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Organoactinide Phosphine/Phosphite Coordination Chemistry. Facile Hydride-Induced Dealkoxylation and the Formation of Actinide Phosphinidene Complexes

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Abstract: This contribution reports a study of the reaction of the organoactinide hydrides $(Cp'_2MH_2)_2$ ($Cp' = \eta^5\text{-}(CH_3)_5C_5$, M = Th, U) with trimethyl phosphite. Quantitative transposition of hydride and methoxide ligands occurs to yield the corresponding $Cp'_2M(OCH_3)_2$ complexes (synthesized independently from Cp'_2MCl_2 and $NaOCH_3$) and the phosphinidene-bridged methoxy complexes $[Cp'_2M(OCH_3)]_2PH$. The reaction is considerably more rapid for M = U than for M = Th. The new compounds were characterized by elemental analysis, ^1H and ^{31}P NMR, infrared spectroscopy, magnetic susceptibility, and D_2O hydrolysis. The molecular structure of $[Cp'_2U(OCH_3)]_2PH$ has been determined by single-crystal X-ray diffraction techniques. It crystallizes in the monoclinic space group $P2/n$ with $a = 13.926$ (3) Å, $b = 10.765$ (3) Å, $c = 15.282$ (4) Å, $\beta = 107.63$ (2)°, and $Z = 2$. Full-matrix least-squares refinement of the structural parameters for the 24 independent anisotropic non-hydrogen atoms has converged to R_1 (unweighted, based on F) = 0.041 for 1677 independent absorption-corrected reflections having $2\theta_{MoK\alpha} < 43°$ and $I > 3\sigma(I)$. The $[Cp'_2U(OCH_3)]_2PH$ molecule has C_2 symmetry, with the $\mu\text{-}PH^{2-}$ ligand lying on a crystallographic twofold axis. The coordination geometry about each uranium ion is of the typical "pseudotetrahedral" $Cp'_2M(X)Y$ type, with U–P = 2.743 (1) Å, U–O = 2.046 (14) Å, ∠U–P–U = 157.7 (2)°, and ∠U–O–C(methyl) = 178 (1)°. Evidence is presented that other >P–OR linkages react in a similar manner.

Although "soft" ligands such as phosphines and phosphites play a unique, central role in d-element organometallic chemistry,[2] the parallel development of a corresponding organo-f-element phosphine/phosphite chemistry has been conspicuously sluggish.[3-5] For actinides, such ligands offer the possibility of stabilizing and solubilizing complexes in low formal oxidation states. Moreover, simple basicity considerations[6] argue that the magnitudes of actinide–phosphorus ligand bonding interactions will be nonnegligible and should give rise to isolable complexes.

We recently reported[5d] that the first organouranium phosphine hydrides could be prepared via the direct route of eq 1 or via an in situ U–C hydrogenolysis approach (eq 2). In both cases, a

$$(Cp'_2UH_2)_2 + 2\text{dmpe} \xrightarrow{-H_2} \underset{\mathbf{1}}{2Cp'_2U(\text{dmpe})H} \qquad (1)$$

$$Cp'_2UR_2 + \text{dmpe} \xrightarrow{H_2} \underset{\mathbf{1}}{Cp'_2U(\text{dmpe})H} + 2RH \qquad (2)$$

$$Cp' = \eta^5\text{-}(CH_3)_5C_5 \qquad R = CH_3 \text{ or } CH_2Si(CH_3)_3$$

$$\text{dmpe} = (CH_3)_2PCH_2CH_2P(CH_3)_2$$

tetravalent starting material is converted into a phosphine-stabilized *trivalent* product. Complex **1** displays rich and vigorous reactivity patterns with CO, olefins, nitrogen and oxygen atom donors, and a variety of other reagents. These will be discussed in detail elsewhere.[7a]

Phosphites are generally viewed as being stronger π acceptors than phosphines.[2,8] Thus, the possibility of further stabilizing low actinide formal oxidation states and/or of observing ligand reactivity modes beyond conventional (**2**) η^1-P donor–acceptor interactions[2,8] (e.g., **3**[9] and **4**[10]) has prompted studies analogous to eq 1 and 2 with phosphite ligands. In the present contribution we report[7b] a chemical, spectroscopic, and structural investigation of this reaction, the course of which represents, to our knowledge, an unprecedented mode of reactivity for a d- or f-element hydride

$M \leftarrow :P(OR)_3$

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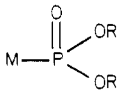

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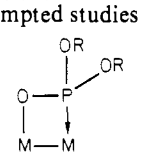

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with trialkyl phosphites. We also report the synthesis and characterization by single-crystal X-ray diffraction of a phosphinidene-bridged binuclear organoactinide which results from this chemistry.

Experimental Section

Synthetic Methods. All organoactinides were handled in Schlenk glassware on a dual-manifold Schlenk line or interfaced to a high-vacuum (10^{-5} torr) system. Solid transfers were accomplished in a Vacuum Atmospheres Corp. glovebox equipped with an atmosphere purification system, maintained under a nitrogen atmosphere. Argon (Matheson, prepurified), nitrogen (Matheson, prepurified), and hydrogen (Linde) were purified by passage through sequential columns of MnO and Davison 4A molecular sieves. Reactions with gases were carried out on the high-vacuum line using a mercury-filled manometer. The starting materials $Cp'_2Th(CH_3)_2$, $Cp'_2U(CH_3)_2$, $(Cp'_2ThH_2)_2$, and $(Cp'_2UH_2)_2$ were prepared as described elsewhere.[11] Trimethyl phosphite and triisopropyl phosphite (Strem) were dried by refluxing over sodium and then distilling under reduced pressure. The ligands $P(C_2H_5)(OCH_3)_2$ (Organometallics, Inc.) and $P(C_2H_5)_2(OCH_3)$ (Strem) were stirred over Na/K alloy overnight, distilled under vacuum, and freeze–pump–thaw degassed. Measured quantities of these reagents were transferred via a 250-μL gastight syringe. Solvents were thoroughly washed, dried, and deoxygenated in a manner appropriate to each and were then distilled under nitrogen. They were stored over appropriate drying agents in evacuated storage bulbs on the vacuum line.

Analytical Methods. Proton and phosphorus NMR spectra were obtained on a JEOL FX 270 (FT, ^{1}H 269.65 MHz; ^{31}P 109.16 MHz), JEOL FX 90Q (FT, ^{1}H 89.55 MHz; ^{31}P 36.19 MHz), or Varian EM-390 (CW, 90 MHz) instrument. Chemical shifts are referenced relative to internal Me_4Si or external 85% H_3PO_4. Samples were prepared either on a high-vacuum line or in the glovebox. Deuterated aromatic solvents were dried overnight over Na/K alloy and were degassed by freeze–pump–thaw cycles on a high-vacuum line. The magnetic susceptibility of $[Cp'_2U(OCH_3)]_2PH$ was measured by the Evans method.[12] Infrared spectra were recorded on a Perkin-Elmer 599B spectrophotometer using Nujol mulls sandwiched between KBr plates in an O-ring-sealed airtight holder. Spectra were calibrated with polystyrene film.

Elemental analyses were performed by Dornis and Kolbe Mikroanalytisches Laboratorium, Mülheim, West Germany.

Synthesis of $[Cp'_2U(OCH_3)]_2PH$ (5). In a 30-mL reaction flask in the glovebox were placed 2.00 g (3.71 mmol) of $Cp'_2U(CH_3)_2$ and 0.15 mL (1.27 mmol) of $P(OCH_3)_3$. The reaction apparatus was then attached to the vacuum line, the reagents were cooled to −196 °C, and 15 mL of dry, degassed pentane was distilled into the reaction flask. After warming to room temperature, the resulting solution was filtered and an atmosphere of H_2 admitted. After stirring for 6 h at room temperature, the solution had become dark green. The volume was next reduced to 5 mL and the solution slowly cooled to −78 °C. Cold filtration yielded a dark green, microcrystalline solid, which was washed with 3 × 3 mL portions of filtrate pentane by Soxhlet extraction. The volatile materials were then removed in vacuo and the product was further dried overnight under high vacuum; yield 0.65 g (42% based upon $P(OCH_3)_3$) of $[Cp'_2U(OCH_3)]_2PH$ as dark green microcrystals.

IR (Nujol mull): 2193 m, 1262 vw, 1100 vs, 1022 s, 950 w, 802 w, 563 w, 422 s cm^{-1}. Anal. Calcd for $C_{42}H_{67}O_2PU_2$: C, 45.41; H, 6.08; P, 2.79. Found: C, 45.89; H, 6.11; P, 2.58.

Synthesis of $[Cp'_2Th(OCH_3)]_2PH$ (6). This reaction was carried out in a manner analogous to the uranium system above, using 1.00 g (1.88 mmol) of $Cp'_2Th(CH_3)_2$ and 0.078 mL (0.66 mmol) of $P(OCH_3)_3$ in 10 mL of dry, deoxygenated pentane. As assessed by ^{1}H NMR, this reaction required 37 h to reach completion. Workup as above gave 0.315 g (43% based upon $P(OCH_3)_3$) of $[Cp'_2Th(OCH_3)]_2PH$ as a light yellow, microcrystalline solid.

IR (Nujol mull): 2200 m, 1105 vs, 1022 m, 800 w, 580 s cm^{-1}. Anal. Calcd for $C_{42}H_{67}O_2PTh$: C, 45.90; H, 6.14; P, 2.82. Found: C, 45.83; H, 6.17; P, 2.93.

Synthesis of $Cp'_2U(OCH_3)_2$ (7). In the drybox, a 30-mL reaction vessel was charged with 0.300 g (0.518 mmol) of Cp'_2UCl_2 and 0.065 g (1.203 mmol) of $NaOCH_3$. The reaction apparatus was then attached to a vacuum line, the reaction flask was cooled to −78 °C, and 10 mL of dry, degassed 1,2-dimethoxyethane was distilled into the reactants in vacuo. An atmosphere of argon was admitted and the red slurry allowed to warm to room temperature. Next the flask was lowered into a 70 °C oil bath, and the reaction was stirred for 14 h at this temperature. The oil bath was then removed and the solvent stripped under high vacuum to yield a yellow-green residue. The residue was dried in vacuo for 1.5 h, after which time it was taken up in 3 mL of dry, degassed pentane. The pentane solution was next cooled to −78 °C for 10 min and cold-filtered to yield a yellow-green filtrate. Slow evaporation of the filtrate and vacuum drying for 2 h yielded 0.130 g (45%) of $Cp'_2U(OCH_3)_2$ as a yellow-green, microcrystalline solid.

IR (Nujol mull): 1113 vs, 1088 vs, 1020 w, 800 w cm^{-1}. Anal. Calcd for $C_{22}H_{36}O_2U$: C, 46.31; H, 6.36. Found: C, 46.26; H, 6.29.

Synthesis of $Cp'_2Th(OCH_3)_2$ (8). In a manner analogous to that above, $Cp'_2Th(OCH_3)_2$ was prepared in 51% yield as colorless microcrystals.

IR (Nujol mull): 1123 vs, 1083 vs, 1020 w, 800 w cm^{-1}. Anal. Calcd for $C_{22}H_{36}O_2Th$: C, 46.82; H, 6.43. Found: C, 46.69; H, 6.42.

Study of the $(Cp'_2ThH_2)_2$ + $P(OCH_3)_3$ Reaction by Toepler Pump. In the glovebox, 0.400 g (0.396 mmol) of $(Cp'_2ThH_2)_2$ was placed in a reaction tube that could be sealed with a Kontes high-vacuum Teflon valve. The tube was next connected to the high-vacuum line, and 5 mL of dry, degassed toluene was distilled into the tube, which had been cooled to −196 °C. Then 0.037 mL (0.314 mmol) of $P(OCH_3)_3$, which was placed in a separate vessel on the vacuum line, was vacuum transferred onto the frozen solution. The tube was then closed and the reaction mixture stirred for 5 days (a time judged by the NMR studies to be adequate for completion) in the dark at room temperature. The evolved gases (0.621 mmol, noncondensable at −196 °C) were then removed by Toepler pump and passed through a CuO catalyst at 280 °C. Combustion was complete at this low temperature and the combustion product was involatile at −78 °C. These results indicate the formation of H_2 in 98% of the theoretical yield given by eq 6.

X-ray Crystallographic Study[13] of $[Cp'_2U(OCH_3)]_2PH$ (5). Dark green crystals of **5** suitable for diffraction analysis were grown by allowing a saturated pentane solution of $Cp'_2U(CH_3)_2$ and 0.35 equiv of $P(OCH_3)_3$ to stand under an H_2 atmosphere at room temperature for 4 days. They are at 20 ± 1 °C monoclinic with a = 13.926 (3) Å, b = 10.765 (3) Å, c = 15.282 (4) Å, β = 107.63 (2)°, V = 2183 (1) Å^3, and Z = 2 [μ_a(Mo Kα)[14a] = 7.09 mm^{-1}; d_{calcd} = 1.690 g cm^{-3}]. The systematically absent reflections in the diffraction pattern were those required by the centrosymmetric space group $P2/n$ (an alternate setting of $P2/c$-C_{2h}^4, No. 13)[15a] or the noncentrosymmetric space group Pn (an alternate setting of Pc-C_s^2, No. 7).[15b] The choice of the centrosymmetric space group was fully supported by the various statistical indicators based on normalized structure factors as well as by all stages of the subsequent structure determination and refinement.

Intensity measurements were made on a Nicolet P1 autodiffractometer using full (1.00° wide) ω scans and graphite-monochromated Mo Kα radiation for a specimen having the shape of a rectangular parallelepiped with dimensions of 0.15 × 0.60 × 0.75 mm. This crystal was sealed under N_2 in a thin-walled glass capillary and mounted on a goniometer with its second longest edge nearly parallel to the ϕ axis of the diffractometer. A total of 2513 independent reflections having $2\theta_{\mathrm{MoK}\alpha} < 43.0°$ (the equivalent of 0.50 limiting Cu Kα spheres) were measured with a scanning rate of 6° min^{-1}. The data collection and reduction procedures which were used are described elsewhere,[16] the scan width and step-off for background measurements were both 1.00°, and the ratio of total background counting time to net scanning time was 0.50. The intensity data were corrected empirically for absorption effects using ψ scans for an intense reflection having 2θ = 10.0° (the relative transmission factors ranged from 0.09 to 1.00).

The structure was solved by using the "heavy-atom" technique. Unit-weighted anisotropic full-matrix least-squares refinement of the parameters for the U and P atoms converged to R_1 (unweighted, based on F)[17] = 0.109 and R_2 (weighted based on F)[17] = 0.154 for 1677

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[13] See paragraph at end of paper regarding supplementary material.

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[17] The R values are defined as

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

and

$$R_2 = \{\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2\}^{1/2}$$

where w is the weight given each reflection. The function minimized is

$$\sum w(|F_o| - K|F_c|)^2$$

where K is the scale factor.

Table I. ^1H and ^{31}P NMR Spectral Data for New Complexes[a,b]

complex	nuclei	η^5-$(CH_3)_5C_5$	other
$\{U[\eta^5\text{-}(CH_3)_5C_5]_2[OCH_3]\}_2PH$	^1H	−2.98 (60 H, s, lw = 17 Hz)	75.5 (6 H, s, lw = 12 Hz, U-OCH_3)
$\{Th[\eta^5\text{-}(CH_3)_5C_5]_2[OCH_3]\}_2PH$	^1H	2.21 (60 H, s)	3.84 (6 H, s, Th-OCH_3), 0.54 (1 H, d, J = 114.7 Hz, Th–P–H)
	^{31}P		74.0 (d, J = 114.7 Hz, P-H)
$U[\eta^5\text{-}(CH_3)_5C_5]_2[OCH_3]_2$	^1H	−0.72 (30 H, s, lw = 7 Hz)	17.5 (6 H, s, lw = 2.5 Hz, U-OCH_3)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2[OCH_3]_2$	^1H	2.11 (30 H, s)	3.79 (6 H, s, Th-OCH_3)

[a] Recorded in C_6D_6 at 30 °C. Chemical shifts are reported in parts per million from Me_4Si for ^1H spectra and from 85% H_3PO_4 for ^{31}P spectra. [b] s = singlet, d = doublet, lw = line width at half-maximum.

independent absorption-corrected reflections having $2\theta_{MoK\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. Inclusions of the remaining 22 non-hydrogen atoms into the model with isotropic thermal parameters gave $R_1 = 0.057$ and $R_2 = 0.068$ for 1677 reflections.

The final cycles of empirically weighted[18] full-matrix least-squares refinement which utilized anisotropic thermal parameters for all non-hydrogen atoms gave $R_1 = 0.041$ and $R_2 = 0.053$ for 1677 independent absorption-corrected reflections having $I > 3\sigma(I)$. Since a careful examination of final $|F_o|$ and $|F_c|$ values indicated the absence of extinction effects, extinction corrections were not made. The three highest peaks (0.83–1.38 e/Å^3) in a difference Fourier calculated at this point were within 1.27 Å of the U atom; the remaining peaks did not correspond to structurally reasonable positions for hydrogen atoms of **5**.

All structure factor calculations employed recent tabulations of atomic form factors[14b] and anomalous dispersion corrections[14c] to the scattering factors of the U and P atoms. All calculations were performed on a Data General Eclipse-S200 computer equipped with 64K of 16-bit words, a floating-point processor for 32- and 64-bit arithmetic, and versions of the Nicolet EXTL interactive crystallographic software package as modified at Crystalytics Co.

Results

Phosphite–Actinide Hydride Reactions. In an initial attempt to study analogues of eq 1 and 2 using trialkyl phosphites as ligands, the reactions of $Cp'_2U(CH_3)_2$ and $Cp'_2Th(CH_3)_2$ with $P(OCH_3)_3$ were investigated under an H_2 atmosphere (eq 3 and 4). Under conditions of excess H_2 and $n > 1$, each reaction yields

$$Cp'_2U(CH_3)_2 + nP(OCH_3)_3 \xrightarrow{H_2} \mathbf{5} + \mathbf{7} \tag{3}$$

$$Cp'_2Th(CH_3)_2 + nP(OCH_3)_3 \xrightarrow{H_2} \mathbf{6} + \mathbf{8} \tag{4}$$

two products, which can be separated by fractional crystallization (**7** and **8** are extremely soluble in pentane). As is typical of U(IV) organometallics,[3,11] the ^1H NMR spectra of **5** and **7** exhibit substantial isotropic shifts (Table I). Thus, compound **5** displays singlet ^1H resonances at −2.98 and 75.5 ppm in an intensity ratio of 10:1 (Figure 1), while **7** exhibits resonances at −0.72 and 17.5 ppm in an intensity ratio of 5:1. The relatively narrow line widths are suggestive of U(IV),[3,5b,d,11] and in each case the more intense resonance is in the chemical shift region generally expected for a $U^{IV}[\eta^5\text{-}(CH_3)_5C_5]_2$ moiety. Although elemental analysis indicates the presence of phosphorus in **5** (but not **7**), it has not been possible to observe a signal in the ^{31}P NMR spectrum. This is not an unexpected observation for phosphorus bound directly to uranium,[5] and apparently ^{31}P spin-lattice relaxation times are rather short in such circumstances.

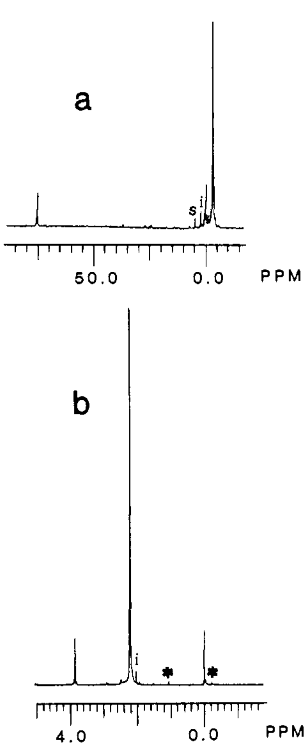

Figure 1. (a) 89.55-MHz ^1H NMR spectrum of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(OCH_3)\}_2PH$ (**5**) in C_6D_6 at 30 °C (s denotes residual proton absorption of solvent and i denotes a small impurity peak which is less than 3% in integrated intensity relative to $(CH_3)_5C_5$ absorption). Peak at 0 ppm is due to Me_4Si. (b) 89.55-MHz ^1H NMR spectrum of $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(OCH_3)\}_2PH$ (**6**). Asterisks denote signals assignable to the P-H proton. The impurity (i) is due to the presence of residual $Th[\eta^5\text{-}(CH_3)_5C_5]_2(OCH_3)_2$ (**7**). Resonance at 0 ppm is due to Me_4Si.

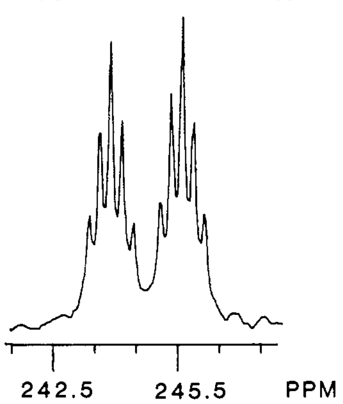

Figure 2. 109.16-MHz Proton-coupled ^{31}P NMR spectrum resulting from deoxygenated D_2O hydrolysis of a C_6D_6 solution of **5**.

Further information on the structures of **5** and **7** derives from infrared spectroscopic and chemical studies. Both complexes exhibit strong, infrared-active transitions in the 1100-cm^{-1} region which are not assignable to a UCp'_2 residue.[11] Rather, these features are assignable to a C–O stretching mode as in a uranium methoxide complex.[19] In addition, the infrared spectrum of **5** displays a non-UCp'_2 transition at 2193 cm^{-1}, which is displaced to 1575 cm^{-1} when eq 3 is carried out under D_2. This vibration

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(18) Empirical weights were calculated from the equation

$$\sigma = \sum_0^3 a_n|F_o|^n = 2.53 + 7.10 \times 10^{-3}|F_o| - 1.28 \times 10^{-5}|F_o|^2 + 1.64 \times 10^{-7}|F_o|^3$$

the a_n being coefficients derived from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$$

where the F_c values were calculated from the fully refined model using unit weighting and an $I > 3\sigma(I)$ rejection criterion.

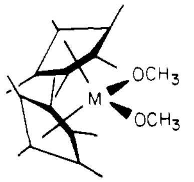
(19) (a) Cuellar, E. A.; Miller, S. S.; Marks, T. J.; Weitz, E. *J. Am. Chem. Soc.* **1983**, *105*, 4580–4589. (b) Cuellar, E. A.; Marks, T. J. *Inorg. Chem.* **1981**, *20*, 2129–2137. (c) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. "Metal Alkoxides"; Academic Press: New York, 1978; pp 116–134. (d) Bradley, D. C. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 259–322. (e) Bradley, D. C.; Fisher, K. J. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *5*, 65–78.

is reasonably assigned to a P–H stretching mode[20] (ν_{P-H}/ν_{P-D} = 1.39). When complex **5** is decomposed with deoxygenated H_2O, the ^{31}P NMR spectrum reveals PH_3[21] (δ −239, $^1J_{P-H}$ = 189.2 Hz (quartet)) as the only phosphorus-containing product. Hydrolysis of **5** with a trace of D_2O produces a quintet ($^1J_{P-D}$ = 30 Hz) in the $^{31}P\{^1H\}$ NMR spectrum and a doublet of quintets ($^1J_{P-H}$ = 189.2 Hz) in the undecoupled spectrum. This information is illustrated in Figure 2. These latter results are consistent with the formation of PD_2H.[21] Isotopic exchange of PH_3 with D_2O is known to be slow under conditions such as these.[22]

The magnetic properties of **5** were investigated in solution by the Evans technique.[12] At 30 °C, the average of three measurements yields χ_M = 10 100 (3500) × 10^{-6} emu mol^{-1}, μ_{eff} = 2.42 (44) μ_B (296 K) per uranium atom. These results, although not definitive, are in best agreement with a U(IV) formulation for **5**, as opposed to U(III) or U(III)–U(IV) mixed valency.[23]

In regard to eq 4, the ^1H NMR spectrum of thorium complex **6** (Figure 1) exhibits singlet resonances at δ 2.21 (60 H) and 3.84 (6 H), which are assignable to η^5-$(CH_3)_5C_5$[11] and OCH_3[19] ligands, respectively. Furthermore, a doublet at δ 0.54 (J = 114.7 Hz, 1 H) is also evident and can be assigned to a P–H functionality.[21] An analogous resonance could not be unambiguously located in the case of **5**. The low magnitude of this one-bond P–H coupling constant indicates the presence of unusually electropositive substituents and/or of unusual valence angles about the phosphorus atom.[21] The $^{31}P\{^1H\}$ NMR spectrum of **6** consists of a singlet at δ 74.0 that splits into a doublet (J = 114.7 Hz) in the absence of heteronuclear decoupling. Selective-decoupling experiments indicate that this phosphorus unit is coupled to the proton resonance at δ 0.54. The ^1H NMR spectrum of **8** consists of singlet resonances at δ 2.11 (30 H) and at δ 3.79 (6 H), assignable to η^5-$(CH_3)_5C_5$ and OCH_3 groups, respectively. The infrared spectra of the pairs **5**,**6** and **7**,**8** are essentially superimposable.

At this juncture, the chemical and spectroscopic results strongly suggested that **7** and **8** were bis(pentamethylcyclopentadienyl)actinide(IV) bis(methoxides) (**9**). This assertion was verified by

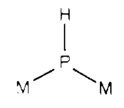


9, M = Th, U

the synthesis and characterization of authentic samples. Methathesis as shown in eq 5 proved to be the most stratightforward

$$Cp'_2MCl_2 + 2NaOCH_3 \xrightarrow[70\ ^\circ C,\ 14\ h]{DME} \underset{\substack{\mathbf{7},\ M = U \\ \mathbf{8},\ M = Th}}{Cp'_2M(OCH_3)_2} + 2NaCl \quad (5)$$

route, while the reaction of methanol with the corresponding hydrides proved to be far less clean. The identity of **5** and **6** does not follow unambiguously from the data at hand, although the presence of a bridging P–H functionality (e.g., **10**) as well as methoxide and η^5-$(CH_3)_5C_5$ ligands is implicated. For these reasons, a diffraction investigation of the molecular structure of **5** was undertaken.



10

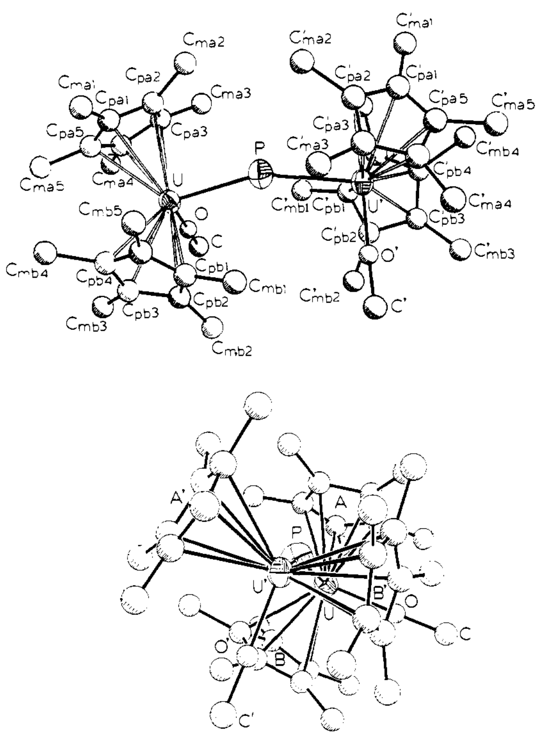


Figure 3. Perspective ORTEP plots showing two different views of the solid-state structure for the $\{U[\eta^5-(CH_3)_5C_5]_2(OCH_3)\}_2PH$ molecule (**5**). The uranium and phosphorus atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density; all carbon and oxygen atoms are represented by arbitrarily sized spheres for purposes of clarity. Hydrogen atoms were not located and are not shown. Atoms labeled with primes are related to those labeled without primes by the crystallographic C_2 axis located at ($^1/_4$, y, $^1/_4$) in the unit cell which passes through the PH^{2-} ligand.

Table II. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $\{U[\eta^5-(CH_3)_5C_5]_2(OCH_3)\}_2PH$ (5)[a]

atom type[b]	10^3x	10^3y	10^3z
U	207.06 (4)	236.04 (5)	410.26 (4)
P	250.0 (-)[c]	285.3 (6)	250.0 (-)[c]
O	101 (1)	100 (1)	366 (1)
C	25 (2)	5 (2)	337 (2)
C_{pa1}	184 (2)	469 (2)	484 (2)
C_{pa2}	142 (2)	478 (2)	392 (1)
C_{pa3}	53 (2)	402 (2)	366 (1)
C_{pa4}	52 (2)	349 (2)	450 (2)
C_{pa5}	134 (2)	391 (2)	519 (1)
C_{ma1}	272 (2)	543 (3)	540 (4)
C_{ma2}	175 (3)	575 (2)	328 (3)
C_{ma3}	-14 (3)	400 (4)	269 (2)
C_{ma4}	−29 (3)	269 (3)	465 (5)
C_{ma5}	131 (4)	357 (4)	617 (2)
C_{pb1}	394 (1)	128 (2)	446 (1)
C_{pb2}	328 (2)	35 (2)	452 (1)
C_{pb3}	305 (1)	63 (2)	535 (1)
C_{pb4}	352 (1)	173 (2)	569 (1)
C_{pb5}	405 (1)	213 (2)	514 (2)
C_{mb1}	461 (2)	125 (4)	381 (2)
C_{mb2}	300 (3)	−82 (3)	400 (3)
C_{mb3}	236 (2)	−8 (5)	579 (4)
C_{mb4}	367 (3)	234 (4)	667 (2)
C_{mb5}	481 (2)	325 (3)	527 (3)

[a] Numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 3. [c] This is a symmetry-required value and is therefore listed without an estimated standard deviation.

Molecular Structure of $\{U[(CH_3)_5C_5]_2(OCH_3)\}_2PH$ (5). The X-ray structural analysis reveals that single crystals of **5** are

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(20) (a) Corbridge, D. E. C. *Top. Phosphorus Chem.* **1969**, *6*, 251–255. (b) Bellamy, L. J. "The Infra-red Spectra of Complex Molecules", 3rd ed.; Chapman and Hall: London, 1975; pp 357–358.

(21) (a) Brazier, J. F.; Houalla, D.; Loenig, M.; Wolf, R. *Top. Phosphorus Chem.* **1976**, *8*, 99–192. (b) Mavel, G. *Annu. Rep. NMR Spectrosc.* **1973**, *5B*, 1–441. (c) Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 1–489.

(22) (a) Weston, R. E.; Bigeleisen, J. *J. Am. Chem. Soc.* **1954**, *76*, 3074–3078. (b) With very larrge excesses of D_2O, we find that there is only ca. 50% exchange after 18 h.

(23) (a) Kanellakopulos, B. In ref 3c, Chapter 1. (b) Marks, T. J.; Seyam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529–5539. (c) For Cp'$_2$U(dmpe)(H), χ_M = 5120 × 10^{-6} emu mol^{-1} and μ_{eff} = 3.47 μ_B.[5d]

Table IV. Bond Lengths (Å) and Angles (deg) in Coordination Groups of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(OCH_3)\}_2PH$[a] (5)

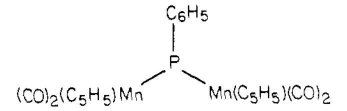
parameter[b]	value	parameter[b]	value
		Lengths	
U-O	2.046 (14)	$U\text{-}C_{pa_1}$	2.80 (2)
		$U\text{-}C_{pa_2}$	2.75 (2)
U-P	2.743 (1)	$U\text{-}C_{pa_3}$	2.71 (2)
		$U\text{-}C_{pa_4}$	2.70 (2)
$U\text{-}C_{ga}$	2.483 (-)	$U\text{-}C_{pa_5}$	2.76 (2)
$U\text{-}C_{gb}$	2.462 (-)	$U\text{-}C_{pb_1}$	2.76 (2)
		$U\text{-}C_{pb_2}$	2.70 (2)
O-C	1.44 (3)	$U\text{-}C_{pb_3}$	2.72 (2)
		$U\text{-}C_{pb_4}$	2.73 (2)
U···U′	5.382 (1)	$U\text{-}C_{pb_5}$	2.75 (2)
		Angles	
PUO	100.0 (4)	$C_{ga}UO$	105.0 (-)
		$C_{gb}UO$	103.5 (-)
$C_{ga}UC_{gb}$	133.1 (-)	$C_{ga}UP$	107.1 (-)
		$C_{gb}UP$	103.6 (-)
UPU′	157.7 (2)		
		UOC	178 (1)

[a] Numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 3.

composed of dinuclear $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(OCH_3)\}_2PH$ molecules like that shown in Figure 3. The bridging μ-PH^{2-} ligand in **5** lies on a crystallographic twofold axis at $^1/_4, y, ^1/_4$ in the unit cell. The U(IV) ion in each structurally equivalent half of the molecule adopts the familiar "pseudotetrahedral" bent-sandwich $Cp'_2M(X)Y$ actinide coordination geometry,[3,5,24] by being π bonded to two $(CH_3)_5C_5^-$ ligands and σ bonded to a terminal OCH_3^- ligand and the bridging PH^{2-} ligand. Final atomic coordinates and anisotropic thermal parameters for the non-hydrogen atoms of **5** are given in Tables II and III,[13] respectively. Bond lengths and angles in the coordination groups and the $(CH_3)_5C_5^-$ ligands of **5** are given with estimated standard deviations in Tables IV and V,[13] respectively. The labeling scheme is shown in Figure 3.

The structural parameters in Table IV for the coordination groups of **5** are typical for a formally 8-coordinate $Cp'_2U(X)Y$ species:[3,5,24] U–C(cyclopentadienyl), 2.74 (2, 3, 6, 10) Å,[25] U–O, 2.046 (14) Å; $\angle C_{ga}\text{–}U\text{–}C_{gb}$,[26] 133.1°; ∠P–U–O, 100.0 (4)°; $\angle C_g\text{–}U\text{–}O$, 104.3 (-, 8, 8, 2)°, and $\angle C_g\text{–}U\text{–}P$, 105.3 (-, 18, 18, 2)°. The metrical parameters for the $(CH_3)_5C_5^-$ ligands are also unexceptional:[3,5,24] ring C–C, 1.38 (3, 3, 8, 10) Å; ring-to-methyl C–C, 1.54 (4, 4, 7, 10) Å; ∠ ring C–C–C, 108 (2, 2, 5, 10)°; ∠ ring-to-methyl C–C–C, 126 (2, 4, 12, 20)°. The five-membered carbon rings of both independent $(CH_3)_5C_5^-$ ligands are coplanar to within 0.03 Å,[27a,b] with the methyl groups displaced by 0.01–0.32 Å from the respective five-carbon least-squares mean plane in a direction away from the U atom. In each Cp′ ligand, the methyl groups nearest the equatorial girdle (C_{ma1} and C_{ma5} in ligand a and C_{mb4} in ligand b) have some of the largest displacements. The least-squares mean planes of these five-membered rings intersect that of the of the "equatorial girdle" defined by U, O, and P[27c] in dihedral angles of 22.8 and 20.8°. The two five-carbon ring mean planes[27a,b] and that of the "equatorial girdle"[27c] intersect the mean plane defined by U and the two five-carbon ring centers of gravity[27d] (C_{ga} and C_{gb}, respectively) in dihedral angles ranging from 88.3 to 89.4°.

In regard to the σ bonded ligands, the 2.743 (1) Å U–P bond length in **5** is significantly shorter than the formally coordinate-covalent U–P bond lengths of 3.211 (8) and 3.092 (8) Å in *trivalent*, formally 9-coordinate $Cp'_2U(dmpe)H$[5d] and 3.104 (6) Å in *tetravalent*, formally 8-coordinate $U(dmpe)_2(OC_6H_5)_4$.[5c] For these coordination numbers, differences in U(III) and U(IV) ionic radii[28] should be on the order of ca. 0.12 Å.[5b,29] The significantly shorter U–P distance in **5** may reflect the lower phosphorus coordination number as well as phosphorus-to-uranium π donation (and multiple-bond character) analogous to that proposed[31] for transition-metal dialkylamides. The rather obtuse U–P–U bond angle of 157.7 (2)° in **5** is significantly larger than the Mn–P–Mn angle of 138 (1)° in the only other well-characterized μ-phosphinidene complex, $[CpMn(CO)_2]_2PC_6H_5$ (**11**).[30] The large angle in the present case may reflect large, repulsive $Cp'_2U(OCH_3)$–$Cp'_2U(OCH_3)$ nonbonded interactions and/or the less directed character of a more polar metal–ligand bonding situation. However, in view of the foregoing discussion, the larger angle could also conceivably reflect π bonding ($sp^3 \rightarrow sp^2$).



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The U–O distance of 2.046 (14) Å in **5** is in favorable agreement with the value of 2.056 (13) Å reported for the terminal alkoxide of $[U(\eta^3\text{-}C_3H_5)_2(O\text{-}i\text{-}C_3H_7)(\mu\text{-}O\text{-}i\text{-}C_3H_7)]_2$.[32a] Somewhat longer are the U(IV)–O distances reported for $U(dmpe)_2(OC_6H_5)_4$ (2.17 (1) Å),[5c] U(catecholate)$_4$ (2.375 (13) Å),[32b] U(hexafluoroacetonylpyrazolide)$_4$ (2.237 (8) Å),[32c] and $U\{\eta^5\text{-}1,3\text{-}[(CH_3)_3Si]_2C_5H_3\}_2[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2$ (2.120 (6), 2.109 (6) Å).[32d] The rather large U–O–C(methyl) angle of 178 (1)° in **5** is comparable to that in the aforementioned U(IV) allyl alkoxide,[32a] 178.0 (10)°, and in a number of early transition-metal alkoxides.[19c–e,33] The angle in the above silyl-substituted cyclopentadienyl aryl oxide is somewhat smaller at 157°.[32d] Such structural features are arguably a consequence of oxygen-to-metal π donation and rather shallow potential surfaces for ∠U–O–C deformation.

There are no intermolecular nonbonded contacts which are significantly shorter than the sum of the appropriate van der Waals radii.[34]

Reaction Mechanism and Stoichiometry. The foregoing chemical discussion provides only circumstantial evidence for the intermediacy of an actinide hydride in eq 3 and 4. More conclusive evidence is provided by the observation that, in the absence of H_2,

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(24) (a) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Organomet. Chem.* **1983**, *250*, 237–246. (b) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357–7360. (c) Marks, T. J.; Manriquez, J. M.; Fagan, P. J.; Day, V. W.; Day, C. S.; Vollmer, S. H. *ACS Symp. Ser.* **1980**, *No. 131*, 1–29.

(25) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

(26) C_{ga} and C_{gb} refer to the centers of gravity for the five-carbon rings of $(CH_3)_5C_5^-$ ligands a and b, respectively.

(27) The least-squares mean planes for the following groups of atoms in $U[Cp'_2(OCH_3)]_2PH$ (**5**) are defined by the equation $aX + bY + cZ = d$, where X, Y, and Z are orthogonal coordinates measured in angstroms along $\vec{a}$, $\vec{b}$, and $\vec{c}^*$, respectively, of the unit cell: (a) C_{pa1}, C_{pa2}, C_{pa3}, C_{pa4}, and C_{pa5} (coplanar to within 0.01 Å): $a = 0.5512$, $b = -0.7652$, $c = -0.3328$, $d = -4.704$; (b) C_{pb1}, C_{pb2}, C_{pb3}, C_{pb4}, and C_{pb5} (coplanar to within 0.03 Å): $a = 0.7878$, $b = -0.5222$, $c = 0.3265$, $d = 5.0618$; (c) U, P, and O: $a = 0.7204$, $b = -0.6934$, $c = 0.0163$, d, $= 0.3060$; (d) U, C_{ga},[26] and C_{gb}:[26] $a = 0.5875$, $b = 0.6137$, $c = -0.5274$, $d = 0.3280$.

(28) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767.

(29) (a) Raymond, K. N.; Eigenbrot, C. W., Jr. *Acc. Chem. Res.* **1980**, *13*, 276–283. (b) Raymond, K. N. In ref 3c, Chapter 8. (c) Baker, E. C.; Halstead, G. W.; Raymond, K. N. *Struct. Bonding (Berlin)* **1976**, *25*, 23–68.

(30) Huttner, G.; Müller, H. D.; Frank, A.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 705–706. **Note Added in Proof**: See also: Huttner, G.; Borm, J.; Zsolnai, L. *J. Organomet. Chem.*, **1984**, *263*, C33–C36 ($[Cr(CO)_5]_2P(t\text{-}C_4H_9)$).

(31) (a) Eller, P. J.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1–95. (b) For an alternative interpretation of the M–N bond lengths in f-element dialkylamides, see ref 29a.

(32) (a) Brunelli, M.; Perego, G.; Lugli, G.; Mazzei, A. *J. Chem. Soc., Dalton Trans.* **1979**, 861–868. (b) Sofen, S. R.; Abu-Dari, K.; Freyberg, D. P.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 7882–7887. (c) Volz, K.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1976**, *15*, 1827–1831. (d) Hunter, W. E.; Atwood, J. L. Proc. First Int. Conf. Chem. Tech. Lanthanides, Actinides; Venice, Sept 5–10, 1983, Abstract A50.

(33) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009–3014 and references therein.

(34) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

there is no detectable reaction between $Cp'_2U(CH_3)_2$ or $Cp'_2Th(CH_3)_2$ and $P(OCH_3)_3$. Furthermore, in NMR tube reactions both $(Cp'_2UH_2)_2$ and $(Cp'_2ThH_2)_2$ were found to react with $P(OCH_3)_3$ as shown in eq 3 and 4, producing the product pairs **5**,**7** and **6**,**8**, respectively. In the case of uranium, the reaction is complete within 1 h, whereas the thorium hydride reaction requires anywhere from one to several days, depending on reactant concentrations. As regards reaction stoichiometry, a Toepler pump quantitation of evolved gases in the thorium hydride reaction (see Experimental Section for details) verifies the stoichiometry shown in eq (6)—98% of the theoretical yield of H_2 is produced. Com-

$$5(Cp'_2ThH_2)_2 + 4P(OCH_3)_3 \rightarrow 2Cp'_2Th(OCH_3)_2 + 4[Cp'_2Th(OCH_3)]_2PH + 8H_2 \quad (6)$$

bustion experiments indicate that >95% of the evolved gas is hydrogen. There is no evidence for PH_3 formation in the NMR experiments.

In the case of the $Cp'_2U(CH_3)_2/H_2/P(OCH_3)_3$ system, monitoring of the reaction by ^1H NMR failed to reveal any intermediates. Indeed, these spectral studies indicated that even detectable quantities of $(Cp'_2UH_2)_2$ were not present—only starting materials and products. In contrast, the kinetically slower $Cp'_2Th(CH_3)_2/H_2/P(OCH_3)_3$ system reveals a variety of intermediates when monitored by ^1H and ^{31}P NMR. In NMR tube reactions of $(Cp'_2ThH_2)_2$ and $P(OCH_3)_3$, the hydride $(Cp'_2ThH_2)_2$ is observed throughout most of the reaction, and in the initial stages (within 1 h) six OCH_3 resonances are evident in the ^1H NMR spectrum. At 109.16 MHz, eight singlets are observed in the $^{31}P\{^1H\}$ spectrum within 1 h, and all split into doublets, with $^1J_{P-H}$ ranging from 97 to 119 Hz in the coupled spectrum. No $^3J_{P-H}$ couplings indicative of $P-OCH_3$ species (J = 7-14 Hz[21]) are detected. Clearly, cleavage of the $P-OCH_3$ bonds and the formation of >P-H groups take place in the initial stages of the reaction.

Survey NMR tube reactions indicate that the $Cp'_2U(CH_3)_2/H_2$ reagent also reacts with $P(O\text{-}i\text{-}C_3H_7)_3$, but at a considerably slower rate than with $P(OCH_3)_3$. The nature of the products appears to be the same as in the trimethyl phosphite reaction.[35a] The $Cp'_2U(CH_3)_2/H_2$ system also reacts with $P(C_2H_5)(OCH_3)_2$ and $P(C_2H_5)_2(OCH_3)$. In the former case, the preliminary ^1H NMR data suggest the formation of a $>P-C_2H_5$-containing product and the uranium bis(methoxide) (**7**).[35b] In addition, some **5** is also observed, suggesting possible $P-C_2H_5$ hydrogenolysis. Curiously, ^1H NMR spectra of the second system reveal only $Cp'_2U(OCH_3)_2$, $(Cp'_2UH_2)_2$, and $(Cp'_2UH)_x$;[11] the fate of the phosphorus-containing starting material is still under investigation. Further studies of these reactions are in progress.

Discussion

This study reveals an unprecedented reaction pattern for an organo-d- or -f-element hydride in which a phosphite alkoxide functionality and the metal hydride ligand undergo rapid, quantitative transposition. Although the greater reactivity of trialkyl phosphite ligands over that of trialkylphosphine ligands is well documented,[2,8-10] the bulk of this chemistry (involving transition-metal complexes) involves Arbuzov-like phosphonato products (**3**) in which R-O bond scission occurs. Reactions involving transition-metal-induced P-O bond cleavage are rare and, to our knowledge, have only been identified in the case of an oxophilic titanium complex (eq 7)[36] or pyrolysis of a trimethyl phosphite

$$Cp_2TiCl_2 + 2(CF_3)_2POP(CF_3)_2 \xrightarrow[85\ ^\circ C]{45\ h} 2(CF_3)_2PCl + Cp_2Ti[OP(CF_3)_2]_2 \quad (7)$$

cluster compound.[37] Rather, the closest analogy to the present chemistry may be the single, brief report that $LiAlH_4$ will dealkoxylate dialkyl alkylphosphonites and alkyl dialkylphosphinites as shown in eq 8 and 9.[38] An extrapolation to trialkyl phosphites

$$RP(OR')_2 \xrightarrow[ether]{LiAlH_4} RPH_2 \quad (8)$$

$$R_2P(OR') \xrightarrow[ether]{LiAlH_4} R_2PH \quad (9)$$

is not unreasonable, and the hydridic, oxophilic character of organoactinide hydrides is well established.[3,11,16,24a,39,40]

The phosphorus-containing products of the present chemistry are binuclear μ-PH (phosphinidene) complexes. As already noted, the only other well-characterized μ_2-phosphinidene complex is $[CpMn(CO)_2]_2PC_6H_5$ (**11**).[30] However, polynuclear μ^3-PR and μ^4-PR cluster compounds are far more common.[41] The complex $CrCo_2(CO)_{11}(\mu_3\text{-}PH)$ is the only other well-characterized μ_n-PH compound.[42]

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Registry No. 5, 89579-17-9; **6**, 89596-62-3; **7**, 89579-18-0; **8**, 89579-19-1; $P(OCH_3)_3$, 121-45-9; $Cp_2'U(CH_3)_2$, 67605-92-9; $Cp_2'Th(CH_3)_2$, 67506-90-5.

Supplementary Material Available: Anisotropic thermal parameters and intra-$(CH_3)_5C_5$ metrical parameters for the nonhydrogen atoms of **5**, crystal structure analysis report, and structure factor tables (16 pages). Ordering information is given on any current masthead page.

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(35) (a) NMR tube reactions under excess H_2 employing 0.4 equiv of $P(O\text{-}i\text{-}C_3H_7)_3$ per equiv of $Cp'_2U(CH_3)_2$ exhibited ^1H resonances after 14 h assignable to $Cp'_2U(O\text{-}i\text{-}C_3H_7)_2$ [δ −0.555 (s, 30 H, Cp′), 1.19 (d, 12 H, J = 5.86 Hz, $CH(CH_3)_2$), 22.95 (septet, 2 H, J = 5.86 Hz, $CH(CH_3)_2$)], resonances due to $(Cp'_2UH_2)_2$,[11] and signals at δ −3.6 (s) and +50.9 (broad, s, line width = 20 Hz) in the correct relative intensities for a $\{Cp'_2U[OCH(CH_3)_2]\}_2PH$ complex. (b) NMR tube reactions involving $P(C_2H_5)(OCH_3)_2$ show signals attributable to $Cp'_2U(OCH_3)_2$ as well as singlets at δ −3.0 (s, 60 H, Cp′?) and +75.5 (s, 6 H, OCH_3?). The bis(methoxide) signals decrease at long (>50 h) reaction times. Although several small signals can be assigned to the ethyl group of a $[Cp'_2U(OCH_3)]_2PCH_2CH_3$ complex, infrared spectra also reveal a P-H stretching mode at 2192 cm^{-1}.

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