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Actinide Organometallic Chemistry

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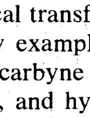
Summary. The stoichiometric and catalytic chemistry of metal-organic compounds having actinide-to-carbon bonds is in a stage of rapid growth. Chemical, structural, and bonding characteristics have been identified which differ in interesting and informative ways from those of *d*-block transition element compounds.

The past three decades have witnessed the rapid development of a new transition element chemistry involving metal-carbon bonds (*1*). Beginning with the excitement generated by such highly nonclassical π-''sandwich'' complexes as ferrocene (**1**) and dibenzenechromium (**2**), this new field at the crossroads of inorganic and organic chemistry has stimulated a vigorous interaction between synthetic, mechanistic, structural, and quantum chemical researchers. With the evolution of *d*-block transition element organometallic chemistry has come a plethora of interesting new molecules, molecular structures, chemical transformations, and modes of bonding. To cite just a few examples, unusual complexes displaying carbene (**3**) (*1, 3*), carbyne (**4**) (*1, 4*), cyclobutadiene (**5**) (*1, 5*), peralkyl (**6**) (*1, 6*), and hydride (**7**) (*1, 7*) ligation as well as metal atom clusters (**8**) (*1, 8*) and multiple bonds between metal atoms (**9**) (*1, 9*) have been prepared and studied. The importance of metal-organic compounds transcends novelty in structure and bonding, however. The chemistry of metal-carbon bonds is inextricably connected with the homogeneous and heterogeneous catalytic processes by which the chemical industry transforms feedstocks into carbon-containing fuels, solvents, polymers, and other products on a massive scale (*10*). It is generally thought that a deeper understanding of the properties of organometallic compounds offers the realistic possibility of major advances in this technology.



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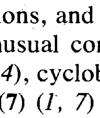

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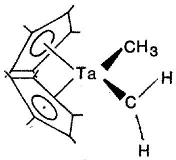

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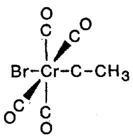

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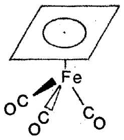

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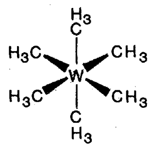

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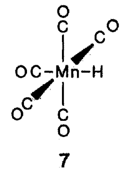

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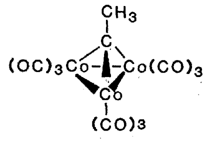

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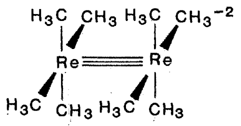

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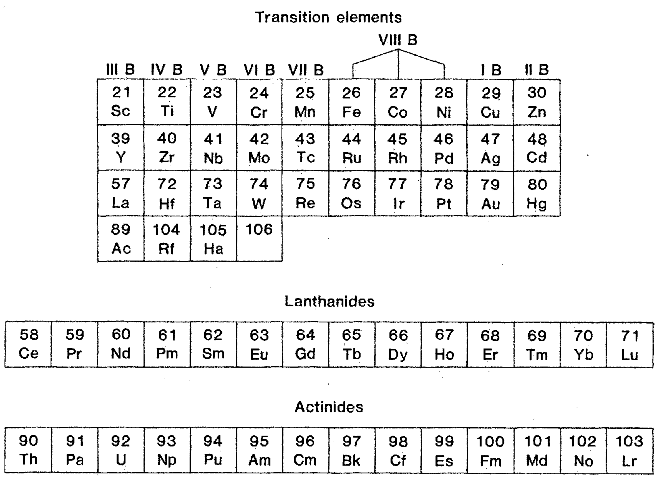
Until recently, this great flowering of organometallic chemistry involving *d*-block elements largely bypassed the actinide elements. The actinides are the elements occupying the final row of the periodic table—the row in which the 5*f* shell is filled with electrons (Fig. 1) (*11*). Although actinides play a major role in nuclear technology and have been used as catalysts or cocatalysts (*12, 13*) (largely for empirical reasons), their organometallic chemistry has been largely unexplored. Historically, organoactinide chemistry dates back to the Manhattan Project and unsuccessful attempts to synthesize volatile compounds such as tetraethyl uranium, $U(C_2H_5)_4$, for isotopic enrichment by gaseous diffusion (*14, 15*). Pioneering efforts by the groups of G. Wilkinson and E. O. Fischer later produced the first cyclopentadienyl complexes (*16*); however, genuine



Transition elements

III B	IV B	V B	VI B	VII B	VIII B			I B	II B
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
89 Ac	104 Rf	105 Ha	106						

Lanthanides

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

Actinides

90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Fig. 1. Partial periodic table showing the location of transition elements, lanthanide (4*f*) elements, and actinide (5*f*) elements.

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Table 1. Some representative actinide cyclopentadienyl complexes (*17*).

Compound	Color	Melting point* (°C)	Sublimation temperature (°C)†
$Th(C_5H_5)_3$	Green		
$Th(C_5H_5)_3Cl$	Colorless		
$Th(C_5H_5)_4$	Colorless	170d	250–290
$Pa(C_5H_5)_4$	Orange-yellow	220d	220d
$U(C_5H_5)_3$	Brown	> 200	
$U(C_5H_5)_3Cl$	Red-brown	260	260
$U(C_5H_5)_4$	Red	250d	200–220d
$Np(C_5H_5)_3Cl$	Brown		
$Np(C_5H_5)_4$	Red-brown	220d	200–220d
$Pu(C_5H_5)_3$	Green	180d	140–165
$Am(C_5H_5)_3$	Flesh	330d	160–200
$Cm(C_5H_5)_3$	Colorless		180
$Bk(C_5H_5)_3$	Amber		135–165
$Cf(C_5H_5)_3$	Red		135–320

*d indicates decomposition. †At a pressure of 10^{-3} to 10^{-4} torr.

excitement in this area did not really begin until the synthesis of the unique sandwich compound uranocene by A. Streitwieser in 1968.

Much of the current research activity in actinide organometallic chemistry reflects the conviction that the unique properties of actinide ions will give rise to a chemistry which is different from *d*-element chemistry, but which, by providing models beyond the frontiers of transition metals, will teach us new things about transition metals as well as actinides. The large size of the actinide ions permits coordination numbers and polyhedra that are unknown or highly unusual for *d*-element ions. This implies that a greater number of potentially reactive species can be coordinated and maintained in spatially unusual orientations; for the same ligand array, an *f*-element ion should be far less coordinatively saturated (that is, should have more vacant coordination sites for ligand or substrate binding or activation) than a *d*-element ion. The availability of 5*f* valence orbitals is also a distinctive feature of actinide ions, and it implies a greater range of metal-ligand bonding possibilities than for *d*-block elements, since the *f* orbitals have different symmetry properties than *d* orbitals, smaller ligand field stabilization energy barriers to exchange of ligands within the coordination sphere, and an ionic character in the bonding which may lead to more electrophilic metal centers and more nucleophilic ligand centers. It will be seen that the unusual oxygen affinity of actinide ions also introduces new possibilities.

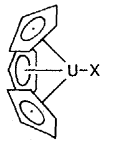
In this article I survey some of the recent highlights in the rapidly developing field of organoactinide chemistry. The article is organized by ligand type. For further details on many of the topics as well as surveys of new results in organolanthanide (4*f*) chemistry, the reader is referred to recent review articles (*17*) and a monograph (*18*).

π-Bonded Ligands

The first organoactinide to be isolated was the complex of the cyclopentadienyl ligand $U(C_5H_5)_3Cl$ (**10**, X = Cl) (*16*). The synthetic approach is a general one for this type of complex: displacement of halide ligands from the actinide ion (Eq. 1). The approximately tetrahedral geometry about uranium (**10**) with a formal coordination number of 10 illustrates the propensity for high coordination numbers (*17, 19*). By modifying the methodology of Eq. 1, it is even possible to introduce a fourth cyclopentadienyl ligand (**11**) and to achieve a formal coordination number of 12. By using an approach analogous to Eq. 1, cyclopentadienyl complexes have now been prepared for eight actinide elements (Table 1). In general, the stoichiometries obtained reflect the stabilities of the various metal oxidation states. Thus, the dominance of the +3 oxidation state for the heavier actinides (*11*) manifests itself in the isolation of tris(cyclopentadienyl) actinide(III) complexes. Because organoactinides are generally exceedingly sensitive to oxygen and moisture, all manipulations of these materials must be conducted in vacuum lines and glove boxes. However, the preparation of transuranium organometallics introduces even further challenges due to the high radioactivity; for example, $Am(C_5H_5)_3$ glows in the dark.

$$UX_4 + 3MC_5H_5 \longrightarrow \underset{\mathbf{10}}{U(C_5H_5)_3X} + 3MX \qquad (1)$$

$$M = Li, Na, Tl \qquad X = Cl, Br, I$$



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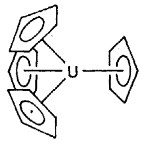

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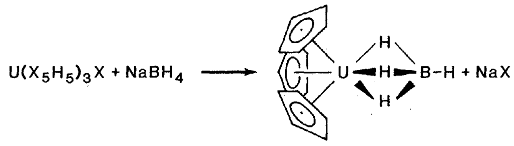
The tetravalent tris(cyclopentadienyl) complexes, as exemplified by $U(C_5H_5)_3X$, undergo reactions such as X^- displacement (*17*) and Lewis base (B) adduct formation (*20*) (for instance, Eqs. 2 and 3). The trivalent tris(cyclopentadienyl)'s undergo Lewis base adduct formation and ring cleavage (*21*) (Eqs. 4 and 5).



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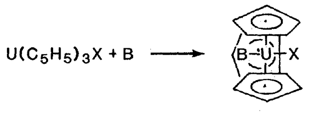

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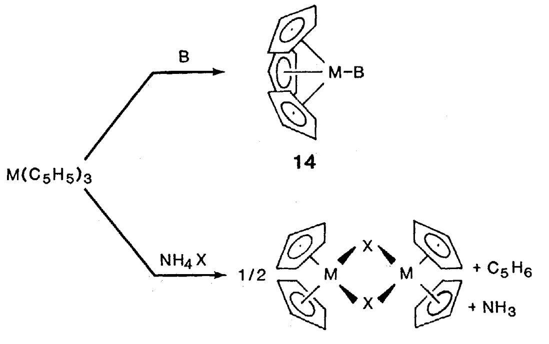
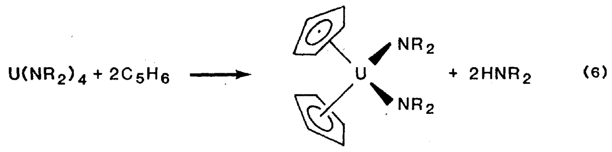


14 (4)

15 (5)

Organoactinides with two or even one cyclopentadienyl ligand can be synthesized by the routes exemplified in Eqs. 6 and 7 (*22, 23*). Peralkylcyclopentadienyl derivatives such as pentamethylcyclopentadienyl can also be prepared (Eqs. 8 and 9) (*24, 25*). The methyl groups impart enhanced solubility, promote coordinative unsaturation (by preventing the binding of other sterically demanding ligands), and stabilize the complexes with respect to various destructive C–H abstraction pathways. As a consequence, **18** and **19** are precursors for some of the chemically most reactive and versatile organoactinides prepared to date.



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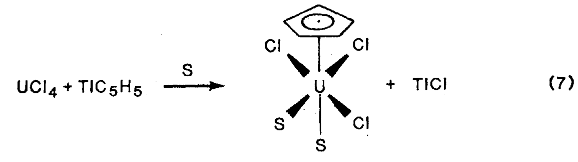

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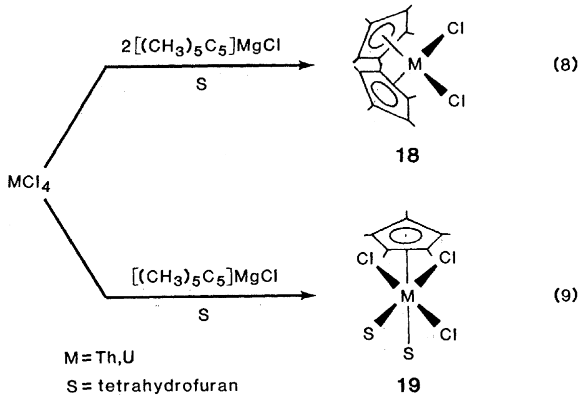
S = basic solvent such as tetrahydrofuran



The cyclopentadienyl organoactinides have been studied by a battery of physicochemical techniques, including x-ray diffraction (*17, 19*), photoelectron spectroscopy (*26*), magnetic susceptibility (*21*), nuclear magnetic resonance (NMR) spectroscopy (*27*), Mössbauer spectroscopy (*28*), and optical spectroscopy (*29*), to elucidate the nature of the metal-ligand bonding. Of central importance have been the questions concerning the extent of metal-ligand orbital overlap (covalency as opposed to ionicity), how it varies as a function of actinide ion and ligand identity, how it compares to that in *d*-element systems, and the role it plays in molecular structure and chemical transformations. Although there is still controversy about the interpretation of some of the results and the degree to which covalency and ionicity can be quantified, it appears that there is substantially more ionic character in the bonding than is found in most *d*-block complexes. However, there is also evidence for some actinide-ligand bond covalency (both 6*d* and 5*f* metal orbitals may be involved), especially for the lighter actinides (Th, Pa, U, and Np), and for surprising similarities to metal-ligand bonding involving early (light) transition metals (*30*). For the heavier actinides, the 5*f* orbitals are far more contracted and the bonding is distinctly lanthanide-like (ionic).

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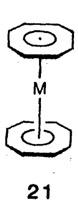

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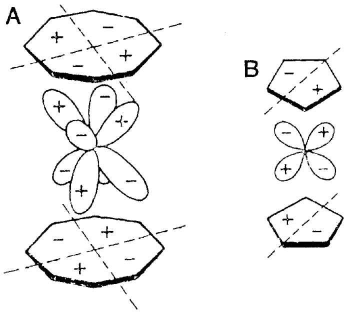


Fig. 2. Cognate metal-ligand orbital interactions in (A) uranocene (metal 5*f* orbital) and (B) ferrocene (metal 3*d* orbital). [From (*31*)]

Sandwich complexes of the cyclooctatetraene ligand (**20, 21**) have also been intensively investigated (*17, 18, 31*). Not only does the large size of the actinide ion facilitate high formal coordination numbers, but a unique interaction can occur between the highest occupied $C_8H_8^{-2}$ molecular orbital (e_{2u}) and the actinide f_{xyz} and $f_{z(x^2-y^2)}$ orbitals. An interesting bonding analogy to ferrocene, but involving *f* orbitals, is illustrated in Fig. 2. The synthetic approach to these "actinocene" sandwich complexes is shown in Eq. 10. In addition, an

$$MCl_4(\text{or } MCl_6^{-2}) + 2K_2C_8H_8 \longrightarrow M(C_8H_8)_2 + 4KCl \qquad (10)$$

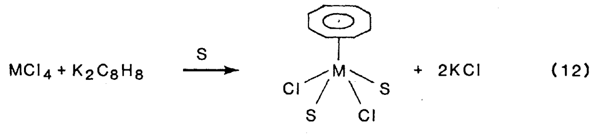
M = Th,Pa,Np,U,Pu

extensive series of ring-functionalized complexes can be prepared by this pathway, starting with substituted cyclooctatetraenes (*31*). Trivalent complexes of heavier actinides are also accessible (Eq. 11) (*17*), as are "half-sandwich" complexes

$$MX_3 + 2K_2C_8H_8 \longrightarrow K^+M(C_8H_8)_2^- + 3KX \qquad (11)$$

M = Np,Pu,Am   X = Cl,Br,I

(Eq. 12) (*31, 32*). These molecules have a "piano stool" structure (**22**) and are expected to have a rich chemistry, based on the high reactivity of actinide-halogen bonds.



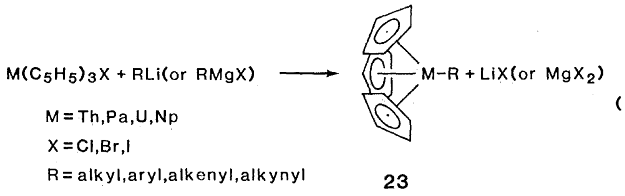
S = tetrahydrofuran

22

Perhaps no class of organoactinides has been subjected to scrutiny by a greater battery of physical techniques than the bis(cyclooctatetraene) series. The principal goal, as for the cyclopentadienyls, has been to understand the nature of the actinide-ligand bonding interactions. Again, the picture that is emerging is one of a large ionic contribution to the bonding, but also a significant contribution due to the overlap of metal 5*f* and 6*d* orbitals with ligand orbitals. Interactions as in Fig. 2 appear to be important (*26, 31, 33*). In comparison to the actinide-cyclopentadienyl complexes, the metal-$C_8H_8^{-2}$ bonding may involve slightly greater orbital overlap. However, such descriptions of the bonding are difficult to quantify and the data for precise conclusions are not at hand. It would also be desirable at this stage to have comparative (actinide versus actinide, actinide versus transition metal) information on chemical reactivity which would probe relative metal-ligand bond polarity.

Actinide-Carbon Sigma Bonds; Synthesis

The two-electron sigma bond between a metal ion and the carbon atom of an organic fragment is one of the cornerstones of stoichiometric and catalytic organo–*d*-element chemistry (*1, 10*). Despite the potential importance of such functionalities for actinide chemistry, the early observations on the thermal instability of simple uranium tetraalkyls discouraged research in this area. Thus, it was three decades after the Manhattan Project studies before the first thermally stable actinide alkyls, aryls, alkenyls, and alkynyls (collectively called hydrocarbyls) were synthesized (Eq. 13) (*17, 34, 35*). In striking contrast to the tetraalkyls, the tris(cyclopentadienyl) actinide hydrocarbyls have a thermal stability that is rather high for any type of metal hydrocarbyl. The explanation appears to reside in the high coordinative saturation and congestion brought about by the three bulky, π-bonded cyclopentadienyl ligands (*34*). Evidence for this comes from the short intraligand nonbonded contacts found in x-ray diffraction studies and hindered rotation about the M–R bonds observed in spectroscopic work (*34*). In terms of chemical reaction mechanism, the unfavorability of further expanding the coordination sphere appears to impede what is frequently the lowest energy thermal decomposition pathway for transition metal hydrocarbyls, β-hydrogen atom abstraction (Eq. 14) (*1, 10*). Instead, cyclopentadienyl hydrogen atom abstraction by the sigma-bonded ligand occurs for these actinide hydrocarbyls (Eq. 15) (*34*). Interestingly, however, β-hydrogen abstraction can be readily induced for the compounds in which M = Th and U by photochemical excitation (Eq. 16) (*36*). A further perspective on the requirements for 5*f* hydrocarbyl thermal stability is provided by experiments on the compounds that have traditionally been formulated as UR_4 (*14, 17, 18*). Here the coordinative unsaturation is anticipated to be greater, and β-hydrogen abstraction products are observed (*37*).



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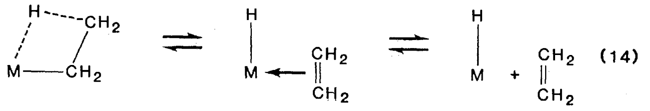

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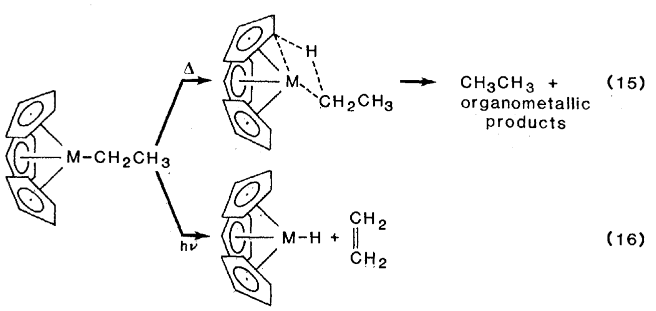

(15)

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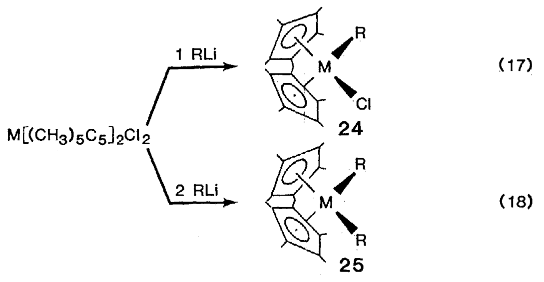

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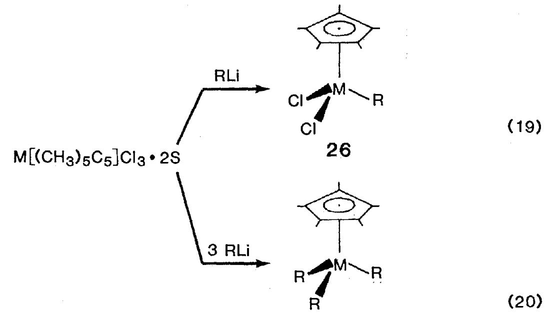
(17)

25

(18)

Although the properties of the tris(cyclopentadienyl) hydrocarbyls are informative, the high degree of saturation and congestion has largely thwarted attempts to probe and to exploit the nature of the actinide-to-carbon sigma bond. A favorable compromise between the extremes of saturation [$M(C_5H_5)_3R$ vis-à-vis MR_4] has recently been achieved in the bis(pentamethylcyclopentadienyl) series. Thus, a new class of thermally stable mono- (**24**) and bishydrocarbyls (**25**) can be straightforwardly synthesized as shown in Eqs. 17 and 18 (*38*). These compounds are highly reactive with respect to a wide range of reagents and provide the first detailed insight into the characteristics of actinide-to-carbon sigma bonds. Furthermore, because the ligand array is identical to that of an extensively studied series of transition metal complexes (M = Ti, Zr) (*39*), it should be possible, for the first time, to develop meaningful chemical and physical comparisons between analogous *d*- and *f*-element molecules.

The logical progression in the trend of decreasing saturation would be to attempt to delete a pentamethylcyclopentadienyl ligand. It has recently proved possible to synthesize the first single-ring actinide trishydrocarbyls (Eqs. 19 and 20) (*40*), although the chemistry is not yet extensively developed. In comparison to the $M[(CH_3)_5C_5]_2R_2$ derivatives, the thermal stability of the $M[(CH_3)_5C_5]R_3$ compounds is more sensitive to the nature of R. Bulky groups and those having no β-hydrogen atoms are the most stable.



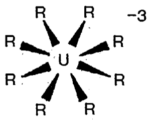
26

(19)

27

(20)

Efforts have also been made to stabilize actinide tetraalkyls by further saturating the metal coordination sphere. Thus, anionic complexes such as those formulated in **28** and **29** (*41*) and phosphine complexes (**30**) (*42*) have been prepared and show enhanced resistance to thermolysis. The phosphine result is also of interest because, in contrast to the rich chemistry of transition metals and phosphines, little is known at present about organoactinide-phosphine complexes (*43*).



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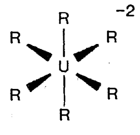

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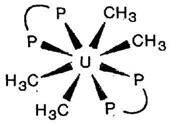

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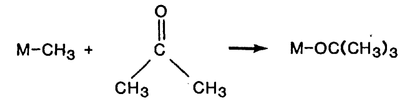
Chemical Characteristics of Actinide-Carbon Sigma Bonds

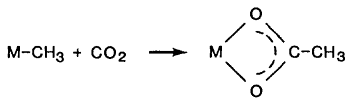
The reactivity of the metal-carbon bonds in the $M[(CH_3)_5C_5]_2(CH_3)_2$ series, with M = Th and U, has been probed with reagents sensitive to bond polarity (Eqs. 21 to 23)

(*38, 44*). The reaction rates are all too great at −78°C to be measured by NMR techniques; competition experiments indicate that the thorium complexes are generally more reactive than those of uranium. These results suggest considerable polarity in the metal-carbon bonds, with the thorium-to-methyl bond being more polar. This latter observation can be rationalized in terms of the higher energies of the metal 5*f* and 6*d* orbitals in the lighter metal (*31, 33*). In competition studies, the $M(C_5H_5)_3CH_3$ complexes were found to be less reactive by a factor of ~ 10^4, reasonably evidencing the diminished steric accessibility of the M–CH_3 bond (*44*). Available data for $Zr(C_5H_5)_2R_2$ compounds (*45*) suggest diminished reactivity for the transition metal systems as well.



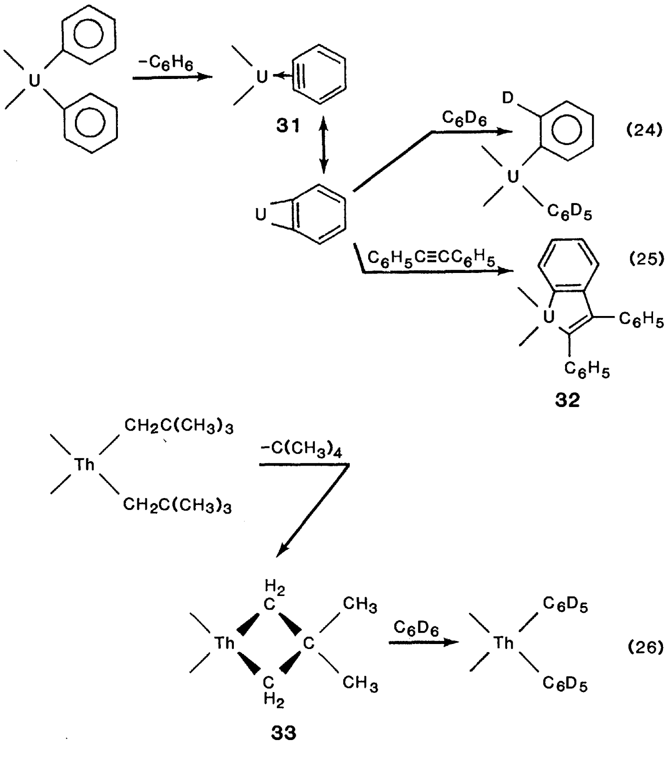
$$M\text{-}CH_3 + (CH_3)_2C{=}O \longrightarrow M\text{-}OC(CH_3)_3 \qquad (21)$$

$$M\text{-}CH_3 + (CH_3)_3COH \longrightarrow M\text{-}OC(CH_3)_3 + CH_4 \qquad (22)$$



(23)

Studies of the $M[(CH_3)_5C_5]_2R_2$ series also reveal pronounced activity for C–H bond cleavage. For two different hydrocarbyl functionalities [R = C_6H_5, $CH_2C(CH_3)_3$], intramolecular hydrogen abstraction produces a high-energy intermediate, which then reacts with an aromatic C–H bond (Eqs. 24 and 26). In the case of the diphenyl uranium complex, the intermediate benzyne (**31**) can be characterized by kinetic and trapping (Eq. 25) experiments (*38*). The thorium system of Eq. 26 (*46*) is instructive because the methyl C–H activation and metallacycle (**33**) formation appear not to require a higher metal oxidation state [Th(IV) has none], which is commonly believed necessary in analogous transition metal–centered reactions (*47*). Intermediate **33** can be isolated and characterized by x-ray diffraction. The net consequence of Eqs. 24 and 26 is a hydrocarbon metathesis process. Under the same conditions, the transformation depicted in Eq. 24 is about 100 times faster than for $Zr(C_5H_5)_2(C_6H_5)_2$ (*48*).



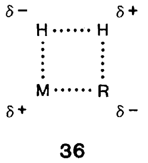
Actinide-Carbon Bond Hydrogenolysis; Hydride Formation

The bis(pentamethylcyclopentadienyl) thorium and uranium dialkyls react rapidly with hydrogen to yield the first organoactinide hydrides (Eq. 27) (*38*). Considering the difficult accessibility of higher actinide oxidation states here (especially for Th), four-center "heterolytic" H_2 activation (*38, 49*) (**36**) rather than an oxidative addition pathway (more common for *d*-elements) (**37**) appears likely. The molecular structure of **34** has been determined by single-crystal neutron diffraction (*50*) and the result is presented in Fig. 3. Both terminal (two-center, two-electron) and bridging (three-center, two-electron) metal-hydrogen interactions take place. The hydride organometallic chemistry is a case where thorium and uranium reactivities diverge markedly. The accessibility of the trivalent uranium oxidation state (*17*) is evident in the reversible hydrogen loss reaction of Eq. 28 to yield a multimetallic trivalent hydride (**38**) (*38*). The monomeric trivalent fragment can be "trapped" if reaction 27 is conducted in the presence of a chelating diphosphine $[(CH_3)_2PCH_2CH_2P(CH_3)_2]$. The result is an unusual uranium phosphine hydride (**39**), which has recently been characterized by x-ray diffraction and other techniques (*51*). This labile molecule even reacts with N_2.

$$2M[(CH_3)_5C_5]_2R_2 + 4H_2 \xrightarrow{0^\circ} \{M[(CH_3)_5C_5]_2H_2\}_2 + 4RH \qquad (27)$$

M=Th, U — **34** M=Th

R=CH_3, $CH_2Si(CH_3)_3$ — **35** M=U



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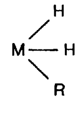
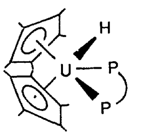


37

$$\{U[(CH_3)_5C_5]_2H_2\}_2 \rightleftharpoons 2/x\{U[(CH_3)_5C_5]_2H\}_x + H_2 \qquad (28)$$

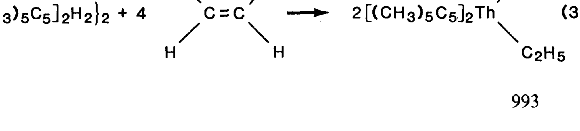
38



39

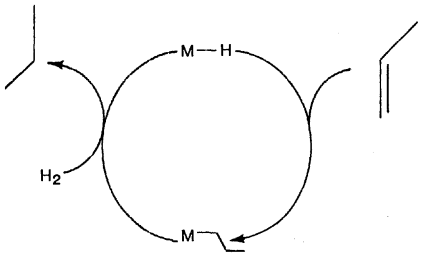
The oxidation state stability of **34** renders it an ideal vehicle for exploring actinide hydride reaction patterns. For example, it is found by ^1H NMR spectroscopy that this molecule reversibly activates H_2 (Eq. 29) with a surprisingly large bimolecular rate constant of ~ 10^5 liters per mole per second at −30°C (*38*). Compound **34** also reacts rapidly with olefins in the reverse of a β-hydrogen abstraction process (Eq. 30). Since it has already been established that actinide-to-carbon bonds suffer facile hydrogenolysis (Eq. 27), the question

$$\{Th[(CH_3)_5C_5]_2H_2\}_2 \underset{H_2}{\overset{^*H_2}{\rightleftharpoons}} \{Th[(CH_3)_5C_5]_2{}^*H_2\}_2 \qquad (29)$$



$$\{Th[(CH_3)_5C_5]_2H_2\}_2 + 4\,H_2C{=}CH_2 \longrightarrow 2[(CH_3)_5C_5]_2Th(C_2H_5)_2 \qquad (30)$$

arises as to whether Eqs. 27 and 30 might be coupled to constitute a cycle for catalytic homogeneous olefin hydrogenation. The simplest possible cycle is illustrated in Scheme 1.

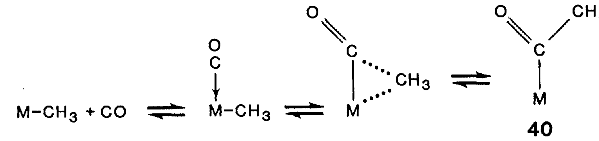


Scheme 1

That organoactinide hydrides can indeed effect this reaction sequence has been confirmed at room temperature for 1-hexene (pressure, 0.9 atmosphere of H_2) with **34** and **35** as catalysts; turnover frequencies (catalytic events per metal atom) of 0.5 and 70 $hour^{-1}$, respectively, are measured (*38*). Furthermore, when $U[(CH_3)_5C_5]_2(CH_3)_2$ is supported on dehydroxylated γ-alumina and then activated with hydrogen, the turnover frequency for propylene hydrogenation at −46°C in a flow reactor (0.6 sec^{-1}) is comparable to that for supported platinum under the same conditions (*52*).

Carbon Monoxide Activation

There is great current interest in understanding and elaborating the processes by which carbon monoxide (likely to be derived from coal in the future) can be catalytically transformed into useful organic chemicals (*10, 53*). Although much of the chemistry of homogeneous catalysis with late transition metals can be understood in terms of well-studied processes such as a migratory insertion reaction to produce a metal acyl (**40**, Eq. 31), there is a great gap in our knowledge as far as the more drastic transformations occurring on metal and metal oxide surfaces are concerned. It would be desirable to attempt to model some of the unusual aspects of these environments in homogeneous solution. The bis(pentamethylcyclopentadienyl) actinide complexes have three unique characteristics that portend distinctly nonclassical CO activation: high coordinative unsaturation, high kinetic lability, and high oxygen affinity (for example, a thorium-oxygen bond is stronger than that involving any *d*-block metal) (*54*). Recent studies of early transition metal CO chemistry also support this idea (*39, 54, 55*).



(31)

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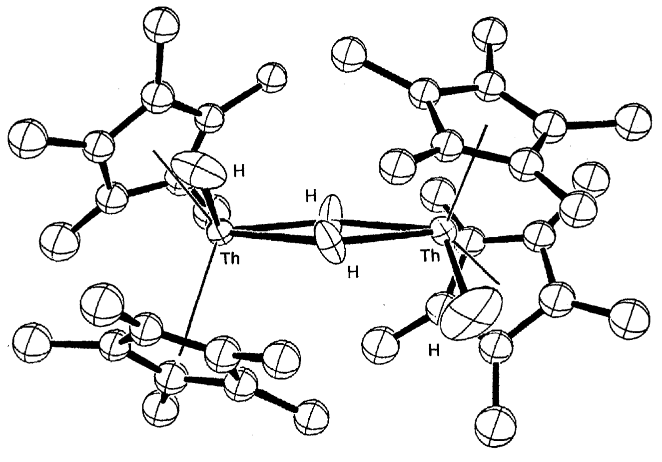
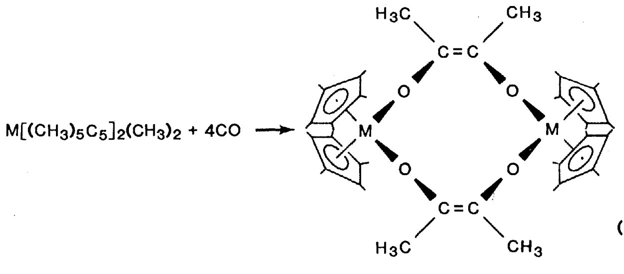


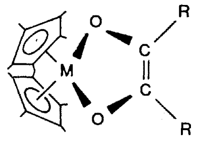
Fig. 3. Molecular structure of the organoactinide hydride $\{Th[(CH_3)_5C_5]_2H_2\}_2$ determined by neutron diffraction. For clarity, the hydrogen atoms on the four $(CH_3)_5C_5$ ligands have been deleted. [From (*50*)]

The actinide dimethyl complexes react rapidly with carbon monoxide at −78°C (Eq. 32) to yield, quantitatively, *cis*-butenediolate complexes (*54, 56*). In effect, four CO molecules are coupled to produce four new Th–O bonds and two carbon-carbon double bonds, exclusively in the *cis* configuration. With bulkier hydrocarbyl functionalities, the carbon-carbon fusion is found to be intramolecular (**43**). How do such unusual species arise? A clue is found when a single equivalent of CO is added to a thorium chloroalkyl (Eq. 33) (*54, 57*).



(32)

41 M=Th **42** M=U



43

M=Th,U

R=$CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$

$$Th[(CH_3)_5C_5]_2(Cl)CH_2C(CH_3)_3 + 1CO \longrightarrow Th[(CH_3)_5C_5]_2(Cl)[COCH_2C(CH_3)_3] \quad (33)$$

44

An acyl complex (**44**) is formed; however, spectroscopic data (the frequency of the C–O stretching vibration and the acyl ^{13}C resonance frequency) and structural data (Fig. 4) show it to be a highly unusual acyl: there is a metal-oxygen interaction of unprecedented magnitude for a molecular compound. The bonding in organoactinide acyls involves a major contribution

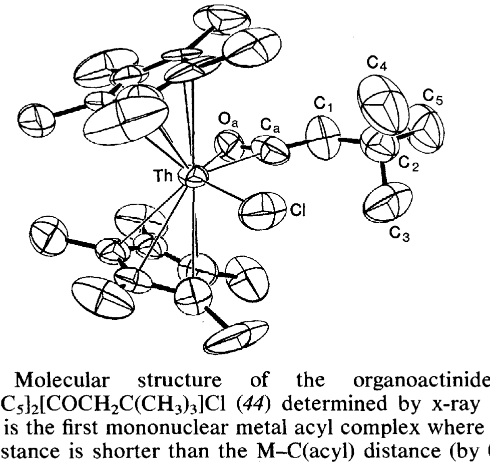
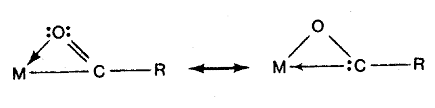


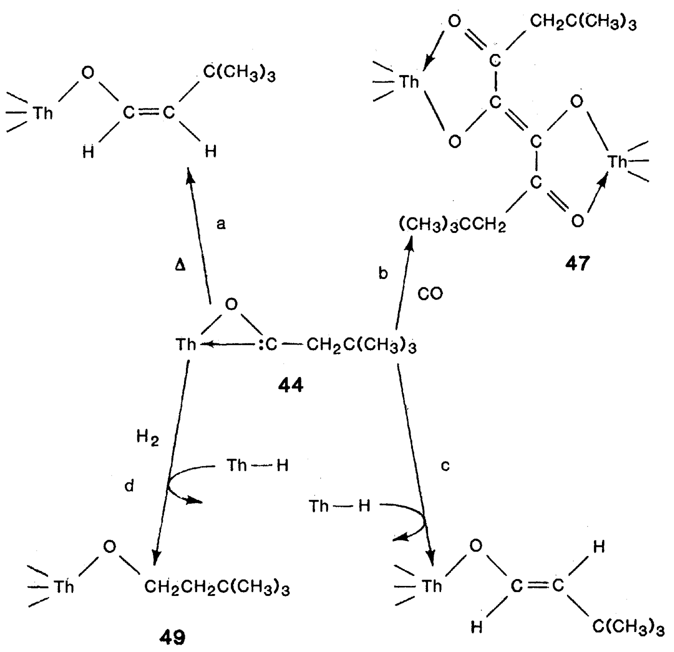
Fig. 4. Molecular structure of the organoactinide acyl $Th[(CH_3)_5C_5]_2[COCH_2C(CH_3)_3]Cl$ (*44*) determined by x-ray diffraction. This is the first mononuclear metal acyl complex where the M–O(acyl) distance is shorter than the M–C(acyl) distance (by 0.07 Å) (*54*). [From (*56*)]

from a carbene-like resonance hybrid (**46**); this is a pivotal concept in understanding the reactivity (*54*).



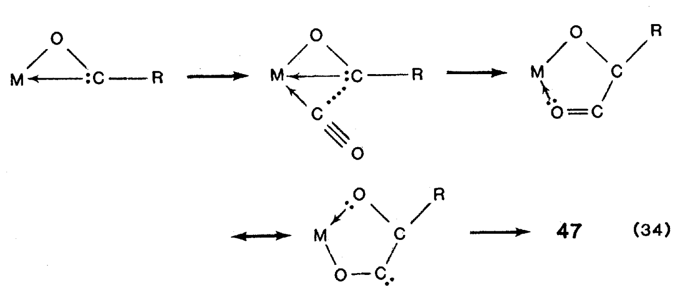
45 **46**

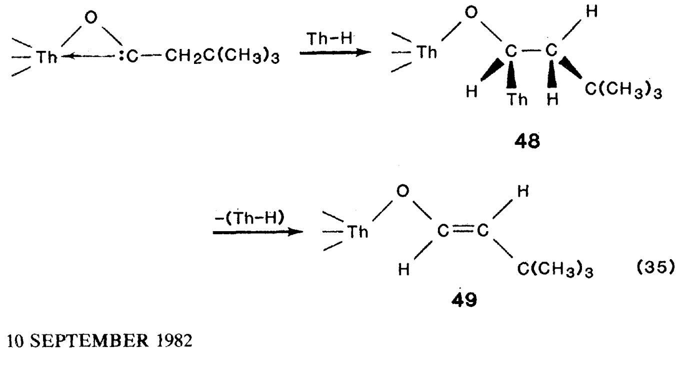
The chemistry of **44** provides an indication of the chemical consequences of activating carbon monoxide in a highly coordinatively unsaturated, oxophilic solution environment (Scheme 2).



Scheme 2

Unlike classical metal acyl chemistry, the behavior of **44** is carbene-like. Reaction *a* is an intramolecular 1,2 hydrogen migration—a common rearrangement process for carbenes. Reaction *b* is a unique CO homologation process in which the actinide acyl suffers further insertion to yield, ultimately, a dionediolate complex (**47**) (Fig. 5) (*56*); Eq. 34 shows a tentative mechanism which is supported by model studies with alkyl isocyanides. When compound **44** comes in contact with a trace of thorium hydride, **34**, a catalytic rearrangement occurs (reaction *c*) (*57*). This transformation proceeds through "insertion" of the acyl carbon unit into the Th–H bond, followed by β-hydrogen abstraction (Eq. 35). Furthermore, intermediate **48** can be intercepted by hydrogenolysis of the actinide-to-carbon sigma bond. The result is catalytic hydrogenation of the inserted CO (reaction *d*) to yield an alkoxide (**49**). The net reaction is thus the formation within the actinide coordination environment of a formaldehyde (CH_2O) equivalent from CO and H_2.





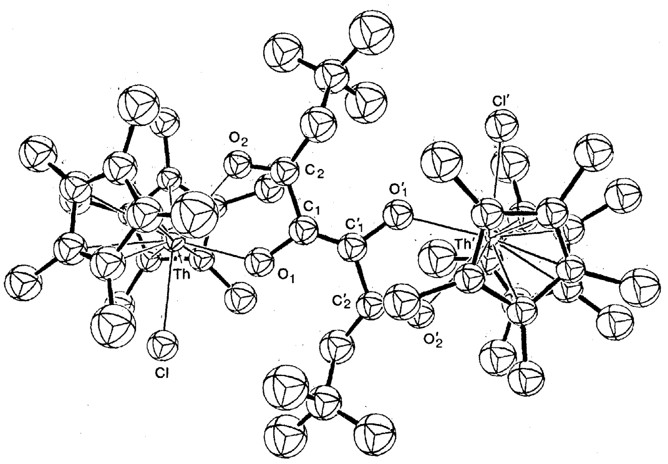
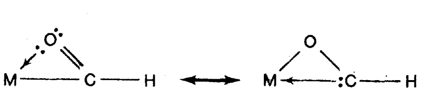


Fig. 5. Molecular structure by x-ray diffraction of the reaction product of the compound in Fig. 4 with an additional equivalent of CO: $\{Th[(CH_3)_5C_5]_2[CO(CH_2C(CH_3)_3)CO]\}_2$ (*47, 54*). [From (*56*)]

Organoactinides also provide a useful perspective on the general nature of the CO migratory insertion reaction (Eq. 36)

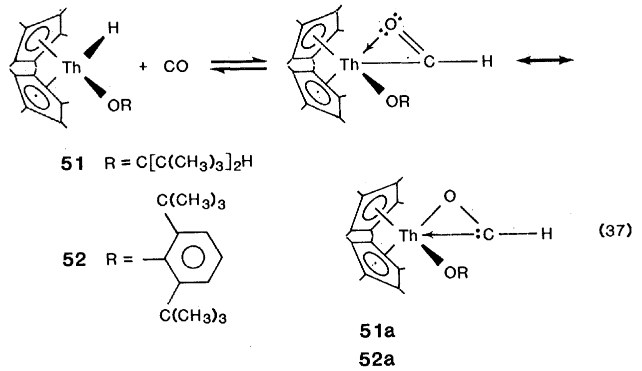
$$M—X + CO \rightleftharpoons MCOX \qquad (36)$$

and how it can be modified by environment. Consideration of available bond energy data indicates that the M–X bond energy will be the dominant factor controlling whether CO insertion is thermodynamically favorable (*54*). Thus, metal-carbon bonds are relatively weak and insertion to form acyl complexes is usually exothermic (Eq. 31). On the other hand, metal-hydrogen bonds are thought to be appreciably stronger, and in homogeneous solution there has been little unambiguous evidence for an insertion reaction when X = H, that is, metal formyl production (*58*). Since formyl complexes have been extensively discussed as key intermediates in the catalytic hydrogenation of CO (*53, 58*), the question arises as to whether a formyl might be stabilized by a metallic center with sufficient unsaturation and oxygen affinity (**50**). Recent results



50

with organothorium hydrides provide both thermodynamic and kinetic information related to this question (*59*). At low temperatures, alkoxyhydrides **51** and **52** undergo reversible migratory CO insertion to yield formyls **51a** and **52a**, respectively (Eq. 37). These reactions are found to be exothermic by about 5 kilocalories per mole. Moreover, at millimolar concentrations, the CO insertion or extrusion process is fast on the ^1H NMR time scale by −40°C. At room temperature, **51** undergoes coupling to produce an enediolate (**53**, Eq. 38), while the steric bulk about **52** precludes this process. Thus, the proper environment can bring about rapid, exothermic insertion of CO into a metal-hydrogen bond. Taking the



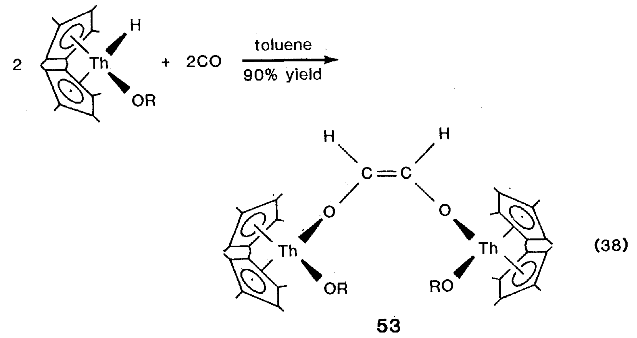
(37)

51 R = C[C(CH$_3$)$_3$]$_2$H

52 R =

51a

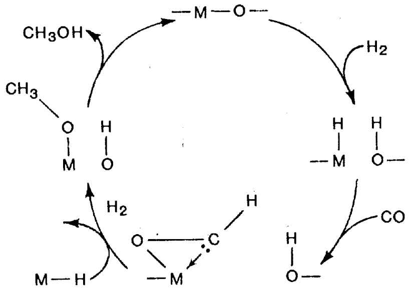
52a



(38)

53

present results along with the established tendency of some metal oxides to cleave H_2 "heterolytically" (*53, 60*) and known reactions of metal alkoxides (*61*), it is possible to advance a plausible mechanistic cycle for the catalytic, heterogeneous hydrogenation of CO to methyl alcohol (*53*). This is presented in Scheme 3.



Scheme 3

Conclusions

Organoactinide chemistry is entering a period of rapid development. It is apparent that a rich and diverse chemistry is emerging, and that "tuning" of the ligation sphere and *f*-electron configuration can exert significant control over the rate and course of many unusual chemical transformations. To place this chemistry in perspective, it appears that there are distinct similarities to main group and transition metal chemistry, but there are also pronounced differences. It is the exploitation of these latter characteristics that offers the greatest challenge and promise.

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