s, 492 s, 467 m cm^{-1}. Vis–near-IR spectrum: 19.3 (1430), 15.7 (240), 15.0 (210), 14.4 (190), 13.8 (120), 13.0 (36), 11.7 (33), 11.0 (35), 10.6 (40), 9.98 (62), 9.36 (55), 8.88 (190), 8.81 (200), 8.73 (190), 7.42 (42), 6.90 (40), 6.73 (55), 6.57 (110), 6.32 (62), 5.78 (27), 5.65 (18) cm^{-1} × 10^{-3} (extinction coefficients in L mol^{-1} cm^{-1} shown parenthetically).

Preparation of Cyclopentadienyluranium(IV) Phosphoylide Complexes. $(\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(C_6H_5)_2]_3$ (IV). A 0.576-g (2.62 mmol) sample of $Li(CH_2)(CH_2)P(C_6H_5)_2$ and 0.407 g (0.89 mmol) of $(\eta^5\text{-}C_5H_5)_3UCl$ were placed in a flask, the solution was cooled, and 50 mL of diethyl ether which had been cooled to -50 °C was added. The mixture was stirred several hours at -50 °C, warmed to room temperature, and filtered. The golden brown filtrate was reduced in volume to about 20 mL and cooled to -15 °C overnight, whereupon gold, rod-shaped crystals formed. These were collected, washed with 5 mL of diethyl ether, and dried under vacuum for 30 min to give 0.774 g (58%) of $(\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(C_6H_5)_2]_3$. Anal. Calcd for $UP_3C_{47}H_{47}$: C, 59.87; H, 5.03; P, 9.85. Found: C, 59.97; H, 5.06; P, 9.80. IR spectrum: 3049 w, 1956 w, 1888 w, 1802 w, 1575 w, 1479 w, sh, 1437 w, 1333 m, 1319 m, 1179 w, 1159 w, 1096 s, 1070 m, 1010 m, 999 m, 940 m, 871 s, 859 s, 805 s, 786 s, 772 s, 733 vs, 685 vs, 500 vs, 470 s, 439 s cm^{-1}. Vis–near-IR spectrum: 24.8 (1720), 20.8 (230), 19.3 (120), 17.9 (110), 16.6 (120), 15.4 (200), 15.0 (220), 14.7 (220), 14.3 (220), 14.0 (200), 10.5 (24), 9.59 (25), 9.22 (41), 9.05 (42), 8.70 (56), 8.30 (160), 8.07 (180), 7.04 (19), 6.62 (25), 6.16 (34), 5.97 (38), 5.70 (24), cm^{-1} × 10^{-3} (extinction coefficients in L mol^{-1} cm^{-1} shown parenthetically).

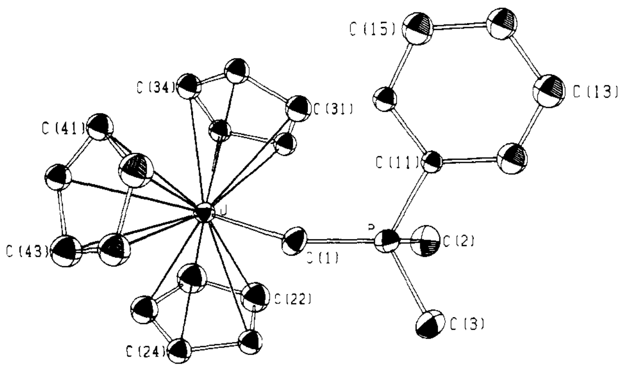

Figure 1. ORTEP drawing of $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$.[16]

The same product can be obtained in THF at -50 °C. Similarly the reaction of $(C_5H_5)UCl_3\cdot 2THF$ with 3 equiv of $Li(CH_2)(CH_2)(C_6H_5)_2$ in THF at -50 °C also gave nearly quantitative yields of $(\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(C_6H_5)_2]_3$. Identical NMR spectra were obtained for each of these products. However all attempts to recrystallize samples prepared in THF failed.

$(\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(CH_3)(C_6H_5)]_3$ (V). A 20-mL solution containing 0.646 g (4.00 mmol) of $Li(CH_2)(CH_2)P(CH_3)(C_6H_5)$ in THF was added to 0.637 g (1.36 mmol) of $(\eta^5\text{-}C_5H_5)_3UCl$ in 40 mL of THF at -50 °C. After this addition the reaction mixture was stirred at -50 °C for 1/2 h, allowed to warm to room temperature, and stirred for an additional 2–3 h, and the solvent was evaporated under vacuum. Following benzene extraction of this solid $(\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(CH_3)(C_6H_5)]_3$ was obtained in nearly quantiative yield. The same material could also be obtained by reaction of $Li(CH_2)(CH_2)P(CH_3)(C_6H_5)$ with $(\eta^5\text{-}C_5H_5)UCl_3\cdot 2THF$ in THF at -50 °C, or from reaction of I and 2 equiv of $Li(CH_2)(CH_2)P(CH_3)(C_6H_5)$ in THF at ambient temperature.

Results and Discussion

The identity of the complexes produced from the reactions of $Li(CH_2)(CH_2)P(C_6H_5)_2$ and $Li(CH_2)(CH_2)P(CH_3)(C_6H_5)$ with $(\eta^5\text{-}C_5H_5)_3UCl$ have been established by the usual chemical and spectroscopic means. Detailed structures, which are reported elsewhere,[13–16] have been determined by X-ray diffraction.

When $Li(CH_2)(CH_2)P(CH_3)(C_6H_5)$ and $(\eta^5\text{-}C_5H_5)_3UCl$ are allowed to react at -50 °C in THF, a green complex forms in nearly quantitative yield according to eq 1. Similarly

$$(\eta^5\text{-}C_5H_5)_3UCl + Li(CH_2)(CH_2)P(CH_3)(C_6H_5) \xrightarrow[-50\ ^\circ C]{THF} (\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5) + LiCl \quad (1)$$

$Li(CH_2)(CH_2)P(C_6H_5)_2$ reacts with $(\eta^5\text{-}C_5H_5)_3UCl$ to produce II, which is also a green, air- and moisture-sensitive material,

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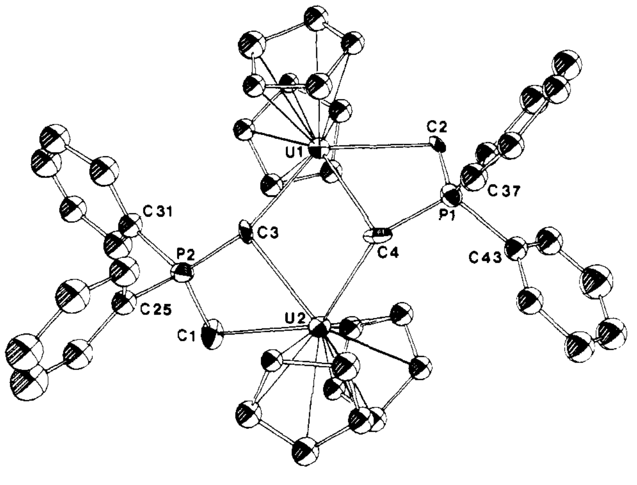

Figure 2. ORTEP drawing of $(\eta^5\text{-}C_5H_5)_2U[CHP(C_6H_5)_2CH_2]_2U(\eta^5\text{-}C_5H_5)_2$.[13,14]

whose NMR and vis–UV spectra indicate it to be a homologue of I.

The structure of I (Figure 1) has been confirmed by X-ray crystallography,[16] and its ^1H NMR spectrum (Table I) is consistent with this structure. The uranium atom in I has the common coordination number of 10. Consistent with this, the visible–near IR electronic spectrum (see Experimental Section) is similar to that reported for other 10-coordinate species of general formula $(\eta^5\text{-}C_5H_5)_3U(X)$ but differs from the spectra of the 11-coordinate $(\eta^5\text{-}C_5H_5)_3U(X)(Y)$.[17]

The mode of ylide attachment of I and II, while having precedent,[18] is not one of those commonly observed in transition metal–ylide complexes. Likewise the proton transfer which transforms a methylene group in the lithiated phosphoylide starting material into a methyl in the final complex is unusual but has been observed previously in, for example, the formation of $(CH_3)_3SiCHP(CH_3)_3$ from the reaction of $(CH_3)_3SiCl$ with $Li(CH_2)(CH_2)P(CH_3)_2$[19] and in a similar reaction of $(CH_3)_2SbCl$.[20]

The methyl protons in II retain some acidic character for when it is mixed with a further equivalent $Li(CH_2)(CH_2)P(C_6H_5)_2$ reaction 2 occurs to produce III. Compound III can

$$\underset{\text{II}}{2(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)(C_6H_5)_2} + 2Li(CH_2)(CH_2)P(C_6H_5)_2 \xrightarrow[\text{reflux}]{\text{THF}} \underset{\text{III}}{(\eta^5\text{-}C_5H_5)_2U(CHP(C_6H_5)_2CH_2)_2U(\eta^5\text{-}C_5H_5)_2} + 2Li(C_5H_5) + 2CH_2P(CH_3)(C_6H_5)_2 \quad (2)$$

also be produced without isolation of II according to eq 3. The

$$2(\eta^5\text{-}C_5H_5)_3UCl + 4Li(CH_2)(CH_2)P(C_6H_5)_2 \xrightarrow[\text{reflux}]{\text{THF}} (\eta^5\text{-}C_5H_5)_2U(CHP(C_6H_5)_2CH_2)_2U(\eta^5\text{-}C_5H_5)_2 + 2LiCl + 2Li(C_5H_5) + 2H_2CP(CH_3)(C_6H_5)_2 \quad (3)$$

structure of III has been determined by single-crystal X-ray diffraction (Figure 2). Both the molecule and its mode of formation are unique. The mode of ylide attachment, where ylide moieties both chelate a single uranium and bridge between two uraniums, has no precedent in ylide metal chemistry. The formation of III from $(\eta^5\text{-}C_5H_5)_3UCl$ is also noteworthy.

Table I. NMR Chemical Shifts[a] (Ppm) and Coupling Constants (Hz)

	C_5H_5	PCH	PCH_2	PCH_3	$P(C_6H_5)$ ortho	$P(C_6H_5)$ meta	$P(C_6H_5)$ para	P
$(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$[b]	+19.28 (s)[c]	+137.8 (d, J_{HCP} = 16)		+20.92 (d, J_{H_3CP} = 12)	−3.69 (dd, J_{HCP} = 12, J_{HCCH} = 7)	−1.30 (t, J_{HCCH} = 7)	−0.35 (t, J_{HCCH} = 7)	+177.54 (m)
$(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$[b]	+19.74 (s)	+123.7 (d, J_{HCP} = 16)		+15.52 (d, J_{H_3CP} = 13)	−10.69 (dd, J_{HCP} = 12, J_{HCCH} = 7)	−3.95 (t, J_{HCCH} = 7)	−1.96 (t, J_{HCCH} = 7)	+213.65 (m)
$[\mu(CH)(CH_2)P(C_6H_5)_2U(\eta^5\text{-}C_5H_5)_2]_2$[b]	+33.92 (s)	+108.1 (s)	−95.5 (s)		−8.05 (s)	−3.07 (t, J_{HCCH} = 7)	−2.44 (t, J_{HCCH} = 7)	+140.44 (m)
$(\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(C_6H_5)_2]_3$[d]	+27.29 (s)		NO[e]		+0.42 (s)	+1.28 (m)	+1.28 (m)	+11.02 (m)
$(\eta^5\text{-}C_5H_5)U[CH_2)(CH_2)P(CH_3)(C_6H_5)]_3$[d]	+30.91 (s)		NO[e]	+10.27 (d, J_{H_3CP} = 10)	+0.15 (s)	+0.90 (m)	+0.90 (m)	−14.42 (m)

[a] Chemical shifts are given in ppm from internal benzene or external H_3PO_4 at 25 °C. [b] Solvent benzene-d_6. [c] Key: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets. [d] Solvent toluene-d_8. [e] See text.

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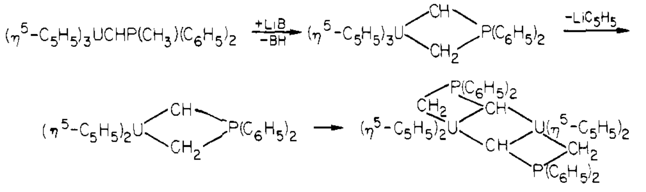
Scheme I



$B = (CH_2)(CH_2)P(C_6H_5)_2^-$

The cyclopentadienyl groups in $(\eta^5\text{-}C_5H_5)_3UCl$ are labile, and this property has been exploited in, for example, the synthetis of complexes of the type $(\eta^5\text{-}C_5H_5)UCl_3{\cdot}2L$ from $(\eta^5\text{-}C_5H_5)_3UCl$ and $UCl_4{\cdot}2L$[21] or $(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5H_4R)UCl$ and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4R)_2UCl$ from the reaction of $(\eta^5\text{-}C_5H_5)_3UCl$ with $C_5H_4R^-$ and from the disproportionation of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4R)_2UCl$.[22] Displacement of $C_5H_5^-$ groups during the formation of actinide–carbon σ bonds, however, has not previously been observed. The ability of the lithiated phosphoylides to do so, no doubt, reflects their nucleophilicity and their ability to form two metal–carbon σ bonds. The fact that one (and two, vide infra) $C_5H_5^-$ groups can be lost from $(\eta^5\text{-}C_5H_5)_3UCl$ during the formation of derivatives rich in U–C σ bonds greatly expands the synthetic utility of this starting material as a precursor to molecules containing fewer than three $C_5H_5^-$ groups. In this context it is also probably worthwhile to mention that III represents the first actinide complex in which the actinide is only bonded to carbon and which contains two $C_5H_5^-$ moieties. While several derivatives of formula $[X(\eta^5\text{-}C_5H_4)_2]MYZ$ are known, the two C_5 rings are linked by a bridging X group.[5] If each $\eta^5\text{-}C_5H_5$ is assumed to occupy three coordination sites and each ylide carbon–metal bond to account for one, the uraniums in III are 9-coordinate which is a new coordination number for uranium in an organometallic compound.

Equations 2 and 3 suggest that III may be formed from II by proton abstraction from the $P\text{–}CH_3$ moiety, followed by chelation to form an 11-coordinate intermediate which eliminates $C_5H_5^-$ and dimerizes (Scheme I). Such a scheme suggests that other bases should convert I into III. In fact III could not be isolated from reactions of I with $LiCH_3$ or $Li(CH_2)(CH_2)P(C_6H_5)(CH_3)$ which casts doubt on Scheme I and suggests that the nature of B^- is important.

The ^1H spectrum of III obtained at ambient temperature shows a single resonance for the $C_5H_5^-$ protons and indicates NMR equivalent phenyl groups. This spectrum can only be consistent with the X-ray structure if III is fluxional. In the structure as depicted in Figure 2 there are two diastereotopic $C_5H_5^-$ sites and two sets of nonequivalent phenyl groups. In addition the $P(C_6H_5)_2$ moiety is a prochiral group. Consequently the process which interchanges nonequivalent groups must also reverse the chirality at the two asymmetric methine protons and at the chiral axis, which is collinear with an approximate twofold axis which bisects the U–U vector. Indeed in ^1H NMR spectra obtained at lower temperatures, the $C_5H_5^-$ signal broadens and reappears as two peaks by −60 °C. The resonances due to the phenyl groups also broaden and merge into the base line of the spectrum. New peaks begin to emerge but have not yet been confidently assigned. The exact nature of the fluxionality of III is, as of yet, uncertain. Several mechanisms including dimer dissociation and inter- or intramolecular methine proton exchange can be postulated to account for the observed behavior. However, definite results must await further study.

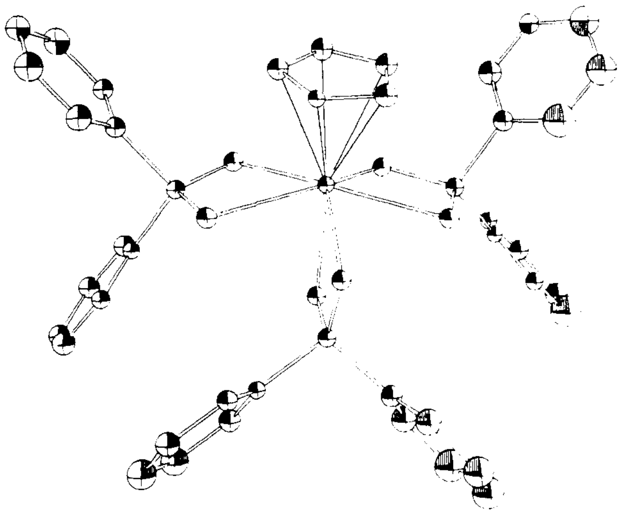


Figure 3. ORTEP drawing of $(\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(C_6H_5)_2]_3$.[15]

In contrast to the formation of I and II where $Li(CH_2)(CH_2)P(C_6H_5)_2$ and $Li(CH_2)(CH_2)P(C_6H_5)(CH_3)$ form similar compounds, no analogue of III could be isolated from the reaction of Cp_3UCl or I with $Li(CH_2)(CH_2)P(C_6H_5)(CH_3)$. Also attempts to form an analogue of III via the reaction of II with $Li(CH_2)(CH_2)P(C_6H_5)(CH_3)$ were unsuccessful, although exchange of ylide moieties was observed (eq 4). The

$$\text{II} + Li(CH_2)(CH_2)P(C_6H_5)(CH_3) \rightleftarrows \text{I} + Li(CH_2)(CH_2)P(C_6H_5)_2 \quad (4)$$

failure of $Li(CH_2)(CH_2)P(C_6H_5)(CH_3)$ to form analogues of III was unexpected but may reflect the need for sterically bulky groups on the ylide in order to stabilize the formally undercoordinated uranium atoms in III.

A third type of compound forms when $(\eta^5\text{-}C_5H_5)_3UCl$ is allowed to react with $Li(CH_2)(CH_2)P(C_6H_5)_2$ or $Li(CH_2)(CH_2)P(C_6H_5)(CH_3)$ according to eq 5. These organo-

$$\begin{aligned}&(\eta^5\text{-}C_5H_5)_3UCl + 3Li(CH_2)(CH_2)P(C_6H_5)(R) \xrightarrow[-50\ °C]{THF}\\ &\qquad (\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(C_6H_5)R]_3 + LiCl +\\ &\qquad \text{IV},\ R = C_6H_5\\ &\qquad \text{V},\ R = CH_3\\ &\qquad\qquad\qquad\qquad 2Li(C_5H_5) \quad (5)\end{aligned}$$

uranium products can also be obtained by eq 6. The structure of IV as determined by X-ray diffraction[15] is shown in Figure 3.

$$\begin{aligned}&(\eta^5\text{-}C_5H_5)UCl_3{\cdot}2THF + 3Li(CH_2)(CH_2)P(C_6H_5)R \xrightarrow{THF}\\ &\qquad (\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(C_6H_5)R]_3 + 3LiCl \quad (6)\end{aligned}$$

The ^1H NMR spectra of IV and V at 25 °C display signals due to the $C_5H_5^-$, PC_6H_5, and PCH_3 groups, but no signals due to the PCH_2 protons. This appears to be due to a dynamic situation placing these protons in the intermediate-exchange region at this temperature. At higher temperatures the PCH_2 signal emerges from the base line and sharpens with increasing temperature. At 95 °C the PCH_2 signal of IV is observed as a broad singlet at +40.54 ppm from internal benzene.

It is interesting to note that IV and V can be formed either from $(\eta^5\text{-}C_5H_5)_3UCl$ or $(\eta^5\text{-}C_5H_5)UCl_3{\cdot}2THF$. To our knowledge these are the first σ-bonded organouranium compounds to be synthesized with use of $(\eta^5\text{-}C_5H_5)UCl_3{\cdot}2B$ as a starting material. In addition these are the first organouranium compounds to contain over three σ C–U linkages and the first to contain only a single $C_5H_5^-$ moiety. This demonstrates that the ability of phosphorus ylides to stabilize M–C σ bonds, which is so notable in ylide transition-metal chem-

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istry,[7] applies to ylide–actinide compounds. While we, as of yet, have been unsuccessful in obtaining an organoactinide which contains only Ac–C σ bonds, the formation and stability of IV and V give hope that further $C_5H_5^-$ substitution can occur if the proper ylide system can be found. The ability of the lithiated ylides to displace $C_5H_5^-$ units from uranium also provides a pathway to complexes rich in Ac–C σ bonds which has not been available before.

Registry No. I, 77357-85-8; II, 77357-86-9; III, 67771-71-5; IV, 77357-87-0; V, 77357-88-1; $(\eta^5\text{-}C_5H_5)_3UCl$, 1284-81-7; $(\eta^5\text{-}C_5H_5)UCl_3\cdot 2THF$, 54674-00-9; $Li(CH_2)(CH_2)P(CH_3)(C_6H_5)$, 59983-61-8; $Li(CH_2)(CH_2)P(C_6H_5)_2$, 59983-62-9.

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Syntheses and Characterization of $(\eta^5\text{-}C_5H_5)_2U(NR_2)_2$ Compounds

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The reaction of 2 equiv of cyclopentadiene with $U(NPr_2)_4$ and $U(NPh_2)_4$ and the reaction of 1.5 equiv of cyclopentadiene with $U(NEt_2)_4$, generated in situ, gives the corresponding $Cp_2U(NR_2)_2$ complexes in good yields. However, $U(N\text{-}i\text{-}Pr_2)_4$ does not react with cyclopentadiene at room temperature and $U(NMe_2)_4$ gives mixture of $Cp_2U(NMe_2)_2$ and $Cp_3U(NMe_2)$. Excess cyclopentadiene also reacts with $Cp_2U(NEt_2)_2$ to produce $Cp_3U(NEt_2)$. The transamination reaction of $Cp_2U(NEt_2)_2$ with pyrrole and 2,3-dimethylpyrrole gives mixtures of products only; however, ethyl 3,4,5-trimethylpyrrole-2-carboxylate gives $Cp_2U[NC_4Me_3(COOEt)]_2$, and the reaction with 1 equiv of diphenylamine yields $Cp_2U(NEt_2)(NPh_2)$. It is argued that the reactivity sequence and the stability of $Cp_2U(NR_2)_2$ compounds are best explained by steric effect considerations. The spectral characteristics of the $Cp_2U(NR_2)_2$ complexes are presented which show that the compounds possess η^5-cyclopentadienyl moieties and monomeric solution behavior with no primary solvent interaction. In $Cp_2U[NC_4Me_3(COOEt)]_2$, additional interaction between uranium and oxygen of the carboxylate functionality is postulated.

Introduction

The synthesis of uranocene,[3] $U(COT)_2$, has rekindled interest in the field of organoactinide chemistry in general and organouranium complexes in particular. Although a large variety of complexes have been synthesized, a quick review of the now extant literature reveals a paucity of Cp_2UX_2-type complexes.[4] The logical entry into this area of chemistry, Cp_2UCl_2,[5] was shown to be incorrectly formulated,[6] and on the basis of best currently available evidences, it appears to be a mixture of Cp_3UCl and $CpUCl_3L_2$ (L = Lewis base).[6c] It is only recently that, by the clever use of the bulky pentamethylcyclopentadienyl ligand system, Marks et al. have succeeded in isolating $[C_5(CH_3)_5]_2UCl_2$[7] and utilized it as a versatile precursor to other $[C_5(CH_3)_5]_2UR_2$[8] complexes which have a very rich chemistry of their own.

Our approach to the synthesis of Cp_2UX_2 complexes was based on the expectation that, given a suitable ligand, a stable and authentic Cp_2UY_2 complex could obtain. Furthermore, if Y happens to be an easily displaceable ligand as well, the material would provide an entry into the elusive area of Cp_2UX_2 (X = some functional group) type compounds.

The utility of transition-metal amides as reactive intermediates has been recognized for years.[9] The reactivity of the metal–nitrogen bond toward molecules containing dipolar double bonds and acidic hydrogens can be exploited in an almost limitless fashion in order to prepare an amazing array of transition-metal complexes.[9] For our purposes, however, the reaction of cyclopentadiene with titanium group amides looked particularly interesting.[10] It was found that zirconium and hafnium amides cleanly gave $Cp_2M(NMe_2)_2$ complexes and this even in the presence of excess cyclopentadiene (eq 1). Since $U(NEt_2)_4$ has been known for a long time[11] and

$$M(NMe_2)_4 + \text{excess CpH} \rightarrow Cp_2M(NMe_2)_2 + 2HNMe_2 \qquad (1)$$
$$M = Zr, Hf$$

many new actinide amides have been synthesized recently,[12] the ramification of eq 1 for the synthesis of $Cp_2U(NR_2)_2$ compounds and their subsequent elaboration to other Cp_2UX_2-type complexes are clear.

The initial results of the substitution reaction using $U(NEt_2)_4$ and cyclopentadiene were encouraging.[13] The com-

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