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New Stoichiometric and Catalytic Organometallic Chemistry with Actinides. C–H Activation and Phosphine/Phosphite Coordination Chemistry

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This short review highlights two areas of recent activity in organoactinide chemistry: actinide-centered homogeneous chemistry in which intra- and intermolecular C–H activation takes place on hydrocarbon fragments, and actinide coordination chemistry involving phosphine and phosphite ligands. It is shown that new metal–ligand bond enthalpy data afford a far greater understanding of observed C–H activation patterns, and, moreover, support the design of successful new strategies for C–H activation on exogenous hydrocarbon molecules. For example, the strain energy of a thoracyclobutane provides the driving force for ring-opening reactions that involve attack on an alkane or arene carbon–hydrogen bond. While phosphines have been shown to be rather unexceptional ligands for organoactinides, the reaction of trialkylphosphites with the organoactinide hydrides $\{M[(CH_3)_5C_5]_2H_2\}_2$, *M* = *Th, U takes a different course. In the case of* $P(OCH_3)_3$, *quantitative demethoxylation of the phosphite occurs under mild conditions to yield μ-phosphinidene complexes of the type* $\{M[(CH_3)_5C_5]_2(OCH_3)\}_2PH$.

Introduction

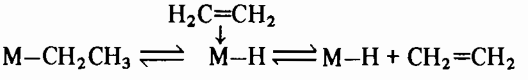
The goal of our exploratory research program in organo-5f-element chemistry [1] is to rationally evolve and characterize new, instructive chemistry deriving from the unconventional structural, bonding, redox, and reactivity properties of actinide ions. As we explore this relatively new field of organometallic chemistry, our aim is not to mimic or duplicate known transition metal chemistry, but to derive new reactivity patterns and to test ideas which will impact upon f- as well as d-element chemistry. For example, f-elements offer the possibility of significantly displacing certain structure/reactivity parameters (*e.g.*, electro- and oxophilicity) beyond what is normally achievable at more conventional metal centers, and of documenting structure/reactivity relationships which might otherwise only obtain under extreme conditions (pressure, temperature) or in less readily studied environments (*e.g.*, on the surfaces of heterogeneous catalysts). Clearly much remains to be learned about stoichiometric and catalytic reaction patterns in situations where conventional two-electron oxidative additions and reductive eliminations, shuttling between relatively low formal oxidation states and coordination numbers, 'soft' metal centers, and a variety of other more classical phenomena appear to be inoperative.

In this contribution we highlight recent results from this Laboratory in two separate areas: C–H activation, and phosphine/phosphite coordination chemistry. In each case, it will be seen that the actinide centers promote new and unusual chemistry. Furthermore, recently acquired [2] thermochemical data on actinide–ligand bond dissociation energies afford a unique perspective both on why certain reactions occur and on how new reactions might be designed.

C–H Activation

The selective cleavage of two-center two-electron bonds on substrates such as endogenous or exogenous hydrocarbon molecules is a major unsolved problem in homogeneous catalysis [3]. A number of C–H activating processes have been observed for organoactinides, and our goal has been to understand both the reaction mechanisms of and the driving forces for such transformations.

One of the simplest and most important C–H activation processes in catalysis is the β-hydride abstraction process (eqn. (1)). Although this reaction is common for many transition metal complexes,



$$M{-}CH_2CH_3 \rightleftharpoons \overset{H_2C=CH_2}{\overset{\downarrow}{M{-}H}} \rightleftharpoons M{-}H + CH_2{=}CH_2 \qquad (1)$$

it has only been observed for organoactinides under unusual circumstances, *i.e.*, photochemically [4], in unusual coordination environments [5], or where

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there is a very stable end product [6]. Why? The answer appears to lie, at least in part, in the thermodynamics of such processes. For a transition metal system where B.D.E.(M–H) – B.D.E.(M–C) ≈ 30 kcal/mol [7] (B.D.E. = bond dissociation enthalpy, formally defined as in eqn. (2)), ΔH for eqn. (1) is predicted to be *ca.* +10 kcal/mol.

$$L_nM{-}R_{(g)} \longrightarrow L_nM^{\bullet}{}_{(g)} + {}^{\bullet}R_{(g)} \qquad (2a)$$

R = hydrocarbyl, H, etc., L = supporting ligand

$$\text{B.D.E.}(L_nTh{-}R) = \Delta H_f^{\circ}(L_nTh)_{(g)} + \Delta H_f^{\circ}(R^{\bullet})_{(g)} - \Delta H_f^{\circ}(L_nTh{-}R)_{(g)} \qquad (2b)$$

Since eqn. (1) creates two particles from one, entropic factors are expected to be on the order of 10 kcal/mol [8] and to render $\Delta G < 0$ kcal/mol under normal conditions. In contrast, B.D.E.(Th–H) – B.D.E.(Th–C) is only *ca.* 15 kcal/mol [2]. Thus, eqn. (1) should be far more endothermic ($\Delta H^{\circ} \approx + 25$ kcal/mol) for thorium. This prediction is supported by our observations [9] (*e.g.*, eqn. (3))

$$(Cp'_2ThH_2)_2 + 4CH_2{=}CH_2 \longrightarrow 2Cp'_2Th(CH_2CH_3)_2 \qquad (3)$$

$C'_p = \eta^5\text{-}(CH_3)_5C_5$) of the facile addition of olefins to actinide hydrides (the reverse of eqn. (1)). Furthermore, eqn. (4) [10] which presumably proceeds via

$$Cp'_2ThCl_2 + 2LiCH(CH_3)_2 \xrightarrow{-78\,^{\circ}C} \xrightarrow{+30\,^{\circ}C} Cp'_2Th(CH_2CH_2CH_3)_2 \qquad (4)$$

an elimination, readdition sequence, argues that kinetic factors such as coordinative saturation are not the sole impediment to β-hydrogen abstraction.

Why is B.D.E.(Th–H) – B.D.E.(Th–CH$_3$) smaller than for many transition metal complexes? Although the answer is not immediately obvious, one explanation may reside in the relatively high polarity of the actinide–ligand bonds. The more polarizable alkyl ligand may simply stabilize the negative charge more effectively than a hydride ligand, thus biasing the energetics of eqn. (2) against the hydride. Such

$$\overset{\delta+\ \delta-}{M{-}CH_3} \qquad \overset{\delta+\ \delta-}{M{-}H}$$

A *B*

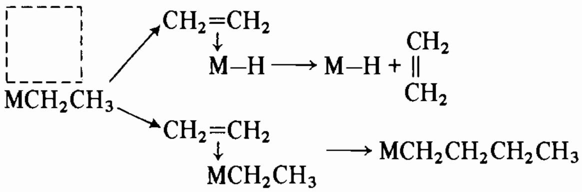
observations are unlikely to be unique for actinides, and certain olefin/hydride reactivity patterns for lanthanides [11] and early transition metals [12] suggest similar bond energy orderings.

The above discussion is, we believe, also relevant to the question of why some actinide [13], lanthanide [11, 14], and early transition metal complexes [15] are such effective olefin polymerization catalysts [15] (few middle and late transition metal complexes [16] exhibit such activity). While the insertion of olefin into a metal–carbon bond (eqn. (5)) should be equally exothermic for any metal, β-hydrogen

$$M{-}CH_3 + CH_2{=}CH_2 \longrightarrow MCH_2CH_2CH_3$$

$$\Delta H \approx -25 \text{ kcal/mole} \qquad (5)$$

abstraction will only be thermodynamically favorable for systems where B.D.E.(M–H) – B.D.E.(M–C) is relatively large. This is an important consideration since it is plausible that the high coordinative unsaturation required for olefin insertion (Scheme I) would also promote competing (and chain-terminating) β-hydrogen abstraction. Thus, in the absence of unusual kinetic factors (more kinetic data are clearly needed), uninterrupted chain growth would be most favorable in coordinatively unsaturated environments where B.D.E.(M–H) – B.D.E.(M–C) is minimized.



Scheme I

Studies of the thermolysis chemistry of actinide hydrocarbyls have revealed more elaborate examples of C–H activation involving saturated hydrocarbon ligands. In the case of $Cp'_2Th[CH_2C(CH_3)_3]_2$ and $Cp'_2Th[CH_2Si(CH_3)_3]_2$, we have recently characterized the cyclometalation processes shown in eqns. (6) and (7) [17]. These reactions exhibit clean first-order kinetics (with negative entropies of activation), and deuterium labelling studies rule out significant α-hydrogen atom or solvent hydrogen atom abstraction in the hydrocarbon extrusion process. Although the course of eqn. (6) bears superficial resemblance to certain Pt(II)-centered cyclometalation processes [18], it is important to note that the Th(IV) center cannot readily undergo formal oxidative addition. Thus, a four-center, heterolytic activation process, promoted by the coordinative unsaturation and electron deficiency of the Th(IV) center (eqn. (8)), appears to be operative. Such a highly organized ('tight') transition state is in accord with the $\Delta S^{\ddagger}$ and structural (*vide infra*) data.

The driving force for eqns. (6) and (7) is not immediately obvious since, as pointed out previously [18], significant strain energy in a metallacycle would appear to favor the reverse reactions. When

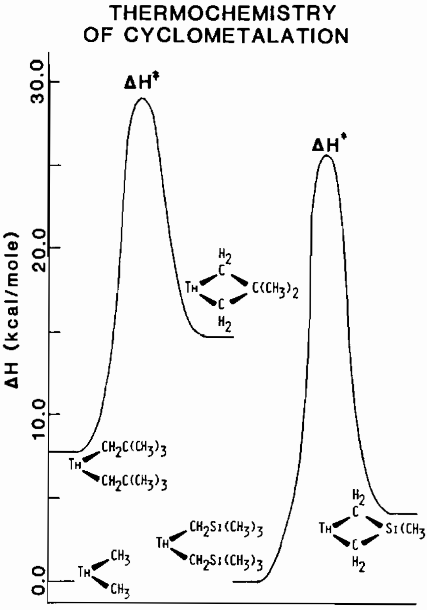
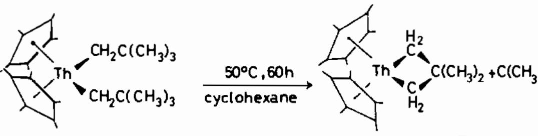
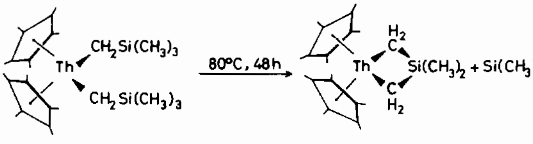


Fig. 1. Approximate solution phase enthalpic relationships for the processes $C \rightarrow E$ and $D \rightarrow F$.



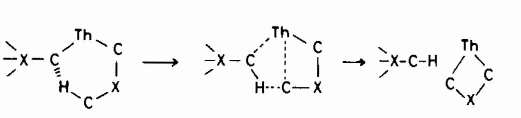
C E (6)

$\Delta H^{\ddagger}$ = 20.6(6) kcal/mol
$\Delta S^{\ddagger}$ = −17(2) eu



D F (7)

$\Delta H^{\ddagger}$ = 25.2(9) kcal/mol
$\Delta S^{\ddagger}$ = −9(1) eu



(8)

X = C, Si

these transformations are viewed in terms of the measured [2] bond dissociation enthalpies (Fig. 1), two features are immediately evident. First, using either $\mathrm{Cp'_2Th(CH_3)_2}$ or the corresponding bis(hydrocarbyl) as the 'unstrained' point of reference (the latter will be seen to be more realistic in view of the structural results for *C* and *D*), it can be seen that the thoracyclobutanes are appreciably strained, as much as *ca.* 17 kcal/mol for *E*. Secondly, the cyclometalation reactions are in both cases endothermic. The driving force for eqns. (6) and (7) thus appears to be entropic: translational and rotational $T\Delta S$ contributions to ΔG are, as already noted, reasonably on the order of 10 kcal/mole or more for such a 1 particle → 2 particle process, under the present reaction conditions.

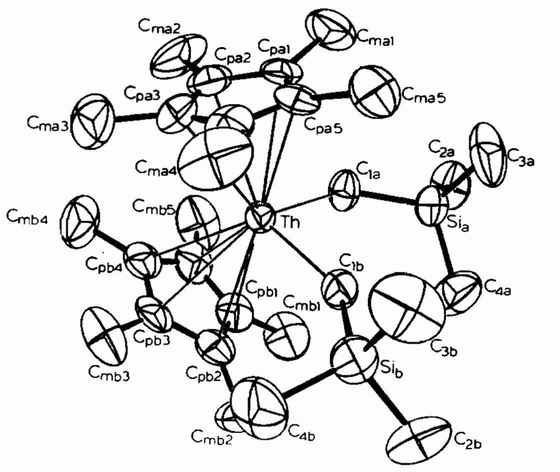
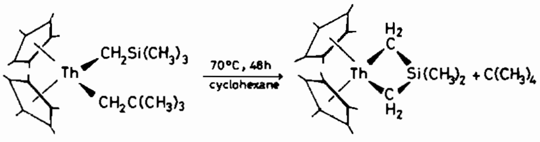


Fig. 2. Perspective drawing [20] of the non-hydrogen atoms in $\mathrm{Th}[\eta^5\text{-}(\mathrm{CH_3})_5\mathrm{C_5}]_2[\mathrm{CH_2Si(CH_3)_3}]_2$, *D*. All atoms are represented by thermal vibrational ellipsoids drawn to encompass 50% of the electron density. Important bond lengths (Å) and angles (deg) for chemically distinct groups of atoms include Th–$\mathrm{C_{1a}}$ = 2.51(1), Th–$\mathrm{C_{1b}}$ = 2.46(1), $\mathrm{Si_a}$–$\mathrm{C_{1a}}$ = 1.86(1), $\mathrm{Si_b}$–$\mathrm{C_{1b}}$ = 1.87(1), Th–C(ring) = 2.81(2) (average), Th–$\mathrm{C_{1a}}$–$\mathrm{Si_a}$ = 132.0(6)°, Th–$\mathrm{C_{1b}}$–$\mathrm{Si_b}$ = 148.0(7)°, $\mathrm{C_{1a}}$–Th–$\mathrm{C_{1b}}$ = 96.8(4)°, ring center-of-gravity–Th–ring center-of-gravity = 134.9°.

The degree to which the thorium-centered cyclometalation proceeds under thermodynamic control has also been of interest [19]. Do the weakest bonds break and the strongest bonds form, or do other factors dictate the course of the C–H activation? Thermolysis of mixed complex *G* (eqn. (9)) results in clean scission of the weakest metal–carbon (Th–neopentyl) bond and the formation of the most stable metallacycle (*F*). The kinetics are unimolecular, and trapping experiments with benzene (*vide infra*) give no evidence for the intermediacy of *E*.



(9)

G F

$\Delta H^{\neq}$ = 19.4(2) kcal/mol
$\Delta S^{\neq}$ = −20.8(5) eu

Further perspective on the cyclometalation process is provided by diffraction-derived structural results on *D*, *C*, and *F*. The structure of *D* [20] is shown in Fig. 2, and that of *C* is rather similar [21]. Although the metrical aspects of $\mathrm{Cp'_2Th}$ ligation [1, 22] are unexceptional, the bonding of the tri-

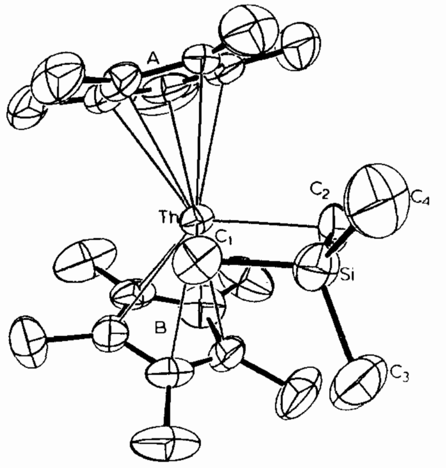


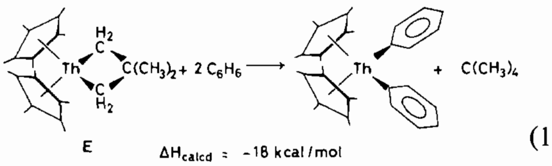
Fig. 3. Perspective drawing [17] of the non-hydrogen atoms in $Th[\eta^5\text{-}(CH_3)_5C_5]_2[(CH_2)_2Si(CH_3)_2]$, *F*. All atoms are represented by thermal ellipsoids drawn to encompass 50% of the electron density. Important bond lengths (Å) and angles (deg) for chemically distinct groups of atoms include $Th-C_1$ = 2.463(13), $Th-C_2$ = 2.485(14), $Si-C_1$ = 1.914(15), $Si-C_2$ = 1.93(14), $Si-C_3$ = 1.912(21), SiC_4 = 1.867(19), Th–C(ring) = 2.807(14) (average), C_1-Th-C_2 = 75.2(4)°, $Th-C_1(C_2)-Si$ = 90.6(5)° (average), ring center-of-gravity–Th–ring center-of-gravity = 138.5°.

methylsilylmethyl and neopentyl moieties is highly unsymmetrical and evidences severe non-bonded repulsions. Most interestingly, while the angle $Th-C_{1a}-Si_a$ is not unusual for an f-element hydrocarbyl (132.0(6)°) [1, 23], the value $\sphericalangle Th-C_{1b}-Si_b$ = 148.0(7)° is, to our knowledge, unprecedented for a d- or f-element hydrocarbyl involving a monohapto, sp^3 carbon atom. Furthermore, the disposition of hydrocarbyl groups has the net effect of placing C_{4a} within 3.97 Å of C_{1b}. Inspection of a diffraction-derived scale model reveals that a relatively small rotation about the $C_{1a}-Si_a$ bond axis brings C_{4a} to within *ca.* 3.4 Å of C_{1b}. Assuming a C–H bond distance of 1.09 Å, subsequent rotation about the Si_a-C_{4a} bond can place a C_{4a} methyl hydrogen atom within *ca.* 2.3 Å of C_{1b}, fully 0.8 Å less than the sum of the C and H van der Waals radii. The situation in *C* is even more dramatic [21], non-bonded repulsions are more severe, the angle analogous to $Th-C_{1b}-Si_b$ has opened to 160°, and the distance analogous to $C_{1b}-C_{4a}$ has further contracted. Besides presenting an explanation for the destabilization of *C* relative to $Cp'_2Th(CH_3)_2$ seen in the bond enthalpy data [2] (Fig. 1), these structural results further support the mechanistic picture of eqn. (8).

The large distortions and close $C_{1b}\cdots C_{4a}$ contacts observed in the hydrocarbyl groups of *C* and *D* appear not to represent deep potential wells nor major perturbations in the bonding. Thus, both neopentyl groups and both trimethylsilylmethyl groups are magnetically equivalent in the 270 MHz ^1H nmr in solution down to −95 °C (but not in the high resolution ^{13}C CP-MAS solid state spectrum) [24]. There is no evidence for unusual C–H interactions in the infrared spectrum. Further resolution of these issues should accrue from neutron diffraction studies now in progress.

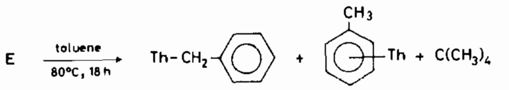
Structural characterization of the first thoracyclobutanes is also in progress. The molecular structure of *F* is shown in Fig. 3 [17]. The pentamethylcyclopentadienyl coordination is typical of an uncongested Cp'_2ThX_2 complex. In terms of Th–C and Si–C distances, the metallacycle is bound symmetrically. The only deviation from planarity is a 6° folding along the C_1-C_2 vector, reflecting a slight non-bonded repulsion between C_4 and a ring methyl functionality.

The relatively high enthalpy content of thorocyclobutane *E* suggests a number of rational approaches to the activation of C–H bonds on exogenous hydrocarbons. Thus, the thermochemical data predict an exothermic reaction of *E* with benzene (eqn. (10)), and this reaction was found to take place

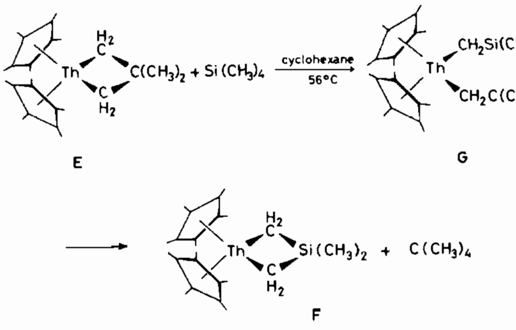


(10)

readily at 70 °C [17]. The kinetics are first-order in *E* and first-order in benzene. Using C_6D_6, $C(CH_3)_2(CH_2D)_2$ is produced and a kinetic isotope effect $(k(C_6H_6)/k(C_6D_6))$ of 1.5(1) is measured. With toluene, attack at both the benzylic (25 ± 10%) and aromatic positions (75 ± 10%) is observed (eqn. (11)) [17, 25]. In regard to activating saturated hydrocarbons, we find that *E* reacts with tetramethylsilane to cleanly yield in steps via *G* (detected by nmr), metallacycle *F* (eqn. (12)) [26]. Studies with other exogenous hydrocarbons are in progress [27].



(11)



(12)

The thermochemical data also indicate that *F* will be far less reactive than *E*. Indeed, to date we have

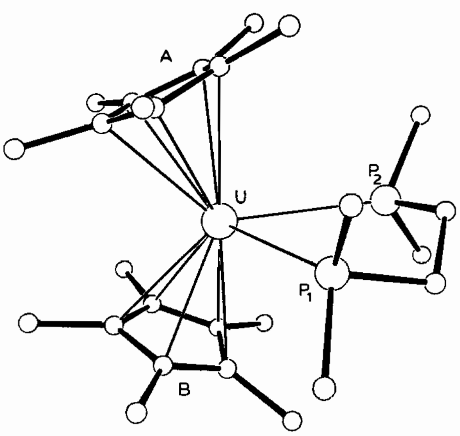
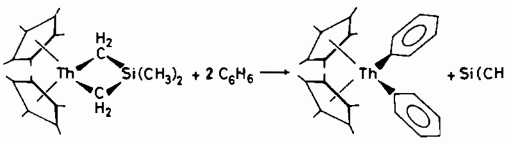


Fig. 4. Perspective drawing [32a] of the non-hydrogen atoms in $U[\eta^5\text{-}(CH_3)_5C_5]_2(H)[(CH_3)_2PCH_2CH_2P(CH_3)_2]$, *H*. All atoms are represented by arbitrarily sized spheres for the purpose of clarity. Important bond lengths (A) and angles (deg) for chemically distinct groups of atoms include $U{-}P_1$ = 3.211(8), $U{-}P_2$ = 3.092(8), U–C(ring)= 2.79(3) (average), $P_1{-}U{-}P_2$ = 63.8(2)°, ring center-of-gravity–U–ring center-of-gravity = 136.2°.

been unable to observe C–H activating reactions such as eqn. (13) under a variety of conditions [17, 25].



(13)

F

$\Delta H_{calcd} \simeq +1$ kcal / mol

These actinide results and other recent reports involving lanthanides [28] forecast a rich, electrophile-based C–H activation chemistry which is not founded upon conventional, transition metal-centered oxidative addition-reductive elimination sequences.

Phosphine/Phosphite Coordination Chemistry

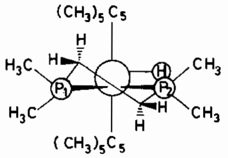
Despite the prodigious growth of organo-f-element chemistry over the past few years, the development of chemistry involving many classes of 'soft' ligands which are ubiquitous in d-element chemistry has been conspicuously absent. For organoactinides, ligands such as phosphines [29, 30] and phosphites offer the possibility of stabilizing low oxidation states, and simple basicity considerations [31] suggest that metal–ligand bonding could well be non-negligible.

$$Cp'_2UR_2 + R'_2PCH_2CH_2PR'_2 \xrightarrow{H_2} Cp'_2U(H)(R'_2PCH_2CH_2PR'_2) \qquad (14)$$

$$(Cp'_2UH_2)_2 + 2R'_2PCH_2CH_2PR'_2 \xrightarrow{-H_2} 2Cp'_2U(H)(R'_2PCH_2CH_2PR'_2) + H_2 \qquad (15)$$

R = alkyl group $\qquad$ *H* R′ = CH_3

The first organouranium phosphine hydrides have been synthesized via the routes shown in eqns. (14) and (15) [32]. The molecular structure of *H* has been determined by single crystal X-ray diffraction, and the result is presented in Fig. 4 [32]. Although the uranium-bound hydrogen atom could not be precisely located in the diffraction analysis, it is evident in the infrared spectrum (ν_{U-H} = 1219 cm^{-1}, ν_{U-D} = 870 cm^{-1}) and in low-temperature ^1H nmr spectra, which indicate instantaneous conformation *I*. Variable temperature nmr studies of *H* reveal at least two dynamic processes [32]. A site permutation process within the molecule interconverts magnetically non-equivalent $\eta^5\text{-}(CH_3)_5C_5$ rings and all dmpe CH_3 substituents as the temperature is raised. This rearrangement presumably involves either spinning of the ligand about the local two-fold axis coupled with inversion of the chelate ring, or stepwise dissociation and reassociation of the phosphorus atoms. In addition, magnetization transfer experiments indicate exchange of the coordinated dmpe with added, free dmpe. Such lability is highly unusual for chelating phosphine ligands. Curiously, an analogous complex could not be prepared with the chelating amine donor $(CH_3)_2NCH_2CH_2N(CH_3)_2$ [32]. Instead, only $(Cp'_2UH_2)_2$ is obtained. Preliminary studies of the chemistry of *H* indicate that the phosphine ligand serves the function of solubilizing, but not interfering with the reactivity of the uranium hydride. Rapid reactions occur with CO, olefins, and ethers, while slower reactions occur with aromatic hydrocarbons. The nature of these products is presently under investigation.

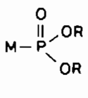


I

Phosphites are stronger π-acceptors than phosphines (suggesting greater stabilization of low oxidation states) and besides the conventional η^1-P (*J*) mode of bonding, complexes are formed with transi-

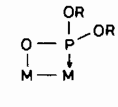
$M \leftarrow :P(OR)_3$

J



$M{-}P(=O)(OR)_2$

K



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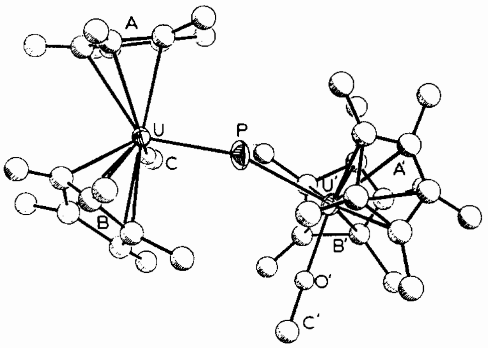

Fig. 5. Perspective drawing [34] of the non-hydrogen atoms in $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(OCH_3)\}_2PH$, *M*. All atoms are represented by arbitrarily sized spheres for the purpose of clarity. Important bond lengths (Å) and angles (deg) for chemically distinct groups of atoms include U–P = 2.745(2), U–O = 2.058(19), C–O = 1.425(48), U–O–C = 177(2)°, U–P–U = 157.4(3)°.

tion metal centers in several other interesting modes (*e.g.*, *K*, *L*) [33]. In contrast to these established possibilities, we were surprised to discover that the reaction of organoactinide hydrides with trimethyl phosphite takes an entirely different course [34]. Under mild conditions, the methoxy functionalities are rapidly and quantitatively stripped from the phosphite molecule according to eqns. (16) and

$$5[Cp'_2UH_2]_2 + 4P(OCH_3)_3 \xrightarrow[\text{toluene}]{25\ ^\circ C,\ 1h}$$

$$\underset{M}{4[Cp'_2U(OCH_3)]_2PH} + 2Cp'_2U(OCH_3)_2 + 8H_2 \qquad (16)$$

(17). The nature of these reactions is supported by ^1H nmr monitoring and by independent syntheses of

$$5[Cp'_2ThH_2]_2 + 4P(OCH_3)_3 \xrightarrow[\text{toluene}]{25\ ^\circ C,\ 40\ h}$$

$$\underset{N}{4[Cp'_2Th(OCH_3)]_2PH} + 2Cp'_2Th(OCH_3)_2 + 8H_2 \qquad (17)$$

the $Cp'_2M(OCH_3)_2$ by-products. Phosphinidene-bridged complexes *M* and *N* have been characterized by ^1H and ^{31}P nmr spectroscopy, infrared spectroscopy (including the P–D derivative of *M*), and by elemental analysis. In addition, *M* has been characterized by magnetic susceptibility measurements and by single crystal X-ray diffraction. Preliminary results of the latter investigation are shown in Fig. 5 [34]. At this stage in the analysis, the U–P interactions are symmetrical, and the U–O–C vectors nearly linear (a common observation for f-element alkoxides [35]). The scope of this reaction for the synthesis of multinuclear, phosphinidene-bridged actinide complexes and for the modification of phosphite ligands is presently under investigation.

Acknowledgements

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