LANTHANIDES AND ACTINIDES

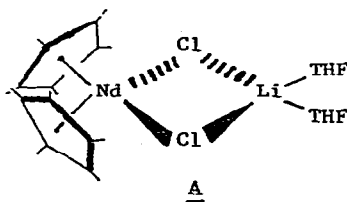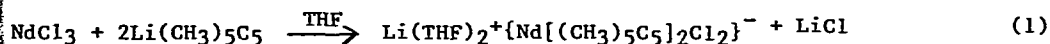ANNUAL SURVEY COVERING THE YEAR 1980 [*]

TOBIN J. MARKS

Department of Chemistry, Northwestern University, Evanston, IL 60201 (U.S.A)

General

An American Chemical Society Symposium Series volume entitled "Lanthanide and Actinide Chemistry and Spectroscopy" has appeared (1). Of particular interest to organometallic chemists are the chapters entitled, "Nonclassical Activation of Carbon Monoxide by Organoactinides"(2), "Alkyl, Hydride, and Related Bis(trimethylsilyl)amide Derivatives of the 4f- and 5f-Block Metals"(3), "Organic Derivatives of the f-Block Elements: A Quest for Orbital Participation and Future Perspective"(4), "Synthesis and Spectroscopy of Novel Mixed-Ligand Organolanthanide Complexes"(5), "Cyclooctatetraeneactinide(IV) Bis-borohydrides"(6), "Nuclear Magnetic Resonance Studies of Uranocenes"(7). The papers in this 472-page volume are taken from a symposium held in September of 1979.
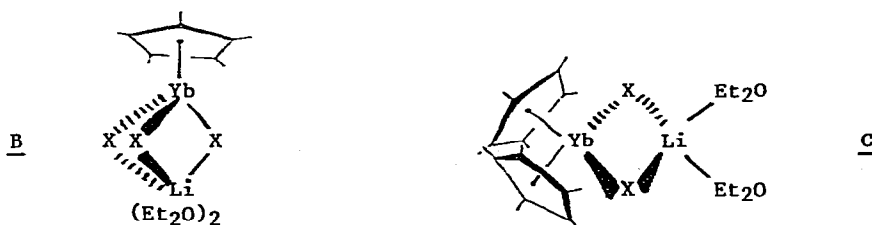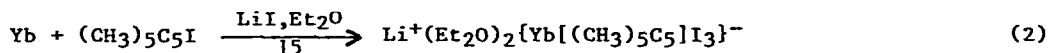
Lanthanides

The year 1980 saw considerable progress in the chemistry of lanthanides with substituted cyclopentadienyl ligands. Wayda and Evans (8) reported that an anionic bis(pentamethylcyclopentadienyl) derivative of neodymium(III) could be prepared via the approach of eq.(1). Structure $\underline{A}$ was proposed for this complex.

$$NdCl_3 + 2Li(CH_3)_5C_5 \xrightarrow{\text{THF}} Li(THF)_2^+\{Nd[(CH_3)_5C_5]_2Cl_2\}^- + LiCl \qquad (1)$$

$\underline{A}$
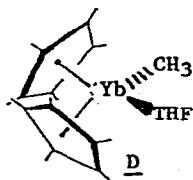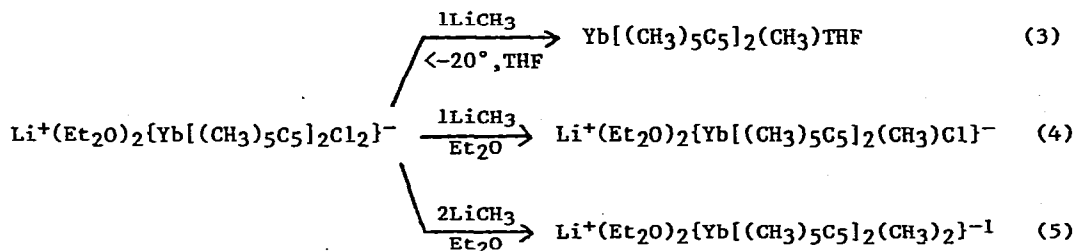
The stability of this compound is believed to reflect the steric demands of the $\eta^5-(CH_3)_5C_5$ ligand, since analogous $\eta^5-C_5H_5$ derivatives of early lanthanides

have not been synthetically accessible (9). This is not, however, the case for the later lanthanides where many bis(cyclopentadienyl) derivatives are known (9). Watson (10) has prepared both Yb(II) and Yb(III) complexes of the $\eta^5-(CH_3)_5C_5$ ligand. In an interesting metal oxidation reaction, $(CH_3)_5C_5I$ (generated _in situ_ from I_2 and $Li(CH_3)_5C_5$) was reported to react with ytterbium metal in diethyl ether according to eq.(2). Structure $\underline{B}$ was proposed for this

$$Yb + (CH_3)_5C_5I \xrightarrow[15]{LiI,Et_2O} Li^+(Et_2O)_2\{Yb[(CH_3)_5C_5]I_3\}^- \tag{2}$$

$\underline{B}$

$\underline{C}$

compound. In longer duration reactions, eq.(2) yields principally $Li^+(Et_2O)_2\{Yb[(CH_3)_5C_5]_2I_2\}^-$, for which a structure ($\underline{C}$) analogous to $\underline{A}$ (_vide supra_) was suggested. Chloride derivatives (X = Cl) of presumably analogous structures could be synthesized from $YbCl_3$ and appropriate quantities of $Li(CH_3)_5C_5$. Various methyl derivatives were then prepared as shown in eqs.(3)-(5). The neutral complex $Yb[(CH_3)_5C_5]_2(CH_3)THF$ was assigned structure $\underline{D}$;
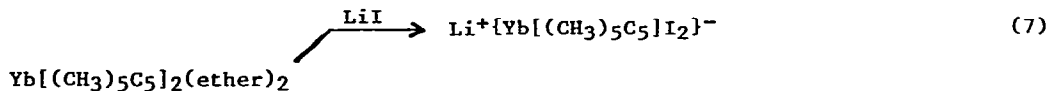
$$Li^+(Et_2O)_2\{Yb[(CH_3)_5C_5]_2Cl_2\}^- \quad \begin{cases} \xrightarrow[<-20°,THF]{1LiCH_3} Yb[(CH_3)_5C_5]_2(CH_3)THF \tag{3} \\ \xrightarrow[Et_2O]{1LiCH_3} Li^+(Et_2O)_2\{Yb[(CH_3)_5C_5]_2(CH_3)Cl\}^- \tag{4} \\ \xrightarrow[Et_2O]{2LiCH_3} Li^+(Et_2O)_2\{Yb[(CH_3)_5C_5]_2(CH_3)_2\}^{-1} \tag{5} \end{cases}$$

$\underline{D}$

it could also be prepared by demethylating $Yb[(CH_3)_5C_5]_2(CH_3)_2^-$ with $Al(CH_3)_3$.

It was also possible to obtain divalent ytterbium compounds via the route of eq.(6). Some but not all of the coordinated ether could be removed by heating
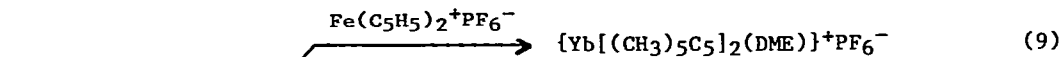
$$YbBr_2 + 2K(CH_3)_5C_5 \xrightarrow{\text{ether}} Yb[(CH_3)_5C_5]_2(\text{ether})_2 \tag{6}$$

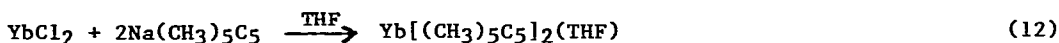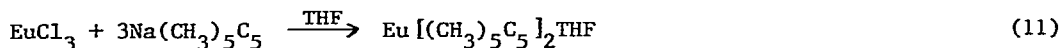$$\text{ether} = Et_2O, THF, 1/2 \text{ DME}$$

in vacuo. The divalent complexes undergo interesting ring displacement reactions, as shown in eqs.(7) and (8). Oxidation proceeds cleanly to give Yb(III)

$$Yb[(CH_3)_5C_5]_2(\text{ether})_2 \begin{cases} \xrightarrow{\text{LiI}} Li^+\{Yb[(CH_3)_5C_5]I_2\}^- \tag{7} \\ \\ \xrightarrow{\text{LiCH}_3} Li^+\{Yb[(CH_3)_5C_5](CH_3)_2\}^- \tag{8} \end{cases}$$

complexes (eqs.(9) and (10)).

$$Yb[(CH_3)_5C_5]_2(DME)_2 \begin{cases} \xrightarrow{\text{Fe(C}_5H_5)_2^+PF_6^-} \{Yb[(CH_3)_5C_5]_2(DME)\}^+PF_6^- \tag{9} \\ \\ \xrightarrow{\text{CH}_2Cl_2} Yb[(CH_3)_5C_5]_2Cl \tag{10} \end{cases}$$

Zalkin, Andersen, et al. (11) have synthesized bis(pentamethylcyclopenta-dienyl) derivatives of europium and ytterbium using Na(CH₃)₅C₅ (eqs.(11) and (12)). In eq.(11), a reduction of Eu(III) to Eu(II) occurs, and

$$EuCl_3 + 3Na(CH_3)_5C_5 \xrightarrow{\text{THF}} Eu[(CH_3)_5C_5]_2THF \tag{11}$$

$$YbCl_2 + 2Na(CH_3)_5C_5 \xrightarrow{\text{THF}} Yb[(CH_3)_5C_5]_2(THF) \tag{12}$$

Eu[(CH₃)₅C₅]₂(THF)·Et₂O is isolated after extracting with ether. Recrystallization from toluene yields Eu[(CH₃)₅C₅]₂(THF). In contrast, the reaction of the YbCl₂ with two equivalents of Na(CH₃)₅C₅ initially yields the red Yb[(CH₃)₅C₅]₂(THF) complex on crystallization of the product extracts from ether. A small yield of the corresponding (green) Yb[(CH₃)₅C₅]₂(Et₂O) complex was later crystallized from the remaining mother liquor. An X-ray structural study was undertaken of the Yb[(CH₃)₅C₅]₂(THF) complex, which crystallizes with half a mole of toluene. As can be seen in Figure 1, the complex is monomeric, with an average Yb-C bond distance of 2.663(2) Å and a Yb-O bond distance of 2.412(5) Å, both of which are shorter than the corresponding distances in Yb(CH₃C₅H₄)₂·THF (vide infra). The ring centroid-Yb-ring centroid angle is 144°, while the ring centroid-Yb-O angles average 108°.

Zinnen, Pluth, and Evans (12) have reported the synthesis of Yb(CH₃C₅H₄)₂(THF) by four different routes (eqs.(13)-(16)). The ytterbium
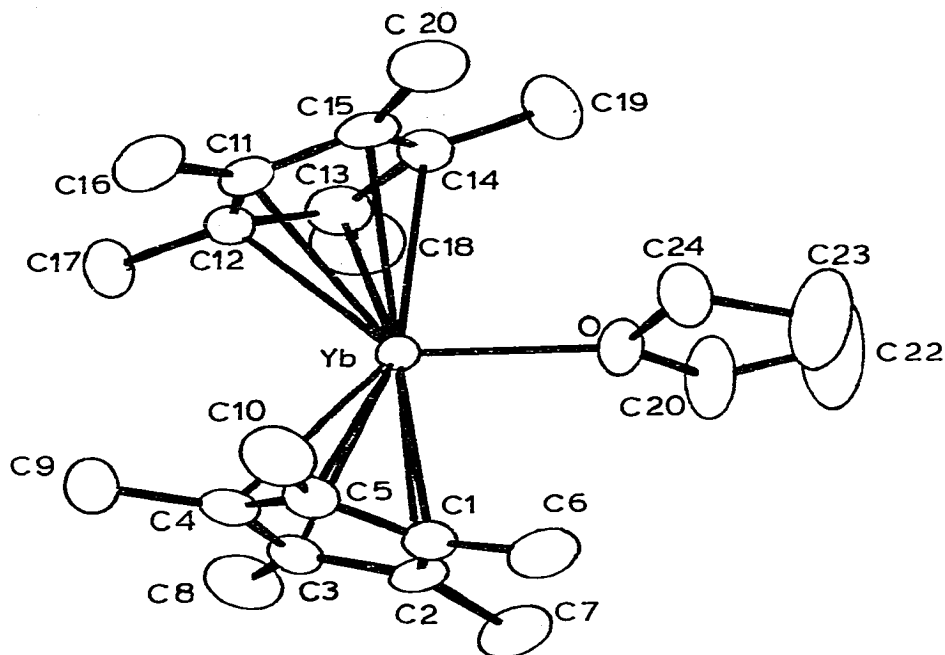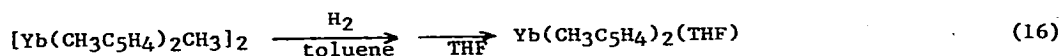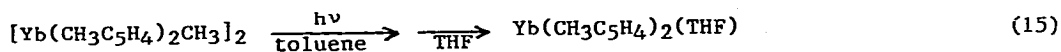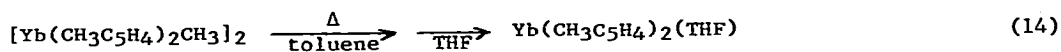
Fig. 1. The molecular structure of Yb[(CH₃)₅C₅]₂(THF) from ref. 5.

$$YbC_6H_{10} + CH_3C_5H_4 \xrightarrow{THF} Yb(CH_3C_5H_4)_2(THF) \tag{13}$$

$$[Yb(CH_3C_5H_4)_2CH_3]_2 \xrightarrow[toluene]{\Delta} \xrightarrow{THF} Yb(CH_3C_5H_4)_2(THF) \tag{14}$$

$$[Yb(CH_3C_5H_4)_2CH_3]_2 \xrightarrow[toluene]{h\nu} \xrightarrow{THF} Yb(CH_3C_5H_4)_2(THF) \tag{15}$$

$$[Yb(CH_3C_5H_4)_2CH_3]_2 \xrightarrow[toluene]{H_2} \xrightarrow{THF} Yb(CH_3C_5H_4)_2(THF) \tag{16}$$
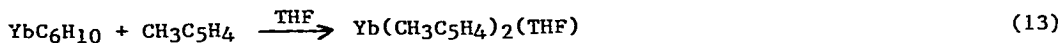
precursor in eq.(13) is prepared by condensing ytterbium vapor with 3-hexyne. Circumstantial chemical evidence was presented to argue that eq.(16) proceeds via an ytterbium hydride. The molecular structure of Yb(CH₃C₅H₄)₂(THF) was determined by single crystal X-ray diffraction and the result is shown in Figure 2. In the solid state the compound exists as a chain polymer where each ytterbium(II) ion is bonded to one terminal CH₃C₅H₄ ligand (Yb-C = 2.76(1) Å), a single THF ligand (Yb-O = 2.53(2) Å), and two shared, bridging CH₃C₅H₄ ligands (average Yb-C = 2.89(2) Å). The Yb-C bond distances are seen to be longer than in related Yb(III) complexes such as [Yb(CH₃C₅H₄)₂Cl]₂ (9), for which Yb-C =
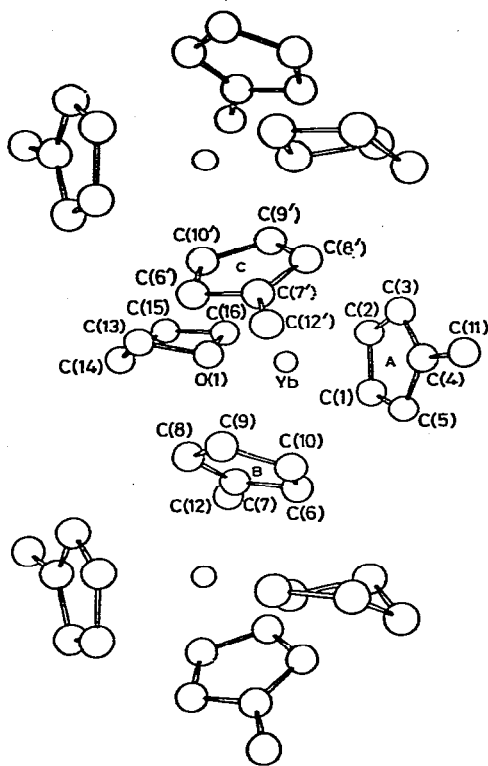
Fig. 2. The solid state structure of Yb(CH$_3$C$_5$H$_4$)$_2$(THF) from ref. 12.

2.58(1) Å. The angles between the various ring centroids and the ytterbium ion in the present case range from 114.6° to 118.0°. This structural result presents an interesting contrast to the aforementioned Yb[(CH$_3$)$_5$C$_5$]$_2$(THF) structure, where the steric bulk of the η^5-(CH$_3$)$_5$C$_5$ ligands apparently impedes molecular association.

An additional example of divalent ytterbium complexes with substituted cyclopentadienyl ligands [(CH$_3$)$_3$SiC$_5$H$_4$] is provided by work of Lappert, Atwood, et al. (13). Reduction of {Yb[η^5-(CH$_3$)$_3$SiC$_5$H$_4$]$_2$Cl}$_2$ proceeds as shown in eq. (17). The THF in the product can be displaced by TMEDA or removed by

$$\{Yb[\eta^5\text{-(CH}_3)_3\text{SiC}_5\text{H}_4]_2\text{Cl}\}_2 \xrightarrow[\text{THF}]{\text{Na/Hg}} 2Yb[\eta^5\text{-(CH}_3)_3\text{SiC}_5\text{H}_4]_2\text{(THF)}_2 \qquad (17)$$
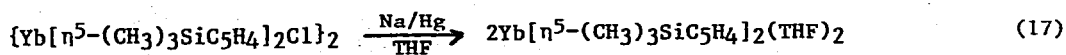
sublimation at ca. 300°C/10^{-3} Torr. Reaction with iodine yields {Yb[(CH$_3$)$_3$SiC$_5$H$_4$]$_2$I}$_2$. The molecular structure of the THF complex was determined by X-ray diffraction techniques and the result is presented in Figure 3. The ligation geometry is approximately tetrahedral with the angles ring

centroid-Yb-ring centroid = 133°; ring centroid-Yb-O(1) = 107°; ring
centroid-Yb-O(2) = 106 and 109°; and O(1)-Yb-O(2) = 85°. The average Yb-C
distance is 2.76 Å (ranging from 2.64(4)-2.84(4) Å), and the Yb-O distances are
2.42(2) and 2.39(3) Å. Clearly, the bulkier trimethylsilyl ring substituents
and the additional coordinated THF molecule inhibit the intermolecular ring
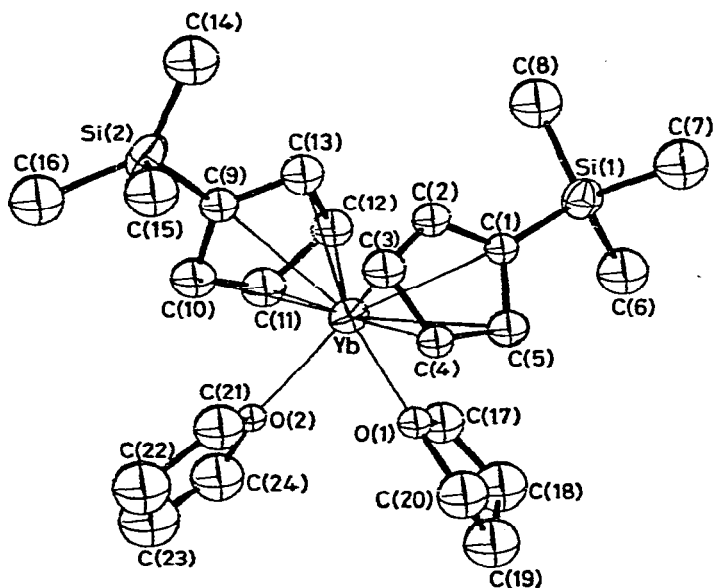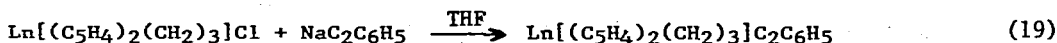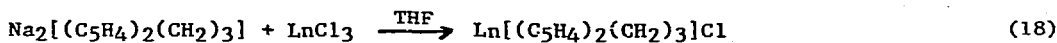sharing found in Yb(CH$_3$C$_5$H$_4$)$_2$(THF) (vide supra).

Fig. 3. The molecular structure of Yb[(CH$_3$)$_3$SiC$_5$H$_4$]$_2$(THF)$_2$ from ref. 13.

In another study with a substituted cyclopentadienyl ligand, John and
Tsutsui (4,14) employed a ring-bridged bis(cyclopentadienyl) ligand,
$^-$C$_5$H$_4$CH$_2$CH$_2$CH$_2$C$_5$H$_4$$^-$ (15), to stablize early lanthanide complexes. The synthesis
of the chloro derivatives is shown in eq.(i8), and conversion to phenylacetylide
compounds in eq.(19). The new complexes were characterized by elemental analy-

$$Na_2[(C_5H_4)_2(CH_2)_3] + LnCl_3 \xrightarrow{THF} Ln[(C_5H_4)_2(CH_2)_3]Cl \qquad (18)$$

$$Ln[(C_5H_4)_2(CH_2)_3]Cl + NaC_2C_6H_5 \xrightarrow{THF} Ln[(C_5H_4)_2(CH_2)_3]C_2C_6H_5 \qquad (19)$$

Ln = La, Ce

sis, infrared, uv-visible, and ^{1}H NMR spectroscopy, and by magnetic suscep-
tibility. No information was provided on the degree of association of these
compounds.

The tris(cyclopentadienyl) lanthanides are known to form adducts with Lewis bases, $Ln(\eta^5-C_5H_5)_3B$ (9), however only one complex, $Pr(C_5H_5)_3CNC_6H_{11}$, has been characterized by diffraction techniques (16). Rogers, Bynum, and Atwood (17) have now reported a structural study of $Gd(C_5H_5)_3(THF)$, prepared by reacting equimolar quantities of $GdCl_3$ and NaC_5H_5 in THF. The pseudotetrahedral coordination geometry found in $Pr(C_5H_5)_3CNC_6H_{11}$ and numerous actinide $M(\eta^5-C_5H_5)_3X$ compounds is again observed (Figure 4). The average Gd-C distance, 2.74(3) Å
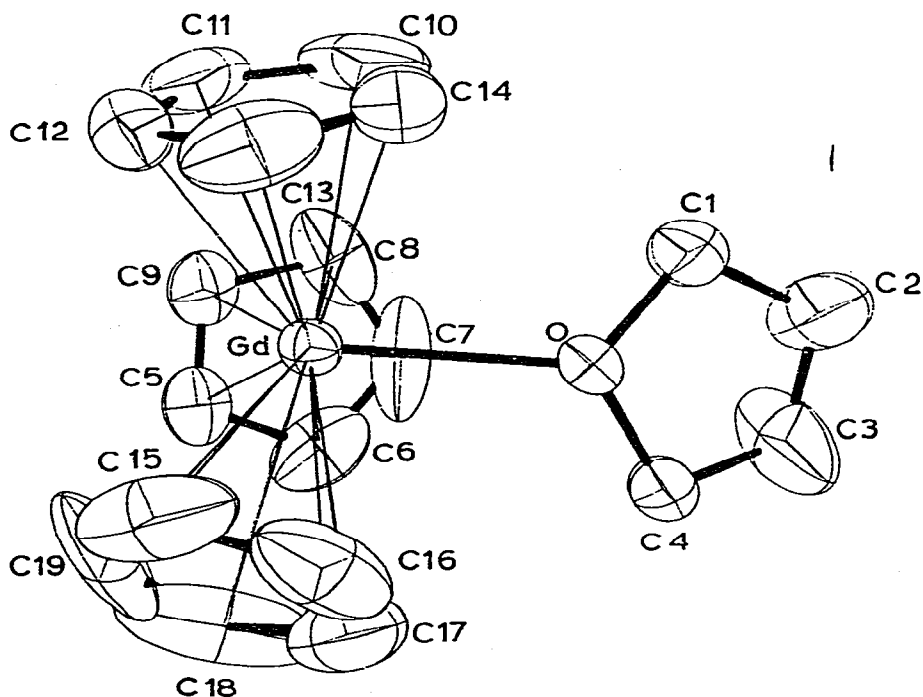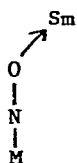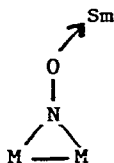
Fig. 4. The molecular structure of $Gd(C_5H_5)_3(THF)$ from ref. 10.

compares favorably with analogous distances in other lanthanide cyclopentadienyl complexes when corrections are made for differences in ionic radii. The ring centroid-Gd-ring centroid angle of 117° and the ring centroid-Gd-O angle of 99° compare favorably with those in $Pr(C_5H_5)_3CNC_6H_{11}$ and the actinide $M(\eta^5-C_5H_5)_3X$ complexes.

Onaka (18) has now published studies of the interaction of $Sm(C_5H_5)_3$ with transition metal nitrosyls. Shifts in ν_{NO} infrared band positions indicate samarium-nitrosyl interactions (E-G) in compounds with terminal (E,

$$\begin{array}{ccc}
\text{E} & \text{F} & \text{G}
\end{array}$$

Cr(C_5H_5)(CO)$_2$NO), doubly bridging (F, [Fe(C_5H_5)NO]$_2$, [Cr(C_5H_5)(NO)$_2$]$_2$, [Mn(CH$_3$C$_5$H$_4$)(NO)CO]$_2$), and triply bridging (G, Mn$_3$(CH$_3$C$_5$H$_4$)$_3$(NO)$_4$) nitrosyls. Addition of diethylamine regenerates the spectrum of the uncoordinated nitrosyl. The approximate order of Lewis basicity with respect to Sm(C_5H_5)$_3$ is found to be terminal NO > μ_2-CO > μ_2-NO $\approx$ μ_3-NO. The greater basicity of the terminally bound ligand is in marked contrast to observations for metal carbonyls (19).

Fischer and Bielang (5,20) have found that ytterbium alkynyls can be readily prepared from the tris(cyclopentadienyl) as shown in eq.(20). Only a single
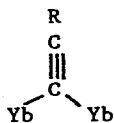
$$Yb(C_5H_5)_3 + HC\equiv CR \xrightarrow{\text{toluene}} [Yb(C_5H_5)_2C\equiv CR]_x + C_5H_6 \qquad (20)$$

R = $\underline{n}$-C$_6$H$_{13}$, x = 3.0 (in benzene)

= $\underline{n}$-C$_4$H$_9$, x = 2.5 (in benzene)

= C$_6$H$_5$

= ferrocenyl

cyclopentadienyl ring could be displaced. ^{1}H NMR spectra of these compounds exhibit large isotropic shifts and Curie-Weiss temperature dependence. The association is proposed to take place through bridging structures such as H.

$$\begin{array}{c}
R \\
C \\
\vert\vert\vert \\
C \\
Yb \diagup \diagdown Yb
\end{array}$$

H

The analogous chemistry with Nd(C_5H_5)$_3$ is considerably less straightforward, and significant amounts of Nd(C_5H_5)$_3$ are present in the product. In closely related work on lanthanide homoleptic hydrocarbyls, Evans and Wayda (21) have found that anionic as well as bis(cyclopentadienyl) alkynyls can be cleanly prepared in a halide-free synthesis by reacting the corresponding alkyl complex with a mono-substituted acetylene (eqs.(21)-(23)). The complexes with R = C(CH$_3$)$_3$ are by

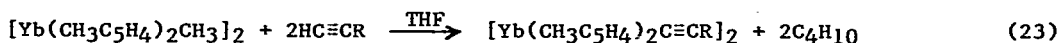$$Li^+(THF)_4Ln(\underline{t}\text{-}C_4H_9)_4^- + 4HC\equiv CR \xrightarrow{THF} Li^+(THF)Ln(C\equiv CR)_4^- + 4C_4H_{10} + 3THF \quad (21)$$

Ln = Sm, Er, Lu

R = C(CH$_3$)$_3$, $\underline{n}$-C$_4$H$_9$, C$_6$H$_5$

$$[Er(C_5H_5)_2CH_3]_2 + 2HC\equiv CR \xrightarrow{THF} [Er(C_5H_5)_2C\equiv CR]_2 + 2C_4H_{10} \quad (22)$$

R = C(CH$_3$)$_3$

$$[Yb(CH_3C_5H_4)_2CH_3]_2 + 2HC\equiv CR \xrightarrow{THF} [Yb(CH_3C_5H_4)_2C\equiv CR]_2 + 2C_4H_{10} \quad (23)$$
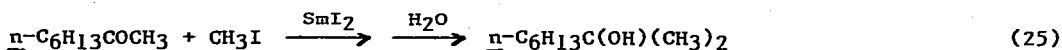
R = C(CH$_3$)$_3$

far the most thermally stable.

The use of lanthanides in organic synthesis continues to attract attention, and Girard, Namy, and Kagan (22) have reported on the properties of SmI$_2$ and YbI$_2$. These reagents were prepared from the metals as shown in eq.(24). In THF

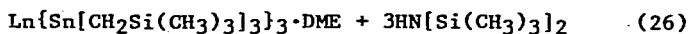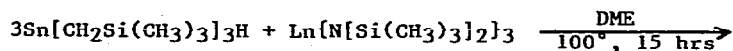$$Ln + ICH_2CH_2I \xrightarrow{THF} LnI_2 + CH_2=CH_2 \quad (24)$$

Ln = Sm, Yb

solution, these complexes deoxygenate expoxides and sulfoxides, as well as reduce some activated double bonds (e.g., cinnamic acid → 3-phenylpropionic acid). In addition, aldehydes are selectively reduced to alcohols in the presence of ketonic functionalities, and most alkyl halides and tosylates are reduced to alkanes. Grignard-like additions to ketones (e.g., eq.(25)) are also

$$\underline{n}\text{-}C_6H_{13}COCH_3 + CH_3I \xrightarrow{SmI_2} \xrightarrow{H_2O} \underline{n}\text{-}C_6H_{13}C(OH)(CH_3)_2 \quad (25)$$

observed with the samarium salt in THF. This reaction appars to be catalyzed by FeCl$_3$.

Compounds containing praseodymium- and neodymium-to-tin bonds have been synthesized by Razuvaev, Kalinina, and Fedorova (23) using the approach of eq.(26). The compounds are nearly colorless, relatively stable thermally,

$$3Sn[CH_2Si(CH_3)_3]_3H + Ln\{N[Si(CH_3)_3]_2\}_3 \xrightarrow[100°, \ 15 \ hrs]{DME}$$

$$Ln\{Sn[CH_2Si(CH_3)_3]_3\}_3\cdot DME + 3HN[Si(CH_3)_3]_2 \quad (26)$$

Ln = Pr, Nd

oxygen- and moisture-sensitive solids which are almost insoluble in both polar and non-polar solvents. They were characterized by elemental analysis and infrared spectroscopy. Reaction with benzoyl peroxide yields [(CH$_3$)$_3$SiCH$_2$]$_3$Sn-Ln(O$_2$CC$_6$H$_5$)$_2$ compounds.

Actinides

The year 1980 saw considerable activity in the area of 5f cyclooctatetraene complexes. LeVanda, Solar, and Streitwieser (6,24) reported that "half-sandwich" cyclooctatet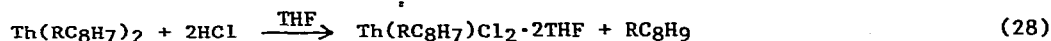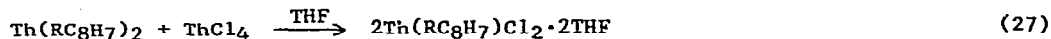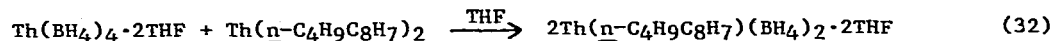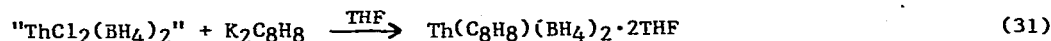raene complexes of Th(IV) can be prepared by the approach of eqs.(27)-(29). Analogous half-sandwich tetrahydroborate compounds ·
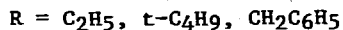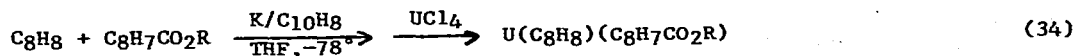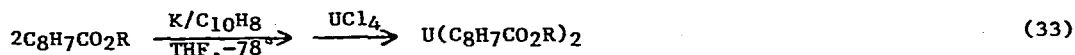
$$Th(RC_8H_7)_2 + ThCl_4 \xrightarrow{THF} 2Th(RC_8H_7)Cl_2 \cdot 2THF \tag{27}$$

$$Th(RC_8H_7)_2 + 2HCl \xrightarrow{THF} Th(RC_8H_7)Cl_2 \cdot 2THF + RC_8H_9 \tag{28}$$

$$R = H, \underline{n}-C_4H_9$$

$$Th[1,3,5,7-(CH_3)_4C_8H_4]_2 + ThCl_4 \xrightarrow{THF} 2Th[1,3,5,7-(CH_3)_4C_8H_4]Cl_2 \cdot 2THF \tag{29}$$

have been synthesized as shown in eqs.(30)-(32).

$$ThCl_4 + 2LiBH_4 \xrightarrow{THF} "ThCl_2(BH_4)_2" \tag{30}$$

$$"ThCl_2(BH_4)_2" + K_2C_8H_8 \xrightarrow{THF} Th(C_8H_8)(BH_4)_2 \cdot 2THF \tag{31}$$

$$Th(BH_4)_4 \cdot 2THF + Th(\underline{n}-C_4H_9C_8H_7)_2 \xrightarrow{THF} 2Th(\underline{n}-C_4H_9C_8H_7)(BH_4)_2 \cdot 2THF \tag{32}$$

Vibrational spectra indicate that the BH_4^- ligands are coordinated in a tridentate fashion. The molecular structure of $Th(C_8H_8)Cl_2 \cdot 2THF$ has been determined by X-ray diffraction for two different crystalline modifications (25), and the result (Figure 5) confirms the half-sandwich structural proposal. The structure of the single molecule present in the α form is in good agreement with the two crystallographically nonequivalent molecules in the β form. The average Th-Cl distance is 2.686(6) Å, the average Th-O, 2.57(2) Å, and the average Th-C(ring), 2.72(2) Å. The Cl-Th-Cl angles range from 99.0(3) to 109.6(1)° and the O-Th-O angles from 130.6(2)° to 136.5(3)°; there is roughly an inverse relationship between the relative magnitudes of these two quantities for a given $Th(C_8H_8)Cl_2 \cdot 2THF$ molecule.

Streitwieser, Burghard, Morrell, and Luke (26) have reported the synthesis of uranocenecarboxylic esters following the methodology of eqs.(33) and (34).

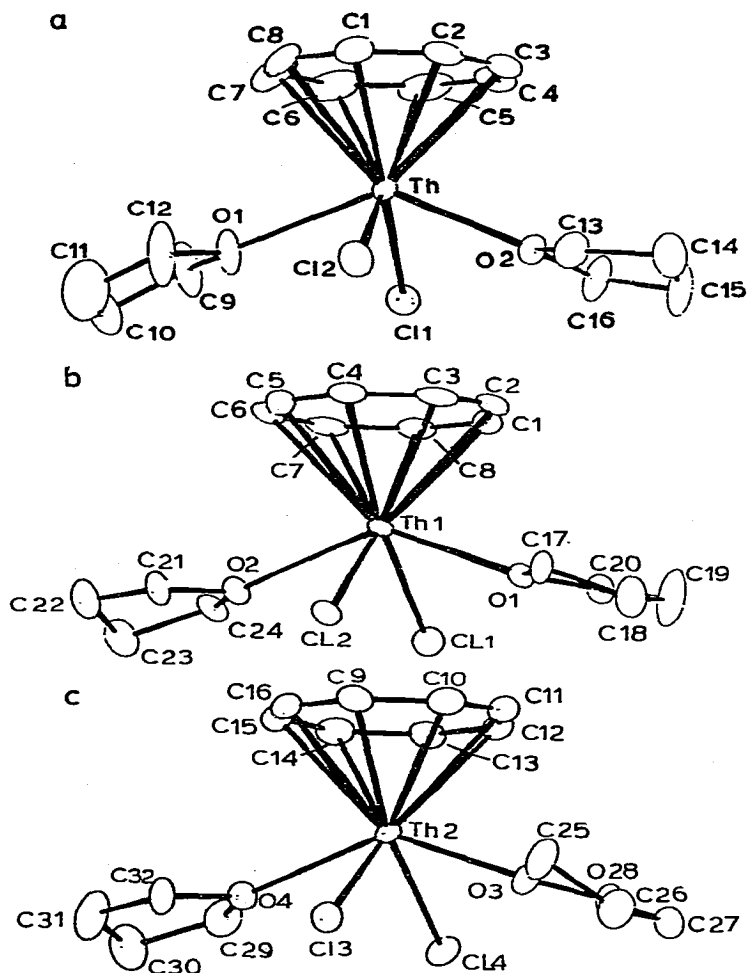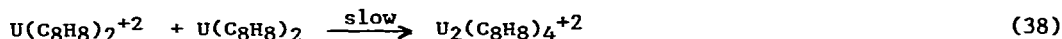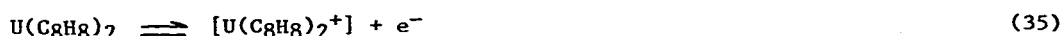$$2C_8H_7CO_2R \xrightarrow[THF,-78°]{K/C_{10}H_8} \xrightarrow{UCl_4} U(C_8H_7CO_2R)_2 \tag{33}$$

$$C_8H_8 + C_8H_7CO_2R \xrightarrow[THF,-78°]{K/C_{10}H_8} \xrightarrow{UCl_4} U(C_8H_8)(C_8H_7CO_2R) \tag{34}$$

$$R = C_2H_5, \underline{t}-C_4H_9, CH_2C_6H_5$$

Fig. 5. Solid state structures of Th(C$_8$H$_8$)Cl$_2$·2THF in (a) and (b,c) crystalline modifications. From ref. 25

The mixed sandwich in eq.(34) was contaminated with small amounts of uranocene (U(C$_8$H$_8$)$_2$) and the corresponding U(C$_8$H$_7$CO$_2$R)$_2$ complex. The new complexes were characterized by a variety of physicochemical techniques. These compounds are considerably more sensitive to protolysis than uranocene, and this was interpreted in terms of greater ionic character in the metal-ligand bonding.

A review of the NMR spectroscopy of uranocene and substituted uranocenes has been published by Streitwieser and Luke (7). The article begins with a general introduction to the sources of isotropic shifts in U(IV) complexes and a review of results on U(C$_5$H$_5$)$_3$X systems. There follows an extensive discussion of variable temperature ^{1}H NMR data on a large number of uranocene derivatives
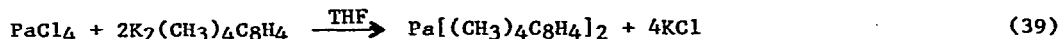
along with complementary magnetic susceptibility data. For the purpose of fac-
toring out the relative contributions of dipolar (pseudocontact) and contact
terms to the observed isotropic shifts, it is concluded that effective axial
symmetry can be assumed. Also, it is not correct to assume that $\chi_\perp$ (the magne-
tic susceptibility transverse to the pseudo-eightfold axis) is zero in uranocene
systems. It is also concluded that the contact shift for uranocene ring protons
is of the same sign as found for the cyclopentadienyl protons in $U(C_5H_5)_3X$
systems (27,28); however it is larger in magnitude, suggesting somewhat greater
metal-ligand bond covalency in the cyclooctatetraene systems. The contact
contribution to the isotropic shifts of ring substituents attenuates rapidly
with the number of intervening sigma bonds.

A full account of uranocene electrochemistry has now appeared (29).
Butcher, Pagni, and Chambers have studied $U(C_8H_8)_2$ cyclic voltammetry in a
number of solvents and over a wide temperature range. The oxidation processes
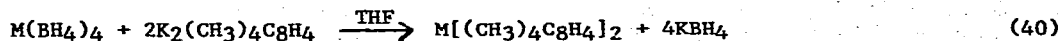observed are best described by eqs.(35)-(38). The first oxidation (eqs.(35),(36))

$$U(C_8H_8)_2 \rightleftharpoons [U(C_8H_8)_2^+] + e^- \tag{35}$$

$$[U(C_8H_8)_2^+] \xrightarrow{\text{fast}} U(C_8H_8)_2^+ \tag{36}$$

$$U(C_8H_8)_2^+ \rightleftharpoons U(C_8H_8)_2^{+2} + e^- \tag{37}$$

$$U(C_8H_8)_2^{+2} + U(C_8H_8)_2 \xrightarrow{\text{slow}} U_2(C_8H_8)_4^{+2} \tag{38}$$

is irreversible, apparently because the initially produced cation, $[U(C_8H_8)_2^+]$,
undergoes an irreversible structural or solvation change. Interestingly, the
cation produced in eq.(36) is more readily oxidized than $U(C_8H_8)_2$ (eq.(37)).
Such behavior has been observed in the cyclic voltammetry of other metallocenes.
The final step to yield $U_2(C_8H_8)_4^{+2}$ (eq.(38)) was shown to be bimolecular.

Bis(1,3,5,7-tetramethylcyclooctatetraene) complexes of protactinium, nep-
tunium, and plutonium have now been reported by Solar, Burghard, Banks,
Streitwieser, and Brown (30). The protactinum complex could be prepared by con-
ventional methodology (eq.(39)), however, the neptunium and plutonium compounds

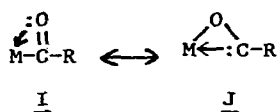$$PaCl_4 + 2K_2(CH_3)_4C_8H_4 \xrightarrow{\text{THF}} Pa[(CH_3)_4C_8H_4]_2 + 4KCl \tag{39}$$

were best prepared from the metal tetrakis(tetrahydroborates) as shown in
eq.(40). It appears that the nonconventional route minimizes competing reduc-

$$M(BH_4)_4 + 2K_2(CH_3)_4C_8H_4 \xrightarrow{\text{THF}} M[(CH_3)_4C_8H_4]_2 + 4KBH_4 \tag{40}$$
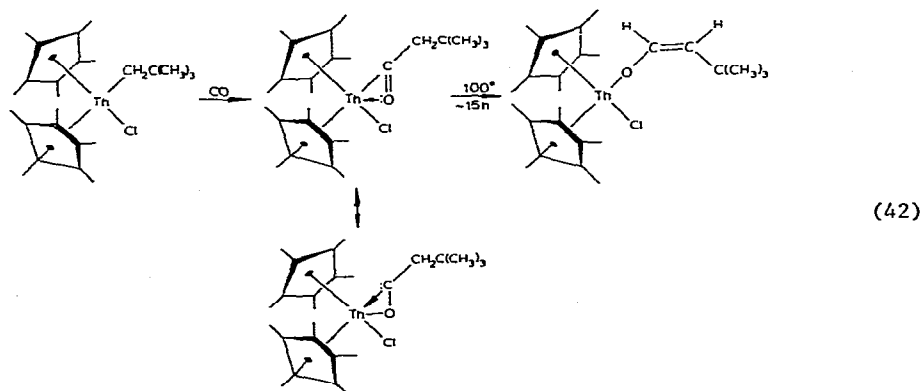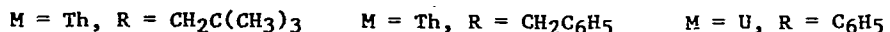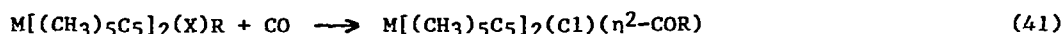
tion to M(III). The new compounds were characterized by uv-visible spectroscopy
and X-ray powder diffraction. Sandwich structures analogous to that of
$U[(CH_3)_4C_8H_4]_2$ (31) are proposed.

Much new information also appeared on pentamethylcyclopentadienyl actinide
compounds during 1980. The $M[(CH_3)_5C_5]_2R_2$ and $M[(CH_3)_5C_5]_2(R)Cl$ derivatives (M
= Th, U) are some of the most reactive actinide hydrocarbyls synthesized to
date. In regard to chemistry with carbon monoxide, the kinetic lability and
oxygen affinity of the actinide ions gives rise to decidedly nonclassical beha-
vior. The pivotal concept here is that this oxophilicity results in dihapto,
oxygen-bound migratory insertion products (I, J) which exhibit carbene-like (J)
chemical, structural, and spectroscopic properties (2,32). Thus the reaction of

the chloro alkyls with carbon monoxide is irreversible and yields unusual dihap-
toacyls (eqs. (41,42)). The C-O stretching frequencies in the range

$$M[(CH_3)_5C_5]_2(X)R + CO \longrightarrow M[(CH_3)_5C_5]_2(Cl)(\eta^2\text{-}COR) \qquad (41)$$

M = Th, R = $CH_2C(CH_3)_3$ M = Th, R = $CH_2C_6H_5$ M = U, R = C_6H_5.

(42)

1430-1480 cm^{-1} are very low in energy; typical nonconjugated transition metal
acyl ν_{CO} values are in the range of ca. 1620-1680 cm^{-1} while ν_{CO} for noncon-
jugated transition metal dihaptoacyls fall in the range 1505-1620 cm^{-1}. In
addition, the ^{13}C chemical shift of the acyl carbon atom in $Th[(CH_3)_5C_5]_2$-
$[\eta^2\text{-}COCH_2C(CH_3)_3]Cl$ (eq.(42)), 360.2 ppm, is in the region of carbene
complexes and far downfield from the shifts found in d-block dihaptoacyls. The
molecular structure of $Th[(CH_3)_5C_5]_2[\eta^2\text{-}COCH_2C(CH_3)_3]Cl$ (Figure 6) confirms that
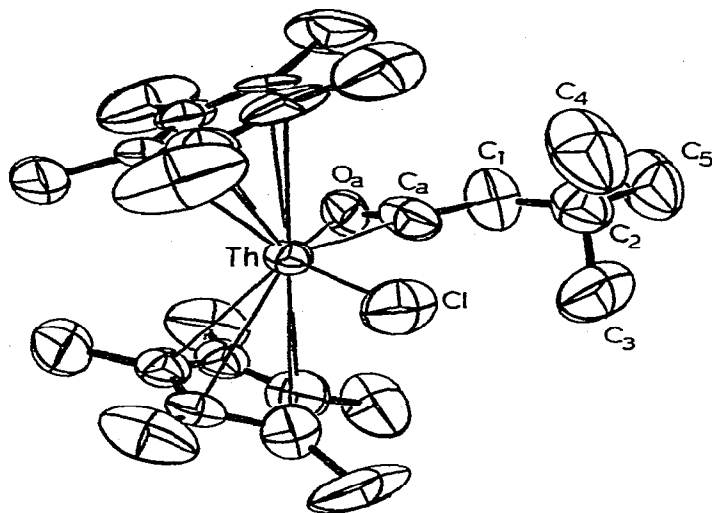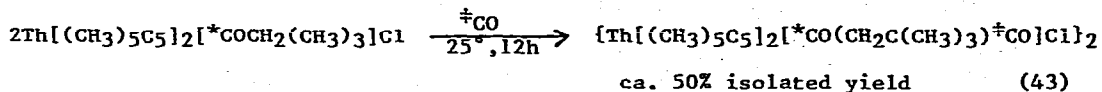
Fig. 6. Molecular structure of $Th[(CH_3)_5C_5]_2[\eta^2\text{-}COCH_2C(CH_3)_3]Cl$ from ref. 32.

this is a dihaptoacyl with a metal–oxygen interaction of unprecedented magnitude. Two features of the dihaptoacyl ligation are particularly striking. First, the Th–O distance (2.37(2) Å) is 0.07 Å _shorter_ than the Th–C distance (2.44(2) Å). This ordering is in contrast to the corresponding M–O vs. M–C parameters in Group IVB dihaptoacyls (33) where the metal–oxygen distance is clearly _longer_ than the metal–carbon distance. The disparity is even greater for Mo and Ru dihaptoacyls. Furthermore, the Th–O distance in the actinide dihaptoacyl is only ca. 0.17 Å longer than a Th–O single bond distance (34)

The chemical consequences of CO migratory insertion in the oxophilic organoactinide environment are a carbene–like reactivity leading to functionalization at the acyl carbon atom and retention of the metal–oxygen bond. Thus, heating $Th[(CH_3)_5C_5]_2[\eta^2\text{-}COCH_2C(CH_3)_3]Cl$ does not result in decarbonylation as is the case for analogous transition metal acyls, but rather in hydrogen atom migration to yield an enolate (eq.(42)). This 1,2 rearrangement is quantitative and stereospecific; it is reminiscent of hydrogen atom migration processes in carbene chemistry. Perhaps the most interesting new reaction of a carbene–like organoactinide dihaptoacyl is a coupling reaction with additional carbon monoxide (eq.(43)). The structure of the dark–violet product has been

$$2Th[(CH_3)_5C_5]_2[^*COCH_2(CH_3)_3]Cl \xrightarrow[25°, 12h]{^\ddagger CO} \{Th[(CH_3)_5C_5]_2[^*CO(CH_2C(CH_3)_3)^\ddagger CO]Cl\}_2$$

$$\text{ca. 50\% isolated yield} \qquad (43)$$

elucidated by X-ray diffraction (Figure 7). Oligomerization of four carbon mon-

oxide molecules has taken place to yield a dimeric thorium enedionediolate complex. The observed metrical parameters are in accord with the valence-bond structure $\underline{K}$. Thus, C_2-O_2 (Figure 7) (1.26(2) Å) is shorter than C_1-O_1 (1.34(2) Å) while $Th-O_2$ (2.53(1) Å) is considerably longer than $Th-O_1$ (2.27(1) Å). The C_1-C_1' distance of 1.35(4) Å suggests appreciable double bond character. One possible mechanism for the formation of $\underline{K}$ is via insertion of CO into the Th-C(acyl) bond to form a ketene ($\underline{L}$, $\underline{M}$) (eq.(44)) which subsequently undergoes intermolecular coupling. Presumably, initial CO interaction could

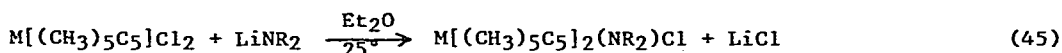Fig. 7. Solid state structure of $\{Th[(CH_3)_5C_5]_2[\mu\text{-}CO(CH_2C(CH_3)_3)CO]Cl\}_2$ from ref. 32.

$\underline{K}$

(44)

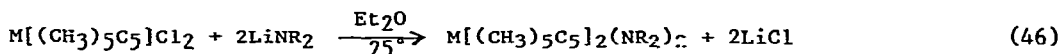$\underline{L}$ $\underline{M}$

involve coordination to the metal ion as shown or to the electrophilic vacant "carbene" p atomic orbital. In view of the affinity of the Th(IV) ion for oxygenated ligands, interaction of the ketene oxygen atom with the metal ion seems reasonable. There is precedent for the reaction of carbenes with CO to form ketenes (35), the transfer of coordinated carbenes to carbon monoxide (36,37), and the formation of complexes between transition metal ions and ketenes (38). The precise manner in which the ketene units formally couple in the present case to form a dimer has not been reported for free ketenes. Isotopic labelling studies ($^*C = {}^{13}C$, $^{\ddagger}C = {}^{13}C$) indicate that the integrity of the different CO moieties is maintained in the oligomerization process.

The reaction of the actinide $M[(CH_3)_5C_5]_2Cl_2$ complexes with dialkylamides yields a series of bis(pentamethylcyclopentadienyl) uranium and thorium chlorodialkylamides and bis(dialkylamides) (eqs.(45) and (46)) (2). The chlorodi-
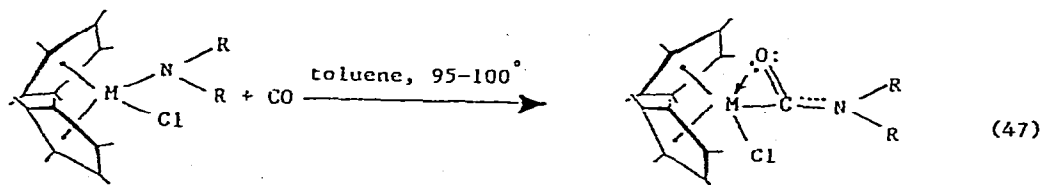
$$M[(CH_3)_5C_5]Cl_2 + LiNR_2 \xrightarrow[25°]{Et_2O} M[(CH_3)_5C_5]_2(NR_2)Cl + LiCl \qquad (45)$$

M = Th, U

R = CH_3, C_2H_5

$$M[(CH_3)_5C_5]Cl_2 + 2LiNR_2 \xrightarrow[25°]{Et_2O} M[(CH_3)_5C_5]_2(NR_2)_2 + 2LiCl \qquad (46)$$

M = Th, U

R = CH_3

alkylamides react irreversibly with carbon monoxide to form, via migratory insertion, carbamoyls (eq.(47)). The low energies of the C-O stretching

$$(47)$$

M = Th, U

R = CH_3, C_2H_5

frequencies (1490–1560 cm^{-1}) suggest dihaptocarbamoyl ligation, consistent with the high oxygen affinity of the actinide ions and the results on analogous organoactinide acyl complexes (vide supra). This conclusion has been verified by a single crystal diffraction study on $Th[(CH_3)_5C_5]_2[CON(C_2H_5)_2]Cl$ (Figure 8) which

shows the simultaneous presence in the solid of two isomers (N and O) which variable temperature NMR studies reveal to be in dynamic equilibrium (eqs.(48) and (49)). For $M = U$, $R = C_2H_5$ $\Delta H = 5.0 \pm 0.4$ kJ mol^{-1} and $\Delta S = 8 \pm 1$ e.u. for
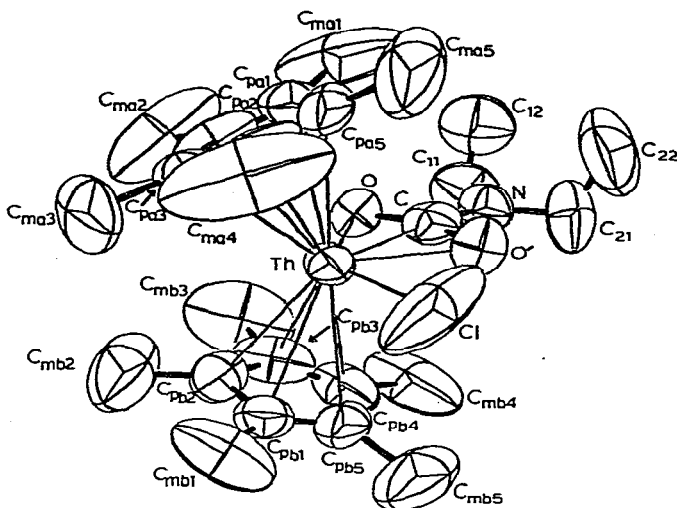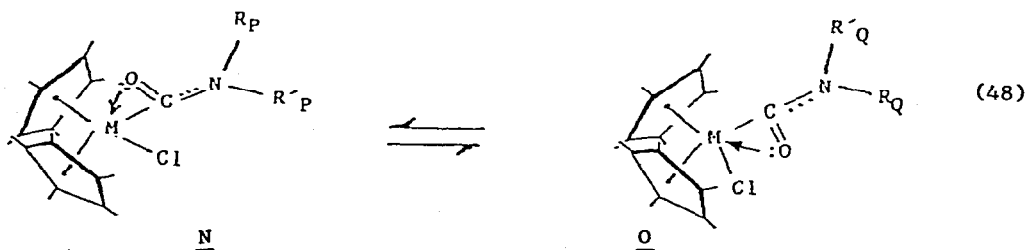

Fig. 8. The molecular structure of $Th[(CH_3)_5C_5]_2[\eta^2-CON(CH_2CH_3)_2]Cl$ from ref. 2.

(48)

(49)

this equilibrium, while $\Delta G^{\ddagger} = 37 \pm 2$ kJ mol^{-1} for this structural interconversion. The barrier to rotation about the C-N bond is very high ($\Delta G^{\ddagger} \gtrsim$ 147 kJ mol^{-1}) this result and the metrical data (vide infra) suggest a large degree of C-N multiple bonding (hybrid Q) in actinide dihaptocarbamoyls,

$$\underline{P} \qquad\qquad \underline{Q}$$

possibly stabilized by the metal-oxygen interaction. The Th-O distances in
Figure 8 are 2.383(31) and 2.460(16) Å, the average Th-C distance, 2.418(20) Å,
and the Th-C-O angles accompanying the above distances, 70.1(15)° and 74.5(1)°,
respectively. The bis(dialkylamides) undergo stepwise migratory CO insertion to
yield mono- and biscarbamoyls (eqs.(50) and (51)). The molecular structure of

(50)

(51)

$$M = Th, U$$
$$R = CH_3, C_2H_5$$

the M = U, R = CH_3 biscarbamoyl is shown in Figure 9. The U-O distances are
2.370(5) and 2.342(7) Å, the corresponding U-C distances, 2.405(8) and 2.402(9)
Å, and the corresponding U-C-O angles, 73.0(4)° and 71.8(5)°.

In the area of cyclopentadienyl compounds, Zanella, Rossetto, de Paoli, and
Traverso (39) have described a new, efficient synthesis of $U(C_5H_5)_3$ using
sodium hydride as the reducing agent (eq.(52)). When the reaction is carried

$$U(C_5H_5)_3Cl + NaH \xrightarrow{\text{benzene}} U(C_5H_5)_3 + NaCl + 1/2\ H_2 \qquad (52)$$
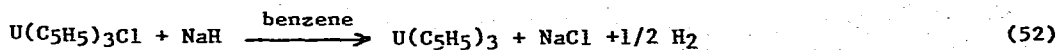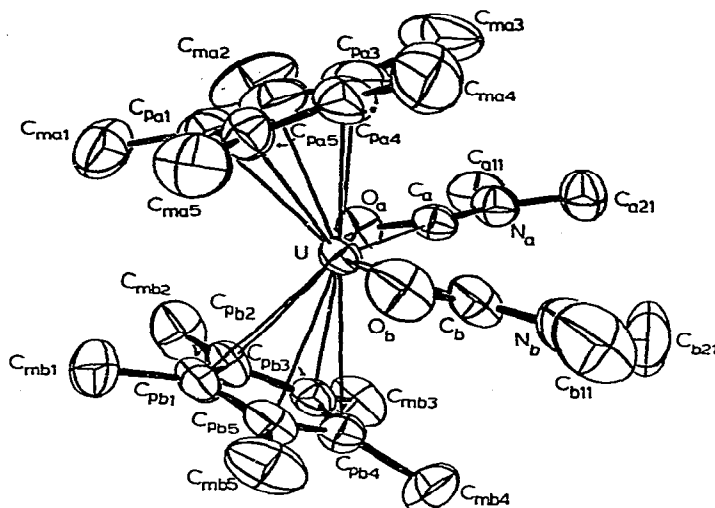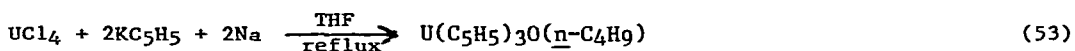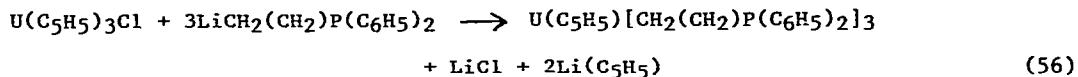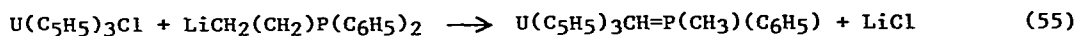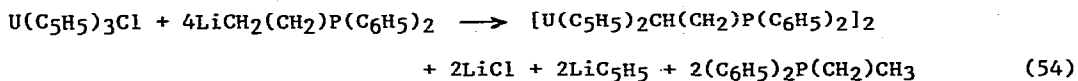
Fig. 9. Solid state structure of $U[(CH_3)_5C_5]_2[\eta^2-CON(CH_3)_2]_2$ from ref. 2.

out in THF, $U(C_5H_5)_3(THF)$ is the product. In related reductive chemistry, McLaren, Kanellakopulos, and Dornberger (40) found that an attempt to prepare cyclopentadienyl uranium complexes in oxidation states lower than +3 resulted in attack on the THF solvent and formation of an n-butoxy compound (eq.(53)).

$$UCl_4 + 2KC_5H_5 + 2Na \xrightarrow[\text{reflux}]{\text{THF}} U(C_5H_5)_3O(\text{n}-C_4H_9) \tag{53}$$

In connection with the assignment of the $U(C_5H_5)_4$ optical spectrum (41), Amberger has studied the vibrational spectra (far infrared and Raman) of $U(C_5H_5)_4$, $Th(C_5H_5)_4$, and $Th(CH_3C_5H_4)_4$ in the region of metal-C_5H_5 stretching and deformation modes (42). He concludes that shoulders on various bands in the $U(C_5H_5)_4$ optical spectrum are not vibronic in origin but likely arise from the fact that the S_4 site symmetry does not closely enough approximate idealized T_d symmetry. Amberger's crystal field analysis for $U(C_5H_5)_4$ (41) is to a certain degree extrapolable to $Np(C_5H_5)_4$, and Kanellakopulos, Klenze, Schilling, and Stollenwerk (43) have reported isotropic shift ^{1}H NMR data for the neptunium compound. The ring proton resonance at 16.0 ppm above TMS is in the region predicted by Amberger's calculations. The temperature dependence of the shift is Curie-like, and the room temperature hyperfine coupling constant, −1.7 MHz, is slightly larger than found for $Np(C_5H_5)_3Cl$ (−1.3 MHz).

Cramer, Maynard, and Gilje (44) have studied the reaction of the phosphoylide $(C_6H_5)_2P(CH_2)CH_2Li$ with tris(cyclopentadienyl) uranium chloride in detail (eqs.(54)−(56)). Two forms of the dimeric product of eq.(54) differing

$$U(C_5H_5)_3Cl + 4LiCH_2(CH_2)P(C_6H_5)_2 \longrightarrow [U(C_5H_5)_2CH(CH_2)P(C_6H_5)_2]_2$$

$$+ 2LiCl + 2LiC_5H_5 + 2(C_6H_5)_2P(CH_2)CH_3 \qquad (54)$$

$$U(C_5H_5)_3Cl + LiCH_2(CH_2)P(C_6H_5)_2 \longrightarrow U(C_5H_5)_3CH=P(CH_3)(C_6H_5) + LiCl \qquad (55)$$

$$U(C_5H_5)_3Cl + 3LiCH_2(CH_2)P(C_6H_5)_2 \longrightarrow U(C_5H_5)[CH_2(CH_2)P(C_6H_5)_2]_3$$

$$+ LiCl + 2Li(C_5H_5) \qquad (56)$$

only in the identity of included solvent molecules have been structurally characterized. An unusual dimeric structure of approximate C_2 symmetry was found (Figure 10) with two bis(cyclopentadienyl) uranium units bridged by two apparently deprotonated (assuming U(IV)) ylide moieties. The coordination geometry about the uranium ions is that of a highly distorted square-pyramid with $\not{\lambda}$ C_3–U–C_4 = 69(1)° and $\not{\lambda}$ C_2–U–C_3 = 130(1)°. Uranium–ylide carbon atom

Fig. 10. The solid state structure of $[U(C_5H_5)_2(\mu\text{–}CH)(CH_2)P(C_6H_5)_2]_2$ from ref. 44.

distances in the more precise of the two structures were found to be 2.66(3) Å (U_2–C_1) and 2.55(3) Å (U_1–C_2). The U–U distance of 3.810(2) Å suggests little metal–metal interaction when compared with a U–U distance of 3.12 Å in uranium metal.

Goffart, Piret–Meunier, and Duyckaerts (45) have now reported further results in the area of indenyl actinide complexes. Monoindenyl complexes were prepared

as shown in eqs.(57) and (58). Complexes with triphenylphosphine oxide as a

$$MX_4 + NaC_9H_7 \xrightarrow{THF} M(C_9H_7)X_3(THF)_2 + NaX \qquad (57)$$

$$M(C_9H_7)_3X + 2MX_4 \xrightarrow{THF} 3M(C_9H_7)X_3(THF)_2 \qquad (58)$$

$$M = U, \ X = Cl, \ Br$$

$$= Th, \ X = Cl$$

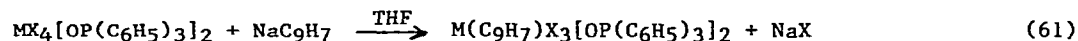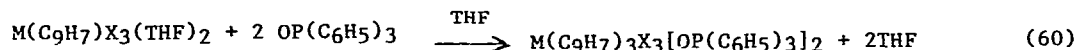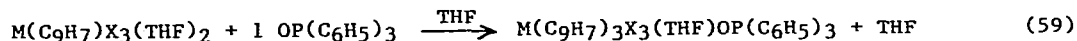ligand are accessible via the approach of eqs.(59)-(61). Heating under high

$$M(C_9H_7)X_3(THF)_2 + 1 \ OP(C_6H_5)_3 \xrightarrow{THF} M(C_9H_7)X_3(THF)OP(C_6H_5)_3 + THF \qquad (59)$$

$$M(C_9H_7)X_3(THF)_2 + 2 \ OP(C_6H_5)_3 \xrightarrow{THF} M(C_9H_7)X_3[OP(C_6H_5)_3]_2 + 2THF \qquad (60)$$

$$MX_4[OP(C_6H_5)_3]_2 + NaC_9H_7 \xrightarrow{THF} M(C_9H_7)X_3[OP(C_6H_5)_3]_2 + NaX \qquad (61)$$

$$M = U, \ X = Cl, Br$$

$$M = Th, \ X = Cl$$

vacuum can be employed to remove one equivalent of base (eq.(62)). In the solid

$$M(C_9H_7)X_3L_2 \xrightarrow{\Delta} M(C_9H_7)X_3L + L \qquad (62)$$

state, the triphenylphosphine oxide complexes are surprisingly stable to air, however gentle heating of, or addition of pentane to THF solutions results in disproportionation (eq.(63)), with the rate being more rapid for M = Th than for

$$3M(C_9H_7)X_3[OP(C_6H_5)_3]_2 \xrightarrow{THF} M(C_9H_7)_3X + 2MX_4[OP(C_6H_5)_3]_2 + 2OP(C_6H_5)_3 \qquad (63)$$
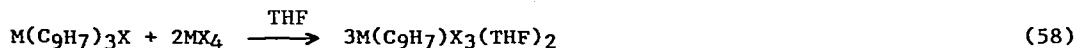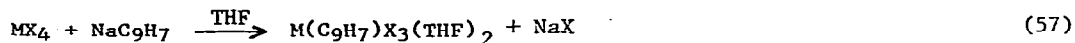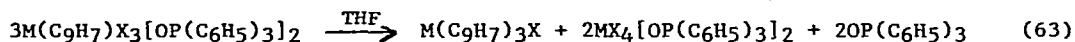
M = U. The new complexes were studied by infrared, mass, and uv-visible spectroscopy, and magnetic susceptibility. The solid state structure of $U(C_9H_7)Br_3(THF)[OP(C_6H_5)_3]$ has been studied by X-ray diffraction (45,46) and the coordination geometry about the uranium ion is the pseudo-octahedral configuration (Figure 11) found for the cyclopentadienyls $U(CH_3C_5H_4)Cl_3(THF)_2$ (47), $U(C_5H_5)Cl_3[OP(C_6H_5)_3]_2$(48), and $U(C_5H_5)Cl_3\{OP[N(CH_3)_2]_3\}_2$ (49). Important bond distances in the present case are U-Br(1) = 2.769(3) Å, U-Br(2) = 2.704(3) Å, U-Br(3) = 2.740(3) Å, U-O(1) = 2.320(14), U-O(2) = 2.479(14) Å, U-C(23) = 2.746(27) Å, U-C(24) = 2.761(26) Å, U-C(25) = 2.801(26) Å, U-C(30) = 2.790(25) Å, and U-C(31) = 2.695(27) Å. Important angles are: Br(1)-U-Br(2) = 90.2(1) Å, Br(1)-U-Br(3) = 163.1(1)°, Br(1)-U-O(1) = 83.3(4)°, Br(1)-U-O(2) =83.0°, and Br(2)-U-Br(3) = 95.2(1)°.

Meunier-Piret, Declerq, Germain, and Van Meerssche (50) have determined the molecular structure of tris(indenyl) uranium by X-ray diffraction. The coor-
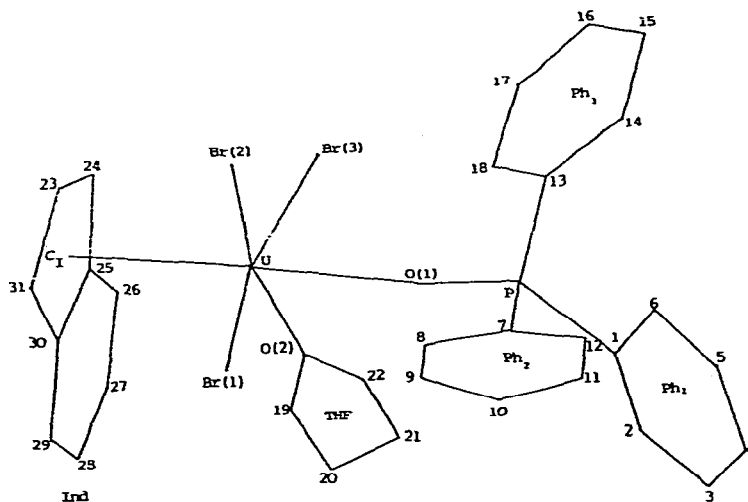
Fig. 11. The molecular structure of U(C9H7)Br3(THF)[OP(C6H5)3] from ref. 46.

dination geometry about the U(III) ion is approximately trigonal (Figure 12) as found for Sm(C9H7)3 (51) with uranium-to-carbon bond distances falling in the range 2.734(21) Å to 2.846(24) Å. The dihedral angles between the planes of the three indenyl ligands are: ${[C(2)-C(10)]-[C(11)-C(19)]} = 123°$, ${[C(11)-C(19)]-[C(20)-C(28)]} = 122°$, ${[C(2)-C(10)]-[C(20)-C(28)]} = 115°$.
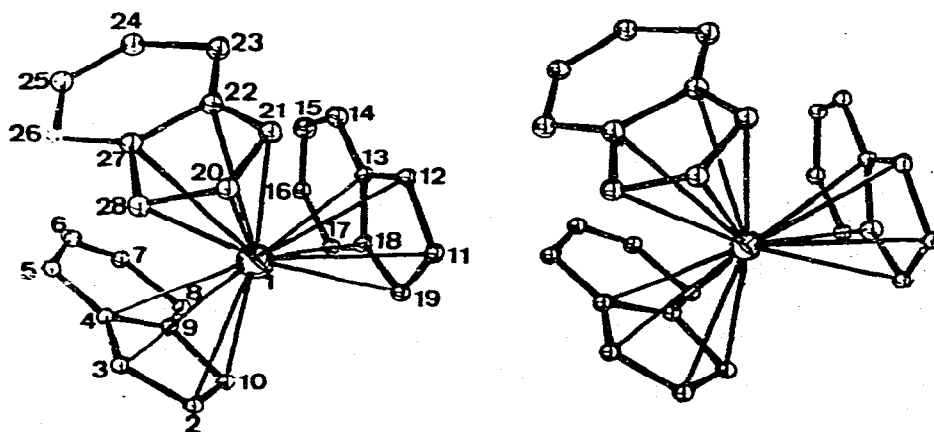
Fig. 12. The solid state structure of tris(indenyl) uranium from ref. 50.

REFERENCES

1 N. Edelstein, Ed., ACS Symposium Series, 131(1980).
2 T.J. Marks, J.M. Manriquez, P.J. Fagan, V.W. Day, C.S. Day and S.H. Vollmer in ref. 1, Ch. 1.
3 R.A. Andersen in ref. 1, Ch. 2.
4 T. Miyamoto and M. Tsutsui in ref. 1, Ch. 3.
5 R.D. Fischer and G. Bielang in ref. 1, Ch. 4.
6 J.P. Solar, A. Streitwieser, Jr. and N.M. Edelstein in ref. 1, Ch. 5.
7 W.D. Luke and A. Streitwieser, Jr. in ref. 1, Ch. 6.
8 A.L. Wayda and W.J. Evans, Inorg. Chem., 19(1980)2190.
9 T.J. Marks, Progr. Inorg. Chem., 24(1978)51.
10 P.L. Watson, J. Chem. Soc., Chem. Comm., (1980)652.
11 T.D. Tilley, R.A. Andersen, B. Spencer, H. Ruben, A. Zalkin and D.H. Templeton, Inorg. Chem., 19(1980)2999.
12 H.A. Zinnen, J.J. Pluth and W.J. Evans, J. Chem. Soc., Chem. Comm., (1980)810.
13 M.F. Lappert, P.I.W. Yarrow, J.L. Atwood, R. Shakir and J. Holton, J. Chem. Soc., Chem. Comm., (1980)987.
14 J. John and M. Tsutsui, J. Coord. Chem., 10(1980)177.
15 For applications of this type of ligand in 5f element chemistry, see: C.A. Secaur, V.W. Day, R.D. Ernst, W.J. Kennelly and T.J. Marks, J. Amer. Chem. Soc., 98(1976)3713.
16 J.H. Burns and W.H. Baldwin, J. Organomet. Chem., 120(1976)361.
17 R.D. Rogers, R. Vann Bynum, and J.L. Atwood, J. Organometal. Chem., 192(1980)65.
18 S. Onaka, Inorg. Chem., 19(1980)2132.
19 S. Onaka and N. Furuichi, J. Organometal. Chem., 173(1979)77.
20 R.D. Fischer and G. Bielang, J. Organometal. Chem., 191(1980)61.
21 W.J. Evans and A.L. Wayda, J. Organometal. Chem., 202(1980)C6.
22 P. Girard, J.L. Namy and H.B. Kagan, J. Amer. Chem. Soc., 102(1980)2693.
23 G.A. Razuvaev, G.S. Kalinina and E.A. Fedorova, J. Organometal. Chem., 190(1980)157.
24 C. LeVanda, J.R. Solar and A. Streitwieser, Jr., J. Amer. Chem. Soc., 102(1980)2128.
25 A. Zalkin, D.H. Templeton, C. LeVanda and A. Streitwieser, Jr., Inorg. Chem., 19(1980)2560.
26 A. Streitwieser, Jr., H.P.G. Burghard, D.G. Morrell and W.D. Luke, Inorg. Chem., 19(1980)1863.
27 R.D. Fischer in Organometallics of the f-Elements, T.J. Marks and R.D. Fischer, Eds., Reidel Publishing Co., Dordrecht, Holland, 1979, Ch. 11.
28 T.J. Marks, A. M. Seyam and J.R. Kolb, J. Amer. Chem. Soc., 95(1973)5529.
29 J.A. Butcher, Jr., R.M. Pagni and J.Q. Chambers, J. Organometal. Chem., 199(1980)223-227.
30 J.P. Solar, H.P.G. Burghard, R.H. Banks, A Streitwieser, Jr. and D. Brown, Inorg. Chem., 19(1980)2186.
31 K.O. Hodgson and K.N. Raymond, Inorg. Chem., 12(1973)458.
32 P.J. Fagan, J.M. Manriquez, T.J. Marks, V.W. Day, S.H. Vollmer and C.S. Day, J. Amer. Chem. Soc., 102(1980)5393.
33 a. G. Fachinetti, C. Floriani and H. Stoeckli-Evans, J. Chem. Soc., Dalton, (1979)2297.
   b. G. Fachinetti, G. Fochi and C. Floriani, J. Chem. Soc., Dalton (1977)1946.
34 J.M. Manriquez, P.J. Fagan, T.J. Marks, C.S. Day and V.W. Day, J. Amer. Chem. Soc., 100(1978)7112.
35 W. Kirmse, Carbene Chemistry, 2nd edn., Academic Press, New York, 1971, pp. 14-16.

36 W.A. Herrmann, J. Plank, M.L. Ziegler and K. Weidenhammer, J. Amer. Chem. Soc., 101(1979)3133.
37 W.A. Herrmann and J. Plank, Angew. Chem. Int. Edn., Engl., 17(1978)525.
38 G. Fachinetti, C. Biran, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Amer. Chem. Scc., 100(1978)1921, and references therein.
39 P. Zanella, G. Rossetto, G. DePaoli and O. Traverso, Inorg. Chim. Acta, 44(1980)L155.
40 A.B. McLaren, B. Kanellakopulos and E. Dornberger, Inorg. Nuclear Chem. Lett., 16(1980)223.
41 H.-D. Amberger, J. Organometal. Chem., 110(1976)59.
42 H.-D. Amberger, Spectrochim. Acta A, 36(1980)933.
43 B. Kanellakopulos, R. Klenze, G. Schilling and A.H. Stollenwerk, J. Chem. Phys., 72(1980)6311.
44 R.E. Cramer, R.B. Maynard and J.W. Gilje, Inorg. Chem., 19(1980)2564.
45 J. Goffart, J. Piret-Meunier and G. Duyckaerts, Inorg. Nuclear Chem. Lett., 16(1980)233.
46 J. Meunier-Piret, G. Germain, J.P. Declerq, M. Van Meersche, Bull. Soc. Chim. Belgique, 89(1980)241.
47 R.D. Ernst, W.J. Kennelly, C.S. Day, V.W. Day and T.J. Marks, J. Amer. Chem. Soc., 101(1979)2656.
48 F. Benetollo, G. Bombieri, G. DePaoli, Z. Zanella and K.W. Bagnall, Abstracts, IX Int. Conf. on Organometal. Chem., Dijon, France, Sept. 1979, p. 63.
49 G. Bombieri, G. DePaoli, A. DelPra and K.W. Bagnall, Inorg. Nuclear Chem. Lett., 14(1978)359.
50 J. Meunier-Piret, J.P. Declerq, G. Germain and M. Van Meersche, Bull. Soc. Chim. Belgique, 89(1980)121.
51 J.L. Atwood, J.H. Burns and P.G. Laubereau, J. Amer. Chem. Soc., 95(1973)1830.