LANTHANIDES AND ACTINIDES

ANNUAL SURVEY COVERING THE YEAR 1981[*]

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General

Several reviews of interest have appeared in 1981. One of these is
entitled "Unusual Carbon Monoxide Activation, Reduction, and Homologation
Reactions of 5f-Element Organometallics - The Chemistry of Carbene-Like
Dihaptoacyls," and presents a thorough coverage of the results obtained by
Marks and coworkers, as well as a large number of pertinent contributions from
other research groups (1). Another review deals with gas phase photoelectron
spectra of organometallic compounds of the d and f block metals, particularly
the bonding information which can be thereby obtained (2). Karraker has
presented a discussion of the use of neptunium-237 Mössbauer spectra in
estimating the extent of covalency in neptunium(IV) organometallic compounds
(3). Mazzei has reviewed results on the polymerization of diolefins brought
about by lanthanide and actinide catalysts, especially π-allyl complexes
(4). In addition, a short review of scandium coordination chemistry for the
year 1979 has appeared (5).

Lanthanides

A variety of studies have been reported on (cyclopentadienyl)lanthanide
compounds. Rogers, Atwood, Emad, Sikora, and Rausch have reported the
preparations of $Y(C_5H_5)_3(THF)$ and $La(C_5H_5)_3(THF)$ by the reaction of excess
NaC_5H_5 with the appropriate metal trichloride in THF (6). X-ray structural
data (Figure 1) for these compounds demonstrate that these molecules are
isostructural with the previously reported gadolinium analog. Thus, the
structures may be described as involving a pseudo-tetrahedral arrangement of
the three cyclopentadienyl groups and the single THF ligand around the central
metal atom. The relative M-C and M-O bond distances for these three compounds
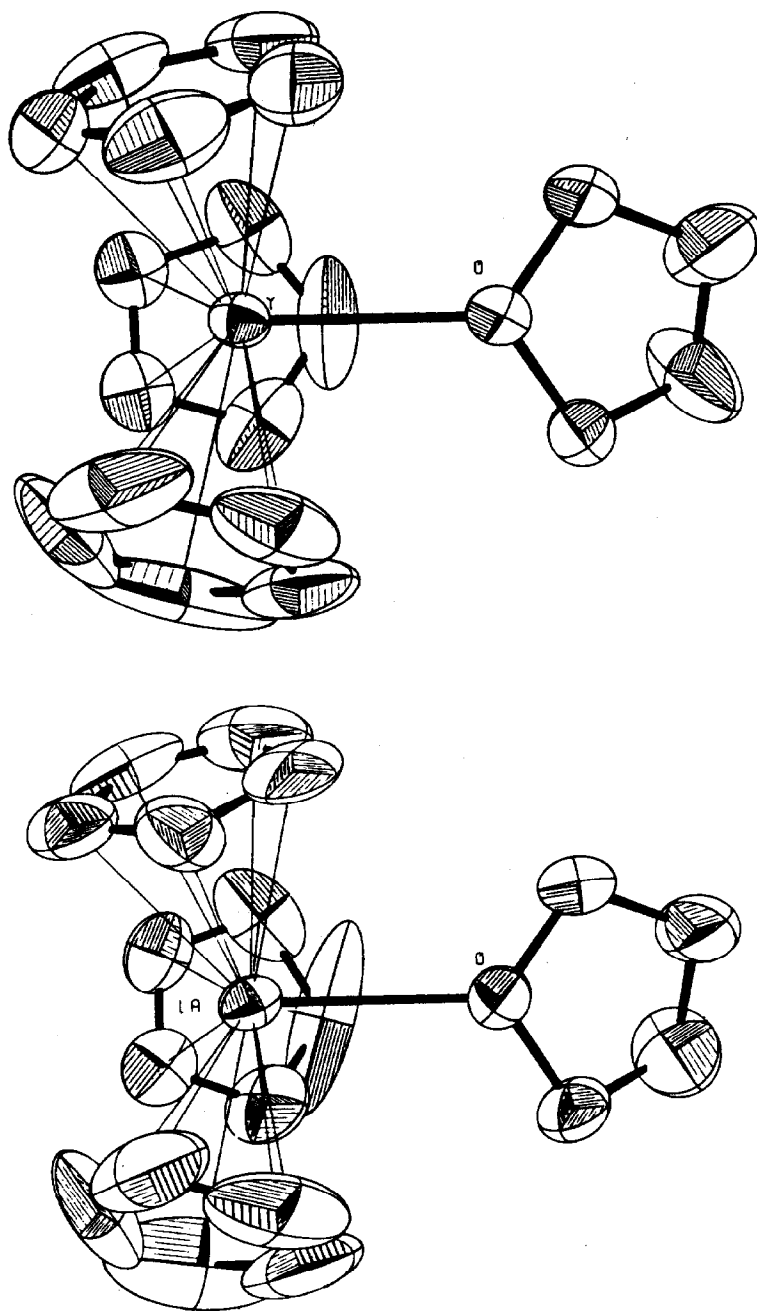
Fig. 1. The structure of $Ln(C_5H_5)_3(THF)$ complexes (Ln = Y, La) from ref. 6.
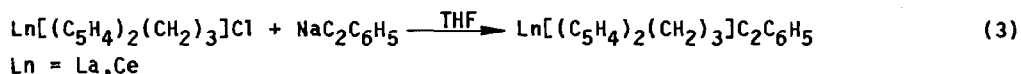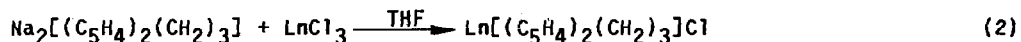
are consistent with the appropriate M^{3+} ionic radii; however, the M-C bond distances are substantially longer than those in related bis(cyclopentadienyl)lanthanide compounds, suggesting a high degree of intramolecular crowding in the $M(C_5H_5)_3(THF)$ compounds.

Namy, Girard, Kagan, and Caro have published complete details for the preparations of SmI_2 and YbI_2 in THF from the metals, preferably in powder form, and various organic diiodide compounds (eq. (1)) (7). In fact, 2,2-

$$Ln + I(CH_2)_nI \xrightarrow{\text{THF}} LnI_2 \tag{1}$$
$$Ln = Sm, Yb; \; n = 1,2$$

diiodobutane could also be successfully employed. However, the nature of the solvent was much more critical. The LnI_2 complexes could not be isolated if the THF was replaced by dioxane, ether, methylal, or DME. The use of 1,2-dibromoethane was reported to lead very slowly to insoluble $SmBr_2$. The above LnI_2 compounds were found to be convenient starting materials for the preparations of other divalent complexes. In particular, the reactions with two equivalents of NaC_5H_5 are reported to lead to the $Ln(C_5H_5)_2$ compounds, although actual details for the isolation of the pure compounds were not provided.

John and Tsutsui have published a full account of the syntheses of ring-bridged bis(cyclopentadienyl) complexes of lanthanum and cerium (8). As in the case of uranium(IV), the use of these ligands allows isolation of bis(cyclopentadienyl) derivatives, even though the unbridged (C_5H_5) complexes are unknown (9). The monochloride compounds with trimethylene bridges were obtained by the route indicated in eq. (2). Reaction of these products with sodium phenylacetylide led to the corresponding σ-alkyl compounds (eq. (3)). For none of these compounds were any molecular weight data provided. The

$$Na_2[(C_5H_4)_2(CH_2)_3] + LnCl_3 \xrightarrow{\text{THF}} Ln[(C_5H_4)_2(CH_2)_3]Cl \tag{2}$$

$$Ln[(C_5H_4)_2(CH_2)_3]Cl + NaC_2C_6H_5 \xrightarrow{\text{THF}} Ln[(C_5H_4)_2(CH_2)_3]C_2C_6H_5 \tag{3}$$
$$Ln = La, Ce$$

complexes are reported to be more soluble when freshly prepared, suggesting that association may be occurring on standing. Various other physical data were reported, including magnetic susceptibility measurements as well as infrared, uv-visible, photoelectron, and nmr spectroscopic data.
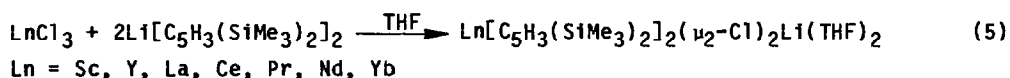
The use of bulky cyclopentadienyl ligands has also successfully been applied to the syntheses of bis(cyclopentadienyl)lanthanide complexes.

Rybakova, Sigalov, Syuthkina, Egorova, and Beletskaya have reported the preparations of bis(fluorenyl)lanthanide compounds in yields of 50 - 60%, as indicated in eq. (4) (10). These compounds are reported to be soluble in THF,

$$LnCl_3 + 2C_{13}H_9Li \xrightarrow{\text{THF}} Ln(C_{13}H_9)_2(\mu_2\text{-Cl})_2Li(THF)_2 \qquad (4)$$
Ln = La, Sm, Ho
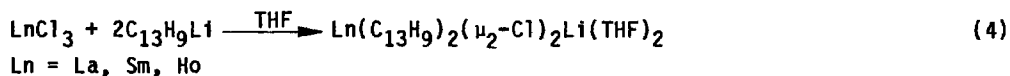
benzene, and also in CCl_4 when freshly prepared. The authors reported that the addition of a third equivalent of $C_{13}H_9Li$ did not bring about a change in composition.

Related compounds have been described by Lappert, Singh, Atwood, and Hunter (11,12). These authors, employing the 1,3-bis(trimethylsilyl)cyclo-pentadienyl ligand, have isolated the analogous bis(cyclopentadienyl)-lanthanide products found in eq. (5). In general, the two THF molecules

$$LnCl_3 + 2Li[C_5H_3(SiMe_3)_2]_2 \xrightarrow{\text{THF}} Ln[C_5H_3(SiMe_3)_2]_2(\mu_2\text{-Cl})_2Li(THF)_2 \qquad (5)$$
Ln = Sc, Y, La, Ce, Pr, Nd, Yb

could be replaced by one DME or TMEDA molecule. Also reported were a variety of dimeric $[Ln[C_5H_3(SiMe_3)_2]_2Cl]_2$ complexes, many of which were prepared by heating the products from eq. (5) in vacuo (eq. (6)).

$$Ln[C_5H_3(SiMe_3)_2]_2(\mu_2\text{-Cl})_2Li(THF)_2 \xrightarrow{\Delta} [Ln[C_5H_3(SiMe_3)_2]_2Cl]_2 \qquad (6)$$
Ln = Sc, Y, La, Ce, Pr, Nd, Yb
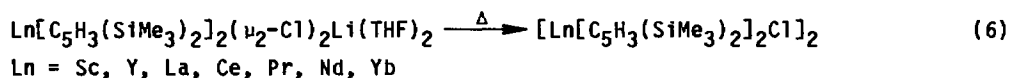
However, somewhat more direct routes could be used for the preparations of the analogous dimeric compounds of samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and lutetium. Structural results have been obtained for the monomeric complex of neodymium (Figure 2) and of the dimeric complexes of scandium, praesodymium, and ytterbrium (Figure 3). In each case, the local environment around the lanthanide metal atom is similar, and can be described as distorted tetrahedral. Reported parameters for the monomeric complex are Nd-Cl = 2.744 Å, Li-Cl = 2.405 Å, ∢ Cl-Nd-Cl' = 82.1°, and ∢ Cl-Li-Cl' = 97.2(9)°. For comparison, in the dimeric complex of the slightly larger praesodymium metal atom, a Pr-Cl distance of 2.81 Å was observed, along with a Cl-Pr-Cl' angle of 78°. Among the dimeric complexes, a general correlation of bonding parameters with ionic radii of the lanthanide metals was observed. Comparison of $[Sc[C_5H_3(SiMe_3)_2]_2Cl]_2$ with $[Sc(C_5H_5)_2Cl]_2$, however, indicated that some steric influences were being experienced in the former complex: while the Sc-Cl bond distances were
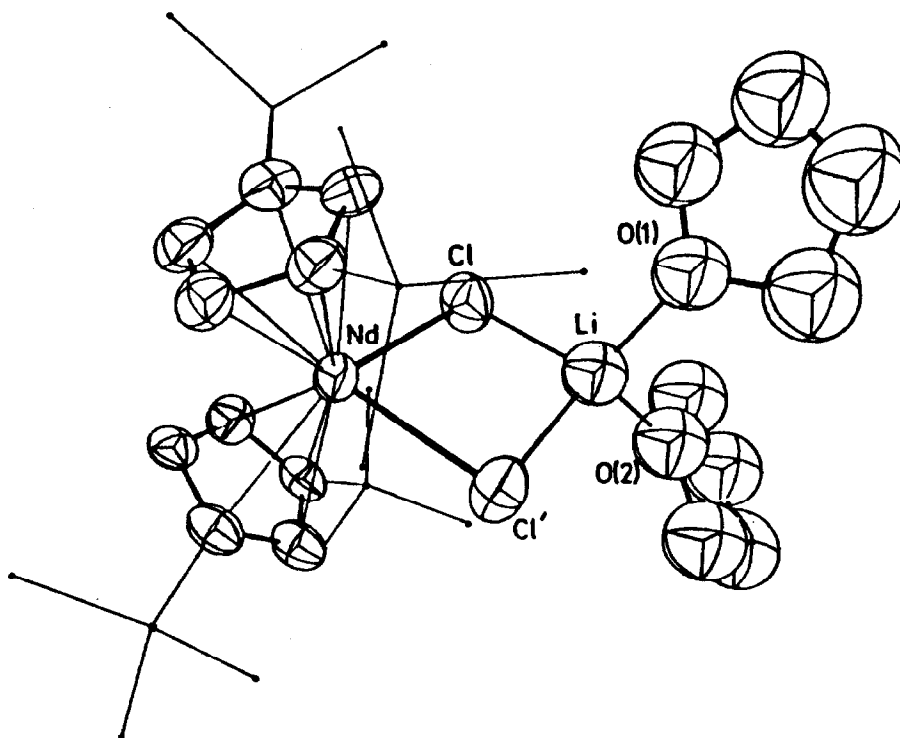
Fig. 2. The solid state structure of $Nd[C_5H_3(SiMe_3)_2]_2(\mu\text{-}Cl)_2Li(THF)_2$ from ref. 11.

essentially identical, the Sc-C bond distances in the former were approximately 0.05 Å longer than in the latter compound.

The pentamethylcyclopentadienyl ligand has continued to bring about interesting influences in organolanthanide chemistry. Tilley and Andersen have prepared a number of complexes of general formula $Ln(C_5Me_5)_2Cl_2ML_n$ (Ln = Nd, Sm, Yb; L = ether, or L_2 = TMEDA, n = 1 or 2; M = Li or Na), from the reaction of the appropriate metal trichloride with two equivalents of MC_5Me_5 in THF (13). Extraction with ether generally leads to the ether adducts, and addition of TMEDA gives rise to the TMEDA complexes. In each case a pseudo-tetrahedral ligand geometry was proposed for the central lanthanide metal, as expected. While the lithium complexes described above are structurally   . very stable, the THF-solvated sodium salts of neodymium and ytterbium readily break up in solvents less polar than THF, yielding the corresponding $Ln(C_5Me_5)_2Cl(THF)$ complexes, which also are expected to contain pseudo-tetrahedral ligand environments. The ytterbium compound could also be
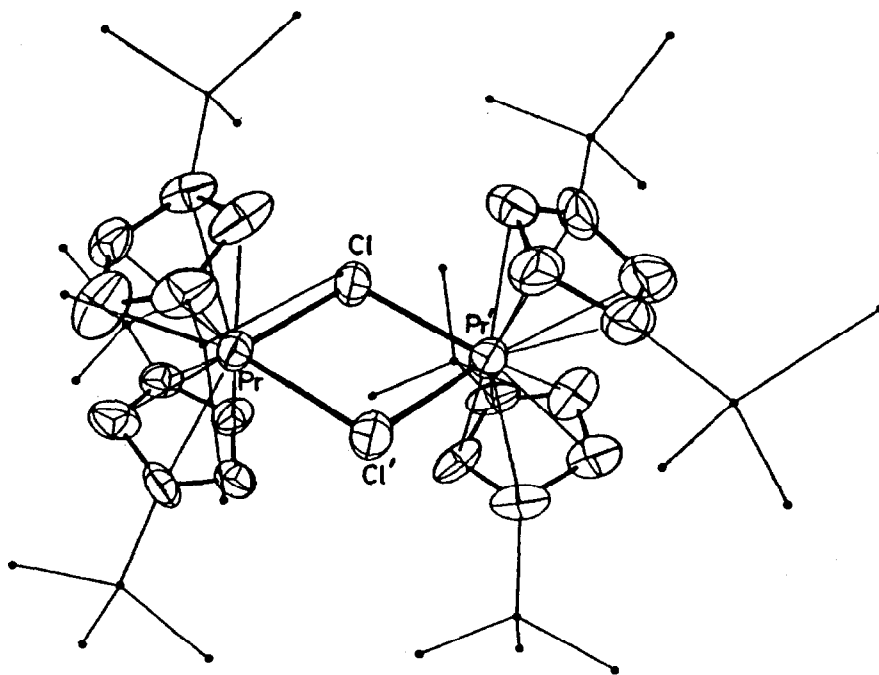
Fig. 3. The molecular structure of $[Pr(C_5H_3(SiMe_3)_2)_2Cl]_2$ from ref. 12.

prepared by the reaction of $Yb(C_5Me_5)_2(THF)$ with either $YbCl_3$ or CH_2Cl_2. The THF ligand in $Yb(C_5Me_5)_2Cl(THF)$ could readily be replaced by one equivalent of pyridine. The authors also found that mono(cyclopentadienyl) complexes may be isolated via the route of eq. (7). Both the mono(cyclopentadienyl) and the

$$NdCl_3 + NaC_5Me_5 \xrightarrow{\text{THF}} \xrightarrow{\text{ether}} Nd(C_5Me_5)Cl_3Na(ether)_2 \qquad (7)$$
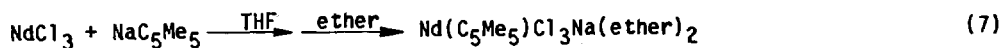
bis(cyclopentadienyl) complexes were found to be useful precursors for the preparations of other derivatives, such as $Nd(C_5Me_5)[N(SiMe_3)_2]_2$ and $Ln(C_5Me_5)_2N(SiMe_3)_2$ (Ln = Nd, Yb).

Watson, Whitney, and Harlow have reported a variety of pentamethylcyclopentadienyl complexes of ytterbium and lutetium (14). Thus, mono(ligand) complexes of stoichiometry $Ln(C_5Me_5)Cl_3Li(THF)$ have been isolated. The ytterbium compound was prepared as described by eq. (8), while the lutetium analog was obtained as a byproduct of a reaction designed to yield

$$YbCl_3 + LiC_5Me_5 \xrightarrow{\text{THF}} Yb(C_5Me_5)Cl_3Li(THF) \qquad (8)$$
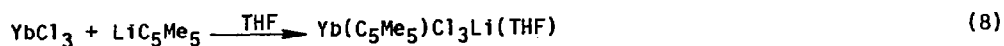
a bis(ligand) complex (vide infra). A similar iodide complex could actually be isolated by a much different reaction (eq. (9)). However, prolonged

$$Yb + C_5Me_5I + LiI \xrightarrow{\text{ether}} Yb(C_5Me_5)I_3Li(\text{ether})_2 \tag{9}$$
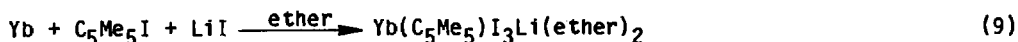
stirring of this reaction mixture led to disproportionation; both $Yb(C_5Me_5)_2I_2Li(\text{ether})_2$, and $YbI_2(\text{ether})$ could thereafter be isolated. Various bis(ligand) complexes were also described. Thus, the reaction of $LnCl_3$ (Ln = Yb or Lu) with two equivalents of LiC_5Me_5 led to the formation of anionic complexes, as in eq. (10). The coordinated ether could readily be removed

$$LnCl_3 + 2LiC_5Me_5 \longrightarrow Ln(C_5Me_5)_2Cl_2Li(\text{ether})_2 \tag{10}$$
Ln = Yb, Lu
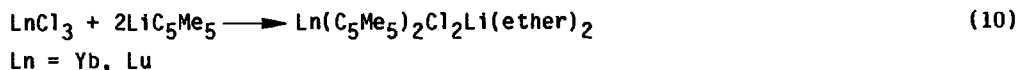
from these complexes, yielding $Yb(C_5Me_5)_2Cl_2Li$ (which was characterized) and presumably $Lu(C_5Me_5)_2Cl_2Li$ as well. Treatment of these unsolvated materials with $AlCl_3$ led to the $Ln(C_5Me_5)_2AlCl_4$ complexes (Ln = Yb, Lu), of which at least the former was found to react with THF to yield $Yb(C_5Me_5)_2Cl(THF)$. Analogous silyl-substituted cyclopentadienyl derivatives having the formulas $Ln[C_5H_4Si(Me)(C_6H_5)_2]_2Cl_2Li(\text{ether})_2$ (Ln = Yb, Lu) were also obtained. Single crystal x-ray structural determinations were reported for $Yb(C_5Me_5)_2(\mu_2-I)_2Li(\text{ether})_2$, $\underline{1}$, $Yb(C_5Me_5)_2(\mu_2-Cl)_2Li(\text{ether})_2$, $\underline{2}$, $Yb[C_5H_4Si(Me)(C_6H_5)_2]_2(\mu_2-Cl)_2Li(\text{ether})_2$, $\underline{3}$, and $Yb(C_5Me_5)_2(\mu_2-Cl)_2AlCl_2$, $\underline{4}$ (see Figures 4 - 7). The average Yb-C bond distances for these compounds were found to be 2.625(5), 2.611(2), 2.634(2), and 2.584(2) Å, while the average Yb-X (X = I or Cl)
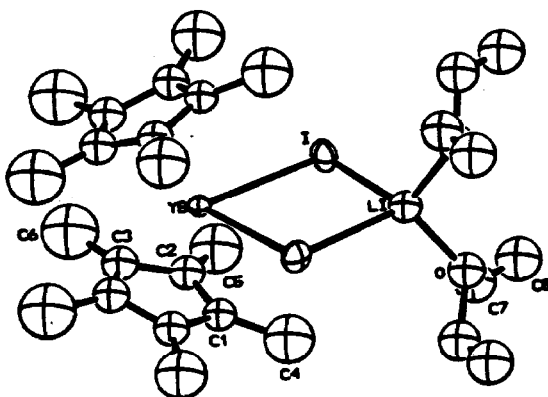
Fig. 4. The structure of $Yb(C_5Me_5)_2(\mu-I)_2Li(\text{ether})_2$ from ref. 14.
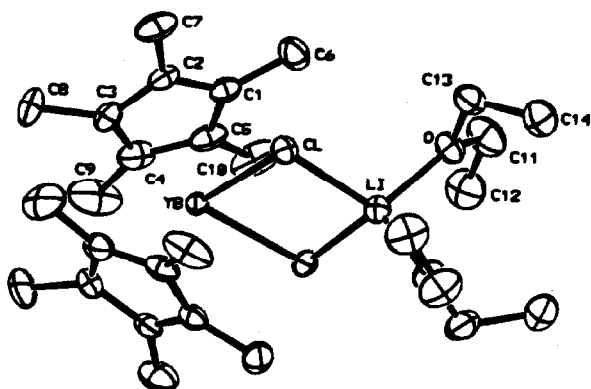
Fig. 5. The molecular structure of $Yb(C_5Me_5)_2(\mu-Cl)_2Li(ether)_2$ from ref. 14.
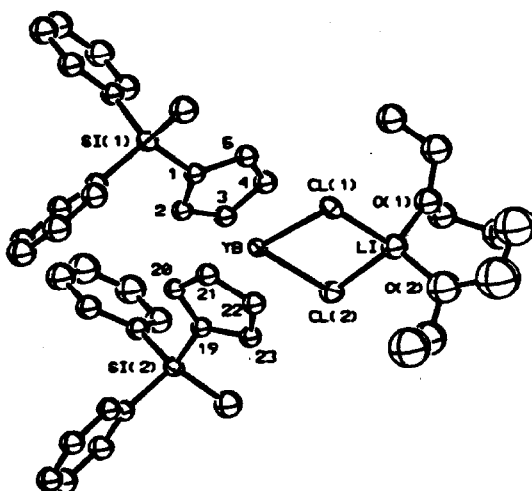
Fig. 6. The solid state structure of $Yb[C_5H_4Si(Me)(C_6H_5)_2]_2(\mu-Cl)_2Li(ether)_2$ from ref. 14.

bond distances were found to be 3.027(1), 2.595(1), 2.593(1), and 2.756(1) Å, respectively. One can note the particularly long Yb-Cl distances in 4, which presumably reflect the greater ability of Al^{3+} relative to Li^+ to abstract the chloride ions from the ytterbium atom. Probably in response to this removal, the Yb-C bond distances in 4 are noticeably shorter than those in 1, 2, or 3. The corresponding X-Yb-X angles were found to be 86.10(2)°, 85.95(2)°, 87.14(3)°, and 73.36(3)°. Once again, the value found for 4 seems to
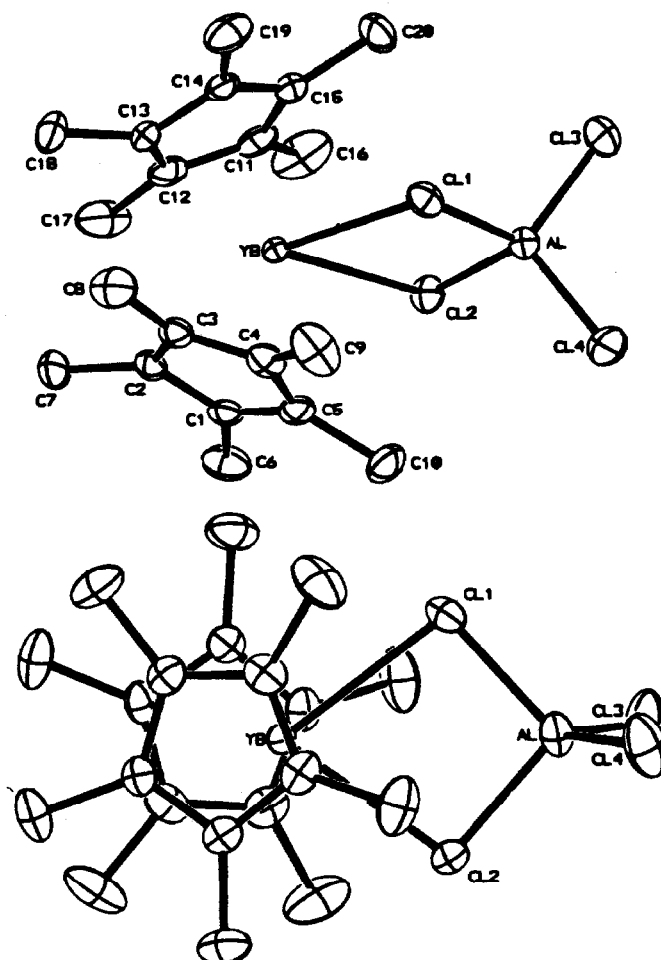
Fig. 7. The structure of $Yb(C_5Me_5)_2(\mu-Cl)_2AlCl_2$ from ref. 14.

stand out. The two cyclopentadienyl ligand planes in a given complex are
reasonably normal in that the angles between the two Yb-(ring centroid)
vectors range from ca. 135-140°. As is generally the case, the methyl ring
substituents in 1, 2, and 4, are bent substantially out of their ligand planes
in a direction away from the ytterbium atom; the distortion is greatest for
those methyl groups which are particularly close to the other C_5Me_5 ligand
plane. The silyl substituents in 3 also experience a similar distortion, and
are bent out of this cyclopentadienyl ligand planes by 0.232(1) and
0.410(1) Å. Finally, the relative orientations between the two
cyclopentadienyl ligands in 2, 3, or 4 may be described as ideally

staggered. In contrast, that of <u>1</u> is virtually eclipsed. This seems to result from intramolecular CH_3--I repulsions, which necessitate a single methyl group in each ligand occupying a position which essentially bisects the I-Yb-I' angle.

The use of the pentamethylcyclopentadienyl ligand also has resulted in the isolation of an interesting divalent samarium compound (15). Evans, Bloom, Hunter, and Atwood have thus reported the synthesis and structural characterization of $Sm(C_5Me_5)_2(THF)_2$. A metal atom vapor reaction between samarium atoms and C_5Me_5H (in a hexane matrix) appeared to lead, after extraction with THF, primarily to a $Sm(C_5Me_5)H(THF)_2$ complex, although some $Sm(C_5Me_5)_2H$ might also have been present. Attempts to crystallize the trivalent product, however, only seemed to lead to $Sm(C_5Me_5)_2(THF)_2$, which could be readily crystallized. An x-ray structural determination for the latter compound demonstrated the expected pseudo-tetrahedral ligand environment (Figure 8), and average Sm-C and Sm-O bond distances of 2.86(3)
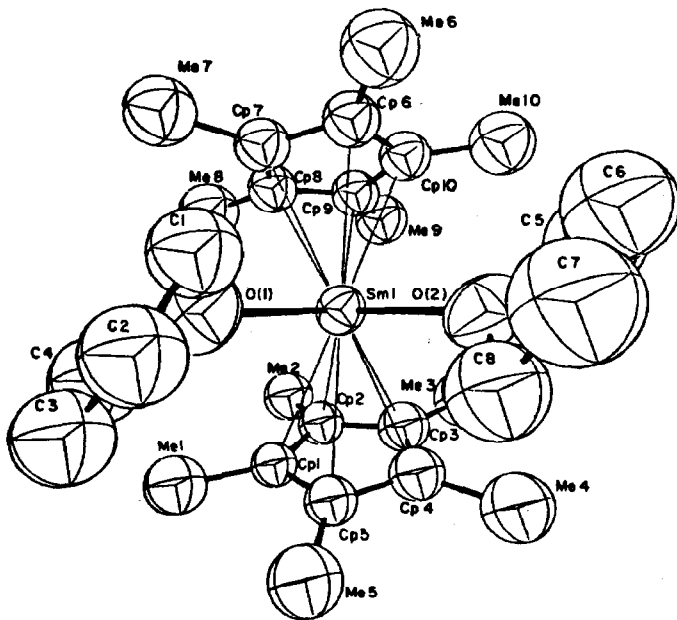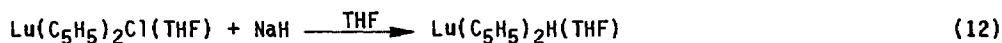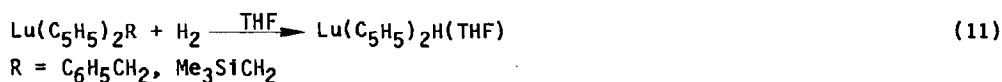

Fig. 8. The solid state structure of $Sm(C_5Me_5)_2(THF)_2$ from ref. 15.

and 2.63(1) Å were found; these distances compare well with the corresponding values of 2.66 and 2.41 Å in $Yb(C_5Me_5)_2(THF)$, when one takes into account the differences in ionic radii and coordination environments for the two

compounds. $Sm(C_5Me_5)_2(THF)_2$ was also observed to react very readily with CO, NO, 3-hexyne, HgR_2, and $Co(PR_3)_4$ compounds, leading to Sm(III) species.

Miller and DeKock have reported that lanthanide(III) complexes of the cycloheptatrienyl trianion, $C_7H_7^{3-}$, may be prepared by treatment of lanthanide trichlorides, specifically those of Er(III) and Gd(III), with one equivalent of the cycloheptadienyl anion (16). Apparently once one molecule coordinates to the lanthanide(III) ion, it may readily undergo two deprotonations by other cycloheptadienyl anions. Specific details were not presented for the lanthanide complexes, but an extensive investigation of a U(IV) complex was carried out, and is summarized in the actinide section.

Significant progress has also been achieved in the areas of hydride and alkyl chemistry. Schumann and Genthe have reported the isolation of bis(cyclopentadienyl)lutetium hydride as a THF adduct (17), by the two routes indicated in eqs. (11) and (12). The compound was characterized analytically

$$Lu(C_5H_5)_2R + H_2 \xrightarrow{THF} Lu(C_5H_5)_2H(THF) \qquad (11)$$
$$R = C_6H_5CH_2, \ Me_3SiCH_2$$

$$Lu(C_5H_5)_2Cl(THF) + NaH \xrightarrow{THF} Lu(C_5H_5)_2H(THF) \qquad (12)$$

and through IR spectroscopy of the hydride and corresponding deuteride. Variable temperature ^{1}H nmr spectra were tentatively interpreted as indicating an equilibrium between monomeric and associated species (eq. (13)). The

$$nLu(C_5H_5)_2H(THF) \longrightarrow [Lu(C_5H_5)_2H]_n \cdot n/2(THF) + n/2(THF) \qquad (13)$$
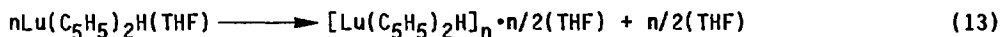
hydride itself did not react with olefins such as ethylene, isobutene, styrene, or cyclohexene. Reaction with $Si(CH_3)_3Cl$ led to the formation of $Lu(C_5H_5)_2Cl$ and $Si(CH_3)_3H$.

A number of new lanthanide alkyl complexes have been reported. Atwood, Hunter, Wayda, and Evans have described the syntheses of dimeric complexes of the type $[Er(C_5H_5)_2(C_2C(CH_3)_3)]_2$ and $[Yb(C_5H_4CH_3)_2(C_2C(CH_3)_3)]_2$ (18). The preparation followed the general course indicated by eq. (14). A dimeric

$$[Ln(C_5H_4R)_2CH_3]_2 + HC_2C(CH_3)_3 \xrightarrow{THF} [Ln(C_5H_4R)_2(C_2C(CH_3)_3)]_2 \qquad (14)$$
$$Ln = Er, \ R = H; \ Ln = Yb, \ R = CH_3$$
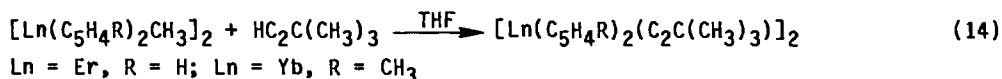
structure was indicated by solution molecular weight measurements, and

confirmed by a solid-state x-ray structural investigation (Figure 9). The compound is located on a crystallographic inversion center. An average Er-C (Cp) bond distance of 2.62(1) Å was observed, and agrees well with expected
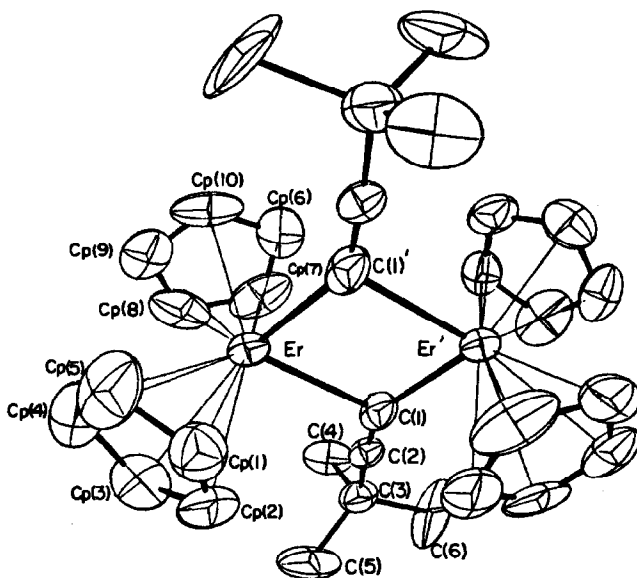
Fig. 9. The structure of $[Er(C_5H_5)_2(C_2CMe_3)]_2$ from ref. 18.

ionic radii for eight-coordinate Er(III) (1.00 Å) and for cyclopentadienyl carbon atoms (1.64 ± 0.04 Å). The two Er-C (alkynide) bond distances are essentially identical, 2.42(2) and 2.47(2) Å, suggesting a symmetrically bridged structure, although the Er-C(1)-C(2) and Er'-C(1)-C(2) bond angles differ at 115 and 149°, respectively. The four-membered Er_2C_2 ring is rigorously planar, with C-Er-C and Er-C-Er angles of 83.4(7) and 96.6(7)°. The Er-C (alkynide) bond lengths actually compare well with analogous (but terminal) Lu-C bond lengths in $Lu[2,6-C_6H_3(CH_3)_2]_4^-$ and $Lu(C_5H_5)_2(C(CH_3)_3)(THF)$. This similarity was attributed to the fact that two counteracting effects are present: metal-alkynyl bond lengths tend to be shorter than metal-alkyl bond lengths, while bridging distances tend to be longer than terminal ones. There was little, if any, evidence to suggest that the carbon-carbon triple bond was interacting with the central metal atom.

Monomeric lanthanide alkyl compounds, of the general formula $Ln(C_5H_5)_2(R)(THF)$, have been reported by Evans, Wayda, Hunter, and Atwood (Ln = Er, Lu; R = $\underline{t}$-C_4H_9) (19), as well as by Schumann, Genthe, and Bruncks, (Ln =

Lu; R = CH_3, C_2H_5, $\underline{n}$-C_4H_9, $\underline{t}$-C_4H_9, CH_2CMe_3, CH_2SiMe_3, $CH_2C_6H_5$, and $\underline{p}$-$CH_3C_6H_4$)
(20). While the methyl, ethyl, and $\underline{n}$-butyl compounds could only be detected
spectroscopically, the use of aryl or large alkyl groups allowed
straightforward isolation and markedly improved thermal stability. The
general method of preparation in each case involved the reaction of
[Ln(C_5H_5)$_2$Cl]$_2$ with the appropriate lithium alkyl in THF or THF/pentane. It
should be noted that [Ln(C_5H_5)$_2$(CH_3)]$_2$ complexes have been previously isolated
by this general method, except that subsequent extraction with toluene
apparently effected removal of the coordinated THF (21,22). Solid state
structures for two lutetium compounds ($\underline{5}$, R = $\underline{t}$-C_4H_9; $\underline{6}$, R = CH_2SiMe_3) have
been determined (Figures 10 and 11). In each case the overall structure could
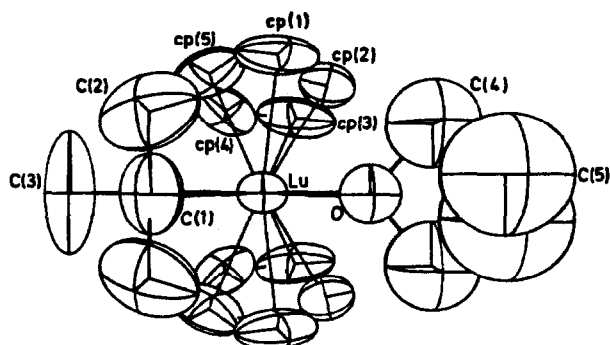be described as distorted tetrahedral. The principal distortions involved the

Fig. 10. The molecular structure of Lu(C_5H_5)$_2$($\underline{t}$-C_4H_9)(THF) from ref. 19.
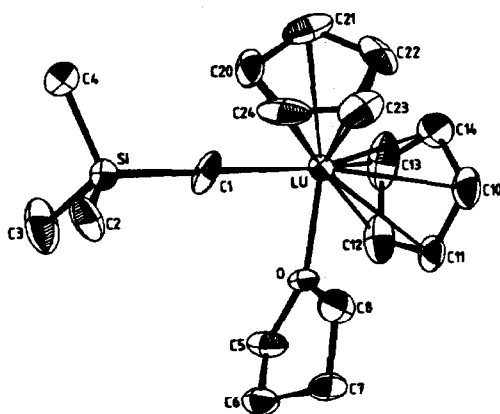

Fig. 11. The solid state structure of Lu(C_5H_5)$_2$(CH_2SiMe_3)(THF) from ref. 20.

C-Lu-O bond angles (94.1° for 5, 96° for 6) and the centroid-Lu-centroid bond angles (125.6° for 5, 130° for 6). The Lu-O bond distances were also quite similar, being 2.31(2) Å for 5 and 2.29 Å for 6. These distances seem shorter than the corresponding distances in $Ln(C_5H_5)_3(THF)$ compounds, possibly a reflection of the higher formal coordination number in the latter species. The Lu-C (alkyl) bond distances for 5 (2.47(2) Å) appear substantially longer than those for 6 (2.38 Å), perhaps indicative of greater steric crowding in 5. Nonetheless, even 6 is evidently crowded, as a Lu-C-Si bond angle of 131° was determined. The Lu-C (Cp) bond distance was found to be 2.63(1) Å in 5, while in 6 a Lu-Cp distance of 2.345 Å was reported (presumably involving the ring centroid).

Schumann, Pickardt, and Bruncks have reported the syntheses and charcterization of hexa(methyl)lanthanate trianions, which may be formulated as $Ln[(\mu_2-CH_3)_2Li(TMEDA)]_3$ for Ln = Pr, Nd, Sm, Er, Tm, Yb, and Lu (23). Previously they had reported the erbium and lutetium compounds (24). The central lanthanide atom thus has a coordination number of 6, with lithium having a value of 4. The overall reaction for their preparation is described by eq. (15). An x-ray structural determination on the erbium compound

$$LnCl_3 + 6LiCH_3 + 3TMEDA \xrightarrow{\text{ether}} Ln(\mu_2-CH_3)_6[Li(TMEDA)]_3 \qquad (15)$$
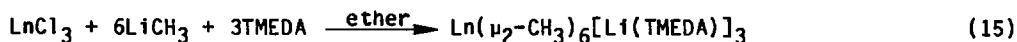
(Figure 12) confirmed the near-octahedral coordination for the erbium atom. The average Er-C and Li-C bond distances were determined to be 2.57(2) and 2.22(4) Å, respectively. Between the erbium atom and any given lithium atom are two bridging methyl groups. The $CH_3-Er-CH_3$ bond angles for each of these four-membered units is 93(1)°. This value and the average value of the Er-C bond distance are remarkably similar to the values observed for methyl-bridged Yb-Yb and Yb-Al pairs.

Evans, Wayda, Hunter, and Atwood have reported single and multiple insertions of CO into the Lu-C(alkyl) bond in $Lu(C_5H_5)_2(\underline{t}-C_4H_9)(THF)$ (25). A 1:1 reaction of CO with this organolanthanide compound in toluene leads to a pale yellow monomeric acyl complex over a period of 2-3 days (eq. (16)).

$$Lu(C_5H_5)_2(CMe_3)(THF) + CO \longrightarrow Lu(C_5H_5)_2(OCCMe_3) \qquad (16)$$
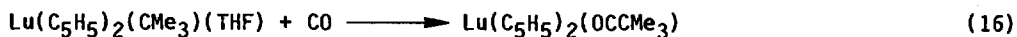
The acyl was characterized analytically and through IR and NMR spectroscopy. The C-O stretching frequency of 1490 cm^{-1} shifted to 1460 cm^{-1} when ^{13}CO was used, and is intermediate between values observed for similar zirconium (1545 cm^{-1}) and thorium (1469 cm^{-1}) compounds. Reaction of the lutetium alkyl compound with excess CO leads instead primarily to a dimetallic, red-purple
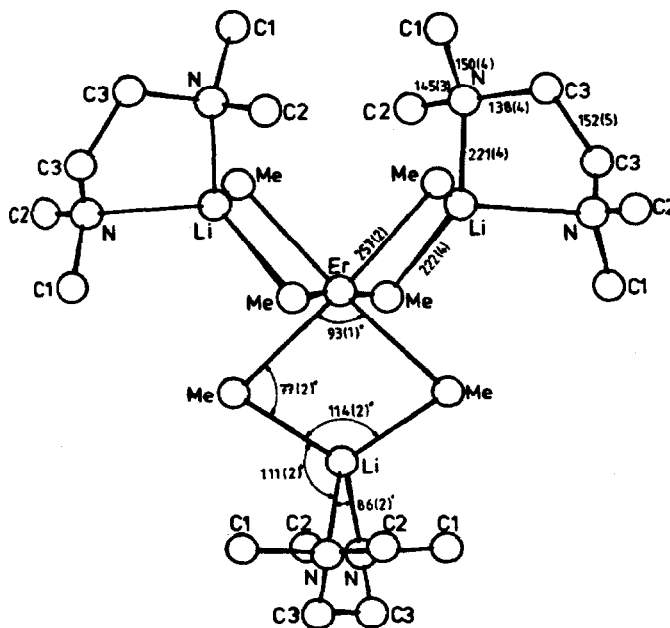
Fig. 12. The molecular structure of [Li(TMEDA)$_3$]$_3$Er(CH$_3$)$_6$ from ref. 23.

enedionediolate complex, characterized analytically and spectroscopically. Two ^{13}CO labelled samples of this compound could be prepared by either treating the normal acyl complex with ^{13}CO, or by treating the ^{13}CO acyl complex with ^{12}CO. ^{13}C NMR spectra of these samples demonstrated that the resonances for the enedionediolate carbon atoms to which alkyl groups were attached appear at 215.4 ppm, while the resonances for the other carbon atoms appear at 153.1 ppm. While these values are similar to those observed for a similar thorium compound, an x-ray structural determination (Figure 13) demonstrated a notably different bonding pattern. While the thorium atom in [Th(C$_5$Me$_5$)$_2$]$_2$ forms a five-membered ring with its chelating ligand (26), the lutetium atom is involved instead in a six-membered ring system (below). The
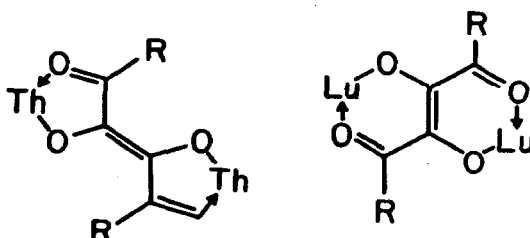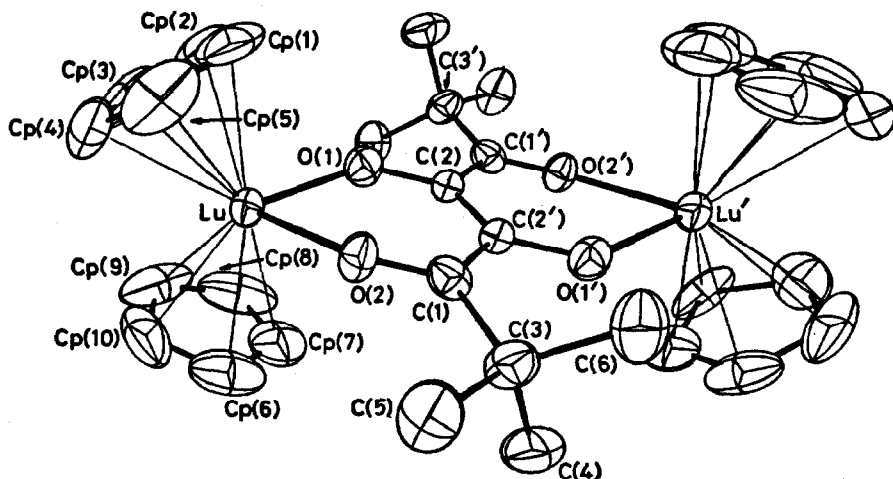
Fig. 13. The structure of the enedionediolate complex formed in the reaction
of Lu(C$_5$H$_5$)$_2$(CMe$_3$)(THF) with excess CO (ref. 25).

isomeric enedionediolate structures can be formally interconverted by 180°
rotations around both of the C-C single bonds. Whether the isomer differences
for these compounds are due to an inherent difference between 4f and 5f
metals, or simply due to steric differences between C$_5$H$_5$ and C$_5$Me$_5$, or between
smaller alkyl groups and $\underline{t}$-C$_4$H$_9$, has not yet been resolved.

Schumann and Reier have reported the isolation of a lutetium σ-ylide
complex (27) from the interaction of methylenetriphenylphosphorane,
(C$_6$H$_5$)$_3$PCH$_2$, with bis(cyclopentadienyl)lutetium chloride (equation (17)).
The colorless compound has been characterized analytically and
spectroscopically. ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies were particularly
diagnostic. For example, the value of the ^{13}C-H coupling constant was

$$(C_5H_5)_2LuCl + \bar{C}H_2\overset{+}{P}(C_6H_5)_3 \xrightarrow{\text{toluene}} (C_5H_5)_2Lu(Cl)\bar{C}H_2\overset{+}{P}(C_6H_5)_3 \qquad (17)$$
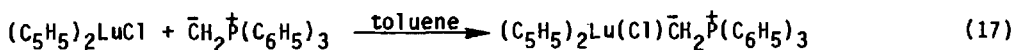
determined to be 118 Hz., similar to other sp^3 hybridized systems, and
differing noticeably from the value of 153 Hz. for the free ylid.

Two reports have appeared dealing with carbon atoms which are engaged in
multiple lanthanide-carbon bonding interactions. Dolgoplosk et al. have
investigated the reactions of yttrium and neodymium trichlorides with
alkyllithium reagents, RLi, where R = C$_6$H$_5$CH$_2$, Me$_3$SiCH$_2$, or C$_6$H$_5$CMe$_2$CH$_2$
(28). Treatment of NdCl$_3$ (or YCl$_3$) with 3 equivalents of benzyllithium led to
the formation of a reasonably stable organometallic compound in good yield,
along with 1.6 - 1.7 equivalents of toluene. Hydrolysis of the organometallic

product led to the consumption of three protons, indicating that the metal still was present in the trivalent oxidation state, even though only one equivalent of toluene was produced. Hydrolysis with D_2O yielded one equivalent of toluene-d_3, while exposure to oxygen, followed by hydrolysis, led to benzoic acid. These results were interpreted in terms of equation (18), which has as the final product some sort of metal-carbyne complex.

$$3C_6H_5CH_2Li + MCl_3 \longrightarrow [C_6H_5CM]_x + 2C_6H_5CH_3 + 3LiCl \qquad (18)$$
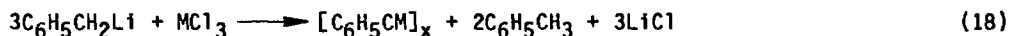
In a similar fashion, the reaction of three equivalents of $C_6H_5CMe_2CH_2Li$ with YCl_3 also seemed to produce a carbyne complex. However, the analogous reaction of three equivalents of Me_3SiCH_2Li with $NdCl_3$ led to a product in which 1.3 - 1.5 silyl groups were incorporated, the balance being released principally as $Si(CH_3)_4$. Hydrolysis with D_2O led primarily to tetramethylsilane-d_2. Thus, it was proposed that in this case the remaining groups were actually carbene ligands, such as would be the case in $Nd_2(CHSiMe_3)_3$.

In a much different fashion, a low valent carbide complex of gadolinium has been prepared and structurally characterized (Figure 14). Simon, Warkentin, and Masse have reported the preparation of $Gd_5Cl_9C_2$ by either the
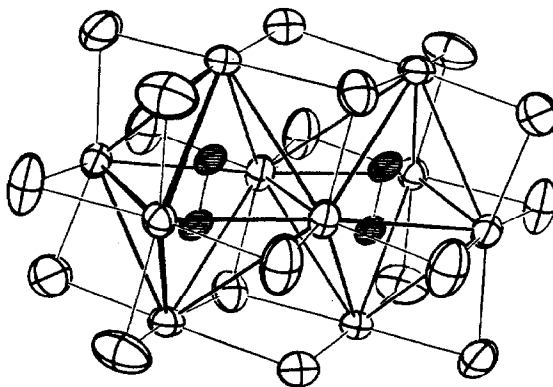
Fig. 14. The structure of $Gd_5Cl_9C_2$ from ref. 29.

electrolysis of fused $GdCl_3$ in a graphite crucible, or by the stoichiometric combination of $GdCl_3$, Gd_2Cl_3, and graphite in a tantalum crucible at 970 K (29). Pertinent structural parameters include the carbon-carbon bond distance of 1.465 Å, the carbon-gadolinium bond distances of 2.21 A to apical metal

atoms, and 2.48 or 2.60 Å to the basal metal atoms. The Gd-Gd and Gd-Cl bond distances fall in the respective ranges of 3.21 - 4.09 Å and 2.61 - 3.26 Å. Similar C_2 fragments are known in transition metal complexes such as $Rh_{12}C_2(CO)_{25}$, which has a carbon-carbon bond distance of 1.48 Å (30).

A number of reports have appeared dealing with reactions which could lead to metal-metal or metal-phosphorus bonding. Tilley and Andersen have described the preparation of a paramagnetic (4.1 μ_B), trivalent compound containing a ytterbium-isocarbonyl interaction (31, 32), as indicated by equation (19). A single crystal x-ray study demonstrated the

$$(C_5Me_5)_2Yb(OEt_2) + 1/2Co_2(CO)_8 \xrightarrow{\text{toluene}} \xrightarrow{\text{THF}} (C_5Me_5)_2Yb(THF)(OC)Co(CO)_3 \quad (19)$$
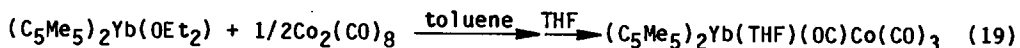
structure to be that shown in Figure 15. The Yb(III) ion is attached to two pentamethylcyclopentadienyl ligands and one THF ligand in normal fashion, and
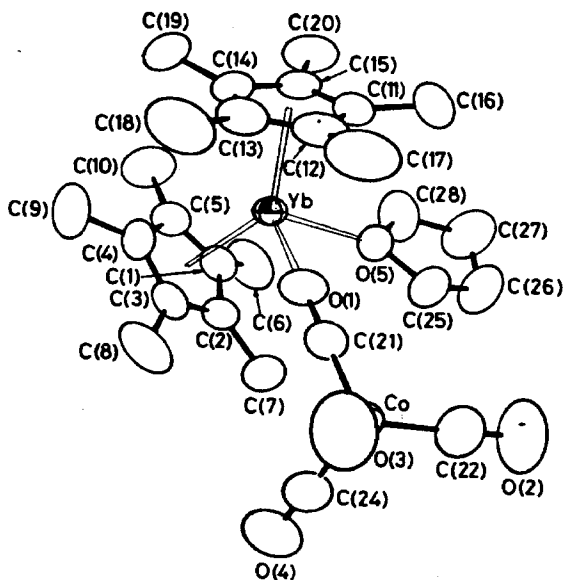
Fig. 15. The solid state structure of $Yb(C_5Me_5)_2(THF)[OCCo(CO)_3]$ from ref. 32.

to a nearly tetrahedral $Co(CO)_4$ unit by a single isocarbonyl interaction. The Yb-O (isocarbonyl) bond distance of 2.258(2) Å is noticeably shorter than the Yb-O (THF) distance of 2.335(2) Å, likely due at least in part to hybridization differences of these oxygen atoms. The coordination of Yb(III) by the carbonyl ligand appears to weaken the C-O bond, and strengthen the Co-C

bond to that carbonyl (1.188(3) and 1.699(3) Å, respectively) relative to the three other ones (1.14 ± 0.02 and 1.77 ± 0.03 Å, respectively). The Yb-C bond distances average 2.596(2) Å, corresponding to a Yb-Cp(centroid) distance of 2.30 ± 0.01 Å.

Suleimanov and Beletskaya have reported similar species from the reactions of various lanthanide chlorides with $NaCo(CO)_4$ (33), as indicated in equation (20). The same products could be obtained from the interaction of

$$LnCl_3 + NaCo(CO)_4 \xrightarrow{\text{THF}} (CO)_4CoLnCl_2(THF)_n \qquad (20)$$
n = 2 - 4, Ln = La, Sm, Dy, Ho, Yb
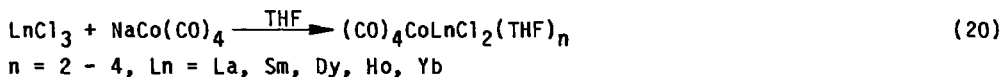
$Co_2(CO)_8$ with $LnCl_3$ in THF. These thermally unstable products displayed C-O stretching frequencies in the ranges of 2000 - 2100 and 1620 - 1640 cm^{-1}. Addition of excess $LnCl_3$ leads to stabilization of these materials. Similar reactions lead to $((C_6H_5)_3P)(CO)_3CoLnCl_2(THF)$ (eq. (21)).

$$LnCl_3 + NaCo(CO)_3(P(C_6H_5)_3) \xrightarrow{\text{THF}} ((C_6H_5)_3P)(CO)_3CoLnCl_2(THF) \qquad (21)$$
Ln = La, Sm, Dy, Ho, Yb
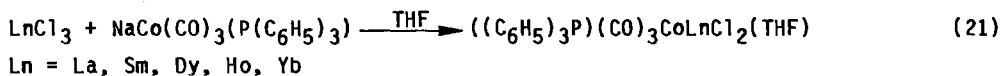
Schumann and Frisch have reported the syntheses of lanthanide-phosphide compounds of the formula $(C_5H_5)_2LnP(\underline{t}-C_4H_9)_2$ and $(C_5H_5)_2LnP(C_6H_5)(\underline{t}-C_4H_9)$ (34). These were prepared by the routes of eq. (22) and eq. (23) in good yields.

$$(C_5H_5)_2LnCl + LiP(\underline{t}-C_4H_9)_2 \xrightarrow{\text{THF}} (C_5H_5)_2LnP(\underline{t}-C_4H_9)_2 \qquad (22)$$
Ln = Tb, Ho, Er, Tm, Yb, Lu

$$(C_5H_5)_2LnCl + LiP(C_6H_5)(\underline{t}-C_4H_9) \xrightarrow{\text{THF}} (C_5H_5)_2LnP(C_6H_5)(\underline{t}-C_4H_9) \qquad (23)$$
Ln = Tb, Ho, Er, Yb, Lu
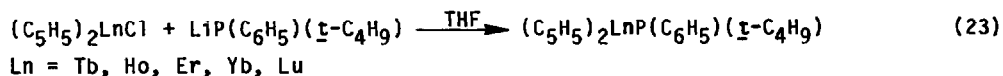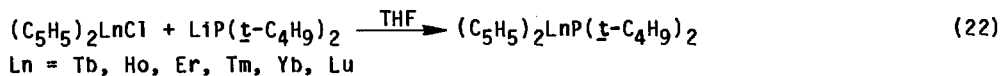
The compounds are extremely moisture sensitive but thermally stable to ca. 120°. Analytical data were obtained, as well as ^{1}H and ^{31}P nmr spectra for the diamagnetic lutetium compounds. Broadening of the ^{31}P resonance by coupling to the [175]Lu nucleus was observed. Molecular weight determinations indicated that these compounds were associated.

Bochkarev, Bochkarev, Radkov, Kalinina, and Razuvaev have reported several ionic germylmercury complexes of praesodymium (35). These were prepared in good yield as shown in eqs. (24) - (26).

$$Pr(O-\underline{t}-C_4H_9)Cl_2 + (C_6F_5)_3GeH + [(C_6F_5)_3Ge]_2Hg \xrightarrow{\text{DME}} \qquad (24)$$
$$[(C_6F_5)_3Ge]_3HgPrCl_2(DME)_3$$

$$Pr(O\text{-}\underline{t}\text{-}C_4H_9)_3 + 3(C_6F_5)_3GeH + 2[(C_6F_5)_3Ge]_2Hg \xrightarrow{\text{DME}}$$

$$[(C_6F_5)_3Ge]_7Hg_2Pr(DME)_3 \tag{25}$$

$$[(Me_3Si)_2N]_3Pr + 2(C_6F_5)_3GeH + 2[(C_6F_5)_3Ge]_2Hg \xrightarrow{\text{DME}}$$

$$[(C_6F_5)_3Ge]_6Hg_2PrN(SiMe_3)_2(DME)_3 \tag{26}$$
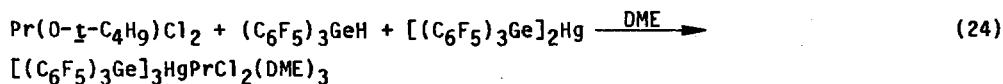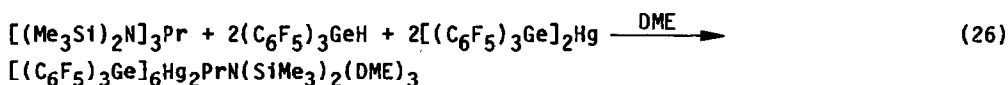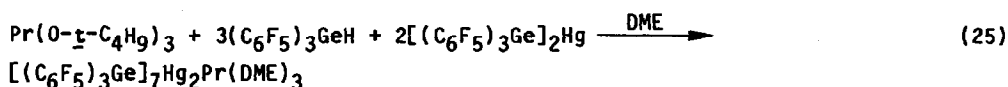
These complexes were characterized analytically and via conductivity measurements, which suggest an ionic structure. It was proposed that these complexes contain $Hg[Ge(C_6F_5)_3]_3^-$ and/or $Hg[Ge(C_6F_5)_3]_4^{2-}$ groups, along with the respective praesodymium cations. Subsequently, Bochkarev, Bochkarev, Kalinina, and Razuvaev have prepared the neodymium and holmium compounds that would be expected from eq. (25), and a similar formulation was proposed on the basis of conductivity and analytical data (36). The reaction of the praesodymium complex with equimolar HCl led to removal of one $Hg[(C_6F_5)_3Ge]_3$ anion, leaving $[(C_6F_5)_3Ge]_4HgPrCl(DME)_3$. Similar results were obtained from the reaction with one equivalent of $(C_6F_5)_3GeBr$, leading to the bromine analog, $[(C_6F_5)_3Ge]_4HgPrBr(DME)_3$.

Nappi and Gingerich have observed the molecule PtLa in the gas phase by Knudsen effusion mass spectroscopy of the Pt-La-graphite system (37). A dissociation energy of 118.5 ± 5.0 kcal/mole was determined. Similarly, Gupta, Nappi, and Gingerich have determined a dissociation energy of 112.4 ± 2.9 kcal/mole for the gas phase PtY molecule (38).

Two spectroscopic studies on organolanthanide and organoactinide compounds have appeared. Green, Kelly, Long, Kanellakopulos, and Yarrow have obtained photoelectron spectra for $Ln(C_5H_4CH_3)_3$ (Ln = Pr, Dy), $[Ln(C_5H_5)_2Cl]_2$ (Ln = Y, Gd), $An(C_5H_5)_4$ (An = Th, U), $An(C_5H_5)_3Cl$ (An = Th, U), $U(C_5H_4Me)_3Cl$, $U(C_5Me_5)_2Cl_2$, and $U(C_5H_5)_3(THF)$ (39). Several interesting trends were observed. The ionizations of the f electrons could readily be seen for the uranium complexes at ca. 6.3 - 7.1 eV, and their relative intensities increased dramatically when the higher energy He-II source was used. This was interpreted as providing evidence for substantial f-orbital covalency. Methylation of the cyclopentadienyl ligands brought about the expected decrease in f orbital ionization potential. In contrast, the spectra for the lanthanides were devoid of such bands, and showed virtually no dependence on the source employed (He-I or He-II). Ionizations for the e_1 orbitals of the cyclopentadienyl ligands were observed in the range 7.0 - 9.5 eV, and tended to be lower for the more ionic complexes (including transition metal species). In contrast, the ionization energies for the chloride ligands (ca. 10.5 - 11.6 eV) tended to be lower for the more covalent complexes. The oxygen atom lone pair in $U(C_5H_5)_3(THF)$ had an ionization energy of 10.03 eV.

Aleksanyan, Garbusova, Chernyslova, Todres, Leonov, and Gramateeva have recorded the vibrational spectra of solid $Th(C_8H_8)_2$ and $KLa(C_8H_8)_2$, and have assigned the various bands by comparison to the spectra of $K_2C_8H_8$ (40). It was observed that the frequencies of all the ligand vibrational modes increased relative to those of $K_2C_8H_8$, even though the in-plane C-C stretching modes in transition metal compounds show the opposite behavior. These increases were greater for the thorium compound, which suggests a greater metal-ligand bonding influence relative to lanthanum. Similarly, bands which would be forbidden under strict D_{8h} symmetry were observed to occur in the thorium, but not lanthanum, spectra. For the thorium compound, bands observed at 226 and 245 cm^{-1} were assigned to the symmetric metal-ligand stretching mode (A_{1g}) and to the degenerate tilting mode (E_{1g}). The antisymmetric stretching mode (A_{2u}) was assigned to a band at 246 cm^{-1}. From these numbers a rough value of the force constant could be obtained as $4.25 \cdot 10^6$ cm^{-2} (cf., $4.89 \cdot 10^6$ cm^{-2} for ferrocene). For the lanthanum compound, corresponding bands were observed at 202 and 216 cm^{-1}, which indicates weaker metal-ligand bonding than in $Th(C_8H_8)_2$.

Several lanthanide metal-atom reaction studies have been carried out. Miller and DeKock have reported the reactions of cyclohexanone with neodymium, uranium, and various transition metal atoms. Two major products were always observed, [1,1'-bicyclohexyl]-1,1'-diol, a pinacol, and 2-(1-cyclohexen-1-yl)cyclohexanone, an aldol-derived product (41). For neodymium, uranium, and chromium, the relative aldol/pinacol ratios were observed to be 2.1, 2.8, and 2.5, whereas for titanium the value was 0.29.

Evans, Coleson, and Engerer have studied the metal atom reactions of erbium, samarium, and ytterbium with ethylene, propylene, cyclopropane, and allene (42). With ethylene, brown matrices are obtained which are composed of ca. 70-80% metal, similar to that expected for the stoichiometry $Ln(C_2H_4)_2$ (73-76%). These materials are insoluble in common organic solvents. Hydrolysis of the samarium and ytterbium products leads primarily to ethane, propane and propene, and butane and butene in a 30:15:45 mole ratio. In contrast, hydrolysis of the erbium compound led primarily to a polymeric solid; interestingly, of the volatile products formed, methane predominated (90%). Both observations were attributed to the lack of a stable divalent oxidation state for erbium, which thereby leads to substantial fragmentation of ethylene to monocarbon units. The lack of substantial quantities of ethylene in any of these products was attributed to the importance of metallocyclopropane resonance hybrids, as opposed to the alternative π resonance forms. In agreement with this, deuterolysis led to multiple incorporation of deuterium atoms, suggestive of extensive metal-

carbon σ bond networks. For the samarium product, it was also found that 0.8 hydride ligands were present per metal atom. The propene reactions followed the above pattern in that samarium and ytterbium atoms behaved similarly. Chemical trapping reactions demonstrated the presence of allyl and hydride ligands in these products (0.5 hydrides per metal), but only traces were observed for erbium, presumably since oxidative addition of an allylic C-H bond would be less favorable for a metal not having a stable divalent oxidation state. Hydrolysis of these products also resulted in substantial propyne evolution, demonstrating a high degree of dehydrogenation of the propene reactant. A fraction of the erbium product mixture was found to be THF-soluble, and it was formulated as $[Er(C_9H_{18})]_n$, where n > 10. Reactions with allene were somewhat similar. Hydrolysis of the products led primarily to propane, propene, and propyne. Only small amounts of allene were liberated, suggesting that little if any π-complex formation was involved. The formation of large amounts of propene and propyne is consistent with the saturation of olefinic bonds by the formation of multiple metal-carbon single bonds. It was also determined that ca. 0.25 hydride ligands were present per metal atom, suggestive of C-H oxidative addition reactions. The cocondensation of erbium atoms with cyclopropane led to an insoluble product, for which hydrolysis led to substantial quantities of propane, propene, propyne, and cyclopropane. The presence of hydride ligands was also detected, an it was believed that oxidative addition of cyclopropane C-H bonds was a major pathway, leading to (cyclopropyl)erbium hydrides. The presence of all three straight chain products suggests that cyclopropyl ring cleavage takes place with substantial hydrogen atom migration.

In a related study, Evans, Engerer, and Coleson investigated the reactions of samarium, ytterbium, and erbium metal atoms with 1-hexyne (43). In the case of ytterbium, a purple product, insoluble in hexane or toluene, was isolated. One fraction was soluble in ether, after which a part of it could be dissolved in toluene. Another fraction could be dissolved in THF. These three components are actually quite similar. Each analyzed for $[Yb(C_9H_{14})]_n$ and contained only ca. 8-15% Yb(III). Each displayed infrared spectral characteristics typical of metal-alkynides, and chemical reactions demonstrated the presence of alkynide and hydride ligands in a ratio of > 3:1. These species were therefore formulated as $[Yb(C_2C_4H_9)_{1.5}H_{0.5}]_n$, with most of the ligands presumably bridging two (or more) metal atoms. In an attempt to locate alternative reaction sites in the terminal alkynes, the authors investigated the same reaction, except that an excess of ytterbium metal was employed. Interestingly, little if any attack occurred at the CH_2 group α to the carbon-carbon triple bond, as indicated by deuterolysis.

Instead it appeared that addition of the metal atoms across the triple bond took place, as indicated by the formation of hexene-d_3 as a minor deuterolysis product. The erbium and samarium reactions with 1-hexyne were completely different, however. The initial brownish products were only soluble in THF, but after this initial exposure, the products could be dissolved in hydrocarbons. Magnetic susceptibility measurements and chemical reactions of these species indicated the metal atoms to be trivalent. Hydrolytic reactions indicated the presence of small quantities of fragmented species, significant amounts of oligomeric species, and indicated as well that multiple metallations of the 1-hexyne ligand (perhaps involving the σ-CH_2 group) were taking place. The above data are consistent with a formulation such as $[M(C_6H_9)_{2-x}(C_6H_8)_xH_{1-x}]_n$. The hydrocarbon-soluble samarium and erbium products were found to be weakly active in the hydrogenation of 3-hexyne, yielding primarily cis-3-hexene.

Several reports dealing with the applications of lanthanide compounds in organic synthesis have appeared. Kagan, Namy, and Girard have published a study on the mechanism of the reductions of alkyl halides, alkyl tosylates, aldehydes, and ketones by SmI_2 in THF (44). For the alkyl halides, the predominant path appeared to involve an electron transfer to the alkyl halide, forming halide ions and alkyl radicals, which could either abstract a hydrogen atom from THF to yield alkane, or be converted to a carbanion by a second molecule of SmI_2. In the latter case, abstraction of a proton would also lead to the formation of alkane, as observed. Chemical evidence for the presence of both radical and carbanionic species was presented. However, the formation of di(alkyl) species was only observed for resonance stabilized groups such as allyl and benzyl. The reduction of ketones to secondary alcohols was similarly interpreted in terms of an initial electron transfer, yielding a ketyl radical anion, whose existence was supported by the isolation of various chemical byproducts (e.g., pinacolization products, etc.). For the Grignard-like conversion of ketones into tertiary alcohols, chemical trapping experiments, and the isolation of by-products, demonstrated the intermediacy of alkyl radicals, ketyl radicals, and radical and/or anionic species derived by abstraction of a proton or a hydrogen atom from THF. Evidence was presented which indicated that in the presence of ketones, alkyl radicals could persist for relatively reasonable lengths of time, whereas in the absence of ketones, these radicals were rapidly converted to carbanions. The use of optically active alkyl halides led to a loss in optical purity, consistent with the above, and ruling out a nucleophilic displacement by a ketone dianion. The addition of catalytic quantities of $FeCl_3$ led to a decrease in the time required for alkylation.

Deacon and Tuong have reported their findings on the reactions of $Yb(C_6F_5)_2$ or $Yb(C_2C_6H_5)_2$ with aldehydes and ketones (45). In most cases, such as with acetone, acetaldehyde, and benzaldehyde, the products resulting were the expected "Grignard-like" products. However, some condensation products were observed in the acetone reactions. Further, with benzophenone, a significant amount (14%) of benzopinacol was formed in the reaction with $Yb(C_2C_6H_5)_2$, and this became the dominant product (84%) in the reaction with $Yb(C_6F_5)_2$. It was believed that the intermediate formation of the benzophenone radical anion took place, and in fact a blue solution was observed, similar in color to that of Na/benzophenone in THF. Analogous results were obtained from YbI_2.

Fukugawa, Fujiwara, Yokoo, and Taniguchi have repoted similar Grignard-like reactivities of phenylytterbium(II) iodide with aldehydes, ketones, esters, and nitriles, to lead to alcohols and/or ketones (46). The conversions of aldehydes or ketones to alcohols generally took place in reasonable yields (18 - 78%), while conversions of nitriles to ketones took place only in low yields (4 - 8%). Reactions with esters produced mixtures of alcohols and ketones, but unlike Grignard reactions, the formation of ketones was favored, especially at lower temperatures. Thus, the competitive reaction of C_6H_5YbI with a 1:1 mixture of methyl benzoate and acetophenone led to benzophenone and 1,1-diphenylethanol in 34% and 17% yields, respectively.

The catalytic applications of lanthanide compounds have continued to attract attention. The hydrogenation of 3-hexyne has been described already (vide supra) (43). Imamura and Tsuchiya have reported that the intermetallic compound $SmMg_3$ reacts with anthracene (0.4 - 2.0:1) in THF to yield dark green products which absorb hydrogen gas instantaneously on exposure, and are active catalysts in the hydrogenation of ethylene (47). In contrast, the pure intermetallic compound is essentially inactive as a hydrogenation catalyst.

Herrmann and Streck have investigated the effects of the presence of additional metal compounds on the polymerization of ethylene and propylene by typical Ziegler-Natta catalysts (48). The catalyst systems were prepared by the combination of titanium alkoxides with acetates or alkoxides of magnesium, aluminum, zinc, or various transition metals or lanthanides, yielding oxide-bridged species to which the alkylating agent ($RAlCl_2$) was added. In general, the effects of adding the lanthanide compounds to the titanium alkoxides were not much different from the effects brought about by some of the other metals.

In a study on the conversion of carbon monoxide to methane, Strelets, Tsarev, and Efimov list various "yttrium compounds" (YCl_3, YCl_4, and $(C_5H_5)_2YCl_2$) which may serve as catalyst precursors for this process (49). Apparently, however, the authors actually were referring to vanadium

compounds.

Actinides

Good progress has been achieved in the area of π-complexes of the actinides. Zanella, Rossetto, De Paoli, and Traverso (50) have reported the facile preparations of $U(C_5H_5)_3$ and $U(C_5H_5)_3(THF)$ from $U(C_5H_5)_3Cl$ and NaH in benzene and THF solutions, respectively. Klähne, Giannotti, Marquet-Ellis, Folcher, and Fischer (51) have also reported the preparation of $U(C_5H_5)_3(THF)$ with yields of up to 70%, from the photolysis of $U(C_5H_5)_3R$ (R = CH_3, n-C_4H_9) complexes. Gas chromatographic analyses of the vapor phase components above the THF solutions indicated the formation of methane or of a butane/butene mixture (93/7), respectively. In contrast, thermolysis of the methyl compound in the dark at 120° led to even more ethane than methane. Interestingly, photolysis in THF-d_8 led to a CH_3D/CH_4 ratio of ca. 70/30, while thermolysis led to a ratio of ca. 30/70. Kinetic data were in accord with a first order reaction. Spin trap ESR experiments did not reveal the presence of free alkyl radicals on photolysis in toluene, but adducts with phenyl-N-t-butylnitrone were observed. Also noted was the presence of another paramagnetic species, formed even under non-photolytic conditions, and tentatively assigned to an adduct of C_5H_5 with the spin trap. In THF solutions, the presence of free methyl and butyl radicals was observed. The authors noted that the initial step in the reduction appeared to involve homolytic scission of the U-C σ-bond, and that this was facilitated in THF relative to toluene.

Sung-Yu, Hsu, Chang, Her, and Chang have reported a novel preparative route to $U(C_5H_5)_3X$ (X = Cl, Br, I) complexes (52). Their method employs the reaction of uranium powder with an excess of cyclopentadiene and alkyl halide (CH_2Cl_2 or CCl_4, C_2H_5Br, C_2H_5I), and leads to generally quite good yields (40% 85%, 90%, respectively). $U(C_5H_5)_3Br$ could also be prepared from $U(C_5H_5)_3$ and C_2H_5Br.

Dormond, Duval-Huet, and Tirouflet have reported the syntheses of various complexes of the general types $U(C_5H_4R)_3Cl$ (R = CH_3, t-C_4H_9, $Si(CH_3)_3$, $CH(CH_3)_2$, and $CH(CH_3)(C_6H_5)$), $U(C_5H_5)(C_5H_4CH(CH_3)_2)_2Cl$, $U(C_5H_5)_2(C_5H_4CH(CH_3)_2)Cl$, $U(C_5H_5)_2(C_5H_4CH(CH_3)C_6H_5)Cl$, $U(C_5H_5)(C_5H_4CH(CH_3)C_2H_4C_5H_4)Cl$, and $U(C_5H_4C(CH_3)_3)(C_5H_4CH(CH_3)C_2H_4C_5H_4)Cl$, the latter two possessing chiral centers at the uranium atom, as well as at one carbon atom, and hence each exists as diastereomeric meso and racemic enantiomeric pairs, which could be distinguished by NMR spectroscopy (53). As complexes such as $U(C_5H_5)_2Cl_2$ are unstable (54), the route employed by the authors involved the initial introduction of a single substituted cyclopentadienyl ligand, yielding a $U(C_5H_5)Cl_3(THF)_2$ type of complex, followed

by the introduction of two equivalents of the other substituted cyclopentadienyl ligand. The authors also observed substantial ligand redistribution for mixtures of $U(C_5H_5)_3Cl$ and $U(C_5H_4C(CH_3)_3)_3Cl$ in THF or toluene after 2 hours at 60°.

The same authors have also reported complexes of the type $U(C_5H_4R)_2(N(C_2H_5)_2)_2$ (R = H, CH_3, $CH(CH_3)_2$, $C(CH_3)_3$), $U(C_9H_7)_2(N(C_2H_5)_2)_2$ (C_9H_7 = indenyl), $U(C_5H_4C_3H_6C_5H_4)(N(C_2H_5)_2)_2$, $U(C_5H_4CH(CH_3)C_6H_5)_2(N(C_2H_5)_2)_2$, $U(C_5H_5)(C_9H_7)(N(C_2H_5)_2)_2$, and $U(C_5H_5)(C_5H_4R)(N(C_2H_5)_2)_2$ (R = CH_3, $C(CH_3)_3$, $CH(CH_3)(C_6H_5)$) (55). The synthetic route which was employed took advantage of the fact that amido groups in $U(N(C_2H_5)_2)_4$ can be selectively replaced with one or two substituted cyclopentadiene molecules to yield the appropriate substituted mono(cyclopentadienyl) or bis(cyclopentadienyl) uranium(IV) complexes. The $U(C_5H_4CH(CH_3)C_6H_5)_2(N(C_2H_5)_2)_2$ complex was found by ^{1}H NMR to exist as the expected pair of meso and racemic diastereomers, due to the presence of two chiral carbon atom centers. $U(C_5H_5)(C_5H_4CH(CH_3)C_6H_5)$-$(N(C_2H_5)_2)_2$ appears to exist as a pair of enantiomers. Some redistribution of cyclopentadienyl ligands could be brought about by the mixing of two different bis(amido) complexes in solution.

Arduini, Edelstein, Jamerson, Reynolds, Schmid, and Takats have published a full report on their preparations of $U(C_5H_5)_2(N(C_2H_5)_2)_2$ complexes, as well as n-propyl and phenyl amido analogs (56). The syntheses were accomplished by the route of equation (27). An attempt to carry out the analogous reaction

$$U(NR_2)_4 + 2C_5H_6 \longrightarrow U(C_5H_5)_2(NR_2)_2 + 2C_5H_6 \qquad (27)$$
$$R = Et, \underline{n}\text{-}Pr, C_6H_5$$
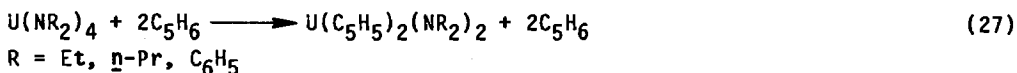
for R = i-Pr led to no reaction (presumably due to steric hinderance), while for R = CH_3, a mixture of $U(C_5H_5)_2(NR_2)_2$ and $U(C_5H_5)_3(NR_2)$ was obtained perhaps due in part to ligand redistribution. In fact, even the R = Et compound was observed to undergo ligand redistribution (to $U(C_5H_5)_3(NEt_2)$) upon standing or sublimation. $U(C_5H_5)_2(NEt_2)_2$ was found to react in hexane with one or two equivalents of diphenylamine to produce solely $U(C_5H_5)_2(NEt_2)(N(C_6H_5)_2)$; mixtures were obtained from THF or benzene. Similarly, the reaction of $U(C_5H_5)_2(NEt_2)_2$ with pyrrole also was reported to lead to a mixture, in this case predominately containing $U(C_5H_5)_2(NC_4H_4)_2$ and $U(C_5H_5)_3(NC_4H_4)$. With 2,5-dimethylpyrrole, a mixture is again obtained, this time appearing to be of $U(C_5H_5)_3(NEt_2)$ and $U(C_5H_5)_2(NEt_2)(NC_4H_2Me_2)$. However, reaction of $U(C_5H_5)_2(NEt_2)_2$ with 3,4,5-trimethylpyrrole-2-carboxylate did lead to the apparent isolation of a single product, $U(C_5H_5)_2(NC_4Me_3(CO_2Et))_2$. In this compound, some interaction between the uranium atom and the carboxylate

functionality was postulated on the basis of the mass spectrum, which
indicated a greater tendency for $U-C_5H_5$ rather than U-amide cleavage, contrary
to the other amide complexes.

Arduini, Jamerson, and Takats have also investigated the reactions of
$U(C_5H_5)_2(NEt_2)_2$ with CS_2, COS, and CO_2, which give rise nearly quantitatively
to insertion products, $U(C_5H_5)_2(XYCNEt_2)_2$ (X, Y = O, S), even when excess CXY
reagent is employed (57). The sulfur-containing products were found to be
monomeric in benzene, while the CO_2 insertion product exhibited variable
degrees of association, depending on solvent and concentration. Mass spectral
data suggested that the first U-Cp bond is broken more readily than that of
the (thio)carbonate ligands, as the major fragment observed was in each case
(parent - C_5H_5). Infrared data suggested that the (thio)carbamate ligands are
all bound in the expected bidentate mode (below). Variable temperature ^{1}H NMR

$$\begin{array}{c} \text{X} \\ \diagup \quad \diagdown \\ \text{M} \qquad \text{C---NR}_2 \\ \diagdown \quad \diagup \\ \text{Y} \end{array}$$
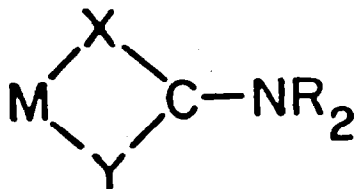
data for the sulfur containing compounds were interpreted as indicating
hindered C-N bond rotation, but rapid metal-centered rearrangement, such as
conversion of a pseudo-octahedral coordination geometry (2 Cp ligands and 4
oxygen or sulfur atoms) to a trigonal prismatic one.

Arduini and Takats have further reported on the reaction of
$U(C_5H_5)_2(NEt_2)_2$ with carboxylic and thiocarboxylic acids (58). From these
reactions, complexes of the composition $U(C_5H_5)_2(XYCR)_2$ (X = O, Y = O,
R = CH_3, C_6H_5, $\underline{t}$-C_4H_9; X = O, Y = S, R = CH_3, C_6H_5) have been isolated.
Attempts to replace only one amido group led to mixtures of products, although
it appeared that ligand redistribution processes were not involved. The
acetate and benzoate compounds appeared to be polymeric, while the pivalate
was dimeric, and the thiobenzoate was monomeric. In the mass spectra of these
compounds, loss of a single C_5H_5 ligand was the predominant process. Infrared
spectra suggested that both atoms (oxygen and/or sulfur) on each carboxylate
or (thio)carboxylate ligand were engaged in coordination, either as a chelate
to one metal, or in bridging fashion to two metals. A slight preference for
bonding to the oxygen atom in the mono(thio)carbamates was noted. Variable
temperature ^{1}H NMR spectra of $U(C_5H_5)_2[OSC(C_6H_5)]_2$ indicated a very facile
metal-centered rearrangement (cf.,(thio)carbamates above), as well as

relatively hindered $C-C_6H_5$ bond rotation.

Eigenbrot and Raymond have reported the preparation of $U(C_5H_5)_3$-(pyrazolate), as outlined in equation (28). An x-ray diffraction

$$U(C_5H_5)_3Cl + NaC_2H_3N_2 \xrightarrow{\text{THF}} U(C_5H_5)_3(C_2H_3N_2) \qquad (28)$$
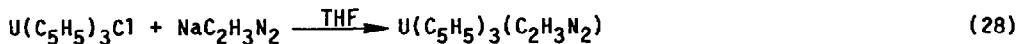
study of the red-brown crystals demonstrated a monomeric structure (Figure 16), containing three $\eta^5-C_5H_5$ ligands for which the average U-C bond distance was 2.76 Å (59). The pyrazolylate ligand was observed to coordinate
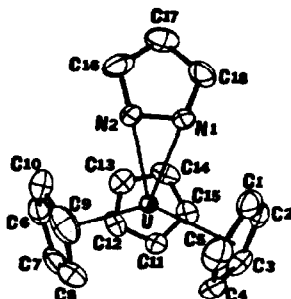
Fig. 16. The molecular structure of $U(C_5H_5)_3(C_2H_3N_2)$ from ref. 59.

in an unprecedented non-bridging η^2 mode, somewhat reminiscent of $Ti(C_5H_5)_3$ (60). The average U-N bond distance was found to be 2.38(1) Å. While most $U(C_5H_5)_3R$ complexes adopt structures in which the centroid(Cp)-U-centroid(Cp) angles and the centroid (Cp)-U-R angles are ca. 117° and 100°, respectively, the corresponding angles here were found in the ranges of 114-115° and 97-108°, indicative of the large size of the pyrazolate ligand. Actually, one of the centroid (Cp)-U-pyrazolate angles here was markedly less than the other two (97° vs. 106° and 108°), and this involved the C_5H_5 ligand which was nearly parallel to the pyrazolate ligand. Apparently, this C_5H_5 ligand can readily slip over toward the pyrazolate ligand in order to lessen steric interactions with the other C_5H_5 ligands. Overall, the metal-ligand bond distances were noted to be quite similar to those in $U(C_5H_5)_3(NCS)(CH_3CN)$ (61).

Goffart, Desreux, Gilbert, Delsa, Renkin, and Duyckaerts have reported the syntheses of $M(1\text{-ethylindenyl})_3Cl$ and $M(1,4,7\text{-trimethylindenyl})_3Cl$ (M = Th, U) complexes, including an x-ray structure determination of the latter uranium compound (62). The preparations involved the stoichiometric reactions of the appropriate metal tetrachloride with the potassium salt of the

substituted indenyl anion in THF. The mass spectra of these complexes were reported, with the strongest peak corresponding in each case to loss of a single substituted indenyl ligand from the parent ion. Only for the 1,4,7-trimethylindenyl compounds could peaks such as $M(indenyl)_2^+$ or $M(indenyl)_3^+$ be observed, suggesting that the chloride ion was more strongly bound in the less substituted complexes. Infrared and Raman spectral results were also reported, with the Th-Cl stretching modes being assigned to bands observed at 260 and 268 cm^{-1} for the two thorium compounds, and 267 cm^{-1} for both of the uranium compounds. The metal-"Cp" ring stretching vibrations were assigned to bands at 211 cm^{-1} and 190 cm^{-1} for the 1-ethylindenyl and 1,4,7-trimethylindenyl compounds (cf., 240 cm^{-1} in unsubstituted indenyls). Magnetic moments of 3.18 and 3.17 μ_B were obtained for the two uranium compounds. The structure of $U(1,4,7-trimethylindenyl)_3Cl$ is shown in Figure 17. Unlike other reported actinide indenyl compounds, the C_2 axis of
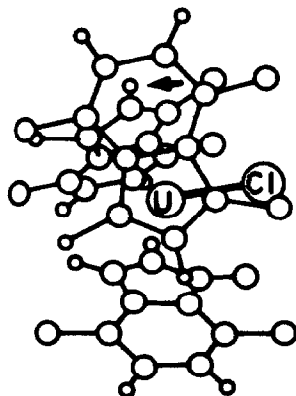
Fig. 17. The structure of $U(1,4,7-trimethylindenyl)_3Cl$ from ref. 62.

each indenyl ligand is not oriented approximately parallel to the U-Cl bond; rather, it is nearly perpendicular in this case. The U-C bonds involving the three outer indenyl carbon atoms were observed to be shorter than those involving the other two carbon atoms which are also part of the six-membered ring (2.72 vs. 2.91 Å); however, whether this should be attributed to true η^3-coordination, or to steric interactions could not be decided. Finally, ^{1}H NMR spectra indicated greatly restricted rotation around the U-indenyl bond axes, in contrast to the situation for less crowded actinide π-complexes.

Goffart, Piret-Meunier, and Duyckaerts have prepared a series of indenyl compounds of thorium and uranium (63, 64), as indicated by eqs. (29) - (34).

$$UCl_4 + NaC_9H_7 \xrightarrow{\text{THF}} U(C_9H_7)Cl_3(\text{THF})_2 \tag{29}$$

$$2MX_4 + M(C_9H_7)_3X \xrightarrow{\text{THF}} 3M(C_9H_7)X_3(\text{THF})_2 \tag{30}$$
M = U, X = Br, Cl; M = Th, X = Cl

$$M(C_9H_7)X_3(\text{THF})_2 + OP(C_6H_5)_3 \xrightarrow{\text{THF}} M(C_9H_7)X_3(\text{THF})(OP(C_6H_5)_3) \tag{31}$$
M = U, X = Br, Cl; M = Th, X = Cl

$$U(C_9H_7)Cl_3(\text{THF})_2 + 2OP(C_6H_5)_3 \xrightarrow{\text{THF}} U(C_9H_7)Cl_3(OP(C_6H_5)_3)_2 \tag{32}$$

$$MCl_4(OP(C_6H_5)_3)_2 + NaC_9H_7 \xrightarrow{\text{THF}} M(C_9H_7)Cl_3(OP(C_6H_5)_3)_2 \tag{33}$$
M = Th, U

$$M(C_9H_7)X_3(L)(\text{THF}) \xrightarrow{60°} \xrightarrow{\text{vacuum}} M(C_9H_7)X_3(L) \tag{34}$$
M = Th, X = Cl, L = THF, OP(C_6H_5)_3; M = U, X = Cl, Br, L = THF, OP(C_6H_5)_3
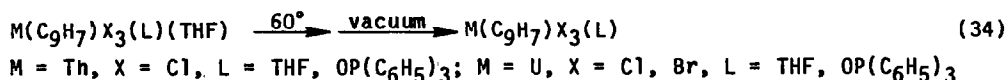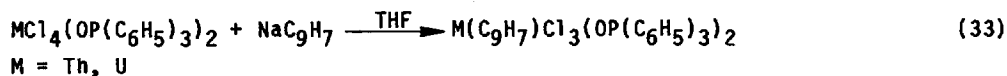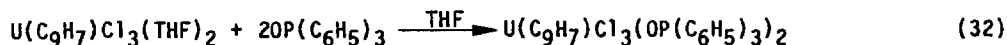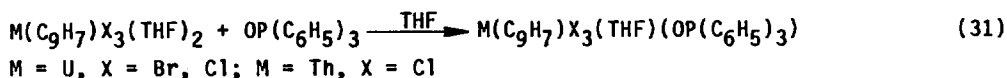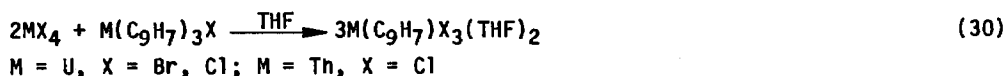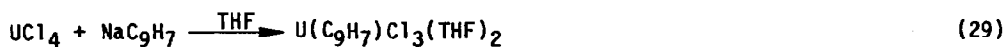
The $OP(C_6H_5)_3$ adducts of the mono(indenyl) complexes were found to be sensitive to ligand disproportionation, particularly for thorium (equation (35)).

$$3M(C_9H_7)_3(OP(C_6H_5)_3)_2 \longrightarrow M(C_9H_7)_3X + 2MX_4(OP(C_6H_5)_3)_2 \tag{35}$$
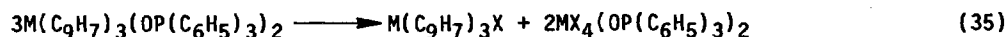
The vibrational spectra of these complexes were interpreted as showing An-Cl stretching modes at ca. 260 - 275 cm^{-1}, and the U-Br stretching mode at ca. 180 cm^{-1}. Magnetic moments of the uranium complexes were found to be ca. 3.6 μ_B (Curie-Weiss, $\theta \approx 220°$) or 2.7 μ_B (Curie).

Finke, Hirose, and Gaughan have reported on oxidative addition and related reactions of $U(C_5Me_5)_2Cl(\text{THF})$ (65). They found the monomeric compound undergoes extraordinarily rapid oxidation to a U(IV) species, the standard reduction potential being -1.3 V vs. saturated calomel electrode. Solutions of the U(III) compound in benzene reacted extremely rapidly with a wide variety of alkyl halides, as well as with iodine, yielding predominately the U(IV) dihalides, although smaller amounts of $U(C_5Me_5)_2(X)(R)$ species, and products resulting from ligand redistribution reactions, were observed. Various redistribution equilibria were measured, such as equation (36).

$$2U(C_5Me_5)_2(Cl)I \longrightarrow U(C_5Me_5)_2Cl_2 + U(C_5Me_5)_2I_2 \tag{36}$$
K = 0.18 ± 0.02.
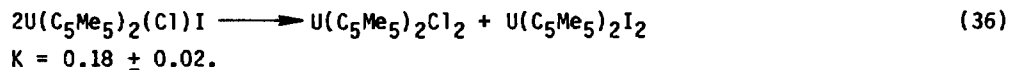
A nearly simultaneous report by Finke, Schiraldi, and Hirose described pertinent kinetic and mechanistic data for the above oxidative addition

reactions (66). These reactions were believed to occur via halogen abstraction by $U(C_5Me_5)_2Cl$, and were found to be first order in both alkyl halide and uranium(III) complex concentrations, and were strongly inhibited by added THF. In fact, the relative reactivities of $U(C_5Me_5)_2Cl$ and $U(C_5Me_5)_2Cl(THF)$ were estimated to be ca. 20:0. A number of observations supported the halogen abstraction process, including evidence for free alkyl radical intermediates (e.g., rearrangement of cyclopropylcarbinyl species, and the relative rates observed for various types of alkyl groups were benzyl ~ tertiary > secondary > primary > neopentyl, and RI >> RBr > RCl). The relative rates for various alkyl halide reactions correlated well with the corresponding reactions for $\cdot Sn(C_4H_9)_3$, which is known to undergo halogen atom abstraction reactions. In fact, $\cdot Sn(C_4H_9)_3$ undergoes such reactions with several alkyl chlorides at a rate only ca. 42 times faster than that of $U(C_5Me_5)_2Cl$. The rates of abstraction for the $U(C_5Me_5)_2Cl$ complex are much greater than for any comparable transition metal complex by a factor of 10^4 – 10^7, and still 4 times more rapid than that by the S_N2 reagent $Fe(CO)_4^{2-}$. As part of this study, the following important equilibrium was measured at 22° in benzene (eq. (37)).

$$U(C_5Me_5)_2Cl(THF) \longrightarrow U(C_5Me_5)_2Cl + THF \qquad (37)$$
$$K = 0.014 \pm 0.002$$
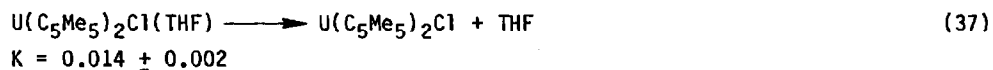
Leonov, Solov'eva, Vertyulina, Kozina, and Arsen'eva have reported a number of reactions of $U(C_5H_5)_4$ with protic compounds (67). Treatment with 10% HCl and hexane led to the dissolution of most of the uranium into the HCl phase as U^{4+}, while a small portion was detected as a uranyl complex. With concentrated HCl, UO_2Cl_2 was formed. The reaction with gaseous HCl led to a product purported to be $U(C_5H_5)_4(HCl)_4$, from which it was claimed two equivalents of HCl could be removed in vacuo. Reactions with acetic acid and methanol (65°) led to uranium(IV) acetate and uranium(IV) methoxide.

A number of reports concerning cyclooctatetraenyl compounds have appeared. Volkov, Legin, and Suglobov have reported details for the high yield (> 90%) synthesis of uranocene, $U(C_8H_8)_2$, from activated uranium powder and cyclooctatetraene at room temperature (68). It was reported that UH_3 would also react with cyclooctatetraene, but that the yields of uranocene were significantly lower. A variation in the synthesis of uranocene has been reported by Evans, Wink, Wayda, and Little (69) in which $K_2C_8H_8$ is prepared by the prolonged reaction of potassium metal with excess 1,5-cyclooctadiene at 180°. Reasonable yields are obtained (68%), but the key advantage to this procedure is that the more expensive cyclooctatetraene need not be used.

Miller, Lyttle, and Streitwieser have reported the syntheses of several $\underline{t}$-butyl substituted cyclooctatetraenes, including 1,4-di($\underline{t}$-butyl)cyclooctatetraene, from which the air-sensitive 1,1',4,4'-tetra-$\underline{t}$-butyluranocene was prepared in ca. 31% yield (70). Similarly, Luke, Berryhill, and Streitwieser have reported the compound bis(cyclobutenocyclooctatetraene)uranium from the reaction of UCl_4 with the potassium salt of the bicyclo[6.2.0]deca-1,3,5,7-tetraenyl dianion (71). Spectroscopic and magnetic data indicated that annulation brought about little if any perturbation on the uranocene complex. Spectroscopic and reaction studies were undertaken to see if any cyclobutene-butadiene type of equilibrium might be established; no such evidence could be found. In a somewhat different fashion, Miller and Streitwieser have reported the compound bis(dicyclooctatetraenyl)diuranium, or "biuranocenylene" (72), as an analog to "biferrocenylene", bis(fulvalene)diiron. The reaction of two equivalents of the dicyclooctatetraenyl dianion with UCl_4 led to a mixture of products, from which the lime green $U(C_8H_7R)_2$ (R = C_8H_7) could be isolated by Soxhlet extraction with hexane (32-45% yield). Subsequent extraction of the residue with hot THF led to isolation of the olive-green $U(C_8H_7-C_8H_7)_2U$ in 45% yield. This compound could also be obtained from the reaction of the above lime-green uranocene complex with finely divided uranium metal (10-20% yield). The presence of a large parent ion in the mass spectrum suggested that the presumed dimetallic compound was not polymeric. ^{1}H NMR data indicated, however, that unlike bis(fulvalene)diiron, the connected C_8H_7 rings appeared to be markedly noncoplanar, and this was correlated with the observed diminished thermal stability of this compound.

Billiau, Folcher, Marquet-Ellis, Rigny, and Saito have reported that uranocene may be reduced to the corresponding U(III) anion (73). Thus, treatment of uranocene with one equivalent of lithium naphthalenide seemed to lead to the desired complex as a THF-solvated lithium salt, which could also be prepared by the direct interaction of "$UCl_3 \cdot THF$" with two equivalents of $K_2C_8H_8$. ESR and electronic spectra evidenced the absence of both starting materials, but the presence of free naphthalene in the initial reaction solution. The ^{1}H NMR spectrum contained a single broad resonance at ca. -30 ppm. That the complex was truly a U(III) compound was indicated by its ESR and variable temberature NMR spectra, as well as the fact that the compound would reduce Ti($\underline{i}$-OC_3H_7)$_4$ to a Ti(III) species, and $U(C_5H_5)_3Cl$ to $U(C_5H_5)_3$.

Levanda and Streitwieser have reported a series of substituted thoracene compounds, prepared as in equations (38) - (40), with yields ranging from low to high (74). The presence of alkyl groups in these complexes substantially
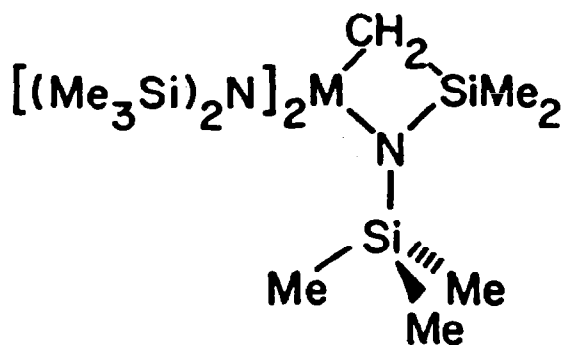
$$ThCl_4 + 2K_2C_8H_7R \xrightarrow{\text{THF or DME}} Th(C_8H_7R)_2 \qquad (38)$$
$$R = H, CH_3, \underline{n}\text{-}C_4H_9, C_6H_5$$

$$ThCl_4 + 2K_2(1,4\text{-}(\underline{t}\text{-}C_4H_9)_2C_8H_6) \xrightarrow{\text{THF or DME}} Th(1,4\text{-}(\underline{t}\text{-}C_4H_9)_2C_8H_6)_2 \qquad (39)$$

$$ThCl_4 + 2K_2(1,3,5,7\text{-}(CH_3)_4C_8H_4) \xrightarrow{\text{THF or DME}} Th(1,3,5,7\text{-}(CH_3)_4C_8H_4)_2 \qquad (40)$$
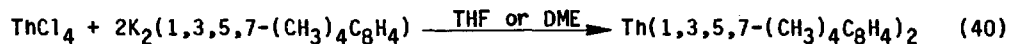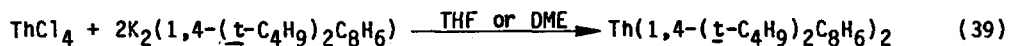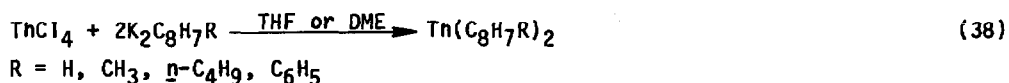
enhanced their solubility relative to $Th(C_8H_8)_2$, and this allowed the
recording of their ^1H and ^{13}C NMR spectra. Interestingly, the ^{13}C chemical
shifts were approximately midway between those of C_8H_8 and $K_2C_8H_8$, which was
interpreted as perhaps indicating a net charge of approximately -1 on each
coordinated C_8H_8 ligand. Similar to uranocene, the substituted thoracenes
were found to react rapidly with organic nitro compounds, yielding, for
example, azobenzene from nitrobenzene. The coordinated cyclooctatetraene
ligands would not undergo exchange with free cyclooctatetraenes, but rapid
exchange was observed with free cyclooctatetraene dianions. Reaction of $Th(\underline{n}\text{-}$
$C_4H_9C_8H_7)_2$ with UCl_4 produced the expected uranocene complex, but only very
slowly.

Miller and DeKock have reported that the interaction of UCl_4 with three
equivalents of lithium cycloheptadienide results in a rapid reaction which
produces an unstable organouranium(IV) complex [16]. However, chemical
evidence indicated that the isolated complex did not contain the expected $C_7H_9^-$
ligand, but instead the aromatic, 10π-electron $C_7H_7^{3-}$, apparently formed by two
deprotonations of coordinated $C_7H_9^-$ by free $C_7H_9^-$ (large quantities of free
cycloheptadiene were detected following the reaction). Thus, deuterolysis of
the initial red complex led only to trideuterated cycloheptadienes, and
hydrolysis of 6-substituted complexes led to a mixture of products in which at
least six substituted cycloheptadienes were present (only three would be
expected for $C_7H_8R^-$ ligands, whereas eight would be expected for $C_7H_6R^{3-}$
ligands). However, after several hours the red complex decomposed to a black
material, which was believed to include U(III) and $C_7H_7^-$ species, formed via an
internal redox reaction. Thus, hydrolysis of the black materials did lead to
some cycloheptatriene, the quantity of which increased with the time the
compound had been standing, and deuterolysis led to some cycloheptatriene-
d_1. The ^1H NMR spectrum of the $C_7H_7^{3-}$ adduct contained a single resonance at
-46.5 ppm, while the $\underline{n}\text{-}C_4H_9C_7H_6^{3-}$ adduct displayed three equal intensity
resonances for the six ring protons (-40.6, -48.6, and -53.0 ppm). Somewhat
similar behavior was also observed for several related lanthanide complexes
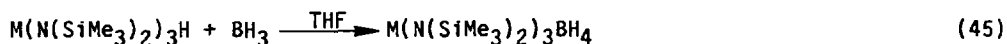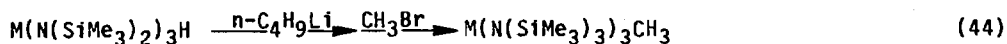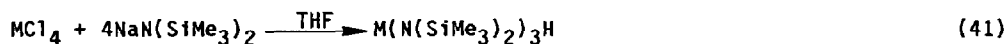(vide supra).

A wide range of new actinide hydride and alkyl complexes has been

reported. Andersen, Zalkin, and Templeton have published a preliminary communication of the structure of the previously described $U(N(SiMe_3)_2)_3H$ complex (75). The compound was found to be isomorphous with related $M(N(SiMe_3)_2)_3$ (M = Nd, U) and $Th(N(SiMe_3)_2)_3H$ complexes. Even though the hydride ligand could not be located, the unit cell differences between the U(III) and U(IV) cyrstals provided good evidence of its presence. The uranium atom position was disordered, but a reasonable U(IV)-N bond distance of 2.237(9) Å was reported.

Simpson, Turner, and Andersen have published a full account of the preparation of various $M(N(SiMe_3)_3)_3X$ (M = Th, U; X = H, D, CH_3, BH_4) complexes, as well as the metallacycles $M(N(SiMe_3)_2)_2(CH_2)Si(Me)_2NSiMe_3$ (76).

$$[(Me_3Si)_2N]_2M \begin{array}{c} CH_2 \\ \diagup \quad \diagdown \\ \quad \quad SiMe_2 \\ \diagdown \quad \diagup \\ N \\ | \\ Si \\ \diagup \quad \diagdown \\ Me \quad Me \\ Me \end{array}$$

Some of the routes available to these compounds are summarized in equations (41) - (45). For the hydride products formed from equation (41), substantial

$$MCl_4 + 4NaN(SiMe_3)_2 \xrightarrow{THF} M(N(SiMe_3)_2)_3H \tag{41}$$

$$MCl_4 + 4NaN(SiMe_3)_2 \xrightarrow{THF-d_8} M(N(SiMe_3)_2)_3D \tag{42}$$

$$M(N(SiMe_3)_2)_3H \xrightarrow{n-C_4H_9Li} \xrightarrow{D^+} M(N(SiMe_3)_2)_3D \tag{43}$$

$$M(N(SiMe_3)_2)_3H \xrightarrow{n-C_4H_9Li} \xrightarrow{CH_3Br} M(N(SiMe_3)_3)_3CH_3 \tag{44}$$

$$M(N(SiMe_3)_2)_3H + BH_3 \xrightarrow{THF} M(N(SiMe_3)_2)_3BH_4 \tag{45}$$

spectroscopic and reactivity data have been obtained. Thus, the M-H and M-D stretching frequencies for the thorium compound were observed at 1480 and 1060 cm^{-1}, while those for the uranium compound were observed at 1430 and 1020

cm^{-1}, respectively. The ^1H NMR spectrum of the thorium hydride contains a peak at 0.63 ppm, which is absent in the deuteride compound. Treatment of the hydrides with CCl_4 leads to the $M(N(SiMe_3)_2)_3Cl$ compounds and $CHCl_3$. Interestingly, the results of equations (43) - (45) suggest that the hydride ligands actually display somewhat amphoteric behavior. Perhaps most interestingly, however, is the fact that the hydride compounds react with D_2, leading to exchange of deuterium for all 55 hydrogen atoms in the molecule. A mechanism was proposed which implicated the metallacycle complexes described above. In this scheme, the starting hydride complexes are believed to split off H_2, which is formed from the hydride ligand and a hydrogen atom in one of the $Si(CH_3)_3$ groups. The resulting complex could then add D_2 to generate a deuteride complex, in which one of the $Si(CH_3)_3$ groups has become a $Si(CH_3)_2(CH_2D)$ group. Subsequently, HD could be lost, regenerating a monodeutero-metallacycle, which could then add D_2, etc. In fact, the thorium metallacycle complex could be prepared by thermolysis of the hydride complexes, and regenerated by exposure to H_2. The metallacycles could also be prepared by thermolysis of the methyl compounds, or by treatment of the $M(N(SiMe_3)_2)_3Cl$ complexes with reagents such as C_2H_5Li, Me_3SiCH_2Li, $(Me_3SiCH_2)_2Mg$, or $(C_2H_5)_2Mg$.

Fagan, Manriquez, Maatta, Seyam, and Marks have presented a full account of the syntheses and properties of $M(C_5Me_5)_2X_2$ (M = Th, U; X = H, Cl, alkyl) compounds (77). Equations (46) - (50) describe some of the synthetic routes. It was found that three pentamethylcyclopentadienyl ligands could not be incorporated into the complexes. Except for the hydrides, pseudotetrahedral

$$MCl_4 + 2Mg(C_5Me_5)Cl(THF) \xrightarrow{\text{toluene}} M(C_5Me_5)_2Cl_2 \qquad (46)$$
M = Th, U

$$M(C_5Me_5)_2Cl_2 + 2LiR \xrightarrow{\text{pentane}} M(C_5Me_5)_2R_2 \qquad (47)$$
M = Th, U; R = CH_3, CH_2SiMe_3, C_6H_5, $CH_2C_6H_5$;
M = Th, R = CH_2CMe_3

$$M(C_5Me_5)_2Cl_2 + LiR \xrightarrow{\text{pentane}} M(C_5Me_5)_2(R)Cl \qquad (48)$$
M = Th, U; R = CH_2SiMe_3, CH_2CMe_3, C_6H_5, $CH_2C_6H_5$

$$M(C_5Me_5)_2Cl_2 + M(C_5Me_5)_2R_2 \xrightarrow{\text{toluene}} 2M(C_5Me_5)_2(R)Cl \qquad (49)$$
M = Th, U; R = CH_3

$$M(C_5Me_5)_2R_2 + H_2 \xrightarrow{\text{toluene}} [M(C_5Me_5)_2(\mu-H)H]_2 \qquad (50)$$
M = Th, U; R = CH_3, CH_2SiMe_3
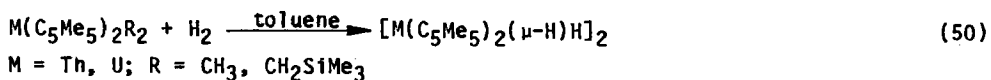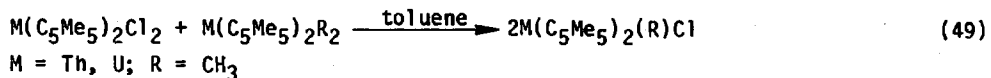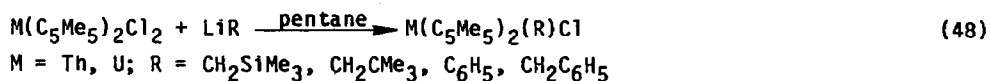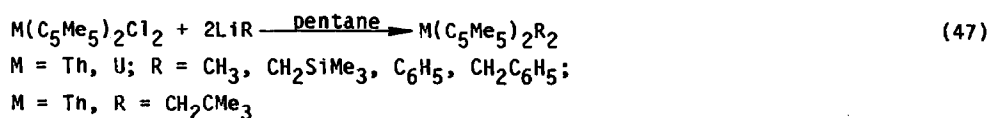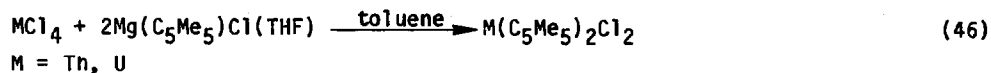
structures were postulated for the above species, most of which were shown to be monomeric. The thorium complexes were observed to be less soluble but generally more thermally stable than those of uranium, and the infrared spectra for analogous thorium and uranium compounds were nearly identical. Variable temperature ^{1}H NMR spectra indicated that hindered rotation takes place around the U-C σ-bonds in $U(C_5Me_5)_2(C_6H_5)_2$ and $U(C_5Me_5)_2(C_6H_5)Cl$, with $\Delta G^{\neq}$ = 12.4 $\pm$ 1.0 kcal/mole at 40° for the first compound, and 13.5 $\pm$ 0.3 kcal/mole at 65° for the second. In addition to the above alkyl compounds, a chelating dialkyl complex of uranium could be prepared from $U(C_5Me_5)_2Cl_2$ and the dilithium salt of tetraphenylbutadiene. The proposed structure of the molecule is shown below. Interestingly, the thermal stabilities of the
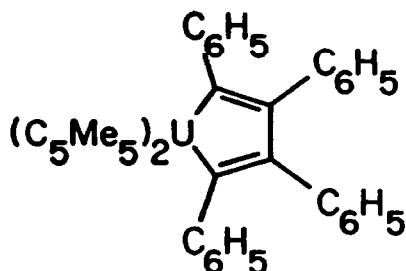
diphenyl compounds were found to be markedly solvent dependent: while these species were stable in refluxing benzene, decomposition occurred in pentane even at room temperature. It was found by NMR that solutions of $U(C_5Me_5)_2(C_6H_5)_2$ in C_6D_6 rapidly underwent first order incorporation of deuterium into the phenyl groups. Isolation of the bis(C_6D_5) complex, followed by dissolution in C_6D_6, led to regeneration of the starting material. The above observations were explained by postulating the abstraction of an <u>ortho</u>-hydrogen atom from one phenyl group by the partner phenyl group, producing free benzene and the benzyne complex, $U(C_5Me_5)_2(C_6H_4)$. The benzyne complex could subsequently react with C_6D_6 to yield $U(C_5Me_5)_2(C_6D_5)(\underline{o}-C_6DH_4)$. Subsequent reformations of similar, but deuterated, benzyne complexes, followed by exposure to C_6D_6, would lead to $U(C_5Me_5)_2(C_6D_5)_2$. In fact, the authors provided further support for this proposal by trapping the postulated benzyne intermediate with diphenylacetylene, leading to the product below, which was formed at a rate indistinguishable from the rate of loss of the C_6H_5 resonances for $U(C_5Me_5)_2(C_6H_5)_2$ in C_6D_6. Interestingly, at 100° $Th(C_5Me_5)_2(CH_2CMe_3)_2$ could also be converted to bis(C_6H_5) and bis(C_6D_5) complexes in C_6H_6 or C_6D_6, respectively. The authors also explored the reactivity of the metal-alkyl

$$(C_5Me_5)_2U \diagdown \overset{\displaystyle \bigcirc}{\underset{\underset{\displaystyle C_6H_5}{|}}{\diagdown}} C_6H_5$$
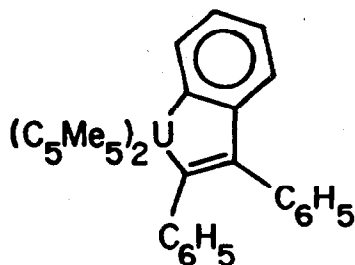
bonds. The dimethyl compounds were found to react rapidly with acetone at room temperature, leading to t-butoxide compounds. From competitive experiments at -78°, it was found that the first methyl group in the thorium compound was converted 30 times more rapidly than that for uranium. The second methyl groups were converted to t-butoxide at much slower rates, with the thorium methyl again being more reactive, by a factor of 20. Similarly, reactions with alcohols led to alkoxides (and alkene). Results of competitive experiments using t-butanol at -78° were similar to the above, with the first thorium methyl group being lost at a rate 1.5 times as rapidly as for uranium, and the second thorium methyl group being lost 4 times as rapidly as that for uranium. Cleavage with I_2 at -78° to yield actinide iodides followed a similar course, with the relative rates for thorium relative to uranium being 3 and 2, for the first and second M-CH3 bonds, respectively. As depicted in equation (50), the actinide dimethyls and bis(trimethylsilylmethyls) react readily with H_2 to yield the dimeric dihydrides. The solid state structure of the thorium complex had previously been reported (78). When deuterium was employed in the above reactions, the corresponding thorium deuteride could be isolated, but for uranium, extensive incorporation of deuterium into the C_5Me_5 ligands occurred. It was also found that exposure of the thorium dihydride to D_2 led rapidly to the dideuteride, which could be reconverted to the dihydride with H_2. In fact, in the ^{1}H NMR spectrum of the dihydride under hydrogen (0.75 atmosphere), one could observe exchange between free H_2 and the hydride ligands. The infrared spectrum of the thorium dihydride contained bands assignable to terminal Th-H stretching modes (1404 and 1370 cm^{-1}) and bridging Th-H stretching modes (650 - 1215 cm^{-1}). The terminal modes were observed to shift to 1002 and 979 cm^{-1} on deuteration. The ^{1}H NMR spectrum of the thorium dihydride contained a single thorium hydride resonance at 19.2 ppm even at low temperatures, assignable to the hydride ligands, indicating facile exchange of the terminal and bridging hydrides. For the uranium dihydride, a resonance at 316.8 ppm could be similarly assigned, and once again this remained a singlet down to low temperatures. Unlike the thermally robust thorium dihydride, the

uranium dihydride was found to lose (reversibly) ca. 0.5 equivalents of H_2 at room temperature under vacuum, apparently leading to a $[U(C_5Me_5)_2H]_x$ complex. The ^{1}H NMR spectrum of this species contained a singlet at -9.37 ppm, which was assigned to methyl groups in the U(III) complex (a hydride resonance was not located). This resonance was broader (18 vs. 4 Hz.) than the corresponding resonance at -2.27 ppm for the U(IV) dihydride. Analogous to the thorium dimethyl complex, the thorium dihydride was found to react with $Th(C_5Me_5)_2Cl_2$ to yield $[Th(C_5Me_5)_2(H)Cl]_2$, which was postulated to have bridging hydride and terminal chloride ligands. Similar attempts for uranium, however, led to $[U(C_5Me_5)_2Cl]_3$. The hydridic nature of the hydride ligands was readily established through chemical reactivity studies. The dimeric thorium dihydride could be quantitatively converted to the dichloride by reaction with 4 equivalents of CH_3Cl. The uranium dihydride reacted similarly, except that a 4:1 ratio of $U(C_5Me_5)_2Cl_2$ to $U(C_5Me_5)_2(CH_3)Cl$ was found. Similarly, the thorium dihydride was found to react with 4 equivalents of acetone or t-butanol to form the di(iso-propoxide) or di(t-butoxide), respectively. The presumed intermediate $Th(C_5Me_5)_2(OR)H$ complexes could not be detected, although $Th(C_5Me_5)_2(O-t-C_4H_9)H$ could be prepared by hydrogenolysis of $Th(C_5Me_5)_2(O-t-C_4H_9)(CH_3)$. Infrared and NMR spectral evidence were consistent with a monomeric structure. The thorium dihydride was also found to react with ethylene, leading to the diethyl compound. While reasonably stable, this compound did appear to decompose during the recording of infrared spectra, with the appearance of new bands similar to those expected for bridging hydride ligands. The formation of $[Th(C_5Me_5)_2(\mu-H)C_2H_5]_2$ was suggested as a possibility. Both the thorium and uranium dihydrides were found to be very active catalysts for the homogeneous hydrogenation of olefins (e.g., 1-hexene and even diphenylacetylene), with the starting metal complex being recovered unchanged after the olefin had been hydrogenated. The uranium catalyst was more active than the thorium one, and over 800 turnovers could be attained without any observable loss of efficiency. It was suggested that the catalytic cycle depended on the breakup of the dihydride dimers into monomers.

Edwards, Andersen, and Zalkin have reported $MX_4(DMPE)_2$ complexes (M = U, X = Cl, Br; M = Th, X = Cl, I), which were prepared by the direct combination of the metal tetrahalide with 1,2-bis(dimethylphosphino)ethane (79). Treatment of the chloride compounds with methyllithium led to the $M(CH_3)_4(DMPE)_2$ complexes, which possessed reasonable thermal stabilities. These complexes were found to react with phenol to yield the respective $M(OC_6H_5)_4(DMPE)_2$ compounds. A single crystal x-ray diffraction study confirmed the nature of $U(OC_6H_5)_4(DMPE)_2$.

Cramer, Maynard, Paw, and Gilje have published a preliminary report on the solid state structure of $U(C_5H_5)_3CHP(CH_3)_2(C_6H_5)$ (80). The compound had been prepared from $U(C_5H_5)_3Cl$ and $Li(CH_2)_2P(CH_3)(C_6H_5)$, during which one methylene group apparently abstracted a hydrogen atom from the other methylene group, somewhat reminiscent of transition metal α-hydride abstractions, which can lead to alkylidene complexes (81). The solid state structure (Figure 18) was found to be based on the common pseudo-tetrahedral geometry adopted by many $U(C_5H_5)_3X$ complexes. Particularly notable, however, was the short U-C bond to the ylide ligand (2.29(3) Å), which seems to suggest the occurrence of some U-C multiple bonding. The U-C-P angle was observed to be somewhat large at 142(1)°, while the U-C(Cp) bond distances averaged 2.79(3) Å.

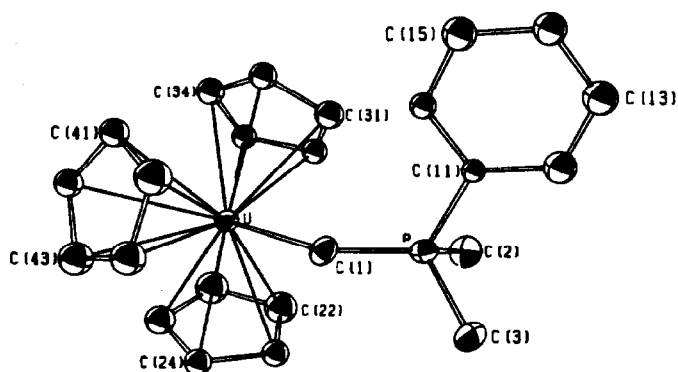Fig. 18. The solid state structure of $U(C_5H_5)_3[CHPMe_2(C_6H_5)]$ from ref. 80.

Cramer, Maynard, and Gilje have also published a full paper dealing with the reactions of lithium phosphoylides in varying proportions with $U(C_5H_5)_3Cl$ (82). Equations (51) - (55) illustrate the variety of products isolated by these authors. The products of equation (51) have essentially been

$$U(C_5H_5)_3Cl + Li(CH_2)_2P(CH_3)_x(C_6H_5)_y \xrightarrow{\text{THF}} U(C_5H_5)_3[(CH)P(CH_3)_x(C_6H_5)_y] \quad (51)$$
$$x = 0, \; y = 2; \; x = 1, \; y = 1$$

$$U(C_5H_5)_3Cl + 2Li(CH_2)_2P(C_6H_5)_2 \xrightarrow{\text{THF}} \tfrac{1}{2} U(C_5H_5)_2[CHP(C_6H_5)_2CH_2]_2- \quad (52)$$
$$U(C_5H_5)_2$$

$$U(C_5H_5)_3Cl + 3Li(CH_2)_2P(CH_3)_x(C_6H_5)_y \xrightarrow{\text{ether}} U(C_5H_5)[(CH_2)_2- \quad (53)$$
$$P(CH_3)_x(C_6H_5)_y]_3$$
$$x = 0, \; y = 2; \; x = 1, \; y = 1$$

$$U(C_5H_5)Cl_3(THF)_2 + 3Li(CH_2)_2P(CH_3)_x(C_6H_5)_y \xrightarrow{THF} U(C_5H_5)[(CH_2)_2- \qquad (54)$$
$$P(CH_3)_x(C_6H_5)_y]_3$$

$$U(C_5H_5)_3[(CH)P(CH_3)_2(C_6H_5)] + 2Li(CH_2)_2P(CH_3)(C_6H_5) \xrightarrow{THF} \qquad (55)$$
$$U(C_5H_5)[(CH_2)_2P(CH_3)(C_6H_5)]_3$$
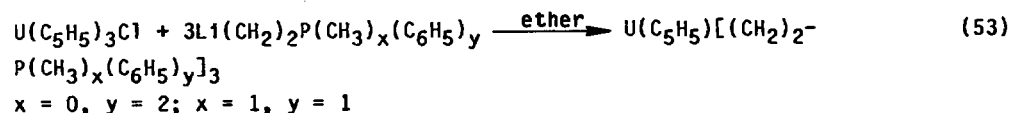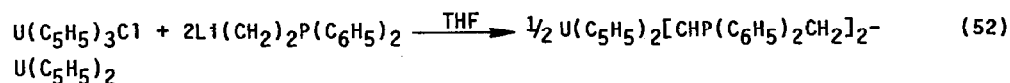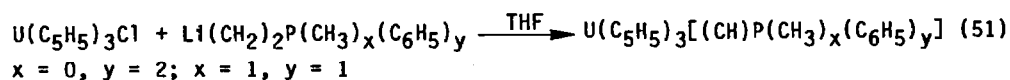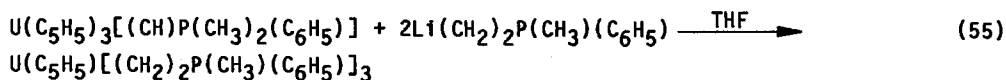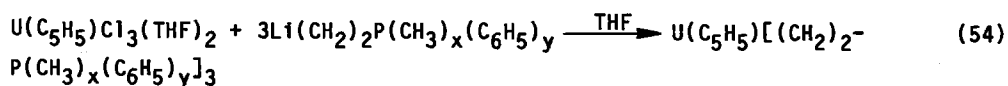
discussed above already; however, it is noteworthy that in a subsequent reaction with two equivalents of a lithium phosphoylide (equation (55)), the α-hydrogen abstraction process seems to be reversed. Treatment of $U(C_5H_5)_3Cl$ with two equivalents of a lithium phosphoylide, equation (52), leads to a novel dimetallic complex, in which two $U(C_5H_5)_2$ units are bridged by the two ylide fragments (Figure 19). In the figure, the CH moieties are
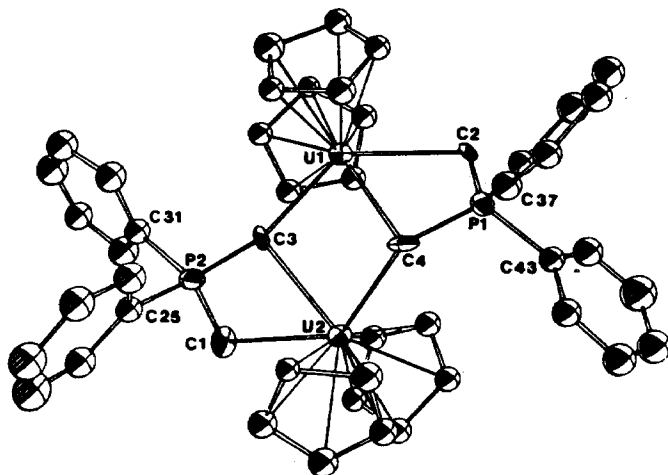
Fig. 19. The structure of $[U(C_5H_5)_2]_2[CHP(C_6H_5)_2CH_2]_2$ from ref. 81.

those (C3 and C4) which bridge the two uranium atoms. It was found that this same complex could be prepared from the product of equation (51) by treatment with an extra equivalent of $Li(CH_2)_2P(C_6H_5)_2$. This suggested that the added ylide might be simply deprotonating the $P-CH_3$ group on the initially coordinated ylide of the starting material. If this were true, it might be expected that other lithium alkyls could be substituted for the second equivalent of $Li(CH_2)_2P(C_6H_5)_2$; however, such attempts did not appear to work. Interestingly, the dimetallic complex was found to be fluxional by variable temperature ^{1}H NMR spectroscopy. Finally, tris(ylide) complexes could be isolated by means of equations (53) - (55). The structure of

$U(C_5H_5)[(CH_2)_2P(C_6H_5)_2]_3$ can be seen in Figure 20. One can note that the coordination geometry may roughly be considered to be pentagonal bipyramidal.
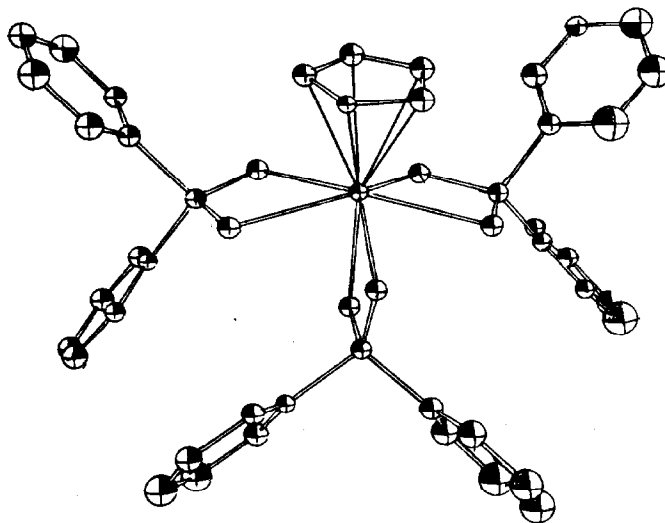
Fig. 20. The molecular structure of $U(C_5H_5)[(CH_2)_2P(C_6H_5)_2]_3$ from ref. 82.

Arnaudet, Folcher, and Marquet-Ellis have reported on the reaction of $U(C_5H_5)_3R$ complexes (R = CH_3, $\underline{n}-C_4H_9$) with SO_2 (83). At -60° a reaction occurred, which was believed to lead to $U(C_5H_5)_3(SO_2R)$ insertion products, and large ^{1}H NMR shifts of the R groups were observed. On warming to room temperature, however, a subsequent reaction led to an insoluble complexes such as $U_2(C_5H_5)_5(SO_2)_4(CH_3)_2$.

Other insertion products have been reported by Simpson and Andersen (84). Using the thorium or uranium metallacycles shown below, they found that insertion reactions for $\underline{t}-C_4H_9CN$, $\underline{t}-C_4H_9NC$, and CO occur (between the U-C bond) although for Me_3SiN_3, only simple adduct formation took place.
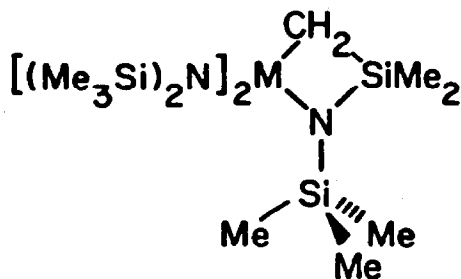
Spectroscopic data for the $\underline{t}$-C_4H_9CN insertion products were interpreted as indicating the product shown below. Interestingly, it appeared that the

$$[(Me_3Si)_2N]_2 M \overset{\displaystyle Me_3Si \quad Me}{\underset{N=\underset{CMe_3}{\overset{\cdots}{\Big|}}}{\overset{N-Si}{\Big|}}}$$
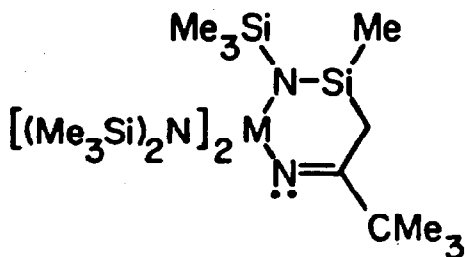
lower nitrogen atom could be protonated or methylated, but these products could not be readily purified. A considerably different course was followed by $\underline{t}$-C_4H_9NC, leading to a product formulated as shown below. One can readily

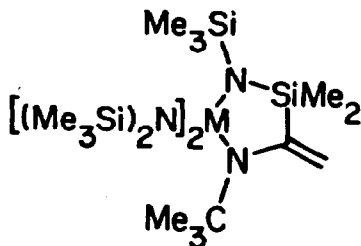$$[(Me_3Si)_2N]_2 M \overset{Me_3Si}{\underset{Me_3C}{\overset{N-SiMe_2}{\underset{N}{\Big|}}}}$$

observe that much more than a single insertion step is involved. The authors favored a process in which insertion into the metal-carbon bond occurred first, followed by insertion of the isocyanide ligand carbon atom into the carbon-silicon bond. In fact, a quite analogous reaction was observed for CO, giving the product below. The $\underline{t}$-C_4H_9CN products could not be protonated or methylated.

$$[(Me_3Si)_2N]_2 M \overset{Me_3Si}{\underset{O}{\overset{N-SiMe_2}{\Big|}}}$$
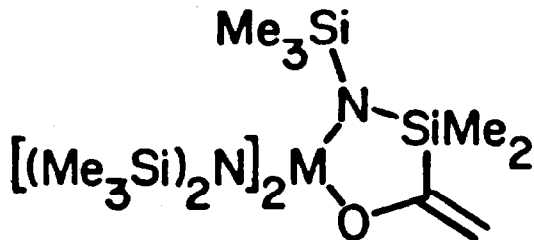
A variety of CO insertion reactions have been reported by the Marks

group. Maatta and Marks (85) have published a preliminary account of the homogeneous hydrogenation of the η^2-acyl complexes, $M(C_5Me_5)_2(\eta^2\text{-OCR})Cl$ (M = U, R = C_6H_5; M = Th, R = CH_2CMe_3), catalyzed by $[Th(C_5Me_5)_2H_2]_2$, which can be quantitatively recovered. In each case, the major product is the alkoxide, $M(C_5Me_5)_2(OCH_2R)Cl$, which could be prepared independently from $M(C_5Me_5)_2Cl_2$ by treatment with one equivalent of alkoxide, or from $M(C_5Me_5)_2(R)Cl$, by treatment with one equivalent of paraformaldehyde. Deuteration studies demonstrated that the incorporation of D_2 took place only at the α-carbon atom of the alkoxide. In the absence of H_2 or D_2, however, the catalyst brought about an isomerization of the thorium acyl complex to a trans-enolate (below). Through deuteration experiments, it was established that H'
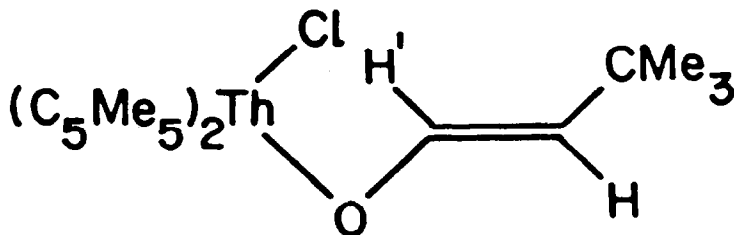
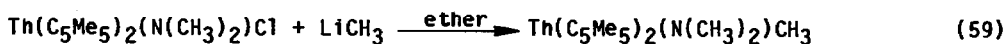originated in the catalyst. In the presence of H_2, the above isomerization is not competitive with hydrogenation. That isomerization is actually somewhat slower demonstrates that the isomerization was not a prerequisite for hydrogenation. A possible scheme to explain these transformations was proposed, based on an initial insertion of the carbon atom of the acyl ligand into a Th-D bond of the catalyst, leading to $[Th(C_5Me_5)_2Cl]\text{-OCD}(CH_2CMe_3)$-$[Th(C_5Me_5)_2D]$. This proposed intermediate could then undergo either β-hydride elimination, yielding $Th(C_5Me_5)_2(D)H$ and the isomerized product, $Th(C_5Me_5)_2(OC(D)=C(H)CMe_3)$, or else it could undergo Th-C bond hydrogenolysis, leading (with D_2) to $Th(C_5Me_5)_2D_2$ and $Th(C_5Me_5)_2(OCD_2CH_2CMe_3)Cl$. The formation of a trans olefin in the isomerization product could readily be explained from this scheme as a result of steric factors.

Fagan, Moloy, and Marks have also communicated evidence for the formation of actinide formyls via migratory insertion of CO into metal-hydrogen bonds (86). For this study, several complexes of stoichiometries $Th(C_5Me_5)_2(OR)H$ (R = t-C_4H_9), $C(t\text{-}C_4H_9)_2H$, o-2,6-$(t\text{-}C_4H_9)_2C_6H_3$) were prepared by various routes. The first complex was found to react with CO, yielding an enediolate, with a half-life of ca. 3 minutes, while the second had a corresponding half-life of ca. 5 hours. The third complex did not seem to form an enediolate. However, while enediolate formation for the latter two compounds was slow,

rapid reactions with CO were observed at -78°, producing yellowish solutions, which suggests (reversible) formation of an η^2-formyl ligand. In fact, the ΔH values for these latter processes could be estimated as ca. -4.5 ± 0.9 and -5.9 ± 1.5 kcal/mole, with ΔS values of -11.7 ± 4.3 eu and -23.9 ± 7.4 eu, respectively. That these complexes were indeed η^2-formyl compounds was demonstrated by infrared spectra (loss of Th-H at 1355 cm^{-1}, gain in C=O at 1477 cm^{-1} for ^{12}CO and 1443 cm^{-1} for ^{13}CO for the second alkoxy hydride) and NMR spectra (^1H resonances for the formyl ligands were observed at 15.2 and 14.7 ppm, respectively; ^{13}C resonances at 372 and 360 ppm, $J(^{13}C-H) = 114$ Hz). The NMR spectra also indicated that the CO insertion/extrusion process was very rapid on the NMR timescale by -40°, and from magnetization transfer experiments on a mixture of $Th(C_5Me_5)_2(OR)H$ compounds ($R = C(\underline{t}-C_4H_9)_2H$, 2,6-$(\underline{t}-C_4H_9)_2C_6H_3$) under CO, it could be concluded that intermolecular transfer of hydride ligands was not important.

Fagan, Manriquez, Vollmer, Day, Day, and Marks have reported extensively on thorium and uranium complexes of stoichiometries $M(C_5^\cdot Me_5)_2(NR_2)Cl$ ($R = CH_3$, C_2H_5) and $M(C_5Me_5)_2(NR_2)_2$ ($M = Th$, U, $R = CH_3$; $M = U$, $R = C_2H_5$) and their chemical and physical properties (87). The appropriate complexes were prepared as outlined in equations (56) - (59). For these complexes, variable

$$M(C_5Me_5)_2Cl_2 + LiNR_2 \xrightarrow{\text{ether}} M(C_5Me_5)_2(NR_2)Cl \tag{56}$$
$$M = Th, U; R = CH_3, C_2H_5$$

$$M(C_5Me_5)_2Cl_2 + 2LiN(CH_3)_2 \xrightarrow{\text{ether}} M(C_5Me_5)_2(N(CH_3)_2)_2 \tag{57}$$
$$M = Th, U; R = CH_3$$

$$U(C_5Me_5)_2(CH_3)_2 + 2(C_2H_5)_2NH \xrightarrow{60°} U(C_5Me_5)_2(N(C_2H_5)_2)_2 \tag{58}$$

$$Th(C_5Me_5)_2(N(CH_3)_2)Cl + LiCH_3 \xrightarrow{\text{ether}} Th(C_5Me_5)_2(N(CH_3)_2)CH_3 \tag{59}$$
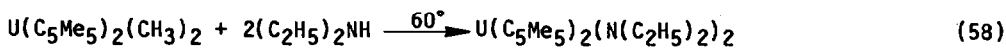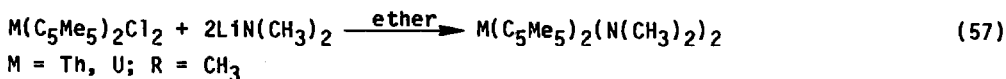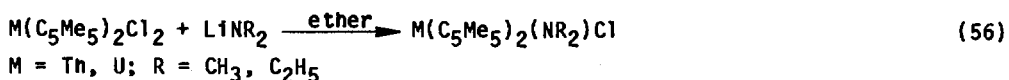
temperature NMR studies indicate that the nitrogen and α-carbon atoms of the amido groups are coplanar with the actinide metal and chloride ligand, and thus, the two amido alkyl groups become nonequivalent at low temperatures. For $U(C_5Me_5)_2(N(CH_3)_2)Cl$, the barrier to U-N bond rotation was determined to be 12.4 ± 1.0 kcal/mole. For $U(C_5Me_5)_2(N(CH_3)_2)_2$, a similar barrier of 9.6 ± 1 kcal/mole was determined. However, such determinations were not made for thorium. Treatment of the $M(C_5Me_5)_2(NR_2)Cl$ complexes with CO in toluene at 95 - 100° led to the formation of η^2-carbamoyl insertion products, $M(C_5Me_5)_2(\eta^2-OCNR_2)Cl$, which were thoroughly characterized spectroscopically, including through incorporation of ^{13}CO. Interestingly, variable

temperature ^{1}H NMR studies of these compounds indicated that the two carbamoyl alkyl groups were nonequivalent, with negligible broadening of their resonances occurring even to 125°, indicating a high barrier (> 23 kcal/mole) to rotation around the OC-NR$_2$ bond. For Th(C$_5$Me$_5$)$_2$(η^2-O^{13}CN(C$_2$H$_5$)$_2$)Cl, the carbamoyl resonance in the ^{13}C NMR spectrum was found to be at 248.5 ppm. The solid state structure for Th(C$_5$Me$_5$)$_2$(η^2-OCN(C$_2$H$_5$)$_2$)Cl was determined (Figure 21), and evidences significant disorder in the η^2-carbamoyl ligand, with the oxygen atom populating two sites nearly equally (site O has a population of 0.57(2), with the O' population being 0.42(3)). The Th-C(C$_5$Me$_5$) bond distances
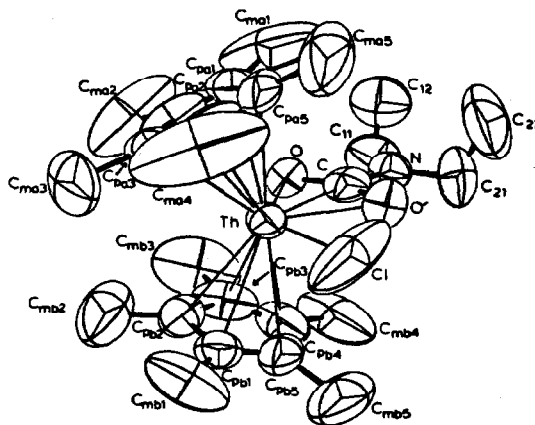
Fig. 21. The solid state structure of Th(C$_5$Me$_5$)$_2$(η^2-OCNEt$_2$)Cl from ref. 87.

averaged 2.78(4) Å, while the Th-C(carbamoyl) distance, subject to extra uncertainty due to the disorder, was 2.418(20) Å. Th-C-O angles of 74.5(11) and 70.1(15)° were observed, as well as Th-O distances of 2.460(16) Å (to O), and 2.383(31) Å (to O'). Notably, the apparently shorter Th-O' distance seemed to be accompanied by a longer C-O' distance of 1.53(4) Å, (cf., C-O = 1.44(3) Å). The C-N distance of 1.34(2) Å appeared reasonable, but the C-O distances were each longer than those observed in analogous transition metal complexes. Interestingly, variable temperature ^{1}H NMR spectra indicated that the two η^2-carbamoyl orientations are in equilibrium with one another in solution, with the rotational barrier ($\Delta G^{\neq}$) being ca. 9.1 $\pm$ 0.3 kcal/mole. In fact, thermodynamic values for the equilibrium could be estimated as ΔH = 1.2 $\pm$ 0.1 kcal/mole, and ΔS = 8 $\pm$ 1 eu. Relatively similar values were obtained for U(C$_5$Me$_5$)$_2$(η^2-OCN(C$_2$H$_5$)$_2$)Cl, with $\Delta G^{\neq}$ being 8.9 $\pm$ 0.5 kcal/mole, ΔH = 0.8 $\pm$ 0.3 kcal/mole, and ΔS = 9 $\pm$ 3 eu. CO insertion could also be realized for the M(C$_5$Me$_5$)$_2$(NR$_2$)$_2$ compounds. In fact, monocarbonylation could be

achieved within 2 hours at 0° under 1 atmosphere of CO, and a number of such
$M(C_5Me_5)_2(\eta^2-OCNR_2)(NR_2)$ complexes were reported (M = Th, R = CH_3; M = U, R =
CH_3, C_2H_5). Under more forcing conditions, a second insertion step could be
realized, and unlike other reported actinide CO insertion processes, this step
could be reversed _in vacuo_ at 100°, with no enediolate formation being
observed. A solid state structural investigation for $U(C_5Me_5)_2(\eta^2-$
$OC(N(CH_3)_2)_2$ was carried out, and the result is shown in Figure 22. The
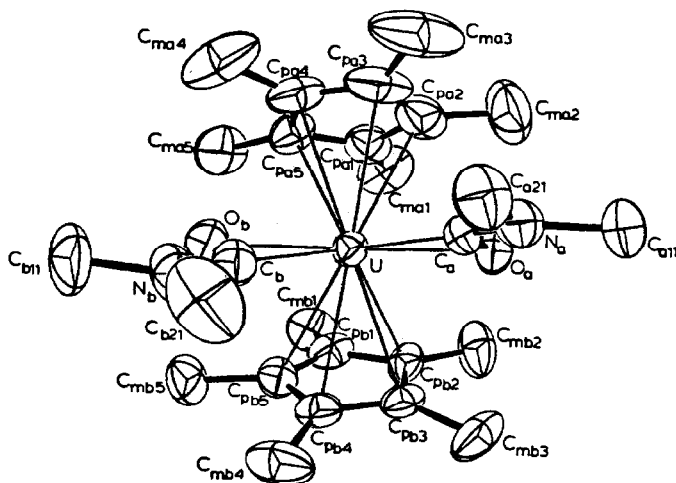
Fig. 22. The structure of $U(C_5Me_5)_2(\eta^2-OCNEt_2)_2$ from ref. 87.

average $U-C(C_5Me_5)$ bond distance was 2.788(13)Å, while the U-C (carbamoyl)
distances averaged 2.404(9)Å. The U-O distances were still shorter at
2.356(6)Å, reflecting the high oxygen affinity of uranium. The C-O and C-
$N(C_2H_5)_2$ bond distances averaged 1.275(11) and 1.333(14) Å. The carbamoyl
ligands are rotated ca. 14° out of the plane defined by the uranium atom and
the midpoints of the two C-O bonds. In order to test the relative
susceptibilities of U-C and U-N bonds to CO insertion, $Th(C_5Me_5)_2(N(CH_3)_2)CH_3$
was prepared as in equation (59). It was found that in this complex,
preferential CO insertion into the Th-C bond took place, yielding
$Th(C_5Me_5)_2(\eta^2-OCCH_3)(N(CH_3)_2)$. Attempts to bring about a second insertion
appeared to lead to mixtures of products.

While not involving an actual organometallic compound, a report by
Prusako, Petrov, Terent'ev, and Simorov has appeared in which evidence for a
uranium-trifluorophosphine complex, perhaps $U(PF_3)_6$, is presented (88). In
their approach, uranium metal vapor was cocondensed with 60 equivalents of PF_3

at liquid nitrogen temperature. Mass spectra of some of the volatile constituents at low temperature indicated the presence of U^+ and $U(PF_3)^+$ fragments. Subsequently, attempts were made to distill or sublime such volatile species from the condenser chamber to a liquid nitrogen cold trap. Once the chamber temperature reached $0°$, the cold trap was allowed to warm to room temperature. After standing one day, no volatile uranium species could be detected from the trap by mass spectroscopy, but substantial quantities of uranium products were reported to be present in the cold trap. It was postulated that $U(PF_3)_6$ may have been prepared under these conditions, analogous to the previously described $U(CO)_6$, which is stable only under cryogenic conditions (89).

Several reports have appeared related to the utilization of organoactinides in catalysis or organic synthesis. Miller and DeKock have investigated the reaction of cyclohexanone with metal vapors including neodymium (vide supra) and uranium (39). As mentioned before, two major products were obtained, [1,1'-bicyclohexyl]-1,1'-diol (a pinacol) and 2-(1-cyclohexen-1-yl)cyclohexanone (an aldol-derived product). For neodymium and uranium, the relative aldol/pinacol ratios were 2.1 and 2.8, while for chromium and titanium the values are 2.5 and 0.29, respectively. For uranium, however, a small amount (3%) of a third product was also observed, bicyclohexylidene.

Wen, Chang, Chuang, Chin, and Chang have reported on the polymerizations of alkynes, dienes, and alkyl halides brought about by uranium powder (90). The authors report that 10 grams of uranium powder brings about varying types of polymerizations with 4 mL of acetylenedicarboxylate, 5 mL phenylacetylene, or 4 mmoles of acetylene. In the first case, a 70% yield of the tetramer, tetramethyl-4-methoxy-5-(1,2,3-tris-(methoxycarbonyl)-2-cyclopentenyl)-1-oxabicyclo-[2.2.1]-hepta-2,5-diene-1,2,3,6-tetracarboxylate, was obtained after only 2 hours. An even faster reaction took place for phenylacetylene, 60% of which was consumed, yielding a product composed 90% of 1,2,4-triphenylbenzene and 5% of 1,3,5-triphenylbenzene. With acetylene itself only a very small yield was obtained (3%), which appeared from spectral data to be a linear polymer. Cocondensation of butadiene onto the powder at $70°$ led to an 80% conversion to polymer after 4 hours. Infrared data indicated it to be composed of 94% cis-1,4-polybutadiene, 3% of the trans isomer, and 3% of 1,2-polybutadiene. Isoprene was similarly converted to the cis polymer, with the consumption being 50%. Uranium allyl catalysts are known also to lead to cis polymerization of butadiene (91). With allyl chloride, a substance grossly formulated as $C_{18}H_{30}Cl_4$ was isolated. On the basis of spectral data, the product was believed to be $CH_3CH=CH-(C_3H_5Cl)_4-CH=CHCH_3$, with mass spectroscopy

suggesting that the $(C_3H_5Cl)_4$ portion is 4,6,9,11-tetrachloromethyl-2,12-tetradecadiene. Similar treatment of allyl bromide led to a material formulated as $C_{21}H_{36}Br_6$, or $CH_3CH=CH-(CH(CH_2Br)CH_2)_5CH(CH_2Br)CH_3$, in which the five central repeating units were assumed to form a 4,6,8,10,12-pentakis(bromomethyl)-2-octadecene unit.

Bowman, Nakamura, Fagan, Burwell, and Marks have reported on the catalytic activities of γ-alumina-supported $M(C_5Me_5)_2(CH_3)_2$ (M = Th, U) complexes toward propene hydrogenation and ethylene polymerization (92). Experiments were carried out using either fully dehydroxylated alumina, or ca. 75% dehydroxylated alumina, and subsequent to being supported on the surface, the organoactinide complexes were activated under He or H_2 streams. It was found that activation of the compound on the fully dehydroxylated support led to little CH_4 evolution, while activation on the partially dehydroxylated support led to large amounts of CH_4. Interestingly, activation under H_2 led to little CH_4 production, which occurs rapidly in homogeneous media forming $[M(C_5Me_5)_2H_2]_2$. A flow reactor was used to study propene hydrogenation with H_2/C_3H_6 = 4.68 at 1 atmosphere total pressure. With the uranium catalyst on dehydroxylated γ-alumina, turnover frequencies of 0.33/second (25°) and 0.55/second were observed, compared to values of 0.16/second and 0.33/second, respectively, for the thorium compound. On the partially dehydroxylated alumina at 120°, it was also established that the uranium catalyst effected over 0.1 turnovers per second. For platinum on silica, the corresponding value is 0.26/second at -46° (93). It was demonstrated that the actinide turnover rates per <u>surface</u> actinide atom must be substantially greater than the above rates per <u>total</u> actinide atoms. Both the thorium and the uranium compounds were also active in catalyzing the polymerization of ethylene. In fact, subsequent to the introduction of as many as 78 equivalents of ethylene in the polymerization experiments, the replacement of helium by hydrogen as the feed gas then allowed for the rapid catalytic hydrogenation of ethylene. Overall, it was noted that the catalytic activities for the supported species were much higher than for the homogeneous systems, and the similarities in catalytic activities for the thorium and uranium compounds suggested that the catalytic cycles involved exclusively the tetravalent state.

A number of physical studies on actinide organometallic compounds have appeared. Studies dealing with photoelectron spectra of lanthanide and actinide cyclopentadienyl compounds (37) and with the vibrational spectra of $Th(C_8H_8)_2$ and related lanthanide compounds (38) have been described in the lanthanide portion of this review. Ciliberto, Condorelli, Fagan, Manriquez, Fragala, and Marks have reported the He(I) and He(II) photoelectron spectroscopy of a number of compounds of stoichiometry $M(C_5Me_5)_2X_2$, where M =

Zr, Th, or U, and X = Cl or CH_3 (94). For these complexes, ionization bands for the 3p orbitals of chlorine were observed in the 9.5 - 11.5 eV region, and showed the expected decrease in cross section (relative to carbon 2p) with the higher photon energies. The patterns for thorium and uranium were reasonably similar to that for zirconium, except that there was some indication that significant mixing was occurring between a_2 (π) orbitals from the chlorine atoms and 5f metal orbitals. For each dimethyl compound, two ionization bands were observed, which could be assigned to the symmetric and antisymmetric M-CH_3 bonding combinations. For zirconium, these ionizations were identified as the bands at 7.18 and 10.27 eV, respectively, while for thorium and uranium the appropriate values were 7.00 and 10.22, and 7.26 and 10.64 eV, respectively. The fact that the differences between the two bands are nearly the same for each metal was interpreted as an indication of similar metal-carbon bonding interactions. In contrast, for the d^2 molybdenum and tungsten compounds (95), the differences were only on the order of 1.5 eV. Bands in the range of 7.4 - 8.0 eV for the $M(C_5Me_5)_2Cl_2$ compounds, and 7.7 - 8.5 eV for the $M(C_5Me_5)_2(CH_3)_2$ compounds, were assigned to ionizations of C_5Me_5 π-electrons. For all dichlorides, these bands were very similar, suggesting that metal-ring interactions were reasonably similar. The corresponding patterns for the dimethyl complexes differed noticeably, however, and it was suggested that enhanced metal-ligand interactions were present for the actinides, by virtue of their 5f orbitals. Finally, for $U(C_5Me_5)_2Cl_2$ and $U(C_5Me_5)_2(CH_3)_2$, low energy bands at 6.85 and 6.64 eV, respectively, were assigned to 5f orbital ionizations. The small difference between these two band energies was noted to be in strong contrast to the situation for related transition metal complexes.

Pyykkö and Lohr have published some relativistically parameterized extended Hückel calculations on a variety of lanthanide and actinide compounds (96). In addition to calculations on a number of oxide and halide species (and $U(BH_4)_4$), a calculation on $U(C_8H_8)_2$ was reported, assuming D_{8h} symmetry. The resulting atomic charges were 4.10 for uranium, -0.31 for carbon, and 0.05 for hydrogen, with the overlap populations being -0.169 for U-C, 1.133 for C-C, 0.962 for C-H, and 0.024 for U-H. As would be expected, the frontier orbitals were highly localized on the metal, being mostly 5f in character and rather close in energy (-9.42 and -9.41 eV). Some mixing was observed to take place between the ligand orbitals and the uranium d and f orbitals. Comparisons to published photoelectron spectra and other MO calculations were provided.

Luke and Streitwieser have published a study on the barriers to ligand rotation in $U(1,4-(\underline{t}-C_4H_9)_2C_8H_6)_2$ and $Fe(1,3-(\underline{t}-C_4H_9)_2C_5H_3)_2$. While $U(C_8H_8)_2$

itself appears to have an extremely low barrier to ligand rotation, the incorporation of 4-$\underline{t}$-butyl groups did allow a barrier to be observed. Thus, above -30°, four resonances were observed with relative intensities of 18:2:2:2, indicating rapid rotation. However, below -80°, a 9:9:1:1:1:1:1:1 pattern is observed, demonstrating that an unsymmetric conformation has been frozen out. From the coalescence temperatures and chemical shifts for the frozen-out conformation, extrapolated to the coalescence temperatures, a value for $\Delta G^{\neq}$ of 8.3 kcal/mole was determined (at -70°). The authors also estimated that $\Delta H^{\neq}$ should be ca. 7 kcal/mole. A simliar study was undertaken for the ferrocene analog, with the value of $\Delta G^{\neq}$ being calculated as 13.1 kcal/mole. The larger value was expected, given the closer proximity of the ligand planes to one another.

Sevast'yanov, Solov'ev, Suglobov, and Volkov have reported on the synthesis and some physical properties of uranocene (98). Their preparation involved the direct combination of activated uranium with C_8H_8. They found that in the 299 - 407° temperature range, uranocene would sublime without decomposition, but that above this point, decomposition would commence. The vapor pressure of uranocene in the above temperature range could be represented approximately as $\log(p)$ (in Pa) = (13.6 $\pm$ 0.5) - (6600 $\pm$ 300)/T. They obtained a value of the ΔH of sublimation for uranocene as being 126.6 $\pm$ 5.6 kJ/mole, and the mean value of ΔS = 201.0 $\pm$ 9.0 J/mole/deg.

Sevasti'yanov, Solov'ev, Leonov, and Il'ynshenkov have published a similar study on 1,1'-dimethyluranocene (99). In this case, reproducible vapor pressure measurements could be obtained in the range 247 - 347°, above which thermal decomposition occurred. In this range, ΔH (sublimation) was found to be 86.53 $\pm$ 0.67 kJ/mole, with ΔS being 151.8 $\pm$ 1.2 J/mole-deg in the middle of the temperature range. The addition of methyl groups to the cyclooctatetraenyl ligands thus rendered the complex more volatile as well as more thermally sensitive. The later observation was interpreted as an indication that decomposition could involve the $C_8H_7-CH_3$ bond.

Anafonov, Shushunov, Gaivoronskii, Spirina, Leonov, Il'yushenkov, Solov'era, and Granoteeva have studied $U(C_5H_5)_4$, $U(C_8H_8)_2$, and $U(CH_3C_8H_7)_2$ by mass spectroscopy (100). For $U(C_5H_5)_4$, the major peaks observed corresponded to loss of C_5H_5 fragments, as well as to loss of C_2H_2, C_2H_4, or C_3H_3 from $U(C_5H_5)_2$ and $U(C_5H_5)$ ions. Various doubly charged ions were also observed. Appearance potentials for the parent ion, and for the ions derived from the loss of the four successive C_5H_5 ligands were reported to be ($\pm$ 0.2 eV) 9.5, 10.3, 14.8, 19.4, and 15.4 eV. The high value for the loss of the third C_5H_5 ligand suggested a preferred process for forming U^+ directly from $U(C_5H_5)_2^+$. For $U(C_8H_8)_2$, the first C_8H_8 ligand was readily removed from the uranium atom,

but loss of the second C_8H_8 ligand occurred in competition to loss of C_2H_2, C_2H_4, C_3H_3, C_4H_4, and other fragments. Doubly charged ions were again observed. The appearance potentials for the parent ion, and for the successive loss of C_8H_8 ligands were 7.3, 9.8, and 12.8 eV for $U(C_8H_8)_2$, and 9.0, 11.0, and 12.6 eV for $U(CH_3C_8H_7)_2$. Values of the mean metal-ligand dissociation energies were estimated to be 225, 325, and 315 kJ/mole for $U(C_5H_5)_4$, $U(C_8H_8)_2$, and $U(CH_3C_8H_7)_2$, respectively, suggesting that the replacement of a hydrogen atom in the cyclooctatetraene ring by a methyl group did not bring about a substantial change in the mean metal-ligand bond energy.

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