# LANTHANIDES AND ACTINIDES
# ANNUAL SURVEY COVERING THE YEAR 1983

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## INTRODUCTION

This review has been restricted to compounds of the lanthanides and actinides containing M—C bonds as defined by Section 29 of Chemical Abstracts. The prelanthanides La and Y have been included with the lanthanides because of their similar size and charge. Abstracts of papers presented at conferences, dissertations, and patents have been excluded.

Several review articles appeared in 1983 covering organolanthanides and actinides. Evans[1] discussed recent advances in organolanthanide chemistry; Palenik,[2] structural chemistry of the lanthanides; and Cardin and Norten,[3] sigma bonded organometallic compounds of the lanthanides and actinides. In addition, Part D6 of the Gmelin Handbook of Inorganic Chemistry appeared (Forsberg, Marcus and Moeller[4]) covering organometallic compounds of Sc, Y, and La—Lu and Schumann discussed homoleptic organometallic compounds of the lanthanides in Comments on Inorganic Chemistry.[5] A review on trends in the chemistry of organometallic compounds of uranium appeared by Sharan, Kapoor, and Pannell.[6]

## LANTHANIDES

### Cyclopentadienyl and Cyclopentadienyl-Like Compounds

As in past years, the majority of the papers published in 1983 dealt with the synthesis of, or the uses in synthetic schemes of cyclopentadienyl or cyclopentadienyl-like ligands. These included cyclopentadienyl itself (Cp), pentamethylcyclopentadienyl (Cp*), methylcyclopentadienyl (CpMe), and bis(trimethylsilyl)cyclopentadienyl (Cp").

Few reports detailed only the synthesis or properties of new Cp compounds. Chen[7] prepared $Cp_2NdCl \cdot THF$ in 29% yield via the reaction of $NdCl_3$ and NaCp in THF at room temperature. The anhydrous compound, $Cp_2NdCl$, was obtained by removal of the THF in vacuo at 180°. Zhu, et al.[8] utilized bis(dibenzoylmethyl)europium acetate and NaCp in THF to prepare $CpEu(CH(COC_6H_5)_2)_2$.

Suleimanov, et al.[9] prepared Cp(HgYb)I·4THF by reaction of CpHgI with $Yb^0$ at 0°C in THF. This reaction produced yellow, insoluble, air-sensitive compounds. Yields were 30-40%. Deacon[10] reported that the reaction of dipyridinium hexachlorocerate(IV) in THF leads to $Cp_3Ce$ and not $Cp_4Ce$ as previously reported.

Fischer, et al.[11] reported the crystal structure of $Cp_3Pr$ (Figure 1) and Deacon, et al.[12] the crystal structure of $Cp_2Yb$(dme) (dme = dimethoxyethane), while Ellis and Schlesener,[13] and Brittain, et al.[14] discussed the electronic spectra of $Cp_3M$ Lewis acid base adducts. The structure of $Cp_3Pr$ consists of a polymeric chain of $Cp_2Pr$ units bridged by two additional Cp ligands. Each Pr is bonded to 3 $\eta^5$- and 1 $\eta^2$-Cp. The Pr-C($\eta^5$ only) distances average 2.765Å, Pr-C($\eta^5$-$\mu$) = 2.875Å average, and the two unique Pr-C($\eta^2$) separations are long at 2.940 and 3.130Å. The structure of $Cp_2Yb$(dme) is shown in Figure 2. The Cp ligands are disordered with Yb-C separations of 2.60 to 2.91Å. The Yb-O distances are 2.45 and 2.50Å. Ellis and Schlesener's[13] report detailed electronic spectra of $Cp_3Yb$ with Lewis bases $NEt_3$, $PEt_3$, pyrrolidine, THF and tetrahydrothiophene. In each case the formation of 1:1 adducts was supported by the spectrophotometric and emission spectra and luminescence titrations. An attempt was made to lay the groundwork for the correlation of the magnitude of the formation constants with the position of a visible absorption band and with the gas-phase basicities of the bases used. Luminescence was observed in the near-IR, f-f spectral region from $Cp_3Yb$ and its adducts. Brittain[14] studied the photoluminescence of $Cp_3Tb$ and $(CpMe)_3Tb$ adducts with THF at room temperature and 77K. Significant differences were observed at 77K between the Cp and CpMe derivatives. Results suggest conclusions regarding molecular symmetries in solution can be drawn by careful analysis of the fine structure within the Tb(III) emission bands.

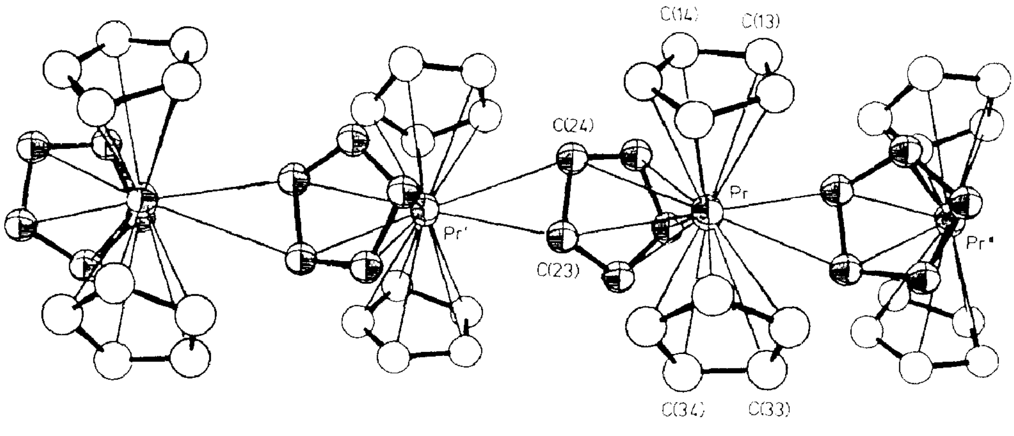


Fig. 1. $Cp_3Pr$. (Reprinted with permission from Journal of Organometallic Chemistry.)

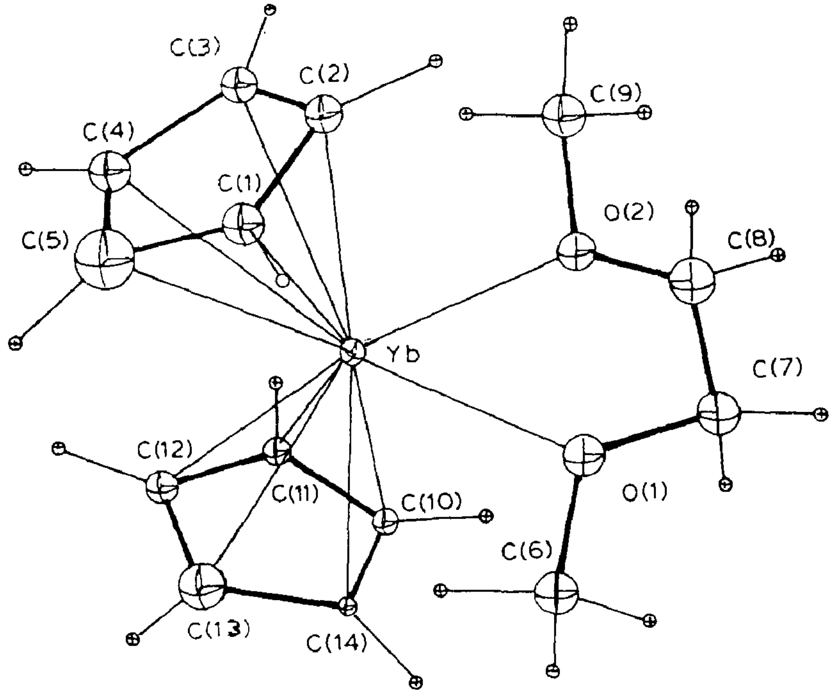


Fig. 2. $Cp_2Yb(dme)$. (Reprinted with permission from Journal of Organometallic Chemistry.)

The majority of papers on cyclopentadienyllanthanide compounds dealt with the synthetic uses of bis-Cp or bis-Cp-like lanthanide(III) compounds. Lappert, et al. in two publications[15,16] made use of $[(Cp'')_2MCl]_2$. In one study[15] excess $NaBH_4$ was allowed to react with the starting dimer in THF at 20°C. The smaller lanthanide Yb and the similar Y and Sc produced bidentate borohydride complexes. For the smallest of these, Sc, the product was solvent-free and is depicted in the ORTEP illustration, Figure 3. The other two compounds, M = Y and Yb, formed mono-THF adducts. The larger La, Pr, Nd, and Sm produced mono-THF adducts containing tridentate $BH_4^-$ as determined by IR-studies. The same starting material was allowed to react with chloride salts as depicted in eq. (1) to prepare $[N(PPh_3)_2][(Cp'')YCl_2]$, $[Li(THF)_4][(Cp'')LaCl_2]$, $[PPh_4][(Cp'')MCl_2]$ (M = Pr, Tm), $[P(CH_2Ph)Ph_3]$-$[(Cp'')MCl_2]$ (M = Nd, Dy) and $[AsPh_4][(Cp'')NdCl_2]$. The crystal structure of the latter was determined and is depicted in Figure 4. The Nd–C($\eta^5$) and Nd–Cl separations average 2.78 and 2.668Å, respectively.

$$\tfrac{1}{2}[(\mathrm{Cp''})_2\mathrm{LnCl}]_2 + [\mathrm{M}]\mathrm{Cl} \xrightarrow{\mathrm{CH_2Cl_2}} \underset{\textstyle\uparrow\; 2\mathrm{Li(Cp'')} + \mathrm{LnCl_3}}{[\mathrm{M}][(\mathrm{Cp''})_2\mathrm{LnCl_2}]} \quad (\mathrm{M} = [\mathrm{Li(THF)_4}]) \qquad (1)$$

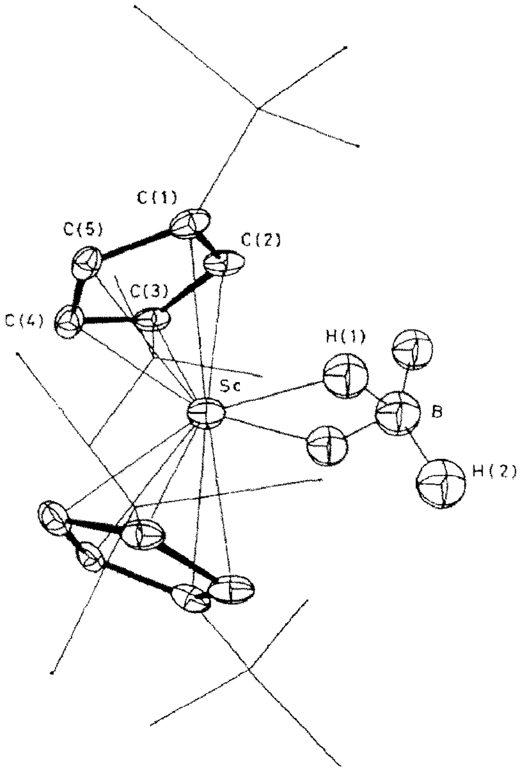


Fig. 3. [$(Cp'')_2ScH_2BH_2$]. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

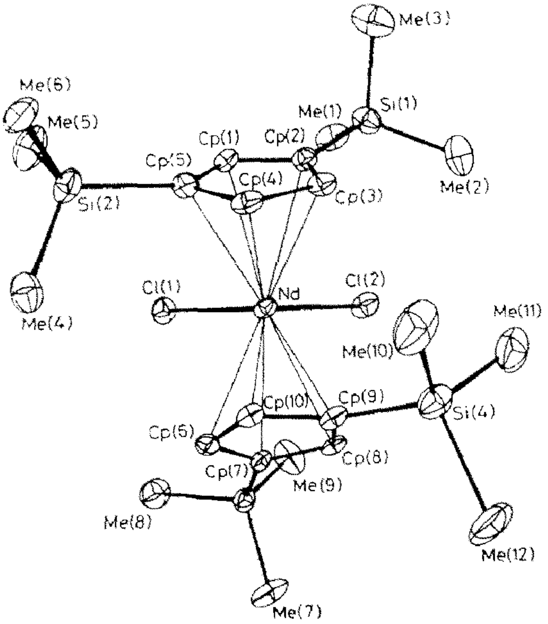


Fig. 4. [$AsPh_4$][$(Cp'')_2NdCl_2$]. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

Evans, et al. used $(CpR)_2MX(THF)$ (R = H, Me; X = H, Cl) to prepare N-alkylformimidoyl[17], alkynyl[18], and phosphide[18] complexes. The compound $[(CpR)_2YH(THF)]_2$ (R = Me) was reacted with t-butyl isocyanide to form $(CpR)_2Y[HCNCMe_3]_2$. The crystal structure of R = H was determined and is shown in Figure 5. The C bridges are 2.545 and 2.561Å from Y. The Y-N distance of 2.325Å is shorter than expected for a dative bond and is more in line with a Y-N single bond. The crystallographically characterized $[(CpMe)_2SmCCCMe_3]_2$ (Figure 6) and the spectroscopically characterized $(CpMe)_2SmPPh_2$ were prepared via eq. (2). The C bridges in the alkynyl groups are equidistant from each Sm center (2.55Å), however, the bridges are not symmetrical with Sm-C-C angles of 151 and 112°. Although this asymmetry is unexpected if no π-component is present in the bonding, the Sm-C(2) distance is too long for any π-interaction (3.20Å).

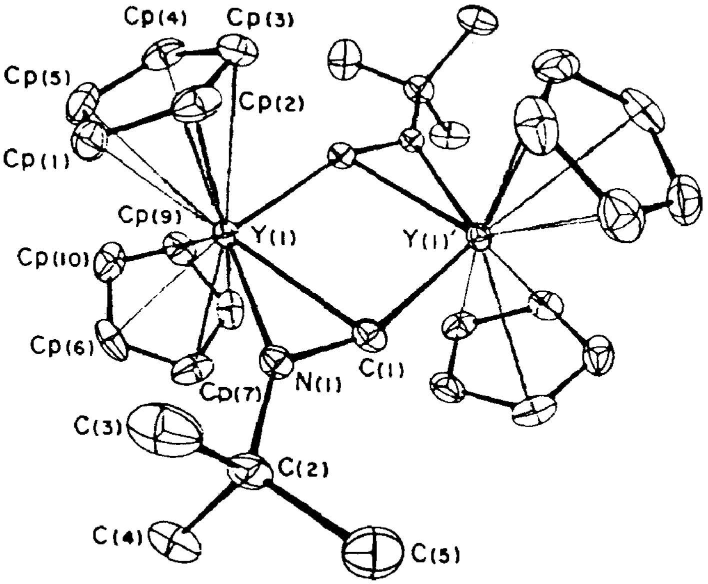


Fig. 5. $Cp_2Y[HCNCMe_3]_2$. (Reprinted with permission from Organometallics. Copyright 1983 American Chemical Society.)

$$2(CpMe)_2SmCl(THF) + 2LiCCCMe_3 \xrightarrow{THF} 2LiCl + [(CpMe)_2SmCCCMe_3]_2 \quad (2)$$

$$[(CpMe)_2SmCCCMe_3]_2 \xrightarrow{2HPPh_2} 2HCCCMe_3 + 2(CpMe)_2SmPPh_2$$

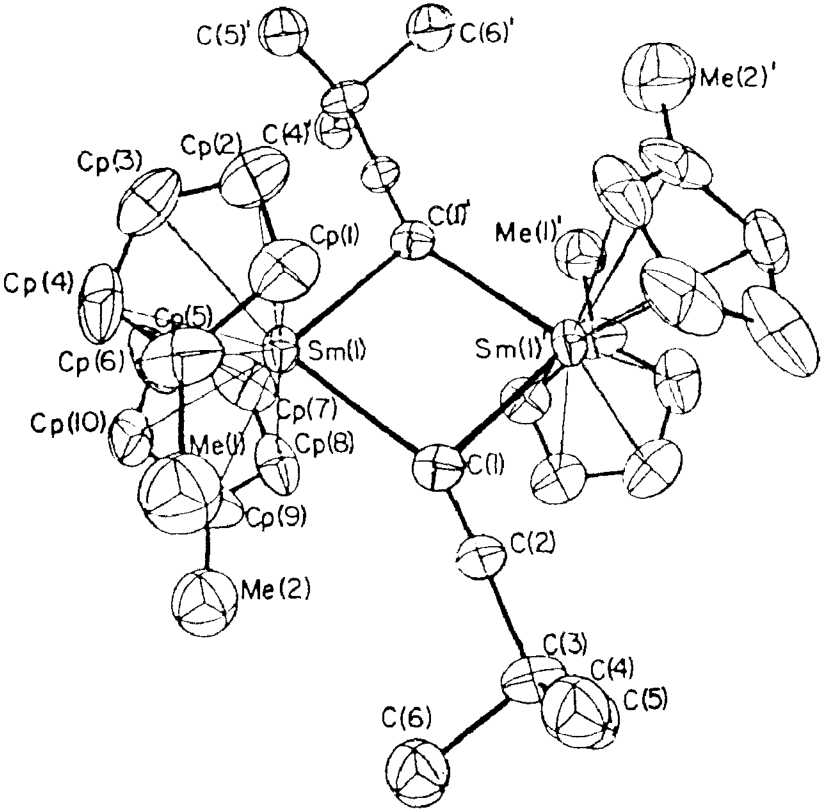


Fig. 6. $[(CpMe)_2SmCCCMe_3]_2$. (Reprinted with permission from <u>Organometallics</u>. Copyright 1983 American Chemical Society.)

In a third report Evans, <u>et al</u>.[19] used the reactivity of low-valent samarium as depicted in eq. (3). The reaction of <u>trans</u>-$(Cp^*)_2Sm(PhCCPh)$-$Sm(Cp^*)_2$ with $H_2O$ produced <u>trans</u>-stilbene and with $H_2$ produced the

$$\begin{tikzcd} (Cp^*)_2Sm(THF)_2 + PhCCPh \arrow[r] & (Cp^*)_2Sm(PhCCPh) \arrow[d, "(Cp^*)_2Sm(THF)_2"] \\ & \text{trans-}(Cp^*)_2Sm(PhCCPh)Sm(Cp^*)_2 \arrow[ul, "THF"] \end{tikzcd} \qquad (3)$$

crystallographically characterized $[(Cp^*)_2SmH]_2$ (Figure 7). The hydride exhibits a bridged structure with the $(Cp^*)_2Sm$ fragments twisted with respect to one another by 87°.

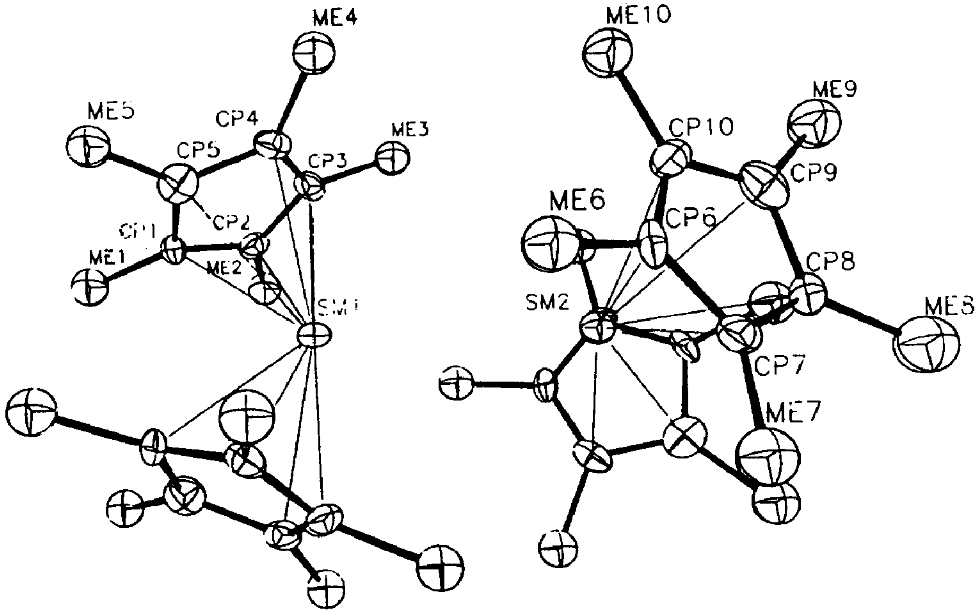


Fig. 7. [(Cp*)$_2$SmH]$_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1983 American Chemical Society.)

Qian, et al.[20] reported the formation of five new saturated compounds containing Ln-C $\sigma$ bonds shown in eqs. (4) and (5). The compounds were

$$\mathrm{(CpMe)_2ErCl + p\text{-}LiC_6H_4CH_3 \xrightarrow{THF} (CpMe)_2ErC_6H_4CH_3\cdot THF + LiCl} \qquad (4)$$

$$\mathrm{Cp_2LnCl + p\text{-}LiC_6H_4X \xrightarrow{THF} Cp_2LnC_6H_4X\cdot THF + LiCl} \qquad (5)$$

(Ln = Er, X = $CH_3$ or Cl; Ln = Yb, X = $CH_3$; Ln = Gd, X = $CH_3$)

characterized by elemental, IR and mass spectral analysis. The unsaturated monomers could be obtained by treatment with an aromatic/hexane mixture. In the same paper two new mixed ligand complexes, $Cp_2(CpMe)Ln$ (Ln = Yb, Er) were reported. The ytterbium complex was prepared from a biscyclopentadienyl ytterbium(III) chloride starting material while the erbium salt was prepared from $(CpMe)_2ErCl$.

Zalkin, Andersen, and Tilley[21] reported the preparation of Cp*-tertiary phosphine complexes of Yb(II), Yb(III), and Eu(II). The reaction schemes employed are shown in eqs. (6) and (7). The products of eq. (5) are predicted

$$\mathrm{(Cp^*)_2LnOEt_2 + dmpe \xrightarrow{C_6H_6} (Cp^*)_2Ln(dmpe)} \qquad (6)$$

(Ln = Eu, Yb)

$$\begin{tikzcd}(Cp^*)_2LnOEt_2 + dmpm(xs) \arrow[r, "C_6H_5Me"] & (Cp^*)_2Ln(dmpm) \arrow[d, "YbCl_3 \quad (Ln = Yb)"] \\ & (Cp^*)_2YbCl(dmpm)\end{tikzcd} \qquad (7)$$

to be coordination polymers and are hydrocarbon insoluble. The dmpm compounds are hydrocarbon soluble and the ligand can be displaced by $OEt_2$. Derivatives of $PMe_3$, $PBu^n_3$ or $Ph_2PCH_2CH_2PPh_2$ could not be isolated. The structure of $(Cp^*)_2YbCl(dmpm)$ was reported (Figure 8). The phosphine is monodentate with an observed Yb-P distance of 2.941Å.

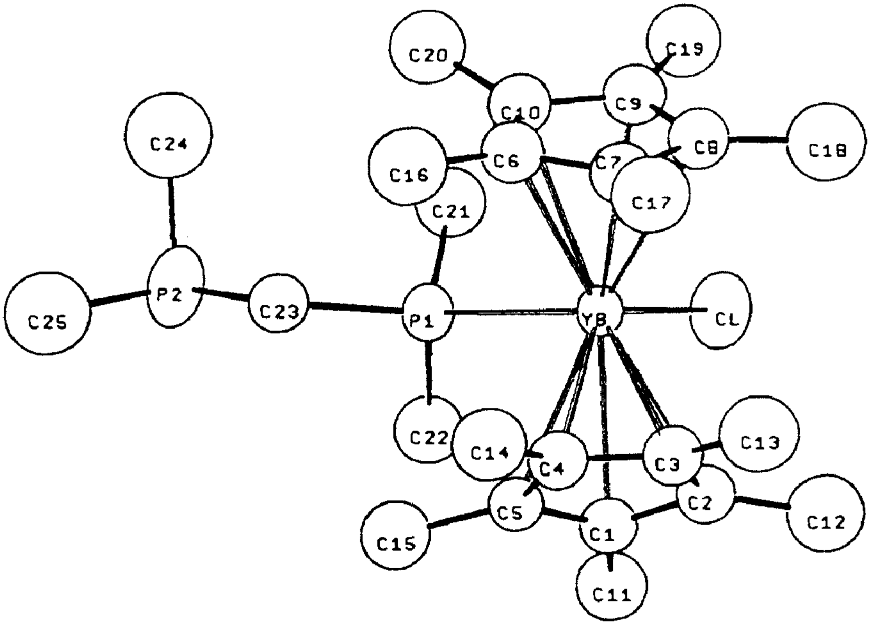


Fig. 8. $(Cp^*)_2YbCl(dmpm)$. (Reprinted with permission from <u>Inorganic Chemistry</u>. Copyright 1983 American Chemical Society.)

Bulychev, et al.[22] reported the reaction products of $Cp_2YCl$ with aluminum hydrides. The compounds $(Cp_2YCl)_2 \cdot AlH_3 \cdot OEt_2$ and $(Cp_2YH)_2 \cdot 2AlH_3$ were assumed to be polymeric. (Structures were determined by their IR spectra.) The structure of $(Cp_2YCl \cdot AlH_3 \cdot NEt_3)_2$[23] was confirmed by single crystal X-ray diffraction and is depicted in Figure 9. It consists of a $Cp_2YCl$ dimer with further

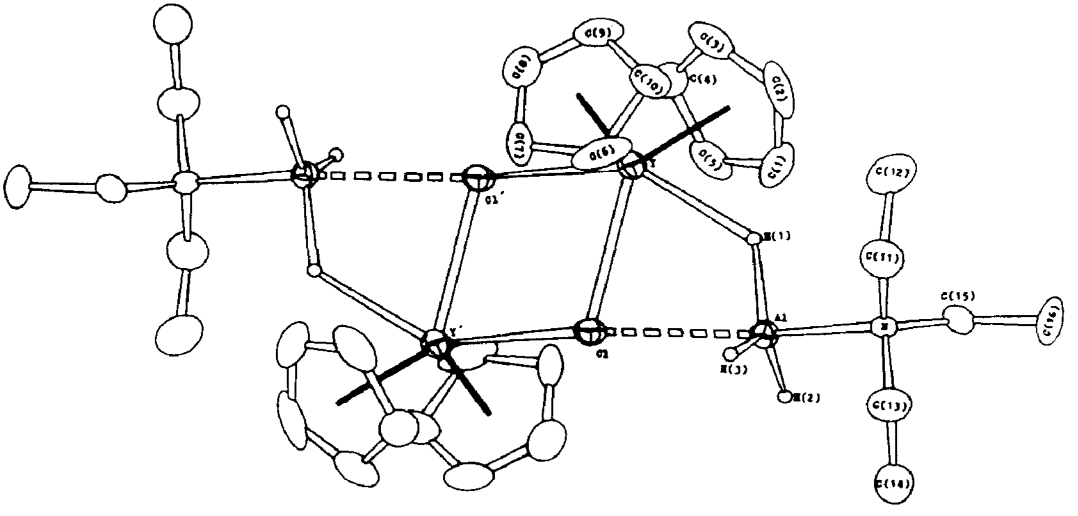


Fig. 9. $(Cp_2YCl{\cdot}AlH_3{\cdot}NEt_3)_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

coordination to each Y center by one hydrogen atom of the $AlH_3$ unit. Short Al···Cl distances suggest a weak interaction.

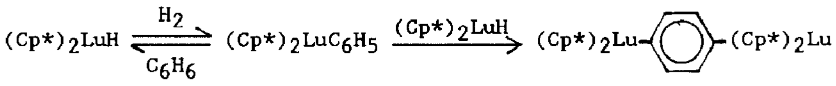
Interest in 1983 in lanthanide alkyl complexes remained high. Three reports on the reactivity of bis-Cp lanthanide alkyl compounds appeared. Schumann[24] allowed $Cp_2LuX{\cdot}THF$ ($X = CMe_3$ or $CH_2SiMe_3$) to react with $CH_2PPh_3$ and $Me_3SiCHPMe_3$ in toluene to produce three new zwitterionic complexes characterized by their NMR spectra: $Cp_2Lu(CMe_3)(CH_2PPh_3)$, $Cp_2Lu(CH_2SiMe_3)(CH_2PPh_3)$, and $Cp_2Lu(CMe_3)(CHSiMe_3PMe_3)$.

Watson published two reports on C–H activation. In one,[25] the exchange reaction in eq. (8) was investigated. Kinetic studies suggested a bimolecular

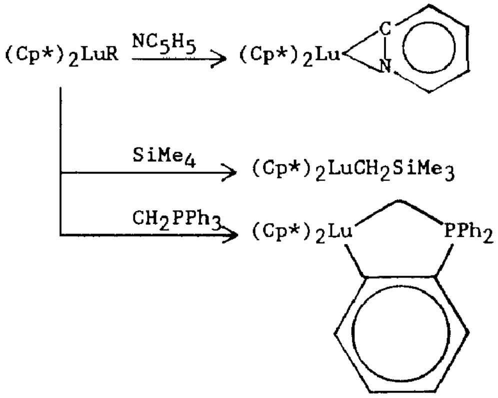
$$(Cp^*)_2LnMe + {}^{13}CH_4 \underset{}{\overset{C_6H_6}{\rightleftharpoons}} (Cp^*)_2Ln^{13}Me + CH_4 \qquad (8)$$

(Ln = Lu, Y)

mechanism zero order in benzene. Solid state $^{13}C$ NMR and crystallographic analysis of the $(Cp^*)_2LnMe$ species revealed a dimeric structure with one terminal methyl and one bridging methyl group, leaving one metal atom with only one Ln–Me interaction. The Ln–Me–Ln angle was reported to be 170°. The second study[26] investigated the reactions of $(Cp^*)_2LuR$ (R = H, Me) in hydrocarbon solvents with benzene, pyridine, $CH_2PPh_3$ and $SiMe_3$ to give products of C–H activation [eqs. (9) and (10)].



(9)

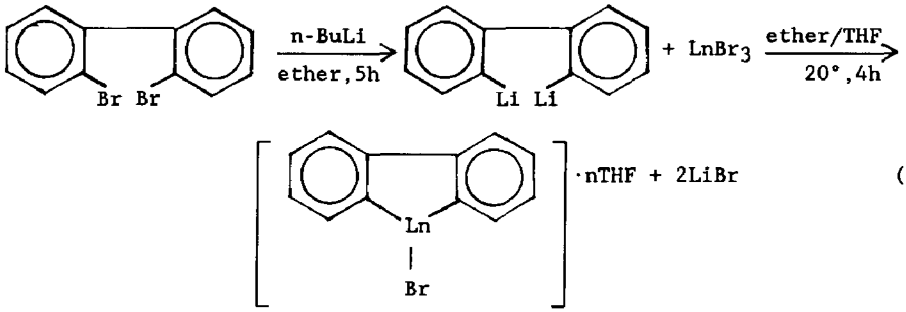


(10)

### Alkyl and Aryl Compounds

Several reports of the preparation of lanthanide alkyl complexes via oxidative addition to the $Ln^0$ metals appeared. Fujiwara, et al.[27] reported the reactions of metallic Pr, Nd, and Dy with EtI at room temperature or 65°C in THF to prepare EtLnI. The metals Gd, Ho, and Er did not react. Dolgoplosk, et al.[28] described the detailed reactions of triphenylmethyl chloride, benzyl chloride and phenyl bromide with metallic lanthanides (Pr, Nd, Gd, Ho) in THF and discussed the reaction mechanism. The composition and stability of the complexes prepared as a function of reaction conditions and metal used were studied. Elemental analyses indicated the general formula $R_nLnX_{3-n}$ ($X = Cl$, Br; $n = 1, 1.5$). In two further reports by Dolgoplosk, et al.,[29,30] the synthesis of benzyllanthanide chlorides ($RLnCl_2$, Ln = Nd, Pr)[29] and triphenylmethyllanthanide chloride ($R_nLnCl_{3-n}$, Ln = Nd, Pr, Gd, Ho; $n = 1$ or 1.5)[30] were accomplished via oxidative addition of the organic chloride to the metallic lanthanide in THF at 20°C. For the latter and Ln = Nd, when the RCl/Ln ratio was $\leq 1$, $R_3Nd_2Cl_3$ was formed. When the ratio was 1.5/2 $RLnCl_2$ formed for Ln = Nd, Pr, Gd, Ho. Yields ranged from 73-100%. Reaction of the corresponding mercuriiodide and $Yb^0$ in THF by Suleimanov, et al.,[9] gave $CF_3(HgYb)I\cdot 4THF$.

Three reports appeared detailing the reactions of aryl ligands with the lanthanides. Sigalov, et al.[31] obtained $C_6F_5YbBr$ via reaction of $C_6F_5Br$ and $Yb^0$ in THF. Bidentate biphenyl lanthanide derivatives were prepared by Syutkina, et al.[32] via eq. (11). The compounds are soluble in THF,



(11)

(Ln = Pr, Sm, Gd, Yb, Ho)

moderately so in benzene, toluene and $CCl_4$. Characterization was accomplished via elemental analysis and NMR and PMR spectra. THF and toluene soluble, fluorenyl (Fl) derivatives, $Fl_2LnCl_2Li \cdot 2THF$,[33] of La, Nd, Sm, Ho, and Lu were prepared by reaction of FlLi and the corresponding $LnCl_3$ in THF at 20°C. Sigalov, et al.[33] report yields of 40-85% and a structure which includes two chloride ions binding the $Ln^{3+}$ and $Li^+$ cations. The final complex composition was reported to be independent of reaction stoichiometry or concentration of reactants.

## Isocarbonyls, Carboranes, Cyclooctatetraenes, Miscellaneous

Bimetallic lanthanide isocarbonyl complexes appeared in reports by Eremenko, et al.[34] and Suleimanov, et al.[35] In the former the synthesis of $La(THF)_5[CpMo(CO)_3]_3 \cdot THF$ was accomplished by reaction of activated powdered La with $[CpMo(CO)_3]_2$ or $Hg[CpMo(CO)_3]_2$ in THF. The X-ray structure of this complex was carried out. The La atom is attached to three $[CpMo(CO)_3]$ fragments through linear Mo—C—O—La bridges. (The average angle is 177.9°, the average La—O separation, 2.444Å.) The second study described the synthesis and thermal stabilities of dimetal metal carbonyl derivatives of the lanthanides from anhydrous lanthanide salts and sodium salts of metal carbonyls. The compounds $(CO)_4CoLnCl_2 \cdot nTHF$ ($Ln = Sm$, $n = 2$; $Ln = Ho, Yb$, $n = 1$) were prepared. Subsequent reaction with NaCp led to $(CO)_3Co—CO—LnCp_2 \cdot nTHF$. These reactions were followed by their IR spectra.

Suleimanov published four reports[36-39] on the synthesis of carboranyl derivatives of the lanthanides. These are summarized in eqs. (12-16).

$$C_6H_5C(B_{10}H_{10})CLi + LnI_2 \xrightarrow[20^\circ C]{THF} C_6H_5C(B_{10}H_{10})CLnI \qquad (12)^{36}$$

(Ln = Sm, Eu, Yb)

$$RC(B_{10}H_{10})CLi + LnCl_3\cdot 3THF \xrightarrow{\text{ether}} RC(B_{10}H_{10})CLnCl_2\cdot LiC(B_{10}H_{10})CR\cdot mTHF \qquad (13)^{37}$$

$(R = Ph,\ Ln = Tm,\ m = 5;\ R = Me,\ Ln = Yb,\ m = 2)$

$$\lfloor\xrightarrow{\text{benzene/THF}} (RC(B_{10}H_{10})C)_nLnCl_{3-n}\cdot mTHF \qquad (14)^{38}$$

$(R = Me,\ Ln = La,\ n = 1,\ m = 0;\ R = Ph,\ Ln = La,\ n = 3,\ m = 1;\ R = Ph,\ Ln = Tm,\ n = 2,\ m = 5;\ R = Ph,\ Ln = Tm,\ n = 3,\ m = 2;\ R = Me,\ Ln = Tm,\ n = 1,\ m = 4;\ R = Me,\ Ln = Yb,\ n = 3,\ m = 1)$

$$R_2Hg + mLn^0 \longrightarrow R_2Ln\cdot THF_n + (m-1)LnHg \qquad (15)^{38}$$

$$3R_2Hg + 2Ln^0 \longrightarrow 2R_3Ln\cdot nTHF + 3Hg^0 \qquad (16)^{39}$$

$(R = H,\ Me,\ Ph;\ Ln = La,\ Sm,\ Tm,\ Yb)$

Wayda[40] reported the extension of the known series $(C_8H_8)LnCl(THF)_n$ to Ln = La, Er, and Lu. The syntheses of these involved slight modifications to the known reaction of $LnCl_3$ with $K_2C_8H_8$ in THF. Subsequently these complexes were used for the synthesis of new alkyl complexes depicted in eq. (17). The

$$(C_8H_8)LnCl(THF) + LiR \xrightarrow[\text{THF}]{-78^\circ C} (C_8H_8)LnR(THF)_x + LiCl \qquad (17)$$

$(R = CH_2SiMe_3,\ x = 2;\ R = o\text{-}C_6H_4CH_2NMe_2,\ x = 1)$

new complexes were characterized by elemental analysis, their IR spectra and X-ray fluorescence.

Rösch and Streitwieser[41] published the quasirelativistic SCF-X$\alpha$ scattered-wave study of cerocene (also uranocene and thorocene). Nonrelativistic treatment gave essentially the same description. The ligand field splitting is less for $(C_8H_8)_2Ce$ than for $(C_8H_8)_2U$ or $(C_8H_8)_2Th$ reflecting the greater ionic character for Ce.

## Organolanthanides in Organic Synthesis

Fujiwara, et al.[27] utilized PhLnI complexes of Eu, Sm, and Yb and N,N-dimethylbenzamide to synthesize benzophenone. The reaction of EtSmI with benzaldehyde was reported in the same paper to yield reduction and coupling products of benzaldehyde. Sigalov, et al.[31] utilized the Yb, Eu, Sm, and Ce derivatives of PhLnI to prepare styrene from vinyl bromide in THF (Kharasch reaction conditions). Biphenyl was a side product (< 10%). Yields were > 90% for Ln = Yb, 10% for Eu, 4% for Sm, and the reaction would not work with Ln = Ce. These same PhLnI compounds were reacted with trans-chalcone, benzalacetone, 9-fluorenone, and benzophenone in a separate paper.[42] Reaction with trans-chalcone proceeded regiospecifically via 1,2-addition in contrast to the same reaction with PhMgI or PhLi. Reaction with unsaturated ketones PhCHCHCOR (R = Ph, Me) in THF at -40°C proceeded as a 1,2-addition with the formation of PhCHCHC(OH)(Ph)R (Sigalov, et al.[43]). The reaction of PhYbI or PhEuI with 1,2,2-trifluorostyrene at 20°C gave trans-1,2-difluorostilbene in high yields (Yb, 100%; Eu, 80-85%: Sigalov, et al.[44]).

Deacon, MacKinnon and Tuong[45] published an extensive paper on the reaction of bis(polyfluorophenyl)ytterbium compounds, $R_2Yb$ (R = $C_6H_5$ or p-$HC_6F_4$) with trans-$Rh(CO)Cl(PPh_3)_2$, $NiCl_2$(2,2'-bipyridyl), $NiCl_2(PPh_3)_2$, $PtCl_2$(2,2'-bipyridyl), $Ph_3SnCl$, $I_2$, and $HgCl_2$. The polyfluorophenyl derivatives trans-$RRh(CO)(PPh_3)_2$, $R_2Ni$(2,2'-bipyridyl), trans-$(C_6F_5)_2Ni(PPh_3)_2$, $(C_6F_5)_2Pt$(2,2'-bipyridyl), $Ph_3SnC_6F_5$, $C_6F_5I$ and $(C_6F_5)_2Hg$ were prepared. Carbonation of $(C_6F_5)_2Yb$ in THF followed by acidification led to pentafluorobenzoic acid and 2,3,4,5-tetrafluorobenzoic acid. Reactivities in general were found to be comparable to Grignard or organolithium reagents.

Evans, et al.[46] published a study examining the catalytic behavior of a number of lanthanide metal vapor systems with alkynes, dienes, and phosphines. The new complexes have the capacity to catalytically activate molecular hydrogen in hydrogenation reactions. These complexes could not be fully characterized.

Yu, Chen, and Wang[47] report the stereospecific polymerization of dienes by new cyclopentadienyl rare earth dichloride catalysts. The catalytic activity was increased when THF or HCl was present. Catalytic activity decreased in the order Nd > Pr > Y >> Ce > Gd. Activity with the alkylaluminum cocatalyst decreased in the order iso-$Bu_2AlH$ > iso-$Bu_3Al$ = $Et_3Al$ >> $Me_3Al$ and had no effect on the stereo structure of the polymer.

## ACTINIDES

### Cyclopentadienyl or Cyclopentadienyl-Like Compounds

(i) Synthesis, characterizations, structural studies of Cp or Cp-like compounds. Leonev, et al.[48] studied the thermal decomposition of $Cp_4U$, $Cp_3UCl$, $(CpMe)_3UCl$, $(C_8H_8)_2U$, and $(BuC_8H_7)_2U$ by thermogravimetry. Thermal stability was found to decrease in the order $Cp_4U > Cp_3UCl \geq (C_8H_8)_2U > (CpMe)_3UCl > (BuC_8H_7)_2U$.

Wasserman and Moody, et al.[49] published the X-ray structure of $Cp_3U \cdot THF$ (Figure 10). Crystals of this complex were obtained from the reaction of $U[N(SiEt_3)_2]Cl_2$ with 2 equivalents of NaCp in THF. It is pseudotetrahedral and isostructural with the analogous $Cp_3Ln \cdot THF$ series. The U—C distances average 2.79Å, the U—O distance is 2.55Å.

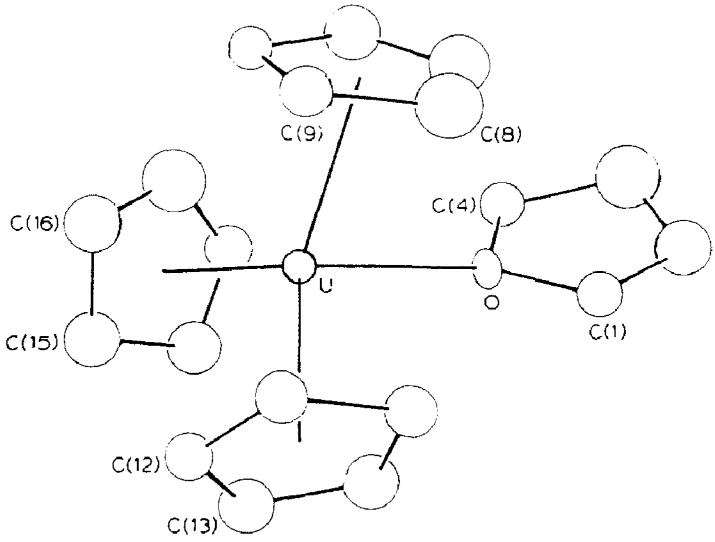


Fig. 10. $Cp_3U \cdot THF$. (Reprinted with permission from Journal of Organometallic Chemistry.)

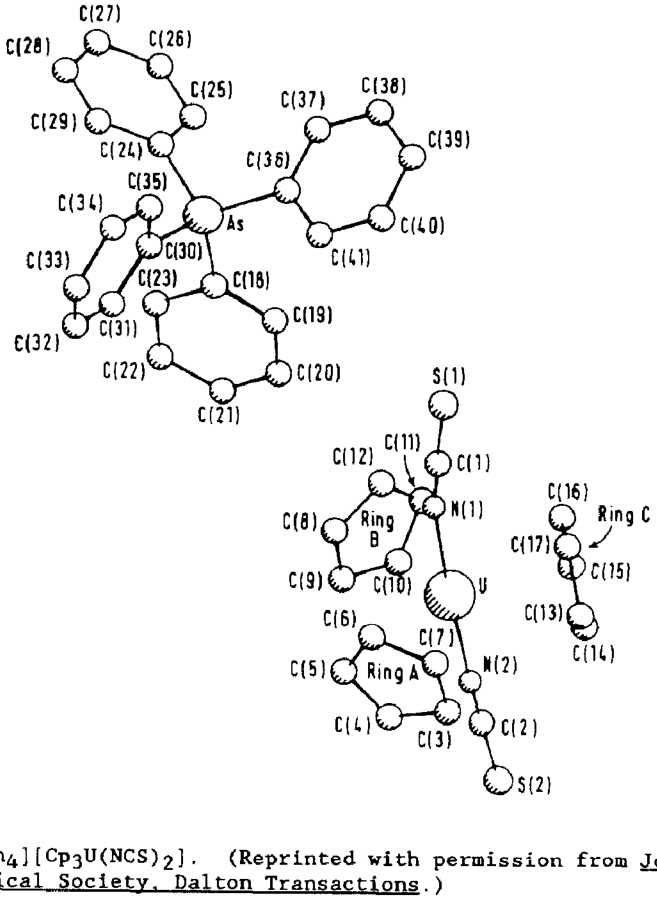


Fig. 11. $[AsPh_4][Cp_3U(NCS)_2]$. (Reprinted with permission from Journal of the Chemical Society, Dalton Transactions.)

The crystal structure of $[AsPh_4][Cp_3U(NCS)_2]$ (Figure 11, Bombieri, et al.[50]) was reported to be essentially trigonal bipyramidal with the Cp ring centroids forming the equatorial plane. The axial U—N separations are 2.46 and 2.50Å.

Karraker[51] studied the bonding in $Cp_2Np^{IV}$ compounds utilizing $^{237}Np$ Mössbauer spectra. Spectra were obtained for a series of $Np^{IV}$ compounds of general composition $NpX_4$, $NpX_2Y_2$, and $NpX_2YY'$ where X = acetylacetonate, bis(1-pyrazolyl)borate, and tris(1-pyrazolyl)borate and Y, Y' = Cl, Cp, CpMe. No evidence for covalent bonding between the Cp ring and $Np^{IV}$ was observed. It was proposed that ligand repulsions lengthen the Nd—Cp and Nd—CpMe bonds and thus prevent appreciable $Np^{IV}$—ligand orbital overlap.

Bagnall, et al.[52] also studied $CpNp^{IV}$ compounds by preparing oxygen donor complexes of $CpNpCl_3$. The compounds prepared included $NpCl_4(Me_3CCONMe_2)$, $CpNpCl_3L_2$, and $(EtCp)Np(Ph_3PO)_2Cl_3$ where L = THF, $MeCONMe_2$, $Me_3CCONMe_2$, $Ph_3PO$, $(Me_2N)_3PO$ and $\frac{1}{2}Ph_2P(O)CH_2CH_2P(O)Ph_2$. Cp complexes with $MeCONMe_2$, $Me_3CCONMe_2$ and $Ph_3PO$ disproportionated to mixtures of $Cp_3NpCl$ and $NpCl_4L_2$ when attempts were made to recrystallize these from THF; the others did not. IR, near-IR and visible solution spectra were reported.

Bursten and Fang[53] reported the valence electronic structures of $Cp_2UX_2$ (X = Cl, Me) giving a quantitative MO description using the $X\alpha$-scattered wave method including relativistic corrections. The results are compared to the He(I) and He(II) photoelectron spectroscopic studies of $(Cp^*)_2UMe_2$ and $(Cp^*)_2UCl_2$.

Fischer and Yünlü[54] described the near-IR/visible and $^1H$ NMR spectra of $[Cp_3U(\mu\text{-}NCBH_3)]_n$ and $[(CpMe)_3U(\mu\text{-}NCBH_3)]_n$. These compounds were shown to be trigonal bipyramidal in the solid state but pseudo-tetrahedral in noncoordinating solvents like $CH_2Cl_2$ and toluene. The $^1H$ NMR spectra of the CpMe derivative indicated a temperature dependent equilibrium involving two rapidly interconverting $\psi$-$T_d$ isomers (eq. 18). In addition a reversible color change (green $\rightleftharpoons$ brown) was observed at 130-150°C suggesting facile rupture of the U—N and U—H bonds.

$$(CpMe)_3U(\eta^3\text{-}H_3BCN) \rightleftharpoons (CpMe)_3UNCBH_3 \qquad (18)$$

Dormand[55] prepared the mixed-bis-Cp complexes $(CpR)(CpR')UX_2$ and $(CpR)(CpR')_2UCl$ starting with $(CpR)UX_3$ (X = Cl, $NEt_2$; R = Me, Et; R' = H, Me, Et). It was observed that if the two Cp ligands have a chiral center, a mixture of one racemic and two meso isomers is obtained.

The $^1H$ and $^{13}C$ NMR of $(CpCH_2Ph)_3UCl$ (Folcher and Dormand, et al.[56]) was used in conjunction with the known solid state structure to analyze paramagnetic induced shift. It was determined that the solid state structure was retained in solution and a mechanism was proposed for spin delocalization by polarization of the electrons of the ligand which were assigned to the $\pi$-bonds.

Lappert, et al.[57] reported the use of bis-trimethylsilylcyclopentadienyl (Cp") ligands as a route to $(Cp")MX_2$ compounds of U and Th (eq. 19).

$$MCl_4 + 2Li(Cp") \xrightarrow[\substack{THF/OEt_2(Th) \\ -23^\circ C}]{THF(U)} (Cp")_2MCl_2 + 2LiCl \qquad (19)$$

(M = Th 60% yield; U 70%)

A crystal structure of $(Cp")_2ThCl_2$ was used to confirm the structure but the details were not presented. As discussed below these compounds were used to access bis–Cp–U and Th alkyls and amides.

Ernst, et al.[58] published the synthesis of an acyclic pentadienyl derivative of U(IV), U(2,4-dimethylpentadienyl)$_3$. The compound was prepared from $UCl_3$ in THF and characterized by IR, NMR, elemental analysis and magnetic susceptibility measurements.

(ii) Cp and Cp-like actinide alkyls, allyls, and ylides. Bruno, Marks, and Morss[59] reported a detailed investigation of the M–L bond disruption enthalpies in $(Cp^*)_2Th$ hydrocarbyls, metallocycles, hydrides, and dialkylamides. The calculated bond disruption enthalpies for the Th–hydrocarbyls fall in the range 60-90 kcal/mol with $C_6H_5 > CH_3 \simeq CH_2SiMe_3 > CH_2CH_3 \geq CH_2C_6H_5 \simeq n\text{-}C_4H_9 \simeq CH_2CMe_3$. The Th–C bonds were reported to appear strengthened by Th–OR coligands and weakened by Th–Cl coligands. In the metallocycles, $(Cp^*)_2Th(CH_2)_2CMe_2$ and $(Cp^*)_2Th(CH_2)_2SiMe_2$, the strain energies are reported as $\simeq$ 16 and 8 kcal/mol, respectively. The Th–H bonds were shown to be $\simeq$ 20 kcal/mol stronger than the Th–alkyl bonds and the Th–$NR_2$ $\simeq$ 18 kcal/mol stronger. In this same report the synthesis of a new compound, $(Cp^*)_2Th(n\text{-}C_4H_9)_2$ was reported as the product of $(Cp^*)_2ThCl_2$ and n-butyllithium at -78°C.

The attempted alkylation of $Cp_3UCl$ by gaseous butadiene (with traces of $O_2$) in $CH_3CN$ was reported by Bombieri, et al.[60] and resulted in the crystallization of $[Cp_3U(NCMe)_2]_2[UO_2Cl_4]\cdot 2C_4H_6$. The crystal structure (Figure 12) and IR of this compound were presented. The structure is essentially trigonal bipyramidal with trans-axial acetonitrile ligands. The U-C distances average 2.74Å, the U–N separations are reported to be 2.61 and 2.58Å.

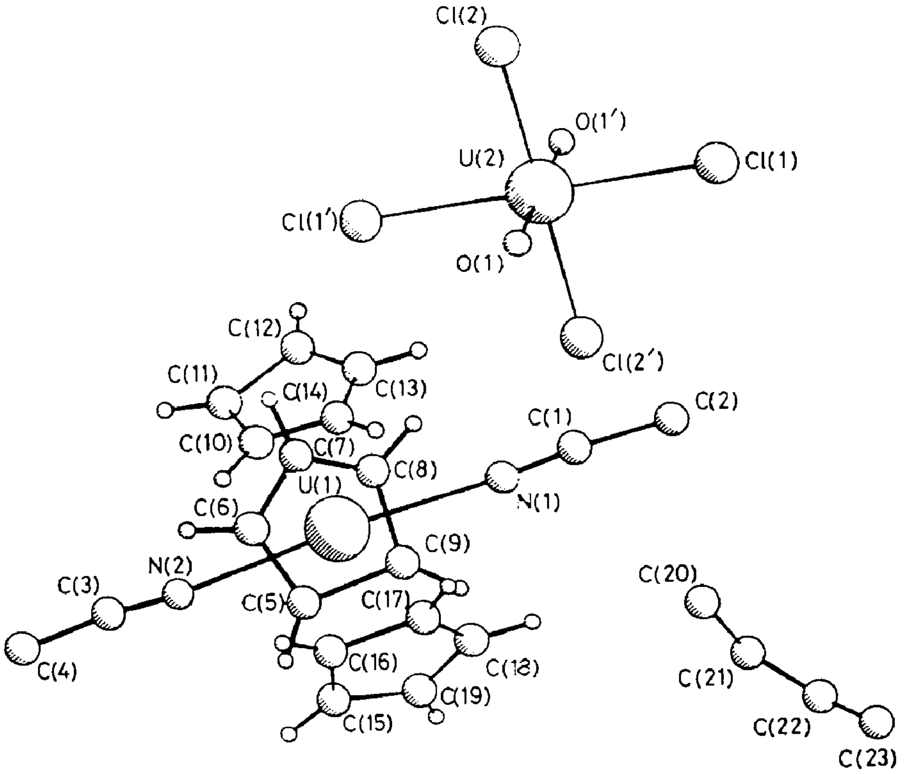


Fig. 12. $[Cp_3U(NCMe)_2]_2[UO_2Cl_4]\cdot 2C_4H_6$. (Reprinted with permission from *Journal of the Chemical Society, Dalton Transactions*.)

Lappert, *et al.*[57] used the product of eq. 19, $(Cp'')_2MCl_2$, to prepare several alkyl and amide derivatives, eqs. 20-22.

$$(Cp'')_2UCl_2 + 2LiR \xrightarrow[-78^\circ C]{OEt_2} (Cp'')_2UR_2 \qquad (20)$$

($R$ = $CH_2Ph$, 60% yield; $CH_2SiMe_3$, 65% yield)

$$(Cp'')_2UCl_2 + 2LiNMe_2 \xrightarrow[-78^\circ C]{OEt_2} (Cp'')_2U(NMe_2)_2 \text{ (60\% yield)} \qquad (21)$$

$$(Cp'')_2UCl_2 + LiNMe_2 \xrightarrow[-78^\circ C]{OEt_2} (Cp'')_2UCl(NMe_2) \text{ (70\% yield)} \qquad (22)$$

Cramer and Gilje, *et al.*[61] published the crystal structure of $Cp_3UCHPMe_2Ph$ (Figure 13), reported to have a U—C double bond. The structure is pseudo-tetrahedral, with U—C(Cp) distances that average 2.79Å. The U-C(ylide) distance is a short 2.29Å with a U—C—P angle of 142°. The P—C(U) bond length is 1.69Å compared to the average P—Me distance of 1.83Å.

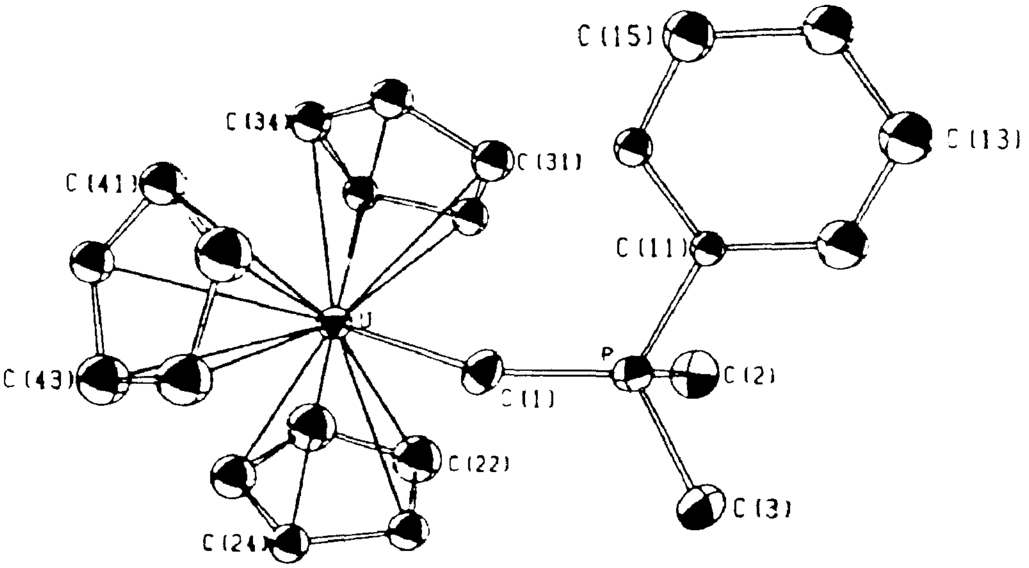


Fig. 13. $Cp_3UCHPMe_2Ph$. (Reprinted with permission from Organometallics. Copyright 1983 American Chemical Society.)

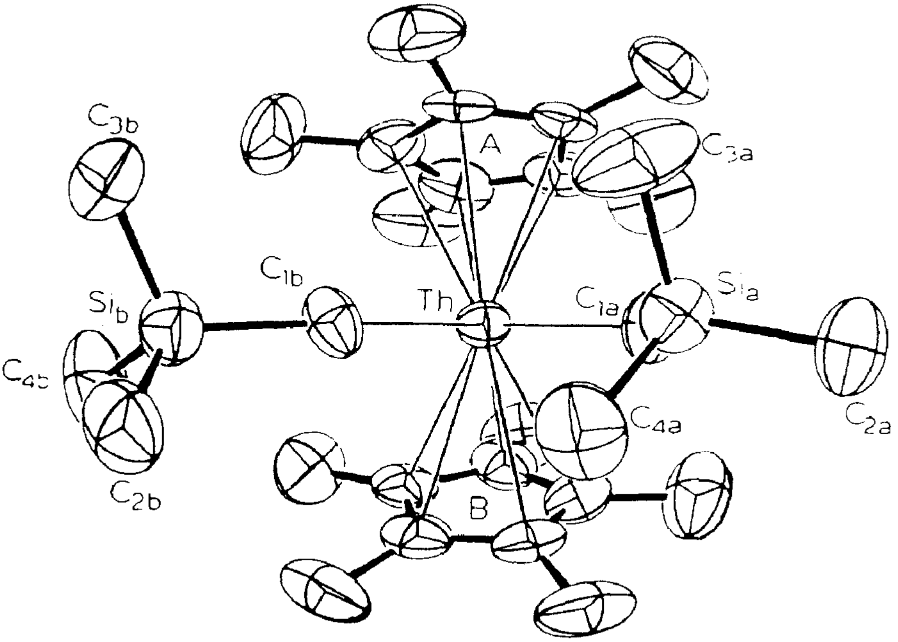


Fig. 14. $(Cp^*)_2Th[CH_2SiMe_3]_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Bruno, Marks and Day[62] reported the crystal structure of $(Cp^*)_2Th[CH_2SiMe_3]_2$ (Figure 14). The $(Cp^*)_2Th$ fragment is normal with an average Th–C distance of 2.81Å, however, the $ThR_2$ portion of the molecule was found to be highly unsymmetrical. The Th–C separation and Th–C–Si angle for the two alkyls are 2.51Å, 132.0° for one and 2.46Å, 148.0° for the other. The asymmetry was ascribed to severe intramolecular nonbonded contacts. The methyl–H of one ligand is 2.3Å from the α–C of the other. The structure was discussed in terms of the facile intramolecular cyclometallation which this molecule undergoes.

He, Burwell and Marks[63] published a report on the reactions of $(Cp^*)_2MMe_2$ and $(Cp^*)_2M(CD_3)_2$ (M = Th, U) with partially dehydroxylated and nearly completely dehydroxylated alumina. The mechanistic and labeling studies revealed that the production of methane occurs via protolysis by surface OH, H atom abstraction, and elimination within the $MR_2$ groups. Chemical evidence is presented to propose the latter pathway to result in alumina-stabilized actinide alkylidenes.

Folcher and Fischer, <u>et al</u>.[64] reported the facile reduction of tris-Cp-uranium alkyls to anionic U(III) alkyl systems via eq. (23). GC/MS studies

$$Cp_3UR + LiR'(xs) \xrightarrow[30\text{-}50^\circ C]{THF} RH + R'H + [Li(THF)_n][Cp_3UR] + [Li(THF)_n][Cp_3UR'] + \text{other products} \quad (23)$$

$(R = Me,\ i\text{-}C_3H_7,\ i\text{-}C_4H_9,\ n\text{-}C_4H_9;\ R' = Me,\ n\text{-}C_4H_9)$

suggested H uptake from MR (coordinated U or Li) and not from the deuterated solvent. An excess of LiR′ and the solvent THF were deemed necessary.

Cymbaluk, Ernst and Day[65] published a detailed study on the synthesis, crystal structure and bonding of $(Cp^*)U(allyl)_3$ (allyl = $C_3H_5$ or $2\text{-}MeC_3H_4$). The compounds were prepared as indicated in eq. (24). The hydrocarbon soluble

$$(Cp^*)UCl_3(THF)_2 + 3(allyl)MgX \xrightarrow[-78^\circ C]{THF} (Cp^*)U(\eta^3\text{-allyl})_3 + 3MgClX \quad (24)$$

$(X = Br, Cl;\ allyl = C_3H_5,\ 2\text{-}MeC_3H_4)$

allyl products were characterized by IR (which indicated $\eta^3$-allyls), NMR, quantitative hydrolysis, elemental analysis and single crystal X-ray diffraction. The crystal structure of the $2\text{-}MeC_3H_4$ derivative is shown in Figure 15. The π-allyls are symmetric, with average parameters of U-allyl(terminal C) = 2.66Å, U-allyl(middle C) = 2.80Å and U-C(Cp*) = 2.79Å.

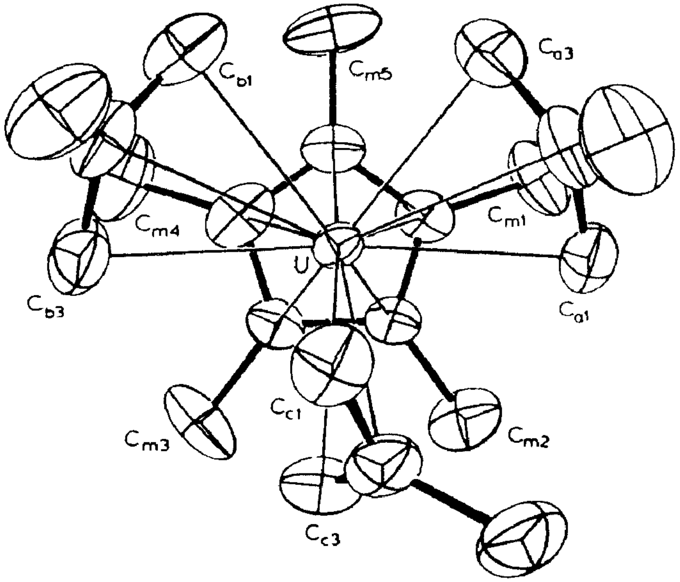


Fig. 15. $(Cp^{*})U(\eta^3\text{-}2\text{-}MeC_3H_4)_3$. (Reprinted with permission from *Organometallics*. Copyright 1983 American Chemical Society.)

(iii) *CO and $CO_2$ activation in cyclopentadienyl or cyclopentadienyl-like actinide compounds*. Leonov, *et al*.[66] published the reactions of $Cp_4U$ with CO and $CO_2$. Carbon monoxide and $Cp_4U$ were reported to produce a polymeric complex of composition $(CpUCO)_n$. The same reaction with carbon dioxide reportedly gave the dimeric $[Cp_2UH_2 \cdot CO_2]_2$. The IR spectra of the new compounds were given.

Cramer and Gilje, *et al*.[67] reported the reaction of $Cp_3UCHPMePhR$ (R = Me or Ph) with $[CpFe(CO)_2]_2$ in THF at 25°C in which coupling of bridging and terminal carbonyls occurred and a new carbon-carbon bond formed between a carbonyl and the ylide ligand. IR spectra indicated both bridging and terminal CO's in the product. The crystal structures of both R = Ph and R = Me were determined. The former is disordered, the latter is not and is depicted in Figure 16.

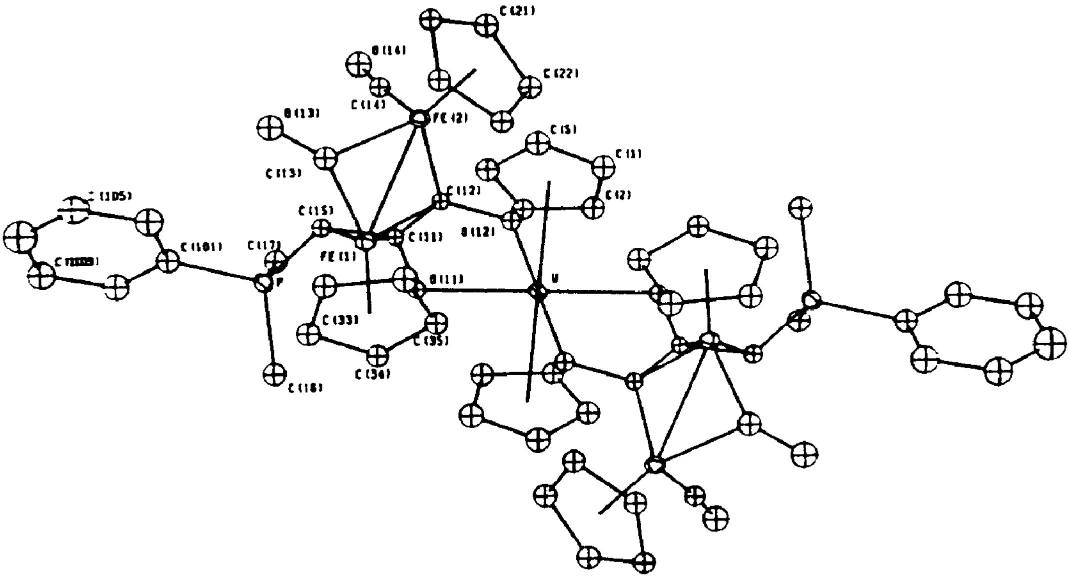


Fig. 16. $Cp_2U[(O_2C_2CHPMe_2Ph)Fe_2Cp_2(CO)_2]_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1983 American Chemical Society.)

Moloy, Marks and Day[68] published a mechanistic study of CO activation via $\eta^2$—acyl—CO coupling and the formation of metal bound ketones. Several new compounds were reported including ylides (eq. 25), and isocyanides (eqs. 26, 27). The crystal structure of the R = Me product of eq. 25 was reported and is shown in Figure 17. The Th—O distances are symmetric and the C—O separation long.

$$(Cp^*)_2Th[\eta^2\text{-}COCH_2CMe_3]Cl + PR_3 \xrightarrow[\text{25°C, 5h}]{\text{1 atm CO} \atop \text{toluene}} (Cp^*)_2ThCl(O_2C_2[CH_2CMe_3][PR_3]) \quad (25)$$

(R = Me, Ph)

$$(Cp^*)_2Th[\eta^2\text{-}COCH_2R]Cl + R'NC \xrightarrow[\text{25°C,½h}]{\text{toluene}} (Cp^*)_2ThCl[OC(CH_2R)CNR'] \quad (26)$$

$$(Cp^*)_2Th[\eta^2\text{-}COCH_2R]Cl + 2R'NC \xrightarrow[\text{25°C,½h}]{\text{toluene}} (Cp^*)_2ThCl(CNR')[OC(CH_2R)CNR'] \quad (27)$$

(R = $CMe_3$, R' = $CMe_3$; R = Ph, R' = $CMe_3$; R = $CMe_3$, R' = $C_6H_{11}$)

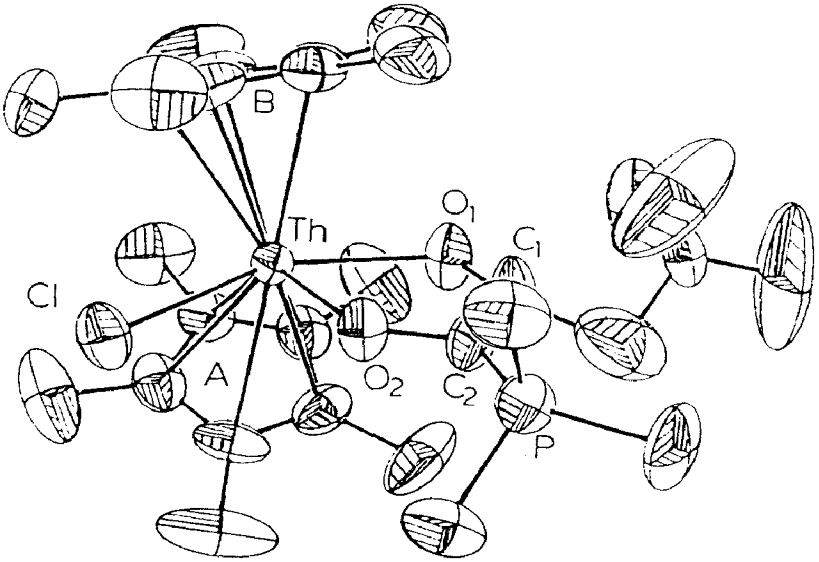


Fig. 17. $(Cp^{*})_2ThCl(O_2C_2[CH_2CMe_3][PMe_3])$ . (Reprinted with permission from Journal of the American Chemical Society. Copyright 1983 American Chemical Society.)

## Cyclooctatetraenyl, Indenyl, and Alkyl Actinide Compounds

Solovev, et al.[69] reported the preparation of thorocene, $(C_8H_8)_2Th$, from $ThCl_4$ and $K_2(C_8H_8)$ and the study of its vapor pressure and thermal stability.

Streitwieser, et al.[70] published a study of dibenzouranocene, $(C_{12}H_{10})_2U$, and related compounds. The reactions of $K_2(C_{12}H_{10})$ and $MCl_4$ (M = U, Th) in THF produced dibenzouranocene and dibenzothoracene. The Diels-Alder product from cyclooctatrienyne and butadiene (7,10-dihydrobenzocycloctatraene) gave bis-(dihydrobenzocyclooctatetrane)uranium which could not be dehydrogenated to dibenzouranocene. Catalytic hydrogenation of this compound resulted in bis(tetrahydrobenzocyclooctatetrane)uranium. This latter compound was also prepared by the reaction of $C_8H_8^{2-}$ with 1,4-dibromobutane to give cis-bicyclo[6.4.0]dodeca-2,4,6-triene which was deprotonated with $KNH_2/NH_3$ and treated with $UCl_4$. NMR and ligand exchange equilibrium between uranocene and dibenzouranocene were studied. The latter was reported to favor the mixed-sandwich compound.

Quasi-relativistic SCF-Xα scattered wave studies of uranocene, thorocene, and cerocene by Rösch and Streitwieser,[41] found similar results to the non-relativistic calculations and reasons for this are given. The study confirmed that the $f_{\pm 2}$ orbitals of the metal atom contribute to the covalent ring-metal bonding and emphasized the role of the 6d orbital (M = Th, U).

Garbe and Boekelheide[71] reported the reduction of the cyclooctatetraene ring of $[2_2](1,6)$cyclooctatetraenyl(1,4)cyclophane via electrochemical reduction or by using lithium metal to give the dianion which reacts with $UCl_4$ to give uranocene.

The only study of actinide indenyl compounds reported in 1983 was the work of Fragalà and Goffart, et al.[72] which detailed the photoelectron spectra of chloro, bromo, methoxy and methyl complexes of tris(indenyl)uranium(IV) and thorium(IV). They observed that the bonding of the ring ligand in the indenyl complexes is similar to that found for Cp complexes even though there are indications of greater 5f covalency in the indenyl compounds. Evidence was presented of a tendency toward ionicity when $X = Me$.

A single study was found in 1983 involving actinide alkyls not containing a $\pi$-bonded coligand. Jacob, et al.[73] reported the existence of dimethylaminopropyl and 1-norbornyl compounds of U and Th prepared via eq. (28).

$$ThCl_4\cdot 2THF + 4RLi \xrightarrow[20^\circ C]{THF} Li_2[R_4ThCl_2] + 2LiCl + 2THF \qquad (28)$$

$$(R = CH_2CH_2CH_2NMe_2)$$

## Organic Synthesis Utilizing Organoactinides

Two reports in this category were found for 1983. Seyam[74] reported the reactions of $UCl_4$ with lithium alkyls as indicated in eq. (29). Yields were reported to be sensitive to the history of the $UCl_4$ and the agitation procedure. Finely pulverizing the $UCl_4$ and drying with $SOCl_2$ increased yields substantially. Ultrasonic agitation led to near quantitative yields.

$$\begin{aligned} UCl_4 + 4RLi &\xrightarrow{heptane} \text{1-butene:n-butane } (R = n\text{-}C_4H_9) \qquad (29) \\ &\xrightarrow{\qquad} \text{isobutene:isobutane } (R = t\text{-}C_4H_9) \end{aligned}$$

Arnaudet, et al.[75] reported the fixation and reduction of $N_2$ by $Cp_3UCH_3Li$ to $NH_3$. The reaction required a strong reductant like lithium napthalide.

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