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## LANTHANIDES AND ACTINIDES

### ANNUAL SURVEY COVERING THE YEAR 1982\*

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#### General

A couple reviews of these areas have appeared in 1982. Lappert and Singh have summarized various aspects of bis(cyclopentadienyl)lanthanide chloride complexes, including their variety, syntheses, structural natures, and reaction chemistry (1). Fay has also reviewed the chemistry of scandium for the year 1980 (2). Several other reports have appeared which, while not dealing directly with organometallic complexes, should still be of general interest to this area. Voronkov and Baryshok have reviewed the area of metallatranes, including examples involving lanthanides (3). Several papers appeared dealing with the applications of lanthanide complexes in NMR spectroscopy. Thus, the diamagnetic La(fod)<sub>3</sub> complex has been found to serve as a useful probe in <sup>13</sup>C NMR spectroscopic studies of π-electron delocalization (4). Other applications of various Ln(fod)<sub>3</sub> complexes have been developed for <sup>1</sup>H NMR spectroscopy (5), and a report of some <sup>139</sup>La NMR spectroscopic studies has also appeared (6). The utilization of lanthanide complexes in organic synthesis has continued to receive attention (7-10), and a structural determination of Y(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>2</sub> has been reported (11).

#### Lanthanides

Several papers have reported the preparation of (cyclopentadienyl)-lanthanide complexes by the use of Hg(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (12-14). In reactions with the activated lanthanide metals themselves, Ln(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>(THF)<sub>n</sub> complexes were generally isolated (Ln = La, Sm, Eu, Yb, Tm; n = 2-4), although for Ln = Sm, Eu, or Yb, and a Hg(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>:Ln ratio of 1:4-5, the Ln(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(THF)<sub>n</sub> complexes were isolated. However, several complications in these latter reactions were observed, and attributed to the formation of side products such as

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\* Previous survey see: *J. Organometal. Chem.*, 318 (1987) 29-82.

$2\text{Ln}(\text{C}_5\text{H}_5)_2(\text{THF})_n \cdot \text{Hg}(\text{C}_5\text{H}_5)_2 \cdot \text{Yb}(\text{C}_5\text{H}_5)_2(\text{THF})$  was found also to react with  $\text{P}(\text{C}_6\text{H}_5)_3$ , yielding  $\text{Yb}(\text{C}_5\text{H}_5)_2[\text{P}(\text{C}_6\text{H}_5)_3](\text{THF})_n$  ( $n = 1-4$ ). The utilization of two equivalents of  $\text{LnCl}_3$  (in place of Ln) per equivalent of  $\text{Hg}(\text{C}_5\text{H}_5)_2$  allowed for the isolation of  $\text{Ln}(\text{C}_5\text{H}_5)\text{Cl}_2(\text{THF})_4$  complexes (Ln = La, Sm, Eu, Tm, Yb) as well, although in general the mono(cyclopentadienyl)lanthanide complexes have been found to contain three equivalents of THF (cf.,  $\text{Er}(\text{C}_5\text{H}_5)\text{Cl}_2(\text{THF})_3$ , *vide infra*).

Similar results have also been reported for reactions of lanthanide metals with  $\text{TiC}_5\text{H}_5$  (15). With samarium or neodymium, the exclusive products are the trivalent species,  $\text{Ln}(\text{C}_5\text{H}_5)_3(\text{THF})$ . For ytterbium,  $\text{Yb}(\text{C}_5\text{H}_5)_2(\text{DME})$  was isolated when an excess of metal was present. The trivalent species  $\text{Yb}(\text{C}_5\text{H}_5)_3$  could best be obtained from the reaction of the isolated  $\text{Yb}(\text{C}_5\text{H}_5)_2$  with  $\text{TiC}_5\text{H}_5$ .

A mass spectroscopic study of presumed  $\text{Ln}(\text{C}_5\text{H}_4\text{R})_3$  complexes ( $\text{R} = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{i-C}_3\text{H}_7$ ; Ln = Sc, Y, La, Pr, Nd, Sm, Gd, Dy, Er, Yb) has been reported (16). In essence, the authors determined that these compounds were actually mixtures in which variable quantities of  $\text{C}_5\text{H}_5$  and  $\text{C}_5\text{H}_3\text{R}_2$  ligands were also present. However, the use of 6,6-dimethylfulvene as a starting material allowed for the isolation of pure compounds.

A structural study on  $\text{Er}(\text{C}_5\text{H}_5)\text{Cl}_2(\text{THF})_3$  has been reported (17). As in the case of the related mer,trans- $\text{U}(\text{C}_5\text{H}_4\text{CH}_3)\text{Cl}_3(\text{THF})_2$ , the coordination geometry may be described as distorted octahedral. In this case a meridional

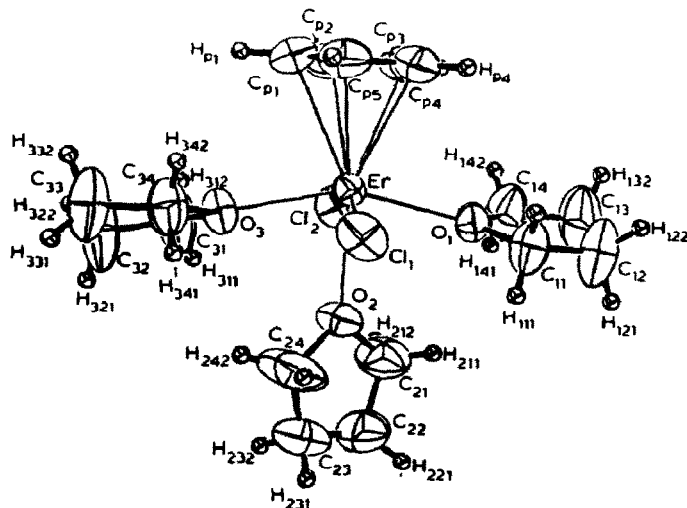


Fig. 1. The solid state structure of  $\text{Er}(\text{C}_5\text{H}_5)\text{Cl}_2(\text{THF})_3$  from ref. 17.

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arrangement of THF ligands and a trans arrangement of the chloride ligands were observed (Figure 1), in line with previous considerations. Thus, the largest ligand is  $C_5H_5$ , and the four ligands cis to it bend down significantly toward the site opposite  $C_5H_5$ , so that the unique site is occupied by the smallest atom possible, an oxygen atom in a THF ligand. The magnitude of the bending distortion may be recognized by the small O-U-O and O-U-Cl angles (ca.  $77-78^\circ$ ) involving the unique oxygen atom. In addition, the erbium atom lies  $0.54 \text{ \AA}$  out of the plane of the four adjacent donor atoms, in a direction toward the  $C_5H_5$  ligand. Finally, the large, flat shape of the THF ligand results in the other two THF ligands adopting a trans orientation to one another. Other pertinent bonding parameters include the Er-C ( $2.667(3) \text{ \AA}$ ), Er-Cl ( $2.616(2) \text{ \AA}$ ), and Er-O ( $2.350(3)$ ,  $2.365(3)$ , and  $2.452(3) \text{ \AA}$ ) bond distances.

The pentamethylcyclopentadienyl ligand continues to find extensive application in organolanthanide chemistry. Tilley, Andersen, Spencer, and Zalkin have reported the solid state structure of  $Yb(C_5Me_5)_2(C_5H_5N)_2$  (18). As would be expected, the compound adopts a pseudo-tetrahedral geometry (Figure 2). The bond distances involving the ytterbium center seemed quite reasonable, with the average values being  $2.74(2) \text{ \AA}$  for Yb-C and  $2.565(6) \text{ \AA}$

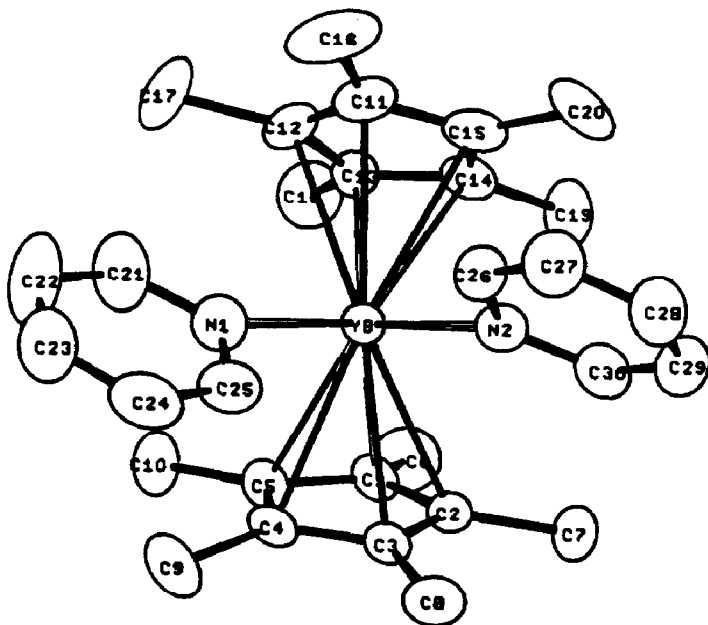
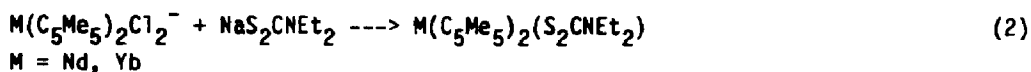
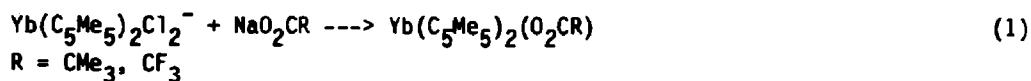


Fig. 2. Perspective view of  $Yb(C_5Me_5)_2(C_5H_5N)_2$  from ref. 18. Copyright 1982 American Chemical Society.

for Yb-N, and average bond angles of  $82.5(2)^\circ$  for N-Yb-N,  $136.3(3)^\circ$  for Cp-Yb-Cp, and  $106.2^\circ$  for Cp-Yb-N.

Related Yb(III) and Nd(III) complexes could be prepared from the reactions of  $M(C_5Me_5)_2Cl_2^-$  complexes with various carboxylates (2,2-dimethylpropionate or trifluoroacetate) or diethyldithiocarbamates, as in equations (1) and (2). In each case, a monomeric complex was presumed, and



for  $Yb(C_5Me_5)_2(S_2CNET_2)$ , this was confirmed crystallographically (Figure 3).

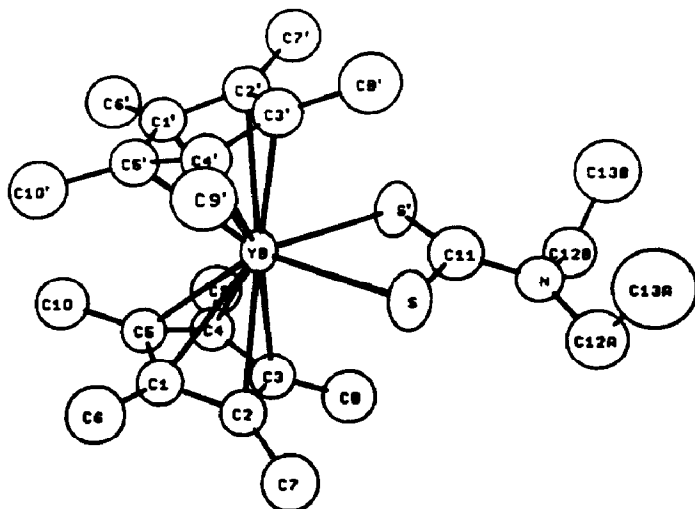


Fig. 3. The structure of  $Yb(C_5Me_5)_2(S_2CNET_2)$  from ref. 19. Copyright 1982 American Chemical Society.

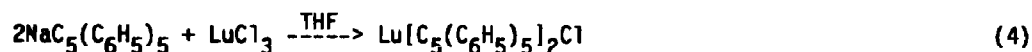
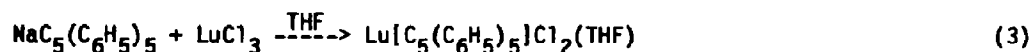
As would be expected, the bonding parameters reflect the smaller size of Yb(III) relative to Yb(II). Thus, the average Yb-C and Yb-S bond distances are  $2.63(3) \text{ \AA}$  and  $2.70(1) \text{ \AA}$ , respectively, while a  $\angle S-Yb-S$  of  $67.1(3)^\circ$  was observed (19).

Qian, Ye, Lu, and Li have reported the syntheses of ring-bridged bis(cyclopentadienyl)lanthanide complexes,  $Ln[(C_5H_4)_2(CH_2)_3]Cl(THF)$ , from the respective lanthanide chlorides (Ln = Pr, Nd, Gd, Dy, Ho, Er, Yb) and

$\text{Na}_2[(\text{C}_5\text{H}_4)_2(\text{CH}_2)_3]$  (20). These species were formulated as either monomers or chloride-bridged dimers.

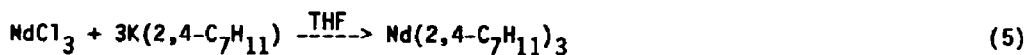
Tsutsui, Chen, Bergbreiter, and Miyamoto have reported the syntheses of heptamethylindenyl (Hmi) complexes of lanthanum, neodymium, and erbium from the metal chlorides and alkali metal heptamethylindenides (21). Apparently the steric bulk and solubilizing nature of these ligands were key factors in allowing the isolation of  $(\text{Hmi})\text{LnCl}_2$  and  $(\text{Hmi})_3\text{Ln}$  complexes, as well as detection of  $(\text{Hmi})_2\text{LnCl}$  species. The  $\text{Ln}(\text{Hmi})_3$  complexes were isolated as THF adducts (e.g.,  $\text{Nd}(\text{Hmi})_3(\text{THF})_5$  and  $\text{Er}(\text{Hmi})_3(\text{THF})_3$ ), although the THF could be removed in vacuo. The mono(Hmi) complexes also displayed varying degrees of solvation, possessing one THF for  $\text{Ln} = \text{La}$ , no THF for Nd, but half a THF for Er. The  $(\text{Hmi})_2\text{LnCl}$  complexes similarly displayed varying degrees of solvation, with the neodymium complex containing one THF while the erbium complex contained none. NMR spectroscopic studies were carried out for the lanthanum compounds, and while  $\eta^5$ -bound structures were favored, rapidly equilibrating  $\eta^3$  structures were not rigorously excluded. Although the  $(\text{Hmi})\text{LaCl}_2(\text{THF})$  complex did not disproportionate in solution over a period of a month,  $(\text{Hmi})_2\text{LaCl}(\text{THF})_n$  was isolated as a mixture of all three possible  $(\text{Hmi})_x\text{LaCl}_{3-x}$  species, and a mixture of  $(\text{Hmi})\text{LaCl}_2(\text{THF})$  and  $(\text{Hmi})_3\text{La}(\text{THF})$  also led to a mixture of the same three species.

Rongben and Tsutsui have reported several new lanthanide complexes containing the tetrahydroindenyl (Thi) ligand (22). Included in this group are both  $\text{Ln}(\text{Thi})\text{Cl}_2(\text{THF})_x$  ( $\text{Ln} = \text{La}$ ,  $x = 2$ ;  $\text{Ln} = \text{Nd}$ ,  $x = 0$ ;  $\text{Ln} = \text{Er}$ ,  $x = 1/2$ ) and  $\text{Ln}(\text{Thi})_2\text{Cl}(\text{THF})_x$  ( $\text{Ln} = \text{La}$  or  $\text{Nd}$ ,  $x = 0$ ;  $\text{Ln} = \text{Er}$ ,  $x = 1$ ) species. These compounds were characterized analytically and spectroscopically, and were found to possess higher hydrocarbon solubility and lower air sensitivity than their simple cyclopentadienyl analogs. These same authors have reported the syntheses of a couple (pentaphenylcyclopentadienyl)lutetium complexes,  $\text{Lu}[\text{C}_5(\text{C}_6\text{H}_5)_5]\text{Cl}_2(\text{THF})$  and  $\text{Lu}[\text{C}_5(\text{C}_6\text{H}_5)_5]_2\text{Cl}$ , through the reactions indicated by equations (3) and (4). The compounds were characterized analytically and



through a variety of spectroscopic methods (IR, NMR, mass, and UV-VIS absorption), and were found to be less air-sensitive than typical organolanthanide compounds (23).

Ernst and Cymbaluk have reported the synthesis and structural characterization of an unusual neodymium complex,  $\text{Nd}(2,4\text{-C}_7\text{H}_{11})_3$  ( $\text{C}_7\text{H}_{11}$  = dimethylpentadienyl) (eq. (5)). This compound is soluble in most organic



solvents, and bright green as a crystalline solid or in solution by reflectance, but red in solution by transmittance (24). A structural study confirmed the monomeric formulation of this species (Figure 4), but was

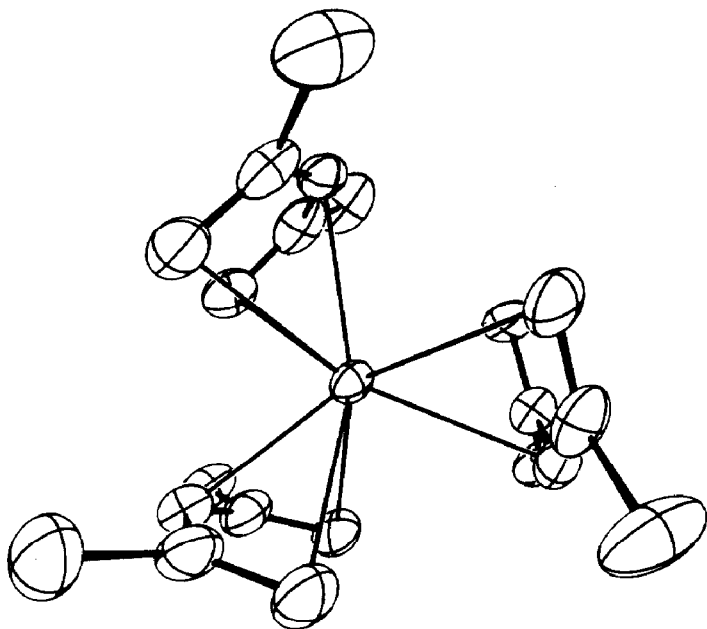


Fig. 4. The molecular structure of  $\text{Nd}(2,4\text{-C}_7\text{H}_{11})_3$  from ref. 24. Copyright 1982 American Chemical Society.

hampered significantly by the presence of disordered ether in the lattice. The complex ideally possesses  $C_{3h}$  symmetry, with the average Nd-C(1,5), Nd-C(2,4), and Nd-C(3) distances being 2.801(9), 2.855(8), and 2.749(10) Å, respectively. It can be noted that these distances correlate well with the relative charges on the carbon atoms, as the central carbon atom tends to have the highest charge, while the carbon atoms in the 2 and 4 positions are formally uncharged. Hence, the simultaneous attraction of the Nd(III) ion for the carbon atoms in the 1, 3, and 5 positions has also brought the Nd(III) ion into close proximity with the formally uncharged C(2) and C(4) atoms. While this is the first crystallographic demonstration of a formally uncharged carbon atom within bonding distance of a lanthanide ion, the interaction appears to be repulsive. Thus, the C(2) and C(4) atoms are all bent out of the planes of their attached C(1,3,5) atoms by ca. 0.07 Å in a direction away

from the Nd(III) ion. The internal and external pentadienyl C-C bonds appeared slightly different, with their distances averaging 1.421(12) and 1.373(12) Å, respectively.

Evans, Meadows, Wayda, Hunter, and Atwood have reported the syntheses and characterizations of dimeric lanthanide hydride compounds of the formula  $[\text{Ln}(\text{C}_5\text{H}_4\text{R})_2(\mu\text{-H})(\text{THF})]_2$  for  $\text{R} = \text{H}, \text{CH}_3$  and  $\text{Ln} = \text{Y}, \text{Er}, \text{Lu}$  (25). These species were prepared by the facile hydrogenolysis of the monomeric  $\text{Ln}(\text{C}_5\text{H}_4\text{R})_2(\text{t-C}_4\text{H}_9)(\text{THF})$  complexes; in contrast, hydrogenolysis reactions of the corresponding, but dimeric, methyl compounds were much slower, requiring weeks rather than minutes to occur. The analogous deuteride species were also preparable utilizing  $\text{D}_2$  in place of  $\text{H}_2$ . The  $\text{R} = \text{H}$  complexes were reasonably soluble in THF only at higher temperatures, whereas the  $\text{R} = \text{CH}_3$  complexes were significantly more soluble, thereby allowing for the isolation of crystalline materials and the determination of solution phase molecular weights. Infrared spectral bands attributable to the hydride ligands could be observed in the range  $1240\text{-}1350\text{ cm}^{-1}$ . These bands were shifted to  $900\text{-}975\text{ cm}^{-1}$  in the corresponding deuterides. The  $^1\text{H}$  NMR spectra for these compounds also provided evidence for the hydrides. In the  $\text{R} = \text{H}, \text{Ln} = \text{La}$  complex, a hydride resonance was observed at 4.69 ppm, whereas for  $\text{R} = \text{H}, \text{Ln} = \text{Y}$ , it was found at 2.02 ppm as a triplet ( $J = 27\text{ Hz}$ ) due to coupling to two equivalent yttrium nuclei ( $I = 1/2$ ). Single crystal x-ray diffraction studies were attempted for several of these species, but only for  $\text{R} = \text{CH}_3, \text{Ln} = \text{Y}$  was an accurate result obtained, including the location of the two (bridging) hydride ligands. The structural result may be seen in Figure 5, and bears a strong similarity to the complex

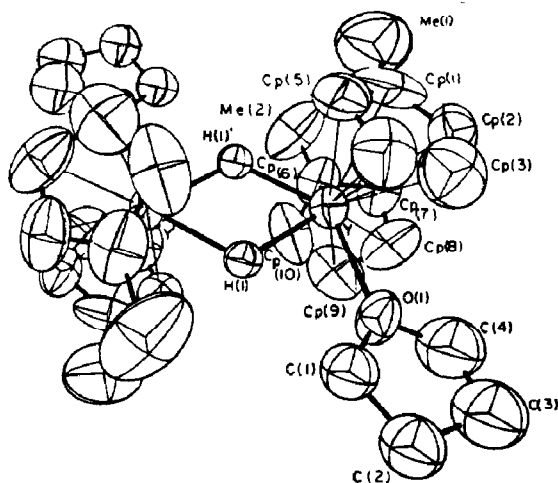


Fig. 5. The structure of  $[\text{Y}(\text{C}_5\text{H}_4\text{CH}_3)_2(\mu\text{-H})(\text{THF})]_2$  from ref. 25. Copyright 1982 American Chemical Society.

$[\text{Zr}(\text{CH}_3\text{C}_5\text{H}_4)_2(\text{H}_2)]_2$  in that the THF ligands of the former, and the non-bridging hydride ligands in the latter, are oriented away from each other (necessitated in the latter case by a crystallographic inversion center). In contrast,  $[\text{Th}(\text{C}_5\text{Me}_5)_2(\mu\text{-H})(\text{H})]_2$  has the two non-bridging hydride ligands pointing out on the same side of the molecule. For the yttrium compound, the Y-H bonds were found to be fairly symmetric, with distances of 2.17 and 2.19 Å, which are quite reasonable distances relative to the zirconium and thorium compounds, when differences in ionic radii are taken into account. The Y-O and Y-C (Cp) distances were found to be 2.460(8) and 2.69(1) Å, and the methyl group was found to lie 0.12 Å out of the cyclopentadienyl ligand plane, away from the metal. Mention was made of a determination of the analogous Ln = Er compound. Although the sizes of yttrium and erbium are quite similar, different imposed crystallographic symmetries resulted, and the bridging hydride ligands were not located. Whether this might allow for the alternative bridging pattern (observed for  $[\text{Th}(\text{C}_5\text{Me}_5)_2(\mu\text{-H})(\text{H})]_2$ ) was not discussed. However, the Er--Er separation of 3.616(5) Å was notably shorter than the value of 3.664(1) Å in the yttrium case.

In a related paper, these same authors have reported on a trimetallic erbium polyhydride complex,  $[\text{Er}(\text{C}_5\text{H}_5)_2(\text{H})]_3\text{Cl}^-$ . While thermal decomposition of  $\text{Er}(\text{C}_5\text{H}_5)_2(\text{t-C}_4\text{H}_9)(\text{THF})$  yields primarily  $[\text{Er}(\text{C}_5\text{H}_5)_2(\text{H})(\text{THF})]_2$ , the presence of small amounts of LiCl leads instead to the isolation of the trimetallic species indicated above, which was isolated as the  $\text{Li}(\text{THF})_4^+$  salt (26). Interestingly, a somewhat unsymmetric structure was adopted, in which one triply bridging hydride ligand was observed, while the other hydrides and the chloride ligand were all found to be doubly bridging, as can be seen in Figure 6. Hydrolytic and infrared spectral data further substantiated this formulation for the product. As a result of the presence of two different types of  $\mu_2$ -bridging ligands, the Er(1)--Er(2) separation of 3.926(2) Å is notably longer than the other two, which were found to be 3.692(1) and 3.684(1) Å, respectively. However, the Er-Cl bonds are somewhat asymmetric, having respective lengths of 2.64(1) and 2.735(9) Å. An average Er-C bond distance of 2.65 Å was reported. In a variation of the above, the thermal decomposition of  $\text{Lu}(\text{C}_5\text{H}_5)_2(\text{t-C}_4\text{H}_9)(\text{THF})$  was attempted at 75° but led to a complex mixture of products. In order to reduce the temperature for decomposition, an attempt to prepare the related ether solvate was made, from the reaction of  $\text{Lu}(\text{C}_5\text{H}_5)_2\text{Cl}$  with  $\text{LiC}(\text{CH}_3)_3$  in ether. Indeed, the initial toluene soluble product decomposes at room temperature, yielding a precipitate soluble in THF. Although a single crystal x-ray study was not successful, the presence of lithium and absence of chloride in the complex, together with chemical evidence, again suggested an anionic lanthanide hydride complex. <sup>1</sup>H



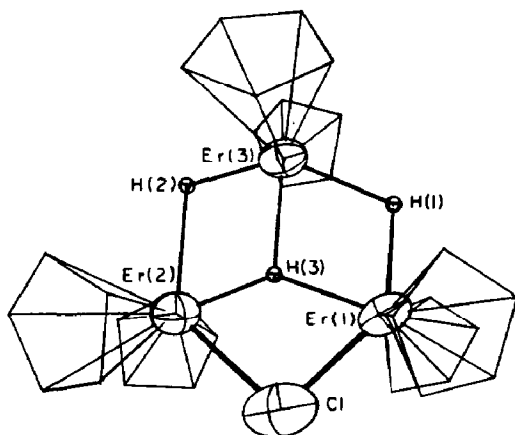


Fig. 6. Perspective view of the  $[\text{Er}(\text{C}_5\text{H}_5)_2(\text{H})]_3\text{Cl}^-$  ion from ref. 26.  
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NMR spectral data (500 MHz) revealed a hydride resonance at 1.83 ppm, occurring as a quartet due to coupling to three other mutually equivalent hydride ligands, which resonated at 3.93 ppm ( $J = 7.8$  Hz). Taken together with the fact that the  $\text{C}_5\text{H}_5$  ligands were found to be equivalent, this led the authors to propose a structural assignment of the anionic species as  $[\text{Lu}(\text{C}_5\text{H}_5)_2(\mu_2\text{-H})]_3(\mu_3\text{-H})^-$ .

From the reaction of  $\text{Y}(\text{C}_5\text{H}_5)_2\text{Cl}$  with  $\text{AlH}_3$  in ether, Lobkovskii, Soloveichik, Erofeev, Bulychev, and Bel'skii have isolated an adduct of formulation  $\text{Y}(\text{C}_5\text{H}_5)_2\text{ClAlH}_3(\text{ether})$  (27). A single crystal x-ray diffraction study has revealed a polymeric structure in which  $\text{AlH}_3(\text{ether})$  groups attach to  $[\text{Y}(\text{C}_5\text{H}_5)_2\text{Cl}]_2$  units via the formation of Al-Cl and Y-H interactions (Figure 7). The resulting local coordination geometry about aluminum closely approximates a trigonal bipyramid, while that for the yttrium center is quite similar to the general type for  $\text{M}(\text{C}_5\text{H}_5)_2\text{X}_3$  complexes. The Y-Cl bonds range from 2.705(5)–2.802(3) Å, while the Y-C and Y-H bond lengths average 2.640(5) Å and 2.35(7) Å, respectively. The Y-H-Al angles average 154(6)°, the Cl-Y-Cl angles average 74.8(2)°, and the more acute type of the H-Y-Cl angles average 68°.

A couple of reports have appeared dealing with simple hydride species. A study of the magnetic properties of  $\text{Th}_{6-x}\text{Y}_x\text{Mn}_{23}$  hydrides has been carried out by Boltich, Wallace, Pourarian, and Malik (28). The hydrogen capacities of these species were found to vary linearly with  $x$ . The Th-rich species ( $x \leq 3$ ) exhibit magnetic ordering and appear ferrimagnetic, while the Y-rich species behave as spin-glasses. The differences between these two groups has been correlated with their nearest neighbor Mn--Mn separations. The second

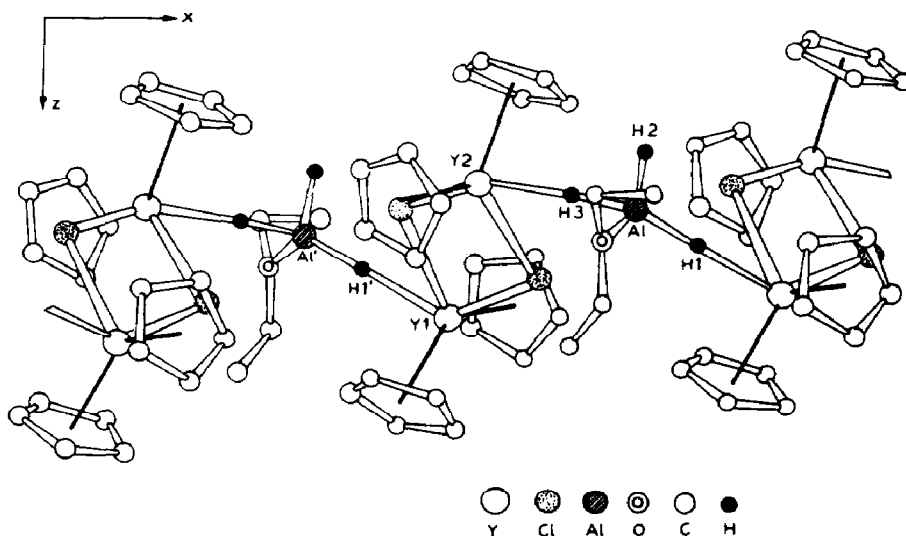
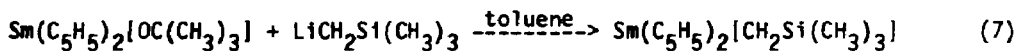
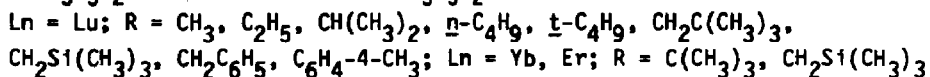
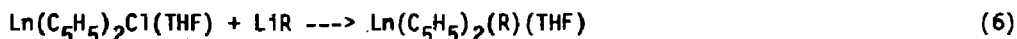


Fig. 7. The structure of  $\text{Y}(\text{C}_5\text{H}_5)_2\text{ClAlH}_3(\text{ether})$  from ref. 27.

study, by Bauslicher and Walch, involved full valence multiconfigurational self-consistent field (MCSCF)/first order CI calculations on the lowest six states of  $\text{ScH}$  (29). Several basis sets were employed at different levels of approximation. At the SCF level, states arising from  $4s4p$  hybrid bonding have similar bond lengths, whereas the  $d$  bonding state ( $^1\Sigma^+$ ) has a much shorter length, but was not the ground state. Full valence MCSCF calculations, utilizing  $3d$ ,  $4s$ , and  $4p$  orbitals for scandium and  $1s$  for hydrogen, instead indicate that the ground state is now  $^1\Sigma^+$ , and retains its short bond. Apparently, the near degeneracy of the  $4s$  and  $4p$  orbitals had led to the poorer SCF results above. Substantiation of these conclusions was obtained through first order CI and CI(single and double excitation) calculations. Calculations involving larger hydrogen basis sets suggested that some  $\text{H}^-$  character contributed to the molecule. However, relatively little effect on the state energies was observed.

Schumann, Genthe, Bruncks, and Pickardt have reported the syntheses of monomeric  $\text{Ln}(\text{C}_5\text{H}_5)_2(\text{R})(\text{THF})_x$  species ( $\text{Ln} = \text{Lu}, \text{Sm}, \text{Er}, \text{Yb}; x = 0, 1$ ), as in equations (6) and (7) (30). Additionally, the substitution of  $\text{NaBH}_4$  for  $\text{LiR}$  in equation (6) allowed for the isolation of  $\text{Lu}(\text{C}_5\text{H}_5)_2(\text{BH}_4)(\text{THF})$ , for which



heating was found to lead to a loss of THF. The infrared spectrum of the borohydride complex as a THF adduct indicated a bidentate mode of coordination. The other adducts would also dissociate upon heating over 120°, and in the  $R = \underline{t}\text{-C}_4\text{H}_9$  case,  $\beta$ -hydride elimination would subsequently be observed. Further heating led to the formation of  $\text{Lu}(\text{C}_5\text{H}_5)_3$ . Solid state x-ray structural determinations were reported for  $\text{Lu}(\text{C}_5\text{H}_5)_2[\text{CH}_2\text{Si}(\text{CH}_3)_3](\text{THF})$  and  $\text{Lu}(\text{C}_5\text{H}_5)_2(\text{C}_6\text{H}_4\text{-4-CH}_3)(\text{THF})$  (Figures 8 and 9). In each case, the expected

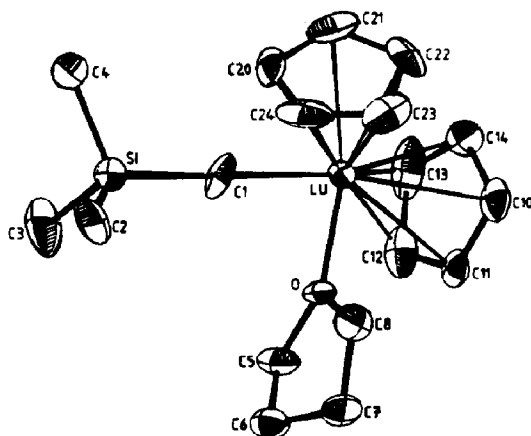


Fig. 8. The solid state structure of  $\text{Lu}(\text{C}_5\text{H}_5)_2[\text{CH}_2\text{Si}(\text{CH}_3)_3](\text{THF})$  (ref. 30). Copyright 1982 American Chemical Society.

pseudo-tetrahedral geometry was observed, with the Lu-C (alkyl) distances being 2.376(17) and 2.345(39) Å, while the Lu-O distances were 2.288(10) and 2.265(28) Å, respectively. The average Lu-C (Cp) distances were 2.606(8) and 2.595(16) Å, while the CM-Lu-CM angles (CM = cyclopentadienyl ligand center of mass) were 130.2 and 128.8 degrees, respectively. Similarly, the O-Lu-C(alkyl) angles were 95.8(9) and 89.6(12) degrees. Watson has also reported the synthesis and reaction chemistry of some very similar species, which are discussed subsequently (vide infra).

Campari and Hart have reported that the reaction of  $\text{LaCl}_3(2,2,2\text{-cryptate})$  with  $\text{LiC}(\text{C}_6\text{H}_5)_3$  in THF gives rise to  $\text{LaCl}_2[\text{C}(\text{C}_6\text{H}_5)_3](2,2,2\text{-cryptate})$  which was characterized by analytical and spectral data (31). These data indicated that the 2,2,2-cryptate ligand was attached to the lanthanum(III) ion, but no conclusion could be reached concerning the  $\text{C}(\text{C}_6\text{H}_5)_3$  and Cl ligands. Related reactions, involving  $\text{LaCl}_3(2,2,2\text{-cryptate})$  or  $\text{NdCl}_3(2,2,2\text{-cryptate})$  and at least 3 equivalents of either  $\text{LiCH}_3$  or  $\text{C}_6\text{H}_5\text{C}_2^-$  failed to yield stable products; in some cases, the presence of uncoordinated cryptate

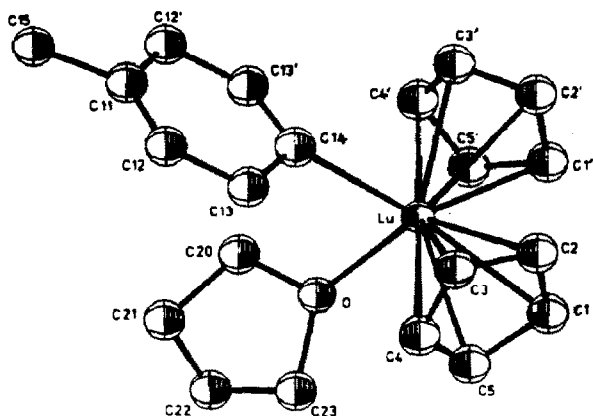
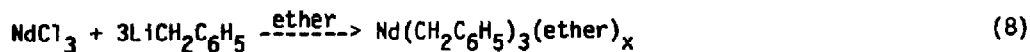


Fig. 9. The structure of  $\text{Lu}(\text{C}_5\text{H}_5)_2(\text{C}_6\text{H}_4-4-\text{CH}_3)(\text{THF})$  from ref. 30. Copyright 1982 American Chemical Society.

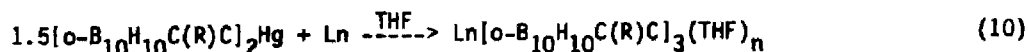
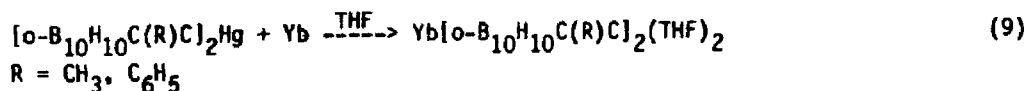
was evident.

Chigir, Guzman, Sharaev, Tinyakova, and Dolgoplosk have reported the synthesis of  $\text{Nd}(\text{CH}_2\text{C}_6\text{H}_5)_3$  (32), as indicated in equation (8). The product is



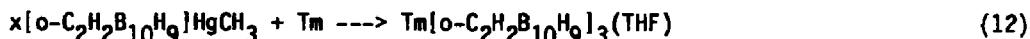
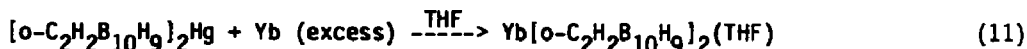
only stable below  $-15^\circ$ , and at higher temperatures decomposes to a previously reported bridging carbyne complex. Acidolysis of the benzyl compound led to the liberation of 3 equivalents of toluene, as well as up to 3 equivalents of ether.  $\text{Nd}(\text{CH}_2\text{C}_6\text{H}_5)_3(\text{ether})_x$  was found to be an active catalyst for the 1,4-trans polymerization of butadiene, for which only a small quantity of the 1,2 polymer was observed as a minor product (ca. 4%). With isoprene, however, the 1,4-trans proportion drops to ca. 91%, while ca. 9% of the product is observed to be the 3,4 polymer. In contrast, the bridging complexes were found to lead to significant proportions of all isomers (1,4-cis, 1,4-trans, 1,2-), while for isoprene nearly equal proportions of the 1,4-trans and 3,4- polymer were observed.

Suleimanov, Bregadze, Koval'chuk, and Beletskaya have communicated the syntheses of carboranyl derivatives of La(III), Tm(III), and Yb(II) (33). Some C-bonded compounds were prepared as indicated in equations (9) and (10).



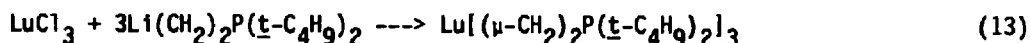
R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>; Ln = La; n = 1; Ln = Tm; n = 3

while the analogous B-bonded species were prepared as indicated by equations (11) and (12).



Watson and Roe have reported the syntheses of Lu(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(CH<sub>3</sub>)(NEt<sub>3</sub>), Lu(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(CH<sub>3</sub>), and Lu(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>[CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>], and have observed that the latter compound can undergo β-methyl elimination, yielding Lu(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(CH<sub>3</sub>) and propene (34). These authors have also studied the mechanistic aspects of the reverse (insertion) reactions, and these will be discussed subsequently (vide infra).

Schumann and Reier have reported the syntheses of new lutetium-ylide complexes (35) as indicated in equations (13) and (14). The <sup>1</sup>H NMR spectrum



of the first product contained two resonances, in a 9:2 ratio, each split into a doublet by coupling with a phosphorus nucleus suggesting a pseudo-octahedral coordination environment. However, complexities in the <sup>13</sup>C and <sup>31</sup>P NMR spectra suggested that an equilibrium was established involving associated species having one ylide group per Lu center function as a bridging ligand, i.e., [(t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>P(μ-CH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Lu(μ-CH<sub>2</sub>)<sub>2</sub>P(t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> for the dimeric species. The complex Lu(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CH<sub>2</sub>)<sub>2</sub>P(t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> was found to exist in the indicated monomeric form with no indication of higher oligomers or isomers such as Lu(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>[CHP(CH<sub>3</sub>)(t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>].

Warkentin, Masse, and Simon have published a full account of the structure of their previously described carbide species Gd<sub>10</sub>C<sub>4</sub>Cl<sub>18</sub> as well as a new complex Gd<sub>10</sub>C<sub>4</sub>Cl<sub>17</sub> (36). In each case, a similar structure is adopted (Figure 10), in which C<sub>2</sub> units are found at the center of Gd<sub>6</sub> octahedra. The first complex, prepared from a stoichiometric mixture of GdCl<sub>3</sub>, Gd, and graphite, occurs as a molecular species, while Gd<sub>10</sub>C<sub>4</sub>Cl<sub>17</sub> achieves a similar structure through the formation of a chloride-bridged chain motif. The Gd--Gd distances in these clusters were found to average ca. 3.72 Å, while the Gd-C distances ranged from 2.19-2.66 Å, and the C-C distances were observed to be 1.47 Å. From Knudsen effusion measurements, Gingerich, Haque, and Pelino

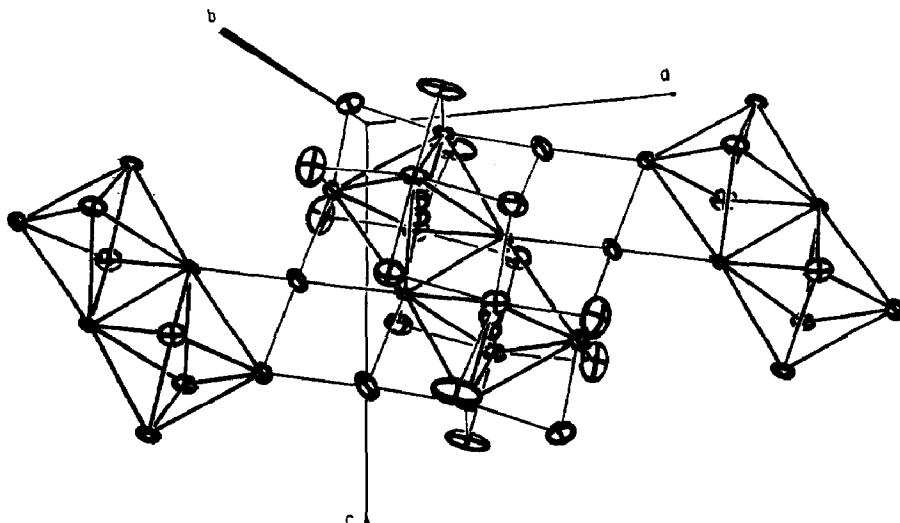
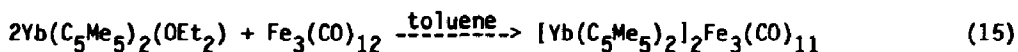


Fig. 10. Carbide-encapsulated bi-octahedral nature of  $Gd_{10}C_4Cl_{17}$  (ref. 36).

have determined the atomization energy and standard heat of formation of  $LaC_7$  to be  $4320 \pm 60$  and  $1095 \pm 50$  kJ/mole, while for  $LaC_8$  the respective values were found to be  $4992 \pm 70$  and  $1140 \pm 60$  kJ/mole (37).

A number of reports have appeared which are pertinent to the area of metal-metal bonding. Tilley and Andersen have reported the preparation of  $[Yb(C_5Me_5)_2]_2Fe_3(CO)_{11}$  through the route indicated by equation (15). A



structural study (Figure 11) was carried out (38), and demonstrated that the ytterbium and iron fragments were held together through Yb-isocarbonyl interactions, resulting in a pseudo-tetrahedral coordination geometry about ytterbium. The  $CM(C_5Me_5)-Yb-CM(C_5Me_5)_2$  angle was found to be  $141.6(6)^\circ$ , while a  $O-Yb-O$  angle of  $70.8(2)^\circ$  was found. An average Yb-O distance of  $2.243(5)$  Å was found, significantly shorter than the average Yb-C distance of  $2.573(13)$  Å. The complex is paramagnetic, and the ytterbium fragments may be regarded as  $Yb(C_5Me_5)_2^+$  units. The Fe(2)-Fe(3) separation is too long for any significant interaction to be occurring. However, the respective Fe(1)-Fe(2) and Fe(1)-Fe(3) distances of  $2.524(1)$  and  $2.538(1)$  Å are comparable to those in triangular 48 electron triferron clusters, such as  $Fe_3(CO)_{12}$ . The related reaction of two equivalents of  $Yb(C_5Me_5)_2(OEt_2)$  with  $Fe(CO)_5$  in THF leads to  $[Yb(C_5Me_5)_2(THF)]_2Fe(CO)_4$ , of presumed formulation  $(OC)_2Fe[CO--Yb(C_5Me_5)_2(THF)]_2$ .

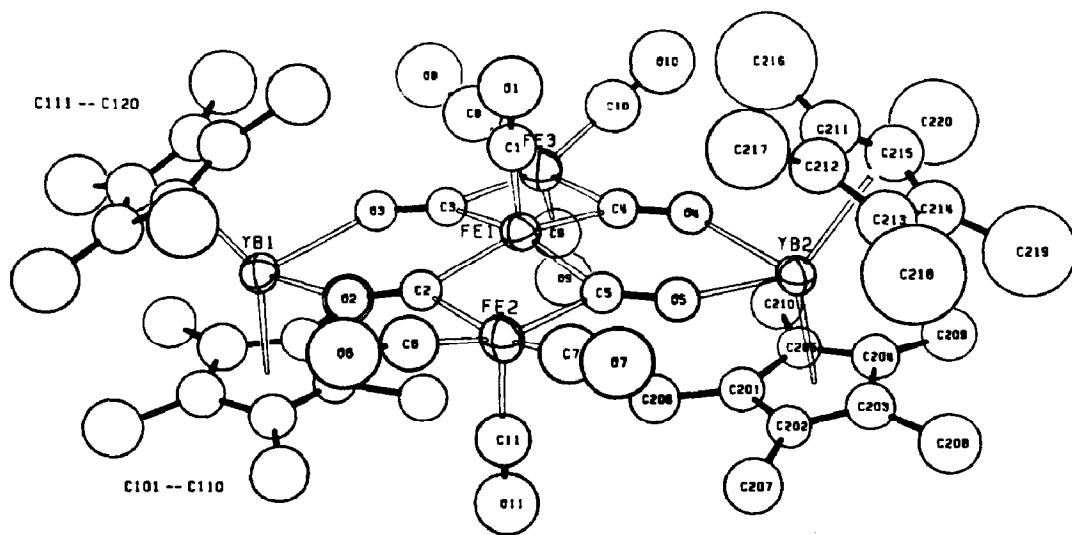
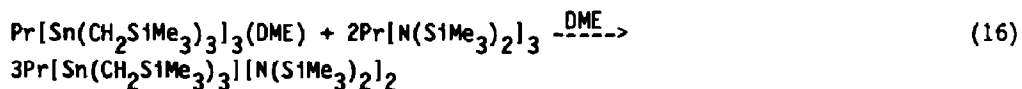


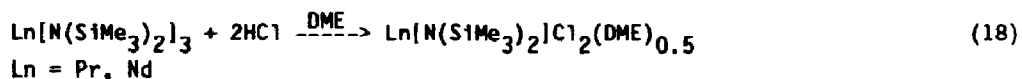
Fig. 11. The structure of  $[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2\text{Fe}_3(\text{CO})_{11}$  from ref. 38. Copyright 1982 American Chemical Society.

Nuriev, Rybakova, Pasynskii, Suleimanov, Gubin, and Beletskaya have reported the preparation of  $\text{Tm}[\text{Co}(\text{CO})_4]_3(\text{THF})_4$  from the reaction of thulium amalgam with either  $\text{Co}_2(\text{CO})_8$  or  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  (39). The product was described both as ionic and containing a metal-metal bond, the latter formulation being supported by the observed C-O stretching frequencies ( $1910\text{--}2080\text{ cm}^{-1}$ ). Manganese and rhenium analogs also appeared isolable.

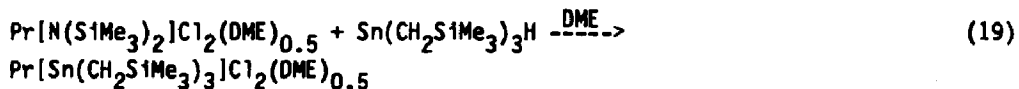
Fedorova, Kalinina, Bochkarev, and Razuvaev have reported the syntheses of some new complexes containing tin-praseodymium bonds (40). The new compounds were prepared via either comproportionation or protonation reactions of their previously reported  $\text{Pr}[\text{Sn}(\text{CH}_2\text{SiMe}_3)_3]_3(\text{DME})$  complex. An example of the former is depicted in equation (16). Similar reactions could also be



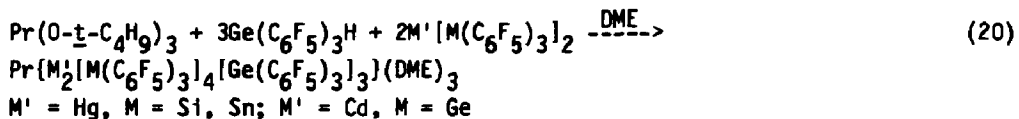
achieved for amide complexes, as in equations (17) and (18). For the latter



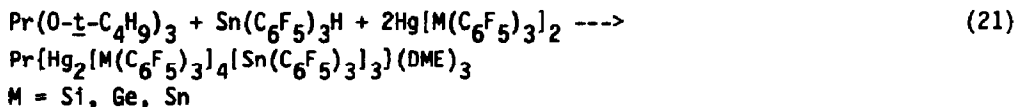
products, evidence was presented which indicated that in DME solution some associated species may form. In addition, the praseodymium compound was found to react with  $(\text{Me}_3\text{SiCH}_2)_3\text{SnH}$ , leading to exchange of the amide ligand by the stannyl group (eq. (19)).



Bochkarev, Rad'kov, Kalinina, Bochkarev, and Razuvaev have reported some ionic compounds containing praseodymium bound to main group metals (41). In an earlier report, they had found that  $\text{Hg}[\text{Ge}(\text{C}_6\text{F}_5)_3]_2$  could be utilized for such preparations, and in the present work they found that  $\text{Ge}(\text{C}_6\text{F}_5)_3\text{H}$  could also be employed, as in equation (20). These species were proposed to contain



polynuclear mercury or cadmium anions,  $\text{M}'[\text{M}(\text{C}_6\text{F}_5)_3]_2[\text{Ge}(\text{C}_6\text{F}_5)_3]^-$  and  $\text{M}'[\text{M}(\text{C}_6\text{F}_5)_3]_2[\text{Ge}(\text{C}_6\text{F}_5)_3]_2^{2-}$ . In a related reaction involving an equimolar ratio of  $\text{Ge}(\text{C}_6\text{F}_5)_3\text{H}$  and  $\text{Pr}[\text{N}(\text{SiMe}_3)_2]_3$ ,  $\text{Pr}[\text{N}(\text{SiMe}_3)_2]_2[\text{Hg}[\text{Ge}(\text{C}_6\text{F}_5)_3]_3]$  is formed. Related tin complexes could also be isolated, as indicated in equation (21).



Schiffman has studied the ytterbium-lead alloy system by vapor pressure measurements using a simultaneous weight-loss-mass-spectrometric Knudsen effusion technique (42). From his thermodynamic measurements the heats of formation (298 K) for  $\text{Yb}_2\text{Pb}$ ,  $\text{Yb}_5\text{Pb}_3$ ,  $\text{YbPb}$ , and  $\text{YbPb}_3$  are -174.6, -461.6, -116.9, and -152.4 kJ/mole, respectively. Wallace and Pourarian have reported photoemission studies on  $\text{LaNi}_{5-x}\text{Cu}_x$  alloys in order to analyze the nature of the hydrogen storage capacity of these materials (43). The apparent major requirement for significant storage capacity is the availability of a partially empty d band of appropriate energy.

Tilley, Andersen, and Zalkin have reported that the coordinated ether in  $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{OEt}_2)_2$  may readily be replaced by dmpe (44), yielding purple, diamagnetic  $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{dmpe})$ , which was structurally characterized (Figure 12). The compound has crystallographically imposed  $\text{C}_2$  symmetry, with Yb-N and



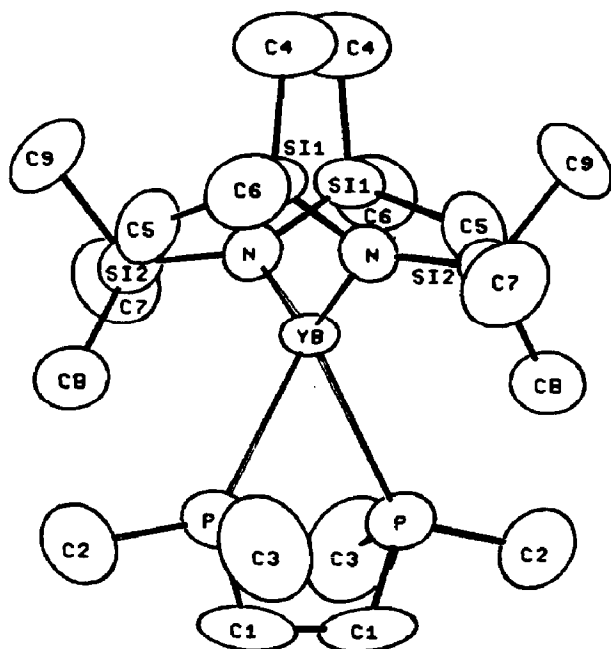


Fig. 12. Perspective view of  $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{dmpe})$  from ref. 44. Copyright 1982 American Chemical Society.

Yb-P bond distances of 2.331(13) and 3.012(4) Å, and N-Yb-N, P-Yb-P, and N-Yb-P bond angles of 123.6(6), 68.4(2), and 101.2(3) degrees, respectively. In addition to the Yb-N and Yb-P interactions, evidence was also presented for an interaction between Yb and C(5). Thus, while the Yb-N-Si(2) angle of 121.0(7)° is not unusual, the Yb-N-Si(1) angle of 108.5(6)° is abnormally small, leading to a Yb--C(5) separation of only 3.04 Å, compared to an expected van der Waals separation of ca. 3.7 Å. In addition some of the three hydrogen atoms bound to C(5) also made close approaches to Yb (2.76(8), 2.85(6), and 3.18(1) Å). Overall, then, it appears that the interaction may involve more Yb-C than Yb-H bonding character, particularly in light of transition metal analogs, which typically involve more M-H character. Also mentioned briefly in this paper were the compounds  $\text{Eu}[\text{N}(\text{SiMe}_3)_2]_2(\text{dmpe})_{1.5}$  and  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2[\text{P}(\text{n-C}_4\text{H}_9)_3]_2$  (M = Eu, Yb).

Lanthanide compounds continue to find applications in organic transformations. Thus, new uses of  $\text{SmI}_2$  as a potent reducing agent have been found (45). In addition, organocerium reagents, prepared from alkyl lithium reagents and  $\text{CeI}_3$ , display interesting reactivities with ketones (46). At -65°, nucleophilic additions occur, yielding tertiary alcohols in generally very good yields, whereas at or above 0°, reductive couplings and/or

reductions of the ketones occur.

Watson has reported the direct insertion of an olefin into the lanthanide-carbon single bond in  $\text{Lu}(\text{C}_5\text{Me}_5)_2(\text{CH}_3)(\text{ether})$  or the ytterbium analog (47). The ether adducts were obtained in several steps from the previously reported  $\text{Li}(\text{THF})_3^+\text{Ln}(\text{C}_5\text{Me}_5)_2(\text{CH}_3)_2^-$  compounds. Thus, heating in vacuum led to the solvent free salts,  $\text{Li}[\text{Ln}(\text{C}_5\text{Me}_5)_2(\text{CH}_3)_2]$ , which react with  $\text{Al}_2(\text{CH}_3)_6$  in pentane to yield  $\text{Ln}(\text{C}_5\text{Me}_5)_2(\text{CH}_3)_2\text{Al}(\text{CH}_3)_2$ . Dissolution of these species in ether then led to the etherates described above ( $\text{Ln} = \text{Yb}, \text{Lu}$ ). For the diamagnetic lutetium compound, NMR spectral data indicated that rapid exchange of free and coordinated ether took place down to at least  $-60^\circ$ . In solution these compounds were found to react with propene in the temperature range of  $-30^\circ$  to  $20^\circ$  to yield an isobutyl compound, which was characterized through various spectroscopic methods and isotopic labelling studies. Hydrolysis led cleanly to isobutane (no *n*-butane). The formation of the isobutyl compound was found to be first order in both propene and the etherate, while an inverse dependence was observed for the ether concentration. Hence, the insertion process depends on an initial dissociation of ether, yielding  $\text{Ln}(\text{C}_5\text{Me}_5)_2(\text{CH}_3)$  in solution. Additionally,  $\text{Lu}(\text{C}_5\text{Me}_5)_2(\text{R})$  species could be observed ( $\text{R} = n\text{-C}_3\text{H}_7, 2,4\text{-dimethylpentyl}$ ), the former apparently through the interaction of propene with  $\text{Lu}(\text{C}_5\text{Me}_5)_2(\text{H})$  (from the beta-hydride elimination of the isobutyl compound), the latter from the direct insertion of propene into the Lu-isobutyl bond. Notably, such direct insertions have been postulated to be important in the Ziegler-Natta catalysis of olefin polymerization.

Watson and Roe have reported some further studies on the lutetium methyl complex  $\text{Lu}(\text{C}_5\text{Me}_5)_2(\text{CH}_3)$ , which could be isolated by heating the triethylamine adduct in vacuo (34). Notably,  $\text{Lu}(\text{C}_5\text{Me}_5)_2(\text{CH}_3)$  exists in a monomer-dimer equilibrium ( $\Delta G^\circ = 2.9 \text{ kcal/mole}$ ), but only one of the methyl groups serves as a bridging ligand, the other remaining terminally bound. This complex reacts readily with propene, yielding the isobutyl complex described above, and much smaller amounts of higher molecular weight multiple insertion products. However, the isobutyl compound then undergoes decomposition (half life ca. 3.4 hr) by several first order processes, yielding significant amounts of the allyl compounds  $\text{Lu}(\text{C}_5\text{Me}_5)_2(\text{C}_3\text{H}_5)$  and  $\text{Lu}(\text{C}_5\text{Me}_5)_2(\text{C}_4\text{H}_7)$  (50-80%) as well as smaller amounts of  $\text{Lu}(\text{C}_5\text{Me}_5)_2(\text{CH}_3)$  (20-40%). The predominant organic product was isobutane (40-60%). The formation of the allyl compounds was postulated to proceed through an intermediate fulvene complex such as  $\text{Lu}(\text{C}_5\text{Me}_5)_2\{\eta^6\text{-C}_5\text{Me}_4(\text{CH}_2)\}$ , while the  $\text{Lu}(\text{C}_5\text{Me}_5)_2(\text{CH}_3)$  product arose from a  $\beta$ -methyl elimination reaction.

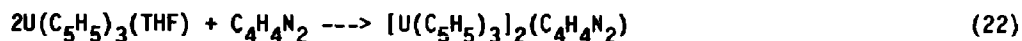
Cao, Qian, Wang, and Zhao have investigated the structure of polyacetylene formed from a neodymium salt-aluminum alkyl catalyst system

(48). Spectroscopic data indicated an initial *cis* content of 70%. Subsequent isomerization to the *trans* form was reported to lead to semicrystalline material, of probable space group *Pnam*. Yang, Tsutsui, Chen, and Bergbreiter have reported that mixtures of THF adducts of lanthanide halides and aluminum alkyls can be used as stereospecific diene polymerization catalysts (49). Thus, in hydrocarbon solvents  $\text{MdCl}_3(\text{THF})_2\text{-Al}(\text{C}_2\text{H}_5)_3$  catalysts were found to be quite active for the polymerization of butadiene and isoprene, yielding products with very high *cis*-1,4 contents (97 and 95% respectively). Similar results were obtained with praseodymium and gadolinium catalysts, although they were not quite as active. It was also found that the polymerization could be quenched with  $\text{CO}_2$ , yielding polymeric carboxylates and, after protonation, polymeric carboxylic acids.

Ramaroson, Kieffer, and Kiennemann have studied the reactions of  $\text{CO}_2\text{-H}_2$  mixtures on various supported palladium catalysts (50). At 0 bar and  $350^\circ$ , palladium on silica yields predominantly methane, while on  $\text{ThO}_2$ , nearly equal amounts of methane and methanol are formed. However, with  $\text{La}_2\text{O}_3$  as the support, a methanol/methane ratio of ca. 90:10 was observed.

Several reports of new actinide cyclopentadienyl compounds have been published. Mugnier, Dormond, and Laviron have reported that  $\text{U}(\text{C}_5\text{H}_5)_3\text{Cl}$  may be reduced reversibly electrochemically in THF to  $\text{U}(\text{C}_5\text{H}_5)_3\text{Cl}^-$ , which appears stable for several hours (51). That the  $\text{Cl}^-$  ion remains attached was surmised by the fact that the cyclic voltammogram was unchanged in the presence of various ligands, and the observation of a broad singlet at -13.30 ppm in the  $^1\text{H}$  NMR spectrum of an exhaustively electrolyzed solution (cf., -21.8 ppm for  $\text{U}(\text{C}_5\text{H}_5)_3(\text{THF})$ ).

Eigenbrot and Raymond have reported the syntheses of  $[\text{U}(\text{C}_5\text{H}_5)_3]_2(\text{C}_4\text{H}_4\text{N}_2)$  and  $[\text{U}(\text{C}_5\text{H}_4\text{Me})_3]_2(\text{C}_4\text{H}_4\text{N}_2)$  ( $\text{C}_4\text{H}_4\text{N}_2$  = pyrazine) by the general route indicated in equation (22) (52). Spectroscopic data were generally similar to those

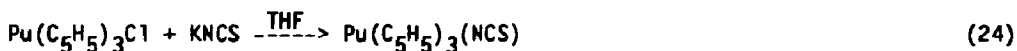
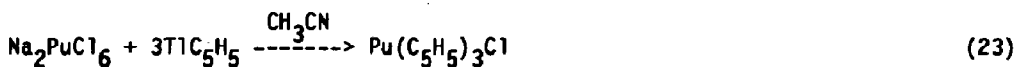


observed earlier for the crystallographically characterized  $[\text{Yb}(\text{C}_5\text{H}_5)_3]_2(\text{C}_4\text{H}_4\text{N}_2)$ , suggesting a similar structure having the two metal centers bridged by the pyrazine ligand. Preliminary magnetic data suggest that some interesting inter-metal communication may be taking place.

Dormond, Dahchour, and Duval-Huet have investigated the reactions of  $\text{U}(\text{C}_5\text{H}_5)_2(\text{NEt}_2)_2$  with various  $\beta$ -diketones (53). In general, selective reactions were observed if the temperatures were kept at  $\leq -20^\circ$ . Thus, the reaction involving two equivalents of  $\beta$ -diketone ( $\text{RC}(\text{O})\text{CHR}'\text{C}(\text{O})\text{R}$ ,  $\text{R} = \text{CH}_3$ ,  $\text{R}' = \text{H}$ ;  $\text{R} = \text{CMe}_3$ ,  $\text{R}' = \text{H}$ ;  $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{R}' = \text{H}$ ) provided the  $\text{U}(\text{C}_5\text{H}_5)_2(\beta\text{-diketonate})_2$  complexes in yields of  $\geq 90\%$ , although for  $\text{R} = \text{OC}_2\text{H}_5$ ,  $\text{R}' = \text{CH}_3$ , a conversion

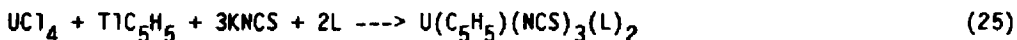
of only 60% was obtained. Lower selectivities were observed for reactions with three equivalents of the  $\beta$ -diketone (90% for  $R = \text{CH}_3$ ,  $R' = \text{H}$  and 30% for  $R = \text{CMe}_3$ ,  $R' = \text{H}$ ). Spectroscopic data suggested "cis-octahedral" coordination geometries for the  $\text{U}(\text{C}_5\text{H}_5)_2(\beta\text{-diketonate})_2$  compounds, and pentagonal bipyramidal for the  $\text{U}(\text{C}_5\text{H}_5)(\beta\text{-diketonate})_3$  species.

Bagnall, Plews, and Brown have reported the syntheses of  $\text{Pu}(\text{C}_5\text{H}_5)_3\text{Cl}$  and  $\text{Pu}(\text{C}_5\text{H}_5)_3(\text{NCS})$  by the routes indicated in equations (23) and (24). While



$\text{Pu}(\text{C}_5\text{H}_5)_3\text{Cl}$  did not sublime readily in vacuo, its infrared spectrum was found to be quite similar to those of the analogous uranium and neptunium compounds. A similar correspondence was observed for  $\text{Pu}(\text{C}_5\text{H}_5)_3(\text{NCS})$  (54). X-ray powder patterns for the two plutonium compounds demonstrated that they were isomorphous with the corresponding uranium and neptunium compounds.

Bagnall and Li have reported the syntheses and characterization of several complexes of the formula  $\text{U}(\text{C}_5\text{H}_5)(\text{NCS})_3(\text{L})_2$  ( $\text{L} = \text{Me}_3\text{CCONMe}_2$  (dmpva),  $\text{Me}_2\text{CHCONMe}_2$  (dmiba),  $\text{OP}(\text{C}_6\text{H}_5)_3$ , and  $\text{OP}(\text{NMe}_2)_3$  (tdpo)) (55). The compounds were prepared in one step procedures, as indicated by equation (25). However,

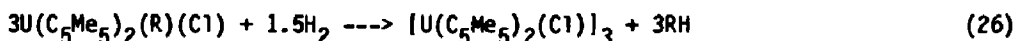


the products were found to contain variable amounts of KCl. Attempts to carry out equation (25) for  $\text{L} = \text{MeCONMe}_2$  (dma),  $\text{EtCONMe}_2$  (dmpa),  $\text{EtCONEt}_2$  (depa), pyridine, or  $\text{L}_2 = 2,2'$ -bipyridine led instead to disproportionation, producing  $\text{U}(\text{C}_5\text{H}_5)_3(\text{NCS})$  and complexes of  $\text{U}(\text{NCS})_4$ . Spectroscopic data suggested that the thiocyanate ligands were bound to the uranium center through the nitrogen atom. Using a model involving first and second order "cone" and "fan" angles, the authors proposed that steric effects were predominantly responsible for determining whether a compound would be stable or unstable to disproportionation.

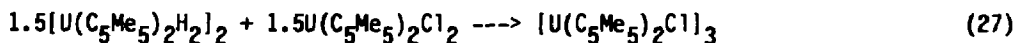
Bagnall, Plews, Brown, Fisher, Klähne, Landgraf, and Siemel have reported a variety of anionic  $\text{An}(\text{C}_5\text{H}_5)_3(\text{X})(\text{Y})^-$  complexes ( $\text{An} = \text{U}, \text{Np}, \text{Pu}$ ;  $\text{X} = \text{NCS}$ ;  $\text{Y} = \text{NCS}, \text{F}, \text{OH}, \text{CN}, \text{NCBH}_3, \text{NCO}$ ) (56). In addition, a new route to the previously reported  $\text{U}(\text{C}_5\text{H}_5)_3(\text{NCS})$  and related  $\text{U}(\text{C}_5\text{H}_4\text{CH}_3)_3(\text{NCS})$  were developed, utilizing the reaction of  $\text{U}(\text{C}_5\text{H}_5)_3\text{Cl}$  or  $\text{U}(\text{C}_5\text{H}_4\text{CH}_3)_3\text{Cl}$  with KNCS in either  $\text{CH}_3\text{CN}$  or aqueous media. The low solubilities and volatilities of these compounds suggested that they possess oligomeric structures with approximate

trigonal bipyramidal coordination at the uranium center. Reactions of the oligomeric  $U(C_5H_5)_3(CN)$  species with an excess of  $CN^-$  did not lead to a monomeric species such as  $U(C_5H_5)_3(CN)_2^-$ , apparently an indication of the stability of the oligomeric compound. A similar reaction could be employed to prepare  $U(C_5H_5)_3(NCBH_3)(L)$  ( $L = H_2O, CH_3CN$ ) species, which under vacuum were converted to the previously reported  $U(C_5H_5)_3(NCBH_3)$  compound. Interestingly, attempts to prepare  $U(C_5H_5)_3(NCBH_3)_2^-$  by the interaction of  $U(C_5H_5)_3(NCBH_3)$  with an excess of  $NaNCBH_3$  led instead to the oligomeric  $U(C_5H_5)_3(CN)$ . Reactions of  $U(C_5H_5)_3(NCS)$  with  $KNCS$  led to  $U(C_5H_5)_3(NCS)_2^-$  salts of varying degrees of purity, depending to some extent on the chosen counterion. The related neptunium and plutonium compounds could also be isolated, and were found to be isomorphous with  $As(C_6H_5)_4^+[U(C_5H_5)_3(NCS)_2^-]$ . Notably, attempts to prepare  $U(C_5H_4CH_3)_3(NCS)_2^-$  salts seemed to encounter even greater difficulties, generally leading to mixtures of products. Both electronic and steric arguments were presented to explain the apparent lower stability of this ion. The mixed ion species,  $U(C_5H_5)_3(NCS)(NCO)^-$ , could be prepared from  $U(C_5H_5)_3(NCO)(NCCH_3)$  and  $KNCS$  in  $CH_3CN$ , but not readily from  $U(C_5H_5)_3(NCS)(NCCH_3)$  and  $KOCN$  in  $CH_3CN$ . The observation that the  $C_5H_5$  ligands in the anionic complexes were much more readily replaced than in neutral or cationic species was interpreted as an indication of weaker  $U-C_5H_5$  bonding.

Fagan, Manriquez, Marks, Day, Vollmer, and Day have reported the syntheses and properties of a variety of bis(pentamethylcyclopentadienyl)-uranium(III) complexes (57). While sodium amalgam reduction of  $U(C_5Me_5)_2Cl_2$  in THF leads to  $U(C_5Me_5)_2(\mu_2-Cl)_2(Na)(THF)_x$  ( $x = 1.5-2$ ), hydrogenolysis of  $U(C_5Me_5)_2(R)(Cl)$  complexes (eq. (26),  $R = CH_3, CH_2SiMe_3$ ) leads to the sodium

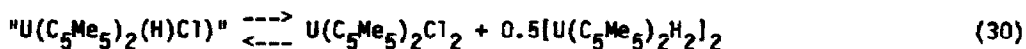


free product. Alternatively, the same complex may be prepared as indicated by equation (27), seeming to suggest that  $U(C_5Me_5)_2(H)(Cl)$  may be unstable with respect to loss of  $H_2$ , unlike the corresponding thorium complexes. However,

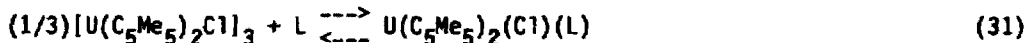


$[U(C_5Me_5)_2H_2]_2$  does exhibit a marked tendency to lose  $H_2$ , thus allowing the alternative possibility indicated by equations (28-30). While  $[U(C_5Me_5)_2Cl]_3$

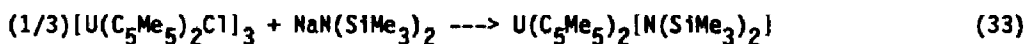
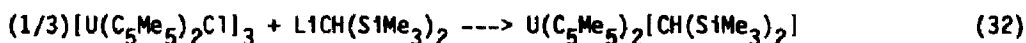




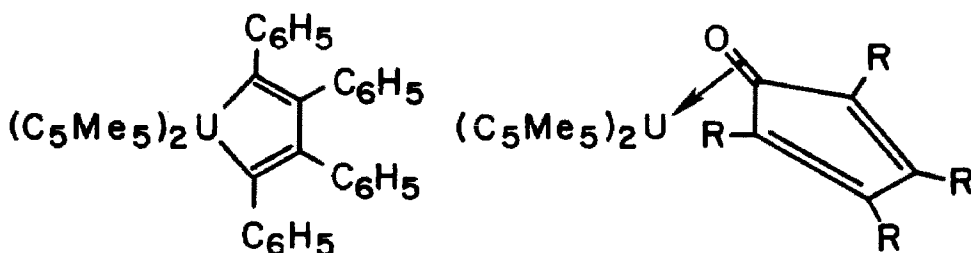
is essentially insoluble in hydrocarbon solvents, it readily dissolves in such solvents in the presence of Lewis bases such as pyridine, THF, ether, or  $PMe_3$  (eq. (31)). The pyridine and THF adducts are reasonably strongly bound, but



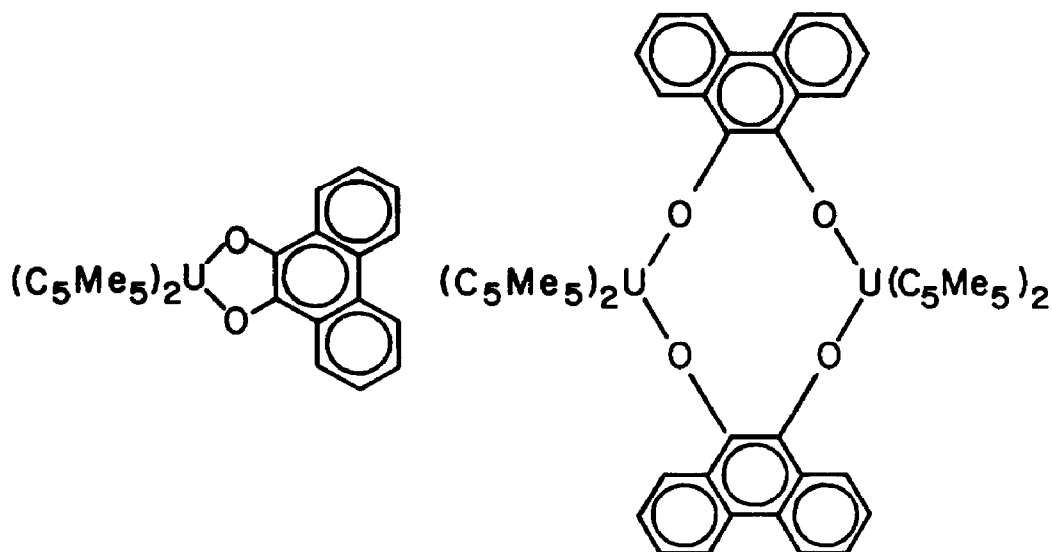
ether and  $PMe_3$  are sequentially more readily lost. In the presence of excess Lewis base, rapid exchange of free and coordinated base is observed on the NMR timescale. Reactions of  $[U(C_5Me_5)_2Cl]_3$  with  $LiCH(SiMe_3)_2$  or  $NaN(SiMe_3)_2$  readily lead to the expected chloride substitution products (eqs. 32, 33),



both formulated as monomeric species, in accord with cryoscopic molecular weight determinations. The alkyl complex reacts very rapidly with hydrogen (much more so than do U(IV) alkyl complexes), yielding  $[U(C_5Me_5)_2H_2]_2$  and  $[U(C_5Me_5)_2H]_n$  in a 4:1 ratio (per uranium atom). Additionally, reactions also occur readily with diphenylacetylene and tetraphenylcyclopentadienone to yield the corresponding products indicated below, together with an equimolar



quantity of  $U(C_5Me_5)_2Cl_2$ . For the former reaction, the intermediacy of  $U(C_5Me_5)_2[\eta^2-C_2(C_6H_5)_2]$  was suggested. Similarly, reaction of  $[U(C_5Me_5)_2Cl]_3$  with 9,10-phenanthrenequinone was found to lead to an equimolar mixture of  $U(C_5Me_5)_2(9,10\text{-phenanthrenequinonate})$  and  $U(C_5Me_5)_2Cl_2$ . The quinonate complex was insufficiently soluble for an accurate cryoscopic molecular weight determination, and both monomeric and dimeric modes of coordination were considered (below). Reactions of  $[U(C_5Me_5)_2Cl]_3$  with  $CH_3Cl$  or  $C_6H_5Cl$  also led to U(IV) species. For the  $CH_3Cl$  reaction, both  $U(C_5Me_5)_2Cl_2$  as well as



$U(C_5Me_5)_2(CH_3)(Cl)$  were formed, in a 6.4:1 ratio, whereas the  $C_6H_5Cl$  reaction led only to  $U(C_5Me_5)_2Cl_2$ . A single crystal x-ray diffraction study was carried out for  $[U(C_5Me_5)_2Cl]_3$  (Figure 13). The molecule was found to possess crystallographic  $C_2$  symmetry, but closely approximated idealized  $D_{3h}$  symmetry. The  $(UCl)_3$  ring was found to be nearly planar (within  $0.015 \text{ \AA}$ ), as were the five membered rings of the  $C_5Me_5$  ligands (within  $0.018 \text{ \AA}$ ). The methyl groups

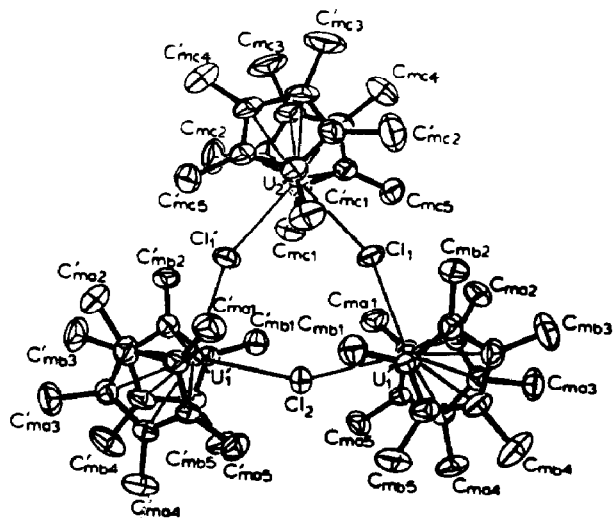
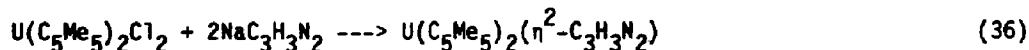
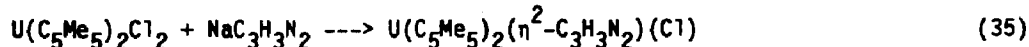
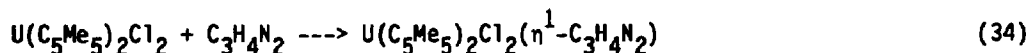


Fig. 13. The solid state structure of  $[U(C_5Me_5)_2Cl]_3$  from ref. 57. Copyright 1982 American Chemical Society.

are located 0.018–0.343 Å out of these planes in a direction away from the metal center. The largest displacements (> 0.33 Å) are exhibited by the methyl groups closest to the other C<sub>5</sub>Me<sub>5</sub> ligand on the same uranium atom. Several other indications of significant CH<sub>3</sub>--CH<sub>3</sub> repulsion effects were observed. A number of intramolecular CH<sub>3</sub>--CH<sub>3</sub> nonbonded contacts were observed to be ca. 0.4–0.5 Å shorter than the expected van der Waals separation of 4.0 Å. The presence of the methyl groups also seems responsible for the adoption of a trimeric structure, as the CH<sub>3</sub>--CH<sub>3</sub> contacts involving methyl groups related by C<sub>3</sub> symmetry were observed to be as short as 3.51–3.70 Å, and would need to be much shorter in a dimeric structure. Two independent CM-U-CM (CM = C<sub>5</sub>Me<sub>5</sub> center of mass, defined by the five metal-bound carbon atoms) angles were observed, 82.0° and 86.4° for U<sub>1</sub> and U<sub>2</sub>, respectively. Average respective U-C and U-Cl bond distances of 2.768(7) and 2.900(6) Å were observed, while the average Cl-U-Cl and U-Cl-U angles were 83.8(11) and 154.9(19) degrees.

Eigenbrot and Raymond have reported the syntheses and structural determinations for several pyrazole or pyrazolate complexes of uranium(IV) (eqs. 34–36) (58). The simple adduct, U(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(Cl)<sub>2</sub>(η<sup>1</sup>-C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>), was found



situated on a site of crystallographic mm (C<sub>2v</sub>) symmetry, necessitating a disorder between N2 and C80 (Figure 14). Pertinent bonding parameters include U-Cl, U-N, and average U-C distances of 2.696(2), 2.607(8), and 2.74(2) Å, with Cl-U-Cl and CM-U-CM angles of 148.29(8) and 137.1 degrees, respectively. Some variable temperature <sup>1</sup>H NMR spectroscopic behavior was observed, and attributed to a fluxionality of the U-N bond. The structure of U(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(η<sup>2</sup>-C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)(Cl) is presented in Figure 15, and involves η<sup>2</sup> coordination of the anionic pyrazolate ligand. The U-Cl and average U-N and U-C distances are 2.611(2), 2.350(4), and 2.73(3) Å, while CM-U-CM and N-U-N angles of 136.2 and 33.3(2) degrees were observed, respectively. All ligands were nearly planar (within 1–2σ), except for the C<sub>5</sub>Me<sub>5</sub> ligands' methyl groups, which generally lied 5–15σ out of the planes of the five metal-bound carbon atoms, in the usual direction. The structure of U(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(η<sup>2</sup>-C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub> may be seen in Figure 16. For this complex, average U-C, U-N, and U-N' bond distances of 2.75(2), 2.404(3), and 2.362(4) (to N2 and N3) Å were observed, while the CM-U-CM and



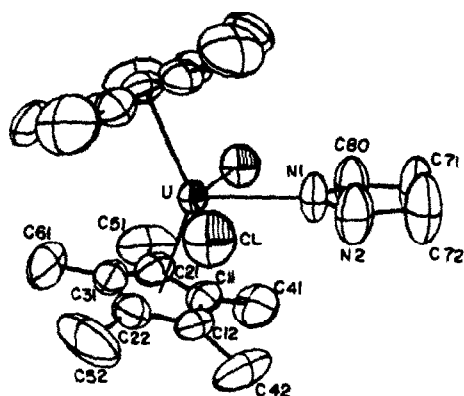


Fig. 14. The structure of  $U(C_5Me_5)_2Cl_2(\eta^1-C_3H_4N_2)$  from ref. 58. Copyright 1982 American Chemical Society.

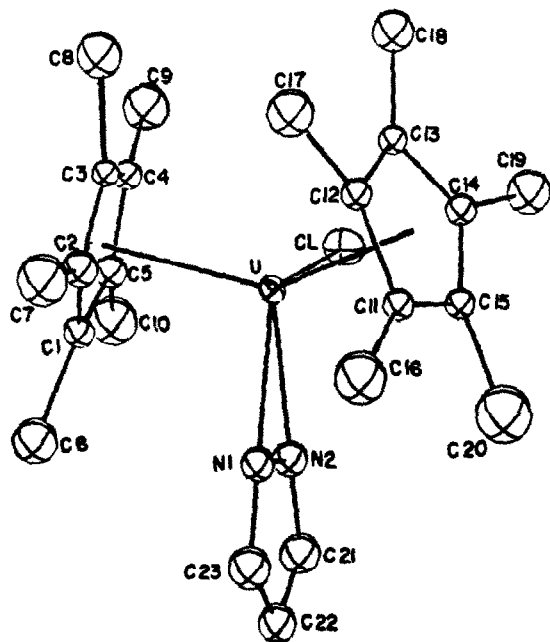


Fig. 15. Perspective view of  $U(C_5Me_5)_2(\eta^2-C_3H_3N_2)Cl$  from ref. 58. Copyright 1982 American Chemical Society.

average intrapyrazolate N-U-N angles were 137.2 and 32.8 degrees, respectively. Interestingly, this compound displays unusual magnetic

behavior, in that its susceptibility is a minimum at low temperature, and initially increases with temperature, until it eventually levels off. In

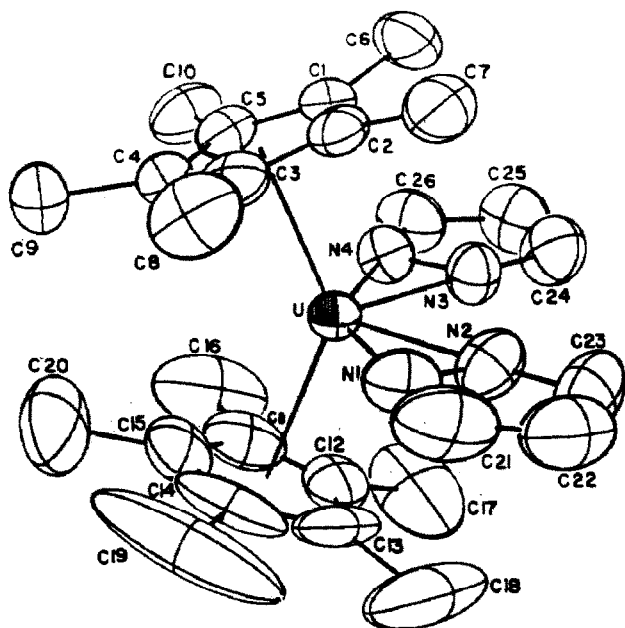


Fig. 16. The molecular structure of  $U(C_5Me_5)_2(\eta^2-C_3H_3N_2)_2$  from ref. 58. Copyright 1982 American Chemical Society.

contrast, the other two complexes have magnetic moments which are high at low temperatures, and decrease with increasing temperature.

Finke, Gaughan, and Voegeli have reported some interesting electrochemical results for  $U(C_5Me_5)_2Cl_2$  (59). They have found that reversible reduction to  $U(C_5Me_5)_2Cl_2^-$  occurs in both  $CH_3CN$  and THF solutions, with observed potentials of -1.30 and -1.22 V vs. SCE. In accord with this and the results of Marks, et al. (*vide supra*), they found it possible to isolate  $U(C_5Me_5)_2(U_2-Cl)_2Na(THF)$  from the stoichiometric reduction of  $U(C_5Me_5)_2Cl_2$  with sodium amalgam. This U(III) species displayed the expected reverse electrochemical behavior as that of  $U(C_5Me_5)_2Cl_2$ . In contrast, however,  $U(C_5Me_5)_2Cl(THF)$  undergoes irreversible electrochemical oxidation in THF. The observed reduction potential for  $U(C_5Me_5)_2Cl_2$  of ca. -1.3 V may be compared to values of -0.8 and -1.8 V for  $Ti(C_5H_5)_2Cl_2$  and  $Zr(C_5H_5)_2Cl_2$ . In contrast, no reduction of  $Th(C_5Me_5)_2Cl_2$  could be observed down to -2.7 V.

Reeb, Mugnier, Dormond, and Laviron have also reported observations on the electrochemical reduction of  $U(C_5Me_5)_2Cl_2$  (60). From NMR spectroscopy

these authors concluded that  $U(C_5Me_5)_2Cl_2$  (I) undergoes slight coordination by THF (as well as DMF and  $CH_3CN$ ). For such a system, a reduction was observed at approximately -1.2 V (vs. SCE), whereas in the presence of  $PF_6^-$ , I is transformed to another species, which is reduced at -1.6 V. In the presence of the better ligand cyclohexyl isocyanide in THF solution, a similar situation was observed. Thus, a reduction process occurred at -1.25 V, while in the presence of  $PF_6^-$ , the reduction at -1.25 V was slowly replaced by another at -1.76 V. However, the presence of an excess of the isocyanide retarded the appearance of this new peak. The various new peaks (-1.6, -1.76 V) were assigned as one electron reductions of  $U(C_5Me_5)_2Cl_2(PF_6)^-$ . It was possible to isolate the reduced isocyanide complex, either from electrochemical or sodium amalgam reduction, and this species could be reoxidized to  $U(C_5Me_5)_2Cl_2(CNC_6H_{11})$ . For the U(III) adduct, the  $^1H$  NMR spectrum could be obtained and, together with the above data, indicated the reduced species to be  $U(C_5Me_5)_2Cl_2(CNC_6H_{11})^-$ .

Spirlet, Rebizant, and Goffart have reported the solid state structure of  $Th(C_{12}H_{13})_3Cl$  ( $C_{12}H_{13}$  = 1,4,7-trimethylindenyl) (61). As may be seen in Figure 17, the authors regard the bonding as being predominantly allylic, and

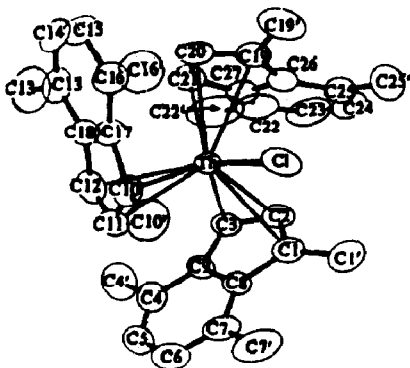
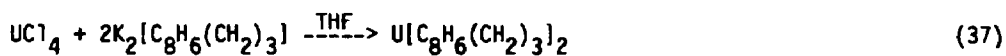


Fig. 17. The structure of  $Th(1,4,7\text{-trimethylindenyl})_3Cl$  from ref. 61.

the average Th-C distances for the three allylic positions (C1-C3 and each of their two equivalents) are 2.845(4), 2.731(4), and 2.742(4) Å, respectively, while the related values for the C8 and C9 positions are significantly longer at 2.946(3) and 2.931(3) Å. The Th-Cl bond length was found to be 2.664(1) Å.

Zalkin, Templeton, Luke, and Streitwieser have reported the synthesis and structure of dicyclopentenouranocene,  $U[C_8H_6(CH_2)_3]_2$  (62). This compound was prepared as indicated by equation (37). The compound was found to possess



a magnetic moment of  $2.4 \mu_B$ . The solid state structure is depicted in Figure 18. The observed conformation is twisted approximately  $8^\circ$  from a staggered

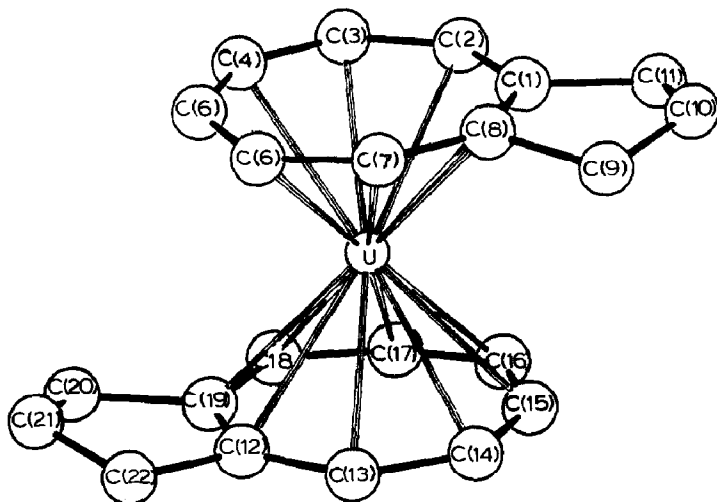


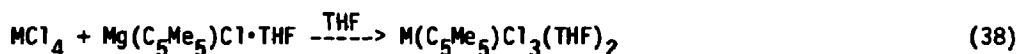
Fig. 18. Perspective view of  $\text{U}[\text{C}_8\text{H}_6(\text{CH}_2)_3]_2$  from ref. 62. Copyright 1982 American Chemical Society.

orientation. The U-C distances all appeared reasonably comparable, averaging  $2.642(7) \text{ \AA}$ .

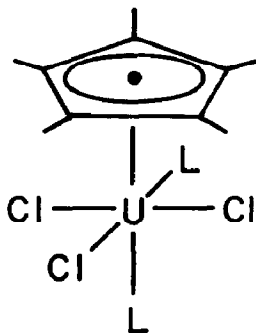
Bruno, Ciliberto, Fischer, Fragala, and Spiegl have studied the He(I) and He(II) photoelectron spectra of a variety of ring-substituted uranocenes  $\text{U}(\text{C}_8\text{H}_7\text{R})_2$  ( $\text{R} = \text{SiMe}_3, \text{P}(\underline{\text{t}}\text{-C}_4\text{H}_9)_2$ ) (63). While some very substantial differences were observed in the photoelectron spectra of  $\text{C}_8\text{H}_7\text{SiMe}_3$  and  $\text{C}_8\text{H}_8$ , the spectra of  $\text{U}(\text{C}_8\text{H}_7\text{SiMe}_3)_2$  are quite similar to those of uranocene itself, interpreted as indicating significant, nearly equally strong contributions to covalent U-C bonding by the uranium 5f and 6d orbitals. For  $\text{U}[\text{C}_8\text{H}_7\text{P}(\underline{\text{t}}\text{-C}_4\text{H}_9)_2]_2$ , once again the absorption energies were quite similar to those of uranocene, with the exception of the additional phosphorus lone pair excitation at 7.46 eV. For the three compounds, the assignments for the observed excitations followed the pattern  $e_{3u}(5f)$  at 6.05-6.15 eV,  $e_{2u}(\pi)$  at 6.70-6.80 eV, and  $e_{2g}(\pi)$  at 7.69-7.84 eV. Thus, the uranium atom was considered by these authors to function as a unique "buffer" for the charge present on the substituted cyclooctatetraenyl ligands.

Mintz, Moloy, Marks, and Day have reported the syntheses and

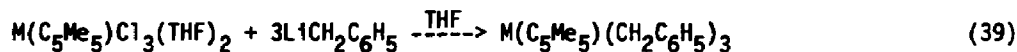
characterization of  $M(C_5Me_5)Cl_3(THF)_2$  complexes ( $M = Th, U$ ) as indicated by equation (38). Analogous to  $U(C_5H_5)Cl_3(THF)_2$ , these complexes were assigned a



mer-cis coordination environment, as below (64). These complexes were found



to react with benzyl lithium to produce the corresponding tris(benzyl) compounds, as in equation (39). Room temperature  $^1H$  NMR spectra indicated



that the three benzyl ligands were equivalent and possessed local  $C_s$  symmetry. However, at lower temperatures the local  $C_s$  symmetry was lost ( $\Delta G^\ddagger = 9.1 \pm 0.3$  and  $8.5 \pm 0.2$  kcal/mole for  $M = Th, U$ ) although the three ligands remained equivalent, mostly in accord with a structural determination for the thorium compound (Figure 19) which revealed essentially  $\eta^3$  coordination by the benzyl ligands. However, it can be seen that in the solid state the three benzyl ligands are actually nonequivalent, and therefore in solution must inter-convert very readily in order to be equivalent even at  $-92^\circ$ . The Th-benzyl interactions appeared largely  $\sigma$  in nature, involving predominantly the benzylic carbon atoms, at which 60% of the negative charge is localized. Thus, these Th-C distances, averaging  $2.58(1) \text{ \AA}$ , were much shorter than those to the C2 ( $2.92(1) \text{ \AA}$ ), C3 ( $3.36(1) \text{ \AA}$ ), and C7 ( $3.50\text{-}3.85 \text{ \AA}$ ) positions. The Th-C( $C_5Me_5$ ) distances averaged  $2.79(1) \text{ \AA}$ .

Duttera, Fagan, Marks, and Day have reported the synthesis and properties of a U(III) hydride complex,  $U(C_5Me_5)_2(H)(dmpe)$ , which was prepared by the route indicated in equation (40) (65). The dmpe ligand appeared symmetric at room temperature on the  $^1H$  NMR timescale, although at lower temperatures an unsymmetrical ground state froze out. In the presence of

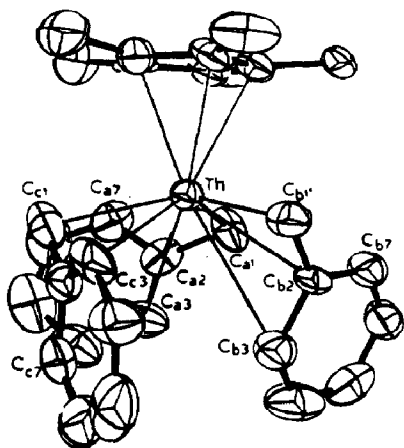
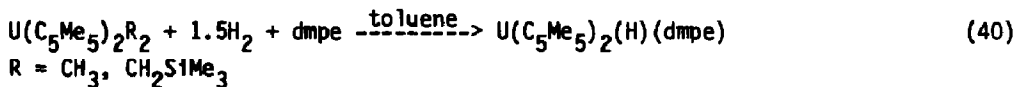


Fig. 19. The solid state structure of  $\text{Th}(\text{C}_5\text{Me}_5)(\text{CH}_2\text{C}_6\text{H}_5)_3$  from ref. 64.  
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free dmpe, exchange between free and coordinated dmpe is observed, which seems to occur more slowly than the site permutation processes for the coordinated dmpe. The resonance for the  $\text{C}_5\text{Me}_5$  ligand is characterized by a line width of 18 Hz, very typical of U(III). The hydride ligand could not be observed by  $^1\text{H}$  NMR spectroscopy, but a band at  $1219\text{ cm}^{-1}$  in the infrared spectrum was assigned to a U-H stretching mode. For the corresponding deuteride, this band shifted to  $870\text{ cm}^{-1}$ . A magnetic moment of  $3.47\ \mu_{\text{B}}$  was observed, consistent also with U(III). A solid state structure determination of this compound (Figure 20) was in accord with the proposed formulation, although not surprisingly the hydride position could not be located. However, the symmetric orientation of the dmpe ligand does suggest that a normal  $\text{M}(\text{C}_5\text{R}_5)_2\text{X}_3$  structural pattern has been adopted. Thus, while  $\text{U}(\text{C}_5\text{Me}_5)_2\text{X}_2$  molecules typically have the two X species located in a symmetrical fashion, the  $\text{P}_2$  unit in this case has twisted ca.  $0.62\ \text{\AA}$  to one side, apparently to make room for the hydride ligand. The  $\text{U-P}_1$ ,  $\text{U-P}_2$ , and average U-C bond distances were found to be  $3.211(8)$ ,  $3.092(8)$ , and  $2.79(1)\ \text{\AA}$ , respectively. Interestingly, the compound must be kept from  $\text{N}_2$ , CO, or THF, with which it readily reacts to form complex mixtures of U(III) and U(IV) products.

Bruno, Kalina, Mintz, and Marks have examined photochemically induced  $\beta$ -hydride elimination reactions for  $\text{M}(\text{C}_5\text{H}_5)_3\text{R}$  ( $\text{M} = \text{Th}, \text{U}; \text{R} = \text{CH}_3, \text{i-C}_3\text{H}_7, \text{n-C}_4\text{H}_9, \text{sec-C}_4\text{H}_9$ ) and related complexes, and have compared these to related thermal transformations (66). In the earlier thermolytic studies, it was

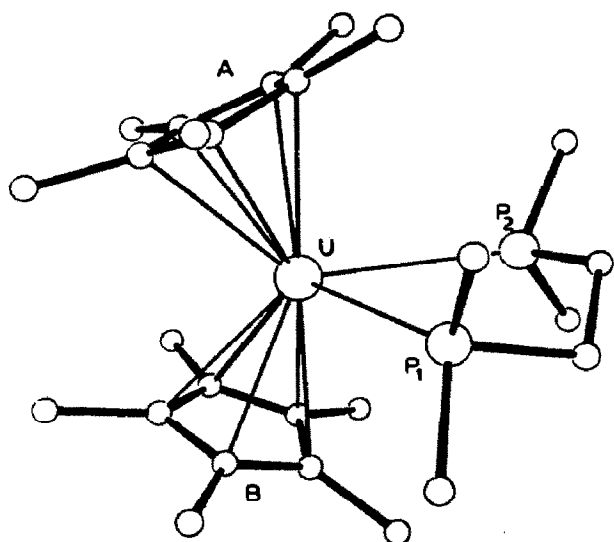


Fig. 20. The structure of  $U(C_5Me_5)_2(H)(dmpe)$  from ref. 65. Copyright 1982 American Chemical Society.

found that abstraction of a  $C_5H_5$  hydrogen atom occurred, stereospecifically for the *cis*- or *trans*-2-butenyl group ( $k_H/k_D = 2.4 \pm 0.2$ ), with half lives at  $170^\circ$  of about 10-1000 h, depending on the particular alkyl group. From these transformations, the dimeric complex  $[(C_5H_5)_2Th(\mu_2-\eta^1, \eta^5-C_5H_4)]_2$  could be isolated essentially quantitatively. In contrast, the  $ThCp_3R$  species ( $Cp = C_5H_5, C_5D_5, CH_3C_5H_4$ ;  $R = i-C_3H_7, n-C_4H_9$ ) undergo facile decomposition upon irradiation at wavelengths below 350 nm, leading to a nearly 1:1 ratio of alkane:alkene, and precipitation of the appropriate dark green  $ThCp_3$  complex. Isotopic labelling studies demonstrated that very little alkane or alkene hydrogen derived from the solvent or Cp ligands, and added ethylene or  $D_2$  neither affected, nor was affected by, the photolytic transformation. In experiments with mixtures of  $Th(C_5H_5)_3(n-C_4H_9)$  and  $Th(C_5D_5)_3(n-C_4H_9)$ , no  $C_5H_5/C_5D_5$  scrambling was observed for the starting materials, but the  $ThCp_3$  products did undergo scrambling, suggesting these species might be analogous to related lanthanide complexes which possess bridging Cp ligands, often in polymeric structures. In accord with a  $\beta$ -hydride elimination mechanism, a quantum yield of 1.7 was obtained for the irradiation of  $Th(C_5H_5)_3(i-C_3H_7)$  at 313 nm. Interestingly, photolysis in glass at  $-196^\circ$  led to an increase in the alkene:alkane ratio, and the detection of  $H_2$  as well. Not surprisingly,  $Th(C_5H_5)_3(CH_3)$  was found to behave much differently. While photolysis of  $Th(C_5H_5)_3(i-C_3H_7)$  and  $Th(C_5H_5)_3(n-C_4H_9)$  required only 2-4 h for complete conversion, the methyl analog was found to undergo only 50% conversion after

20 h. The nonmetallic products formed, and their relative yields, were methane (90%), ethane (4%), and hydrogen (6%). Labelling studies indicated that the Cp rings and solvent were major sources of the added hydrogen. However, the photolysis of  $\text{Th}(\text{C}_5\text{D}_5)_3\text{CH}_3$  in  $\text{C}_6\text{D}_6$  still led only to a 39%  $d_1$  content for the methane. Interesting results were obtained when additional species were added to the mixtures. For example, the  $\text{Th}(\text{C}_5\text{H}_5)_3(\text{CH}_3)$  photolysis, in the presence of  $\text{C}_2(\text{C}_6\text{H}_5)_2$ , led to a deep red-brown solution, and isolation of  $\text{Th}(\text{C}_5\text{H}_5)_4$  in 20% yield. A mixture of  $\text{Th}(\text{C}_5\text{H}_5)_3\text{R}$  complexes (R =  $\text{CH}_3$ , R =  $\underline{1}\text{-C}_3\text{H}_7$ , 6:1 ratio) led to increased quantities of  $\text{CH}_4$  relative to photolysis of  $\text{Th}(\text{C}_5\text{H}_5)_3\text{CH}_3$  itself, and to higher propene:propane ratios than would be obtained for pure  $\text{Th}(\text{C}_5\text{H}_5)_3(\underline{1}\text{-C}_3\text{H}_7)$ . As the R =  $\underline{1}\text{-C}_3\text{H}_7$  photolysis is more facile than that of R =  $\text{CH}_3$ , it appears that once the propene and " $\text{Th}(\text{C}_5\text{H}_5)_3\text{H}$ " are formed from the photolysis, the latter is more efficiently trapped by  $\text{Th}(\text{C}_5\text{H}_5)_3\text{R}$  for R =  $\text{CH}_3$  than for R =  $\underline{1}\text{-C}_3\text{H}_7$ , leading to the observed product differences. The natures of  $\text{Th}(\text{C}_5\text{H}_5)_3$ ,  $\text{Th}(\text{C}_5\text{H}_4\text{CH}_3)_3$ ,  $\text{Th}(\text{C}_5\text{H}_4\text{C}_2\text{H}_5)_3$ , and  $\text{Th}(\text{indenyl})_3$ , all prepared via photolysis, were investigated. No evidence of hydride ligands could be observed spectroscopically, while mass spectral studies revealed expected ions such as  $\text{Th}(\text{C}_5\text{H}_5)_3^+$  and  $\text{Th}(\text{C}_5\text{H}_5)_2^+$ . The complex is paramagnetic, having  $\mu = 0.404 \mu_B$  at room temperature, but  $\mu = 0.10 \mu_B$  at 4 K. Treatment of  $\text{Th}(\text{C}_5\text{H}_5)_3$  with  $\text{I}_2$  or  $\text{CHCl}_3$  led to the expected  $\text{Th}(\text{C}_5\text{H}_5)_3\text{X}$  complexes, while with four equivalents of  $\text{CH}_3\text{OH}$ ,  $\text{Th}(\text{OCH}_3)_4$  was obtained, as well as the expected quantities of  $\text{C}_5\text{H}_6$  and  $\text{H}_2$ . On exposure of  $\text{Th}(\text{C}_5\text{H}_5)_3$  to  $\text{H}_2$ , 0.31 equivalents of  $\text{H}_2$  were incorporated, leading to an off-white complex whose infrared spectrum was consistent with the presence of hydride ligands. This material was very photosensitive, and exposure to light led to regeneration of  $\text{Th}(\text{C}_5\text{H}_5)_3$ . Interestingly, reactions of the previously reported purple " $\text{Th}(\text{C}_5\text{H}_5)_3$ " with iodine or  $\text{CH}_3\text{OH}$  led only to half the expected quantities of  $\text{Th}(\text{C}_5\text{H}_5)_3\text{I}$  or  $\text{H}_2$ . Related Th(III) complexes,  $\text{Th}(\text{C}_5\text{H}_4\text{CH}_3)_3$  and  $\text{Th}(\text{C}_5\text{H}_4\text{C}_2\text{H}_5)_3$  could also be obtained, and displayed optical spectra similar to that of  $\text{Th}(\text{C}_5\text{H}_5)_3$ . However, exposure of the  $\text{C}_5\text{H}_4\text{CH}_3$  complex to aromatic solvents led to slow decomposition, while the  $\text{C}_5\text{H}_4\text{C}_2\text{H}_5$  complex was observed to dissolve in benzene or toluene with rapid discharge of its dark green color, and formation of hydrogen gas and a pale yellow solution. Photolysis of  $\text{Th}(\text{C}_9\text{H}_7)_3(\underline{n}\text{-C}_4\text{H}_9)$  ( $\text{C}_9\text{H}_7$  = indenyl) led to a 96% yield of organic product, consisting of 96% butane and 4% 1-butene. Hence,  $\beta$ -hydride elimination is not the major pathway for photolytic decomposition, perhaps due to the greater indenyl ligand bulk. Little (ca. 4%) hydrogen incorporation took place from solvent, the primary source being the indenyl ligands. In addition, a soluble, red-orange product, formulated as  $\text{Th}(\text{C}_9\text{H}_7)_3$ , was obtained. This species was found to react with  $\text{CH}_3\text{OH}$ , leading to 0.46 equivalents of  $\text{H}_2$ , and with  $\text{I}_2$  or  $\text{CHCl}_3$ , leading to the appropriate  $\text{Th}(\text{C}_9\text{H}_7)_3\text{X}$  complex, although in



only ca. 40% yield. For comparison to the thorium results, similar photolytic studies were also carried out for  $U(C_5H_5)_3R$  ( $R = n-C_4H_9$ ,  $sec-C_4H_9$ ) complexes. Earlier thermolysis studies had demonstrated that these species were less stable than their thorium analogs, but also decomposed by stereospecific abstraction of cyclopentadienyl ring protons. In photolytic decomposition, some  $\beta$ -hydride elimination is observed, as in the thorium studies, but this pathway does not dominate. Instead, larger alkane:alkene ratios are observed (e.g., 91:9 for  $n-C_4H_9$ , 71:29 for  $sec-C_4H_9$ , and 98:2 methane:ethane for  $CH_3$ ), the larger alkane yields reflecting a homolytic U-C bond cleavage pathway to decomposition. From labelling studies it was established that the hydrogen incorporation resulted from Cp ligands and solvent, especially the former. Some incorporation of deuterium was also observed for the alkene products, which may help explain the observation that photolysis of  $U(C_5D_5)_3(n-C_4H_9)$  in  $C_6D_6$  only led to 73% incorporation of deuterium (as  $d_1$ -butane). Photolysis at  $-196^\circ$  led to higher alkene:alkane ratios of 42:58 and 47:53 for  $n-C_4H_9$  and  $sec-C_4H_9$ , respectively. Variable amounts of  $U(C_5H_5)_3(THF)$  were formed in these reactions. Photolysis in THF led to higher quantities of  $U(C_5H_5)_3(THF)$  than found from toluene solutions which were later extracted with THF, suggesting THF served as an efficient trap for the  $U(C_5H_5)_3$ . The relative quantity of  $U(C_5H_5)_3(THF)$  isolated paralleled the yields of olefin (i.e., the favorability of  $\beta$ -hydride elimination), suggesting the  $\beta$ -hydride elimination process to be the source of the  $U(C_5H_5)_3(THF)$ .

Evans, Wink, and Stanley have reported their observations on the reactions of varying ratios of  $Li(t-C_4H_9)$  or  $Li(n-C_4H_9)$  with  $UCl_4$  (67). They found that the addition of one equivalent of  $Li(t-C_4H_9)$  to  $UCl_4$  led to the formation of a reddish-purple solid which liberated 0.45 equivalents of  $D_2$  on deuterolysis. Approximately 0.75 equivalents of a 1.4:1 ratio mixture of isobutane and isobutene were also liberated. Near-visible infrared spectra of this solid, dissolved in THF, were almost identical to those of " $UCl_3(THF)_x$ ", indicating a related formulation. Not surprisingly, this material was found to react with three equivalents of  $NaC_5H_5$  to yield  $U(C_5H_5)_3(THF)$ . The reaction of  $UCl_4$  with two equivalents of  $Li(t-C_4H_9)$  led to changes in color from green to brown to black, and also appeared to yield a U(III) product, in this case as a black solid. After several days of reaction, 1.3 equivalents of isobutane and isobutene (in a 1.5-2:1 ratio) were observed, the ratio being larger for longer reaction times, suggesting that the uranium complex formed was serving as a hydrogenation catalyst. A small quantity, 0.1 equivalents, of 2,2,3,3-tetramethylbutane was also observed. Deuterolysis of the black solid took place in stages, yielding first a purple solution with the liberation of 0.53 equivalents of gas (60% HD, 40%  $D_2$ ). After stirring overnight, a green product resulted, along with 0.40 equivalents of gas (20%

HD, 80% D<sub>2</sub>). The possibility of a fast hydrolysis of a "UCl<sub>2</sub>H" species, yielding primarily HD, followed by a slower oxidation of U(III) to U(IV), yielding primarily D<sub>2</sub>, was mentioned. Notably the reaction which led to the formation of "UCl<sub>2</sub>H" could be envisioned as a two-step process, in which the first equivalent of Li(t-C<sub>4</sub>H<sub>9</sub>) served as a reducing agent, generating "UCl<sub>3</sub>", while the second equivalent served as an alkylating agent, generating "UCl<sub>2</sub>(t-C<sub>4</sub>H<sub>9</sub>)", which could then form "UCl<sub>2</sub>H" by β-hydride elimination. This would then lead to the formulation of slightly less than one equivalent of isobutane/isobutene in a 1:1 ratio for the first (reduction) step, as a result of t-butyl radical disproportionation and dimerization, and only isobutene in the second step. This is, however, inconsistent with the observation of isobutane/isobutene ratios greater than 1:1, even if one allows for hydrogenation of the isobutene by "UCl<sub>2</sub>H". It was therefore suggested that additional hydrogen was obtained either from solvent or from excess Li(t-C<sub>4</sub>H<sub>9</sub>), especially in reactions involving 4 equivalents of Li(t-C<sub>4</sub>H<sub>9</sub>) (*vide infra*). For solvent participation to occur, it was suggested that "UCl<sub>2</sub>H" might recombine with isobutene to yield "UCl<sub>2</sub>R", which then with "UCl<sub>2</sub>H" could form RH and two equivalents of "UCl<sub>2</sub>", which could then abstract hydrogen atoms from solvent. Alternatively, it was mentioned that perhaps U(III) could abstract hydrogen atoms from solvent, although such processes were pointed out to be uncommon. The reaction of UCl<sub>4</sub> with four equivalents of Li(t-C<sub>4</sub>H<sub>9</sub>) was found to proceed almost identically to that involving two equivalents. The authors observed only 1.5-1.8 equivalents of isobutane and isobutene, in a ratio of ca. 2.5-3:1. Significant quantities of unreacted Li(t-C<sub>4</sub>H<sub>9</sub>) were detected by hydrolysis of octane extracts. As in the previous reaction with two equivalents of Li(t-C<sub>4</sub>H<sub>9</sub>), black solids were formed. Deuterolysis led to traces of isobutane, and ca. 0.1 equivalents of isobutene. Washing the black solid with ether led to a brown solution (leaving most of the black solid behind), which seemed to be the source of the isobutene on deuterolysis. Also produced in the deuterolysis of the black solids were 0.75-0.96 equivalents of HD and 0.63-0.65 equivalents of D<sub>2</sub>. Color changes (black ---> purple ---> green) were observed in the deuterolysis. The formation of HD suggests the presence of uranium hydride in the black solid. The black solid ("UCl<sub>2</sub>H") was found to undergo some other chemical reactions. With cyclooctatetraene, ca. 5% yields of uranocene could be isolated. Treatment of the black solid with cyclopentadiene or t-butylacetylene led to the formation of hydrogen gas and the appropriate "anions" formed by deprotonation. The black solid also was found to effect catalytic hydrogenation of isobutene, 3-hexyne, and 1-hexene. Analytical data for the black solid were in accord with a 8:4:1 mixture of LiCl, "UCl<sub>2</sub>H", and ether. About 90% of this material is soluble in THF, leading to an intense purple solution containing U(III). For comparative

purposes, a 4:1 reaction of  $\text{Li}(\underline{n}\text{-C}_4\text{H}_9)$  with  $\text{UCl}_4$  also was carried out. Again a black solid was produced, along with 1.6 equivalents of a 1.2:1 mixture of butane and butene. Unlike the  $\underline{t}$ -butyl reaction, this ratio is not consistent with the expected disproportionation/dimerization ratio for the alkyl radical ( $\underline{t}\text{-C}_4\text{H}_9$ , 7.2:1;  $\underline{n}\text{-C}_4\text{H}_9$ , 0.13-0.14:1), possibly indicative of a higher contribution of the  $\beta$ -hydride elimination (as opposed to reduction) pathway for the less reducing  $\text{Li}(\underline{n}\text{-C}_4\text{H}_9)$ . After separation of the black solid from the supernatant solution, hydrolysis of the latter was carried out, leading to 2.1 equivalents of butane, while deuteration of the black solid led to 0.65 equivalents of HD, 0.63 equivalents of  $\text{D}_2$ , and 0.1 equivalents of butane.

Seyam has reported on the thermal decomposition of presumed  $\text{UO}_2\text{R}_2$  species, formed by the reaction of  $\text{UO}_2\text{Cl}_2$  with two equivalents of  $\text{LiR}$  or  $\text{Mg}(\text{R})\text{Cl}$  at  $-78^\circ$  in THF or toluene (68). In each case, a dark brown solid,  $\text{UO}_2$ , was produced, along with hydrocarbons. It was concluded from the hydrocarbon distributions that three pathways to decomposition were operative, and are relatively unaffected by the choice of solvent. For example, for  $\text{R} = \text{C}_6\text{H}_5$ , the decomposition occurs mainly via reductive elimination of diphenyl. For  $\text{R} = \underline{i}\text{-C}_3\text{H}_7$ ,  $\underline{n}\text{-C}_4\text{H}_9$ , or  $\underline{t}\text{-C}_4\text{H}_9$ , the reactions lead to mixtures of alkane and alkene. For  $\text{R} = \underline{i}\text{-C}_3\text{H}_7$ , these are formed in a nearly 1:1 ratio, as would be expected for  $\beta$ -hydride elimination; however, for  $\text{R} = \underline{n}\text{-C}_4\text{H}_9$  or  $\underline{t}\text{-C}_4\text{H}_9$ , significantly larger alkane:alkene ratios were observed. Similarly, decomposition of " $\text{UO}_2(\text{CH}_3)_2$ " and " $\text{UO}_2(\text{CHCH}_2)_2$ " led to formation of methane and ethylene, respectively, via hydrogen atom abstraction. Thus, decomposition of " $\text{UO}_2(\text{CH}_3)_2$ " in toluene- $\text{d}_8$  was found to lead to the formation of some  $\text{CH}_3\text{D}$ .

Bruno, Marks, and Day have communicated results on the inter- and intramolecular activation of C-H bonds in organothorium compounds (69). Thus, thermolysis of  $\text{Th}(\text{C}_5\text{Me}_5)_2(\text{CH}_2\text{MMe}_3)_2$  ( $\text{M} = \text{C}, \text{Si}$ ) leads to  $\text{MMe}_4$  and the metallacycles  $\text{Th}(\text{C}_5\text{Me}_5)_2(\text{CH}_2)_2\text{M}(\text{CH}_3)_2$ . Deuteration studies demonstrated that neither solvent nor  $\alpha$ -hydride abstraction were directly involved in the process. Kinetic studies revealed the thermolysis to be first order in dialkyl, with  $E_a$ 's of  $21.3 \pm 0.6$  kcal/mole ( $\Delta H^\ddagger = 20.6 \pm 0.6$  kcal/mole and  $\Delta S^\ddagger = -17 \pm 2$  eu) and  $25.9 \pm 0.9$  kcal/mole ( $\Delta H^\ddagger = 25.2 \pm 0.9$  kcal/mole and  $\Delta S^\ddagger = -9 \pm 1$  eu), respectively, for  $\text{M} = \text{C}$  and  $\text{Si}$ , in accord with the observation that the former is about 20 times more reactive than the latter. The large negative values of  $\Delta S^\ddagger$  indicate highly ordered transition states, in marked contrast to thermolytic observations for  $\text{Pt}(\text{CH}_2\text{CMe}_3)_2(\text{PEt}_3)_2$  and related compounds. A structural determination was reported for  $\text{Th}(\text{C}_5\text{Me}_5)_2(\mu\text{-CH}_2)_2\text{-SiMe}_2$  (Figure 21), and revealed a rather normal coordination geometry about thorium, with the average Th-C (alkyl) bond distance being 2.474(12) Å. The four-membered  $\text{Th}_2\text{Si}$  ring was slightly nonplanar, experiencing a  $5.8^\circ$  fold along the  $\text{C}_1\text{-C}_2$  vector. A small  $\text{C}_1\text{-Th-C}_2$  angle of  $75.2(4)^\circ$  was found. The

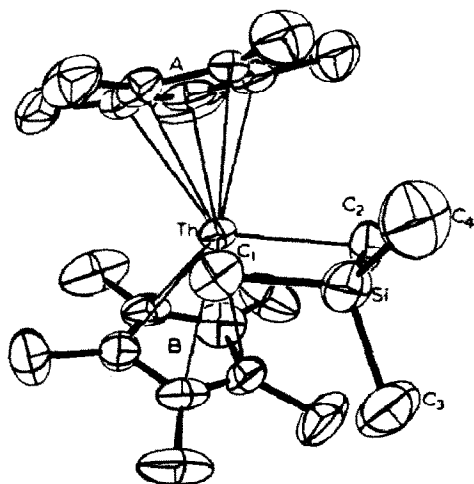


Fig. 21. The structure of  $\text{Th}(\text{C}_5\text{Me}_5)_2(\mu\text{-CH}_2)_2\text{SiMe}_2$  from ref. 69. Copyright 1982 American Chemical Society.

$\text{Th}(\text{C}_5\text{Me}_5)_2(\text{CH}_2)_2\text{CMe}_2$  metallacycle was observed to be more reactive than  $\text{Th}(\text{C}_5\text{Me}_5)_2(\text{CH}_2)_2\text{SiMe}_2$ . Thus, the former reacts with  $\text{C}_6\text{H}_6$  or  $\text{C}_6\text{D}_6$  to yield  $\text{Th}(\text{C}_5\text{Me}_5)_2(\text{C}_6\text{H}_5)_2$  or  $\text{Th}(\text{C}_5\text{Me}_5)_2(\text{C}_6\text{D}_5)_2$ , respectively (along with neopentane- $d_2$  in the latter case). These reactions were found to be first order in both thorium complex and  $\text{C}_6\text{H}_6$  concentrations, and a  $k_H/k_D$  value of  $1.5 \pm 0.1$  was observed. Notably,  $\text{Th}(\text{C}_5\text{Me}_5)_2(\text{CH}_2\text{CMe}_3)_2$  was found to react with  $\text{C}_6\text{H}_6$ , also yielding  $\text{Th}(\text{C}_5\text{Me}_5)_2(\text{C}_6\text{H}_5)_2$ , via the metallacycle.  $\text{Th}(\text{C}_5\text{Me}_5)_2(\text{CH}_2)_2\text{CMe}_2$  was also found to react with toluene, yielding neopentane and a mixture of benzylic and (mostly,  $75 \pm 10\%$ ) ring-metallated species. The metallacycle was additionally found to react with olefins such as propene to yield complex mixtures of ring-opened products, without olefin metathesis occurring. By NMR spectroscopy, some  $\text{ThCH}_2\text{CMe}_3$  species was evident, and deuterolysis led to the formation of  $\text{Me}_3\text{CCH}_2\text{D}$ . In contrast to the  $\text{M} = \text{C}$  metallacycle,  $\text{Th}(\text{C}_5\text{Me}_5)_2(\text{CH}_2)_2\text{SiMe}_2$  (as well as  $\text{Th}(\text{C}_5\text{Me}_5)_2(\text{CH}_2\text{SiMe}_3)_2$ ) was not observed to react with benzene.

Two reports have appeared dealing with the insertions of CO into actinide-carbon bonds. Cramer, Maynard, Paw, and Gilje have found that  $\text{U}(\text{C}_5\text{H}_5)_3(=\text{CHPR}_3)$  complexes react readily with CO to yield  $\text{U}(\text{C}_5\text{H}_5)_3[\eta^2\text{-OCC(H)(PR}_3)]$  species ( $\text{PR}_3 = \text{PMe}(\text{C}_6\text{H}_5)_2, \text{PMe}_2(\text{C}_6\text{H}_5)$ ) (70). A structural determination revealed the compound to be monomeric (Figure 22), and roughly tetrahedral about uranium. Two resonance forms (below) were proposed for the new ligand, to account for the observed C1-C2, C1-O, U-C1, U-O, and P-C2 distances of 1.37(3), 1.27(3), 2.37(2), 2.27(1), and 1.77(2) Å, respectively, as well as the near planarity of the  $\text{UOC}_2\text{P}$  framework.

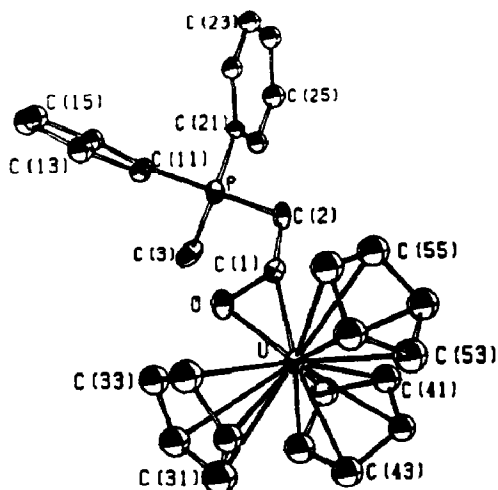
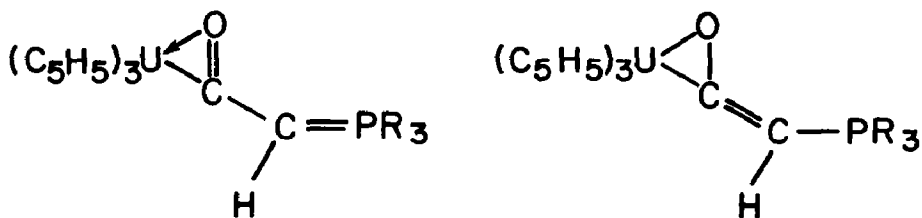
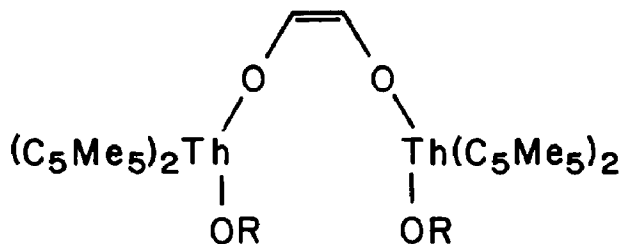


Fig. 22. The solid state structure of  $U(C_5H_5)_3[n^2-OCC(H)(PMe(C_6H_5)_2)]$  from ref. 70. Copyright 1982 American Chemical Society.



Katahira, Moloy, and Marks have studied carbonylation reactions of  $Th(C_5Me_5)_2(OR)(H)$  ( $R = CH(CMe_3)_2$ ) (71). Earlier it had been demonstrated that a mononuclear formyl complex,  $Th(C_5Me_5)_2(n^2-OCH)(OR)$ , was formed rapidly and reversibly, which could be followed by a slower dimerization yielding cis-enediolates (below). Three mechanistic pathways for dimerization were considered in the present paper, involving (subsequent to formyl formation) either binuclear hydride insertion, ketene formation, or formyl dimerization. The first pathway should lead to a rate of formation proportional to  $[complex]^2[CO]$ , while the second should be proportional to  $[complex][CO]^2$ , and the third,  $[complex]^2[CO]^2$ . Kinetic measurements revealed that the rate of cis-enediolate formation was proportional to  $[complex]^2[CO]$ , supporting the first pathway, hydride insertion. Additional support for this process was provided by experiments in which the starting thorium complex was exposed to a mixture of CO and  $H_2$  (0.1 and 6 atmospheres, respectively). Under these conditions, the yield of the cis-enediolate is reduced to 10%, while the major product is the methoxide,  $Th(C_5Me_5)_2(OCH_3)(OR)$ , presumably formed via



hydrogenation of  $(\text{C}_5\text{Me}_5)_2(\text{OR})\text{Th}(\text{OCH}_2)\text{Th}(\text{OR})(\text{C}_5\text{Me}_5)_2$ , an expected intermediate in the hydride insertion pathway.

Two papers relating to actinide metal-metal bonding have appeared. Beck and Strobel have reported the synthesis and structural characterization of  $\text{ThI}_3$ , which was prepared from  $\text{ThI}_4$  and thorium metal (72). Two crystalline modifications of  $\text{ThI}_3$  were obtained. When short reaction times (2-3 days) were employed, shiny-black, monoclinic, cylindrical rods were obtained ( $\alpha$ - $\text{ThI}_3$ ), while tempering for 4-6 weeks led to dark crystals with a slight green to brass-colored luster ( $\beta$ - $\text{ThI}_3$ ). A structural determination of  $\beta$ - $\text{ThI}_3$  (Figure 23) revealed the presence of three independent thorium atoms, one

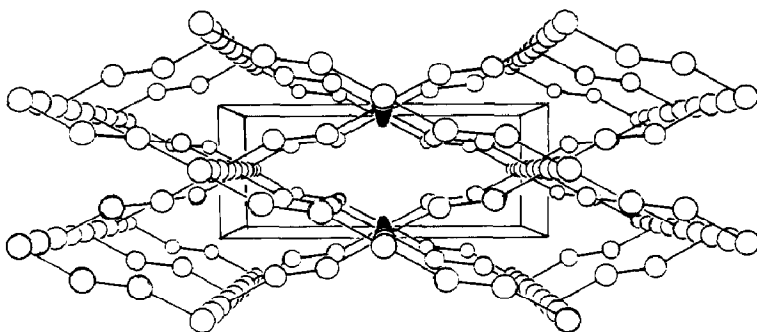


Fig. 23. Perspective view of the metal atom arrangement in  $\beta$ - $\text{ThI}_3$  (ref. 72).

having cubic, while the other two square-antiprismatic, coordination by the iodide ions, with the respective average distances being 3.30, 3.22, and 3.25 Å, similar to those in  $\text{ThI}_4$  and  $\text{ThI}_2$ . The compound was formulated as  $\text{Th}^{4+}(\text{I}^-)_3(\text{e}^-)$ , in which the electron could either be considered to be delocalized in quasi-metal bonding (as in  $\text{ThI}_2$ ) or engaged in localized Th-Th interactions. For  $\text{ThI}_3$ , both of these possibilities contribute. Along the [001] direction, a strictly equidistant (3.665 Å) linear chain of thorium atoms resulted, with the thorium atom coordination spheres (defined by the iodide ions) alternating between cubic and square prismatic. At the cubically

coordinated thorium atoms, other thorium chains propagate, parallel to the [110] and  $[1\bar{1}0]$  axes. In these chains, long and short Th-Th separations were found, 3.800 and 3.460 Å (cf., Th metal, 3.60 Å, ThI<sub>2</sub>, 3.97 Å). This structure is therefore unusual in that one chain contains equidistant bonds, while the others have alternating short and long bonds.

Paine, Duesler, and Moody have reported that UCl<sub>4</sub> reacts with four equivalents of Ni(C<sub>5</sub>H<sub>5</sub>)[OP(OCH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> to yield U{Ni(C<sub>5</sub>H<sub>5</sub>)[OP(OCH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}<sub>4</sub> (73). Not surprisingly, no uranium-nickel bonds were present (U-Ni = 4.750(2) Å); instead, an x-ray structural determination revealed that the uranium atom was bound to the eight terminal oxygen atoms on the phosphorus atoms (Figure 24).

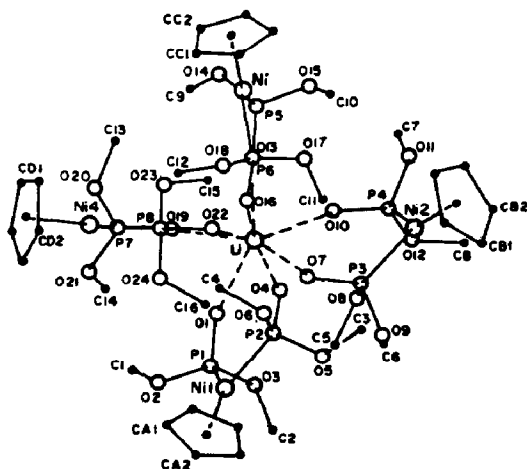


Fig. 24. Solid state structure of U{Ni(C<sub>5</sub>H<sub>5</sub>)[PO(OCH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}<sub>4</sub> from ref. 73. Copyright 1982 American Chemical Society.

A square-antiprismatic coordination geometry resulted, similar to that in U(acac)<sub>4</sub>, with the U-O distances ranging from 2.346(9)-2.381(10) Å.

Some new applications of uranium compounds in catalytic transformations have been reported. Folcher, Le Maréchal, and Marquet-Ellis have found that solutions of UCl<sub>3</sub> in THF can be used as homogeneous catalysts for olefin hydrogenation (74), the hydrogen coming from either LiAlH<sub>4</sub>, or LiH (somewhat less active). For example, treating 0.1 mmoles of UCl<sub>4</sub> in 20 mL THF with 4 mmoles of LiAlH<sub>4</sub> led to a "UCl<sub>3</sub>" solution. Thirty minutes after addition of 2 mmoles of ethylene, it was observed that half of the ethylene had been hydrogenated. With excess olefin, the reaction stops when the LiAlH<sub>4</sub> is consumed, but addition of more LiAlH<sub>4</sub> leads again to hydrogenation. Similar results were found for propene, 1-butene, and cis- or trans-2-butene.

Isobutene was found to undergo slow hydrogenation, while butadiene underwent a two-step hydrogenation via cis- and trans-butenes. Hydrogenation of ethylene by  $\text{LiAlH}_4$  in  $\text{THF-d}_8$  and  $\text{LiAlD}_4$  in THF led to incorporation of deuterium only in the latter case (as  $\text{C}_2\text{H}_4\text{D}_2$ ). The formation of an aluminum mirror was also noted, leading the authors to propose a homolytic cleavage pathway. In contrast,  $\text{U}(\text{C}_5\text{H}_5)_3(\text{THF})$  was found to be inactive in such hydrogenations.

Baussart, Delobel, Le Bras, Le Maguer, and Leroy have reported the synthesis of high purity  $\text{USb}_3\text{O}_{10}$ , which is a catalyst for the selective oxidation of propene to acrolein (75). The compound, formulated as containing both pentavalent antimony and uranium, is weakly paramagnetic ( $\mu = 1.77 \mu_B$ ), and the authors favored a  $6d^1$  electron configuration for uranium. Apparent activation energies in the range of 17-20 kcal/mole were observed for the propene oxidation. The used catalyst was found to contain both Sb(III) and Sb(V) by Mössbauer spectroscopy.

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