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LANTHANIDES AND ACTINIDES
ANNUAL SURVEY COVERING THE YEARS 1987-1989

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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 abbreviations will be found throughout this review. These include Cp = η^5-$C_5H_5^-$, Cp* = η^5-$C_5Me_5^-$, CpMe = η^5-$C_5H_4Me^-$, Cp' = η^5-$C_5H_4SiMe_3^-$, Cp" = η^5-$C_5H_3(SiMe_3)_2^-$, Ind = indenyl - $C_9H_7^-$, COT = cyclooctatetraene dianion - $C_8H_8^{2-}$, dme = dimethoxyethane, Ar = aryl, Bz = benzoyl - $CH_2C_6H_5$.

Several review articles appeared in the period covered by this review. The annual survey in this series covering the year 1981 was published by Ernst and Marks[1] (100 references). Two general reviews were published by Miller covering the years 1986 (178 references)[2] and 1987 (197 references).[3] Winter prepared reviews of Y, La, lanthanide, and actinide compounds containing metal-carbon sigma bonds in 1987 (302 references)[4], 1988 (358 references),[5] and 1989 (339 references).[6] Evans published an account of the organometallic chemistry of the lanthanides in low oxidation states (160 references)[7] and a review of organosamarium syntheses by metal vapor deposition (69 references).[8] Organometallic divalent Sm, Eu, and Yb compounds were the subject of a review by Beletskaya and Suleimanov[9] (108 references) and by Swamy[10] (56 references). Short reports discussing organometallic lanthanide electronic structure (21 references)[11] and early lanthanide organometallic compounds (28 references[12], 25 references[13]) appeared in 1988 and 1989. Bulychev prepared a

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*Lanthanides and Actinides, Annual Survey covering the years 1984-1986, see J. Organomet. Chem., 416 (1991) 201.
Reprints for this Survey are not available.

short review of the structural and catalytic chemistry of Cp_2LnCl-aluminum hydrides (28 references).[14] Evans reviewed paramagnetism in organolanthanides (63 references),[15] Kagan the use of organolanthanides in organic chemistry (28 references[16]; 29 references[17]), and Kahn and Rieke carbonyl coupling reactions using lanthanides and actinides (104 references).[18] Organic derivatives of rare earth elements were reviewed by Bochkarev, et al. in a book.[19] Rothwell published a review of the homogenous activation of C-H bonds by f-metal systems (128 references).[20] Marks, et al. reviewed progress in the study of the thermochemistry of 4f and 5f organometallic compounds (49 references).[21] Orpen, et al.[22] tabulated average lengths for 325 different metal-ligand bonds with intraligand distances as determined by both x-ray and neutron diffraction data. A total of 9,802 crystal structures were used to obtain the average values tabulated. Marcalo, et al.[23] derived ligand effective radii for the f-elements by study of the bond lengths in 274 structurally characterized f-element compounds. The derived values were discussed in terms of metal ion oxidation state and ionic radius, coordination geometries, and bonding type. Burns and Bursten[24] examined covalency in f-element organometallic complexes by review of theoretical and experimental techniques (136 references).

LANTHANIDES

Cyclopentadienyl and cyclopentadienyl-like compounds

(i) Monocyclopentadienyl compounds. The preparation and crystal structure of $CpNdCl_2(THF)_3$ (Figure 1) was published by Yang, et al.[25] The Nd-C separations were reported to average 2.779(9)Å. Schumann reported the synthesis of $CpYbCl(THF)_2$,[26] $Cp^*YbCl(THF)_2$,[26] CpYbCl(dme),[26] $Cp^*YbCl(dme)$,[26] and $[Cp^*LuS^tBu(\mu\text{-}S^tBu)_2Li(tmeda)]$.[27] Zhongsheng, et al.[28,29] published the crystal structure of $[CpNd(THF)(\mu\text{-}Cl)_4Li_2(THF)_4]$ (Figure 2). The average Nd-C distance reported was 2.77Å. The La derivative was established to be isomorphous. The synthesis of the La and Nd derivatives were also reported in reference 30. The X-ray photoelectron spectra of cyclopentenylcyclopentadienyl derivatives of $CeCl_2^+$, $PrCl_2^+$, $NdCl_2^+$ and $SmCl_2^+$ were reported.[31] Nie, et al.[32] prepared and characterized $Cp'LnCl_2\cdot nTHF$ (Ln = Nd, Sm, Gd; n = 0, 1, 2) while Wang, et al.[33] reported making cyclopentenylCp and alkylCp compounds $(C_5H_9C_5H_4)LnCl_2 \cdot nTHF$ and $(C_3H_5C_5H_4)LnCl_2 \cdot nTHF$ (Ln = Nd, Sm, Gd; n = 0, 1, 2, 3).

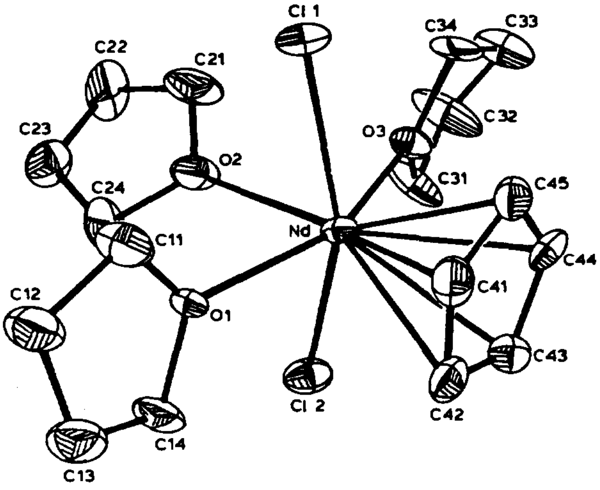

Fig. 1. $CpNdCl_2(THF)_3$. (Reprinted with permission from Journal of Organometallic Chemistry.)

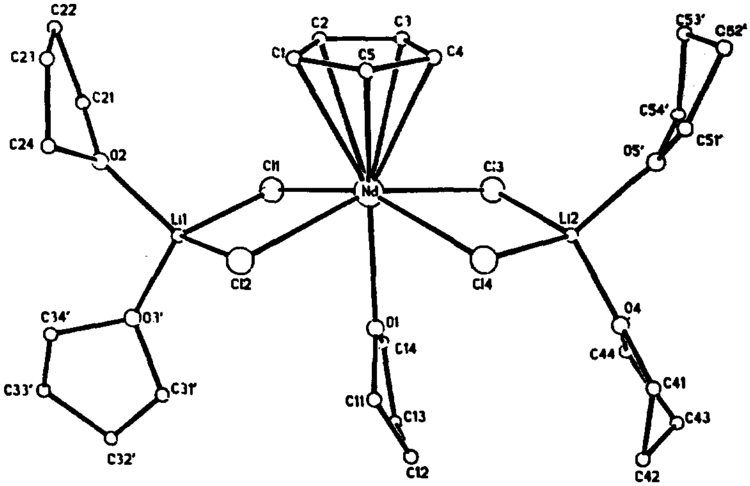

Fig. 2. $[CpNd(THF)(\mu\text{-}Cl)_4Li_2(THF)_4]$. (Reprinted with permission from Inorganica Chimica Acta.)

A Cp*Yb cluster was crystallographically characterized by Zalkin and Berg[34] (Figure 3). The compound, [Yb$_5$O(OEt$_2$)$_2$Cp$^*{}_5$Cl$_8$], has chloro and oxo bridges. One Yb has two Cp* ligands and one has none. A tetrametallic cluster, Cp$^*{}_6$Yb$_4$(μ-F)$_4$, was characterized by Andersen, et al.[35] (Figure 4). The mixed valence cluster contains two Yb(II) ions with one Cp* and two Yb(III) ions with two Cp* ligands. The Yb(II)-C distances were reported to average 2.65(2)Å, the Yb(III)-C separations 2.62(2)Å.

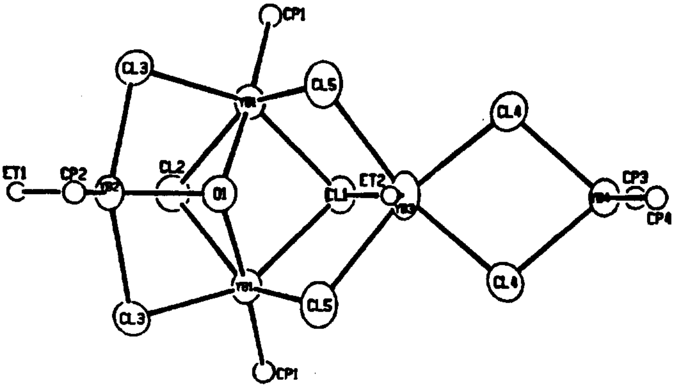

Fig. 3. [Yb$_5$O(OEt$_2$)$_2$Cp$^*{}_5$Cl$_8$]. (Reprinted with permission from Acta Crystallographica.)

Wayda[36] published the synthesis of (Cp^{t}Bu)LuCl$_2$(THF)$_2$ via the reaction of LuCl$_3$ with NaCp^{t}Bu in THF. Bruno, et al.[37] prepared and crystallographically characterized Cp*CeI$_2$(THF)$_3$ (Figure 5; Ce-C(Cp*) = 2.80(3)Å). Also prepared were the La analog and [Cp*CeCl$_2$(THF)$_x$]$_y$. Evans, et al.[38] studied the reactions of ceric ammonium nitrate with NaCp in THF and prepared CpCe(THF).

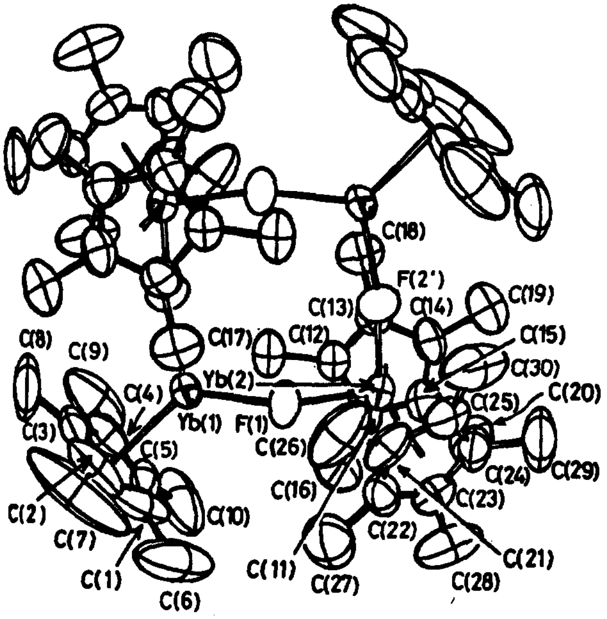

Fig. 4. $Cp^*_6Yb_4(\mu\text{-}F)_4$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

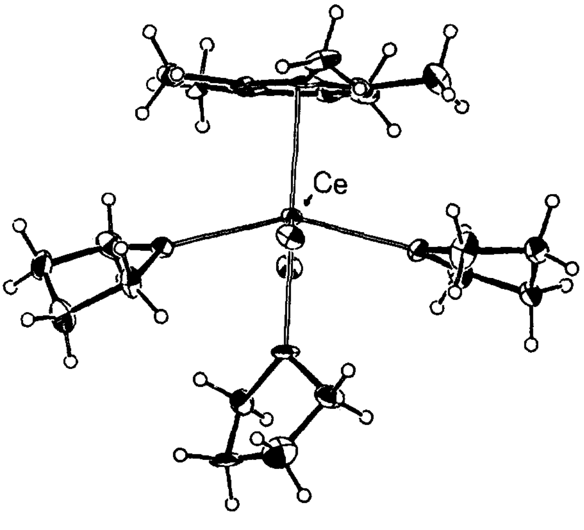

Fig. 5. $Cp^*CeI_2(THF)_3$. (Reprinted with permission from Organometallics. Copyright 1987 American Chemical Society.)

Ma and Ye[39,40] reported the synthesis of CpYb(β-dikenato)$_2$ complexes by reaction of Cp_3Yb with the β-diketone in n-hexane. Elemental, IR, mass spectral and thermal decomposition data were reported for β-dikenato = MeCOCHCOMe, $Me_3CCOCHCOCMe_3$, $MeCOCHCOCF_3$, PhCOCHCOMe, $SCH{=}CHCH{=}CCOCHCOCF_3$, OCN(Ph)N=C(Me)CCOPh. In addition the bis-acetylacetonate complexes, CpLn(acac)$_2$ (Ln = Nd, Sm, Gd, Dy, Er),[41] the bis-8-hydroxyquinoline,[42] bis-o-aldehydophenolato,[43] and bis-furfuralcoholato[43] complexes of CpNd and CpYb and the bis-o-aminophenol complex of CpYb[42] were reported. Thiele, et al. prepared [Cp_2Co][CpCe(acac)$_3$] by the reaction of Cp_3Ce(THF) and Co(acac)$_3$.[44]

Teuben[45,46] published the preparation and crystal structure of Cp^*Ce(2,6-di-^{t}Bu-phenoxide)$_2$ (Figure 6). This compound was utilized as a precursor for $Cp^*Ce[CH(SiMe_3)_2]_2$ (Figure 7) and $Cp^*Ce[N(SiMe_3)_2]_2$ (Figure 8) by reaction with $LiCH(SiMe_3)_2$ or $NaN(SiMe_3)_2$, respectively. Both were crystallographically characterized. All three compounds were reported to have secondary agostic interactions between the Ce ion and methyl hydrogen atoms. Bonding parameters include: for the 2,6-di-^{t}Bu-phenoxide compound, Ce-C(Cp*) = 2.76(1)Å; for the $CH(SiMe_3)_2$ compound, Ce-C(Cp*) = 2.79(3)Å, Ce-C(σ) = 2.53(2)Å; and for the $N(SiMe_3)_2$ compound, Ce-C(Cp*) = 2.77(1)Å.

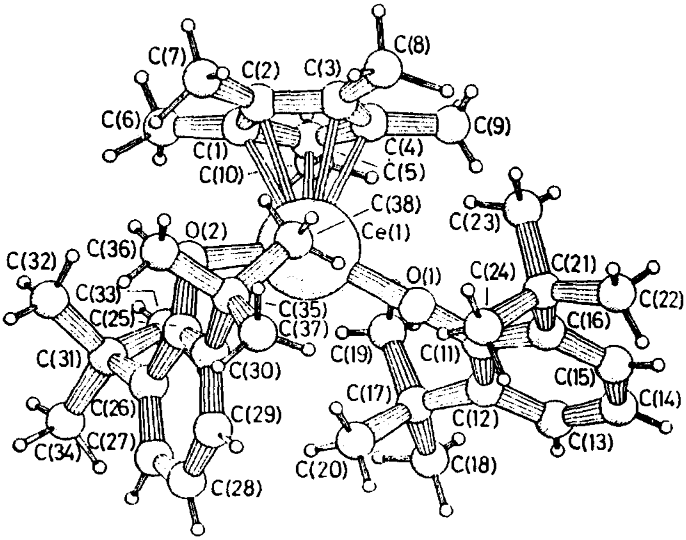

Fig. 6. Cp*Ce(2,6-di-^{t}Bu-phenoxide)$_2$. (Reprinted with permission from *Journal of the Chemical Society, Chemical Communications*.)

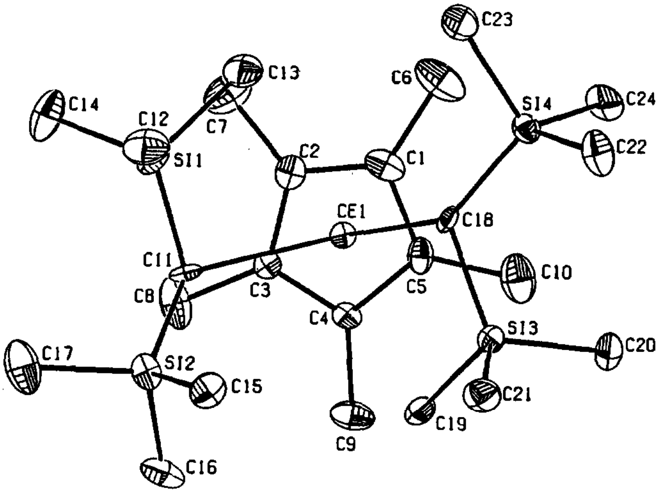

Fig. 7. Cp*Ce[CH(SiMe$_3$)$_2$]$_2$. (Reprinted with permission from *Organometallics*. Copyright 1989 American Chemical Society.)

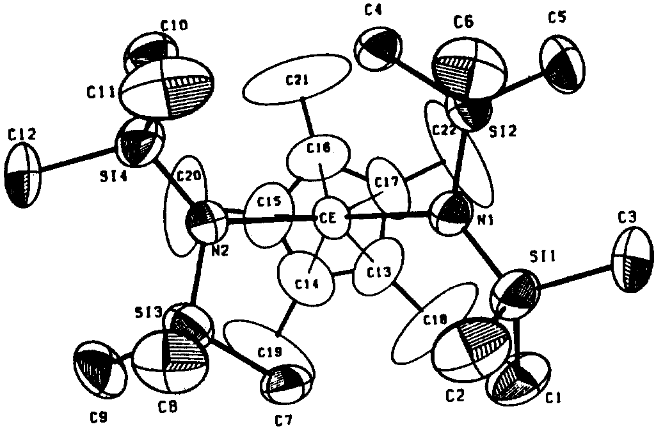

Fig. 8. $Cp^*Ce[N(SiMe_3)_2]_2$. (Reprinted with permission from <u>Organometallics</u>. Copyright 1989 American Chemical Society.)

The dimeric $[Cp^*Ln(OCMe_3)_2]_2$ (Ln = La, Ce: Figure 9)[47] were prepared via reaction of $Cp^*_2LnCH(SiMe_3)_2$ with $HOCMe_3$. Teuben, <u>et al</u>.[48] also investigated the transmetallation of $LnCl_3(THF)_x$ with $LiCp^*$ to produce mono-Cp derivatives. Reaction of LnR_3 with Cp^*H generally gave Cp^*_2LnR. Similar compounds were reported by Schaverien, <u>et al</u>.[49,50] by a different route. Reaction of $Cp^*LaI_2(THF)_3$ with $KCH(SiMe_3)_2$ in hexane/OEt_2 resulted in $Cp^*La[CH(SiMe_3)_2]_2(THF)$[49] (Figure 10). Further treatment with Me_3SiI gave $Cp^*La[CH(SiMe_3)_2]_2$ (Figure 11). When the chloro salt of Lu(III) was utilized, μ-chloro complexes were obtained.[51] Both $Cp^*Lu[CH(SiMe_3)_2](\mu\text{-}Cl)_2Li(tmeda)$ (Figure 12) and $Cp^*Lu[CH(SiMe_3)_2]_2(\mu\text{-}Cl)Li(THF)_3$ (Figure 13) were crystallographically characterized.

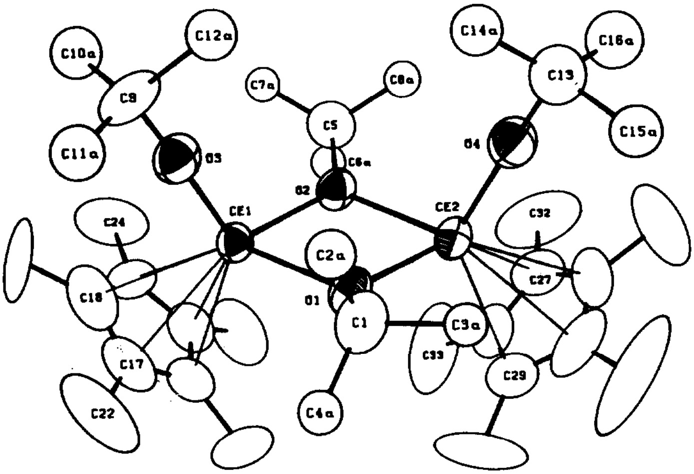

Fig. 9. [$Cp^*Ce(OCMe_3)_2]_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

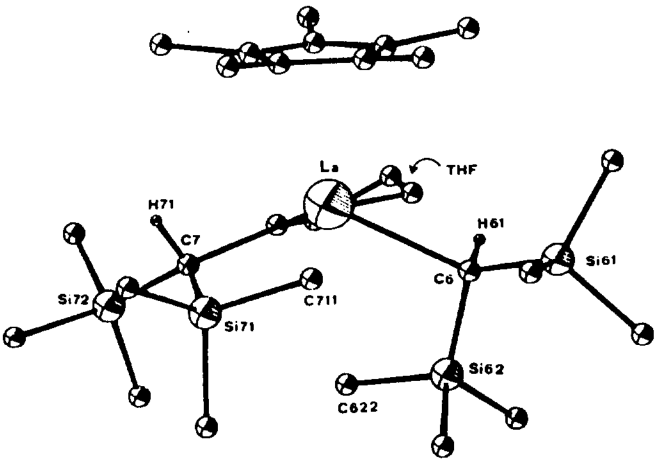

Fig. 10. $Cp^*La[CH(SiMe_3)_2]_2(THF)$. (Reprinted with permission from Organometallics. Copyright 1989 American Chemical Society.)

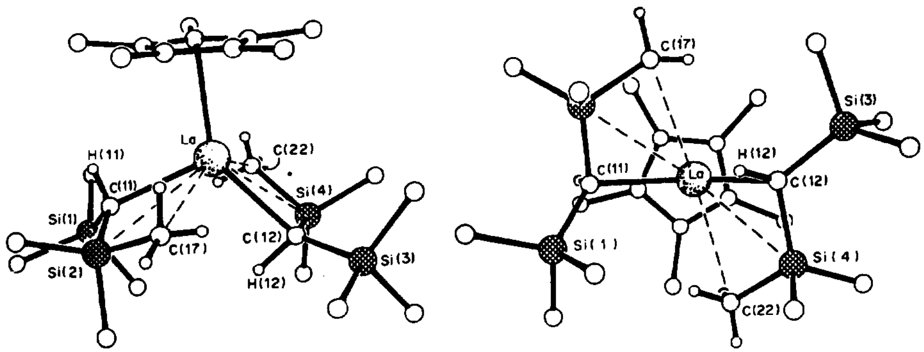

Fig. 11. Cp*La[CH(SiMe$_3$)$_2$]$_2$. (Reprinted with permission from Polyhedron. Copyright 1989 Pergamon Press plc.)

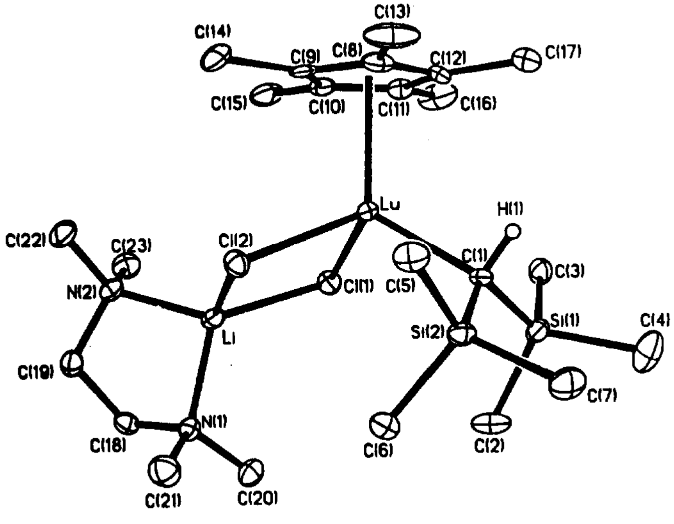

Fig. 12. Cp*Lu[CH(SiMe$_3$)$_2$](μ-Cl)$_2$Li(tmeda). (Reprinted with permission from Organometallics. Copyright 1989 American Chemical Society.)

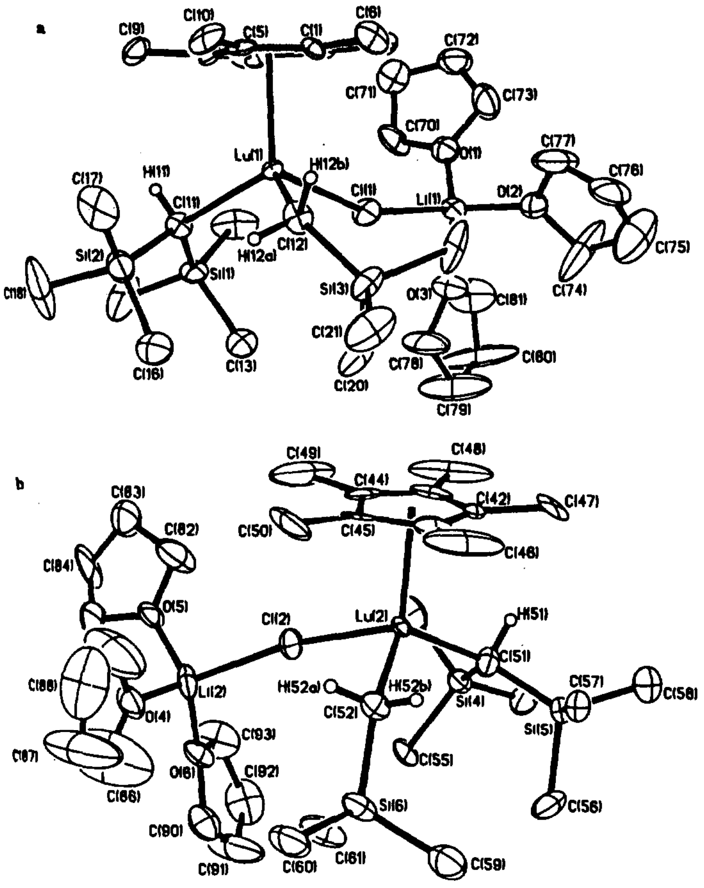

Fig. 13. $Cp^{*}Lu[CH(SiMe_3)_2]_2(\mu\text{-}Cl)Li(THF)_3$. (Reprinted with permission from Organometallics. Copyright 1989 American Chemical Society.)

The $Cp^{*}Y$-σ-aryl compounds, $Cp^{*}Y(o\text{-}C_6H_4CH_2NMe_2)_2$ (Figure 14) and $Cp^{*}Y[o\text{-}C_6H_4CH_2NMe(\mu\text{-}CH_2)][\mu\text{-}o\text{-}C_6H_4CH_2NMe(\mu\text{-}CH_2)]YCp^{*}(THF)$ (Figure 15) were prepared and crystallographically characterized by Teuben and Spek, et al.[52] The former was prepared by reaction of $Y(o\text{-}C_6H_4CH_2NMe_2)_3$ with $Cp^{*}H$. Thermolysis of this compound gave the latter. The thermolysis pathway was reported to follow activation of an agostic C-H bond.

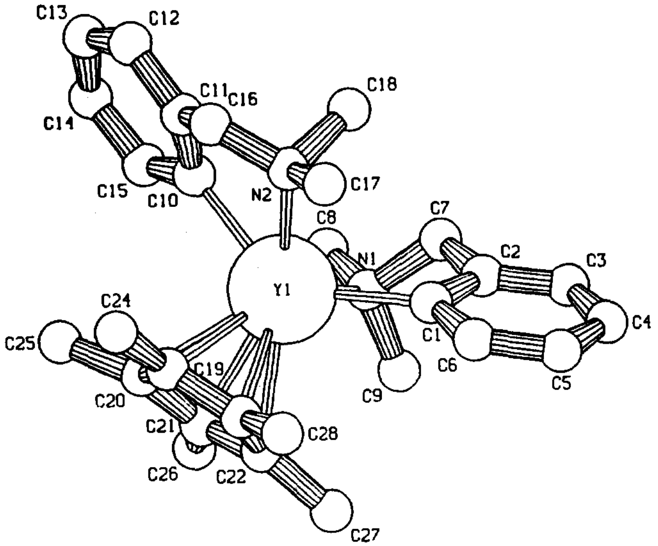

Fig. 14. Cp*Y(o-$C_6H_4CH_2NMe_2$)$_2$. (Reprinted with permission from <u>Organometallics</u>. Copyright 1989 American Chemical Society.)

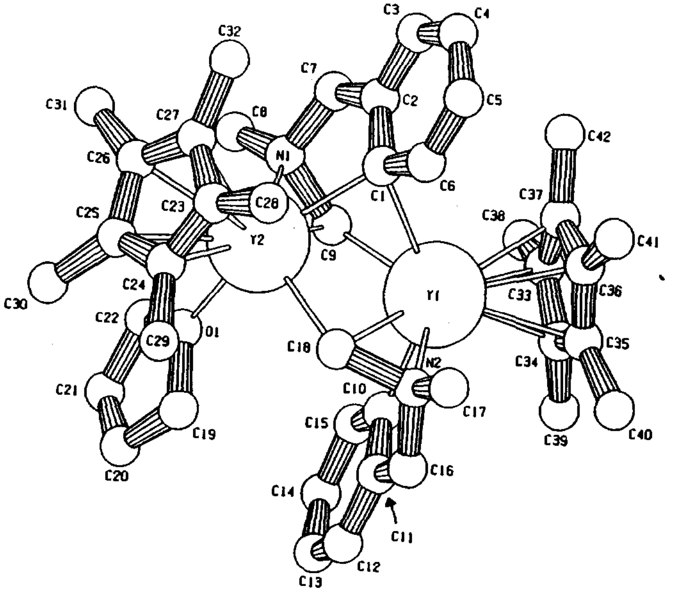

Fig. 15. Cp*Y[o-$C_6H_4CH_2NMe(\mu\text{-}CH_2)$][$\mu$-o-$C_6H_4CH_2NMe(\mu\text{-}CH_2)$]-YCp*(THF). (Reprinted with permission from <u>Organometallics</u>. Copyright 1989 American Chemical Society.)

Schumann, et al.[53] reported the preparation of Cp^*LnCOT (Ln = Pr, Sm, Gd, Tb, Dy, Er, and Lu) by the reaction of $COTLnCl(THF)_n$ with $NaCp^*$ in THF. The crystal structure of M = Lu was determined (Figure 16). The synthesis and crystal structure of $(C_5(CH_2Ph)_5)LuCOT$ (Figure 17) were also published.[54] The last structure has a centroid-Lu-centroid angle of 167.7°. Teuben, et al.[55] published the synthesis, IR spectra, and UPS studies of the Y and La derivatives of Cp^*LnCOT. The La compound was found to be polymeric in the solid state and the THF adduct $Cp^*LaCOT(THF)$ could be isolated.

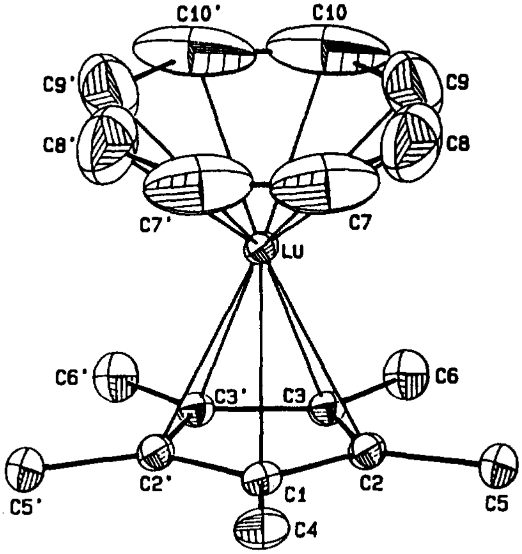

Fig. 16. Cp^*LuCOT. (Reprinted with permission from Organometallics. Copyright 1989 American Chemical Society.)

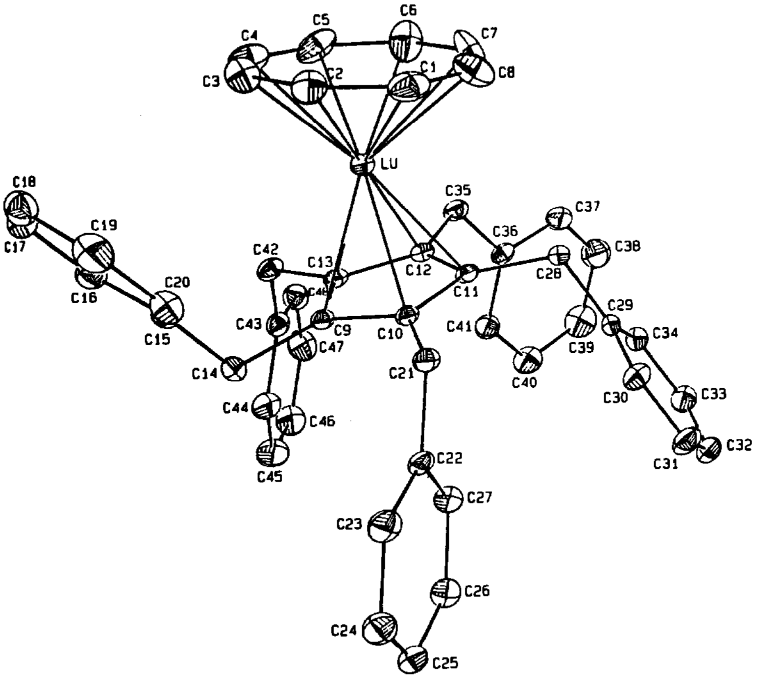

Fig. 17. ($C_5(CH_2Ph)_5$)LuCOT. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

Schumann, *et al*.[56] reported the reaction of $Lu(OSO_2CF_3)_3$ with NaCp in THF which gives $CpLu(OSO_2CF_3)_2(THF)_3$ and $Cp_2Lu(OSO_2CF_3)(THF)$. The crystal structure of the former is presented in Figure 18.

Lobkovskii, *et al*.[57] prepared and structurally characterized the polynuclear complex, $[(Cp^tBu_2)LuH(AlH_4)]_4(OEt_2)_2]\cdot OEt_2$. There is a tetrahedral metal core.

Bruno, Brittain, and Hazin[58] studied the luminescence spectra of halide, alkyl, aryl, ether, nitrile, Cp, Cp*, and COT Ce(III) compounds. Covalancy of up to 20-25% was indicated by the results, increasing in the order: halides < alkyls, aryls < Cp < COT, Cp*.

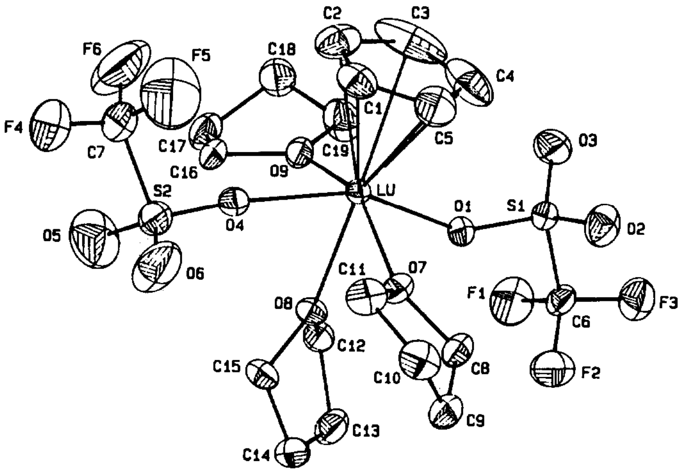

Fig. 18. $CpLu(OSO_2CF_3)_2(THF)_3$. (Reprinted with permission from Journal of Organometallic Chemistry.)

(ii) Tetra- and triscyclopentadienyl compounds. The tetrakiscyclopentadienyl compounds $Na[Cp_4Ln]\cdot(THF)_n$ (Ln = La, Ce, Nd) and $Na[Cp_4Pr]$ were synthesized and characterized by Thiele, et al.[59] The compounds are reported to contain three pi and one sigma Cp ligands.

Evans, et al.[38] and Thiele, et al.[44] published the synthesis of $Cp_3Ce(THF)$ from $[NH_4]_2[Ce(NO_3)_6]$ by reaction with NaCp. The compounds $(Cp^tBu)_3Sm$ and $(Cp^tBu)_3La(THF)$ by Wayda[36] and $(CpCHMe_2)_3Ce$ by Zverev, et al.[60] were also prepared. Optimized preparative routes to $Cp_3Nd(THF)$, $Cp_3Sm(THF)$, and $Cp_2Yb(dme)$ are given by Deacon, et al.[61] The structures of Cp_3La (Rebizant, et al.,[62] Figure 19), Cp_3Yb (Eggers, et al.,[63] Figure 20), and $(CpMe)_3Yb$ (Weidlein, et al.,[64] Figure 21) were crystallographically characterized. The La complex was reported to be a polymer containing one $\mu,\eta^5:\eta^1$-Cp and two η^5-Cp's, while the Yb complexes crystallized as discrete molecular units.

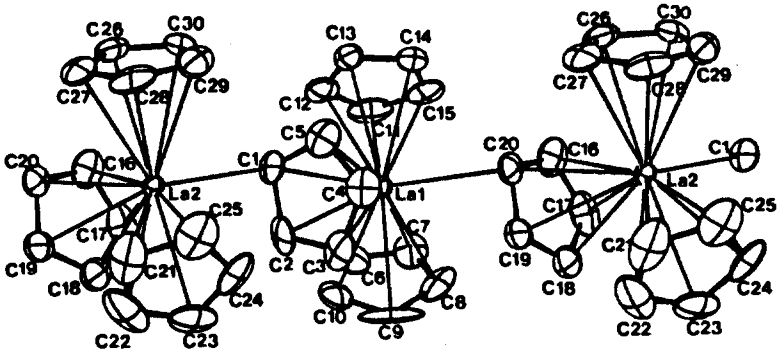

Fig. 19. Cp_3La. (Reprinted with permission from Acta Crystallographica.)

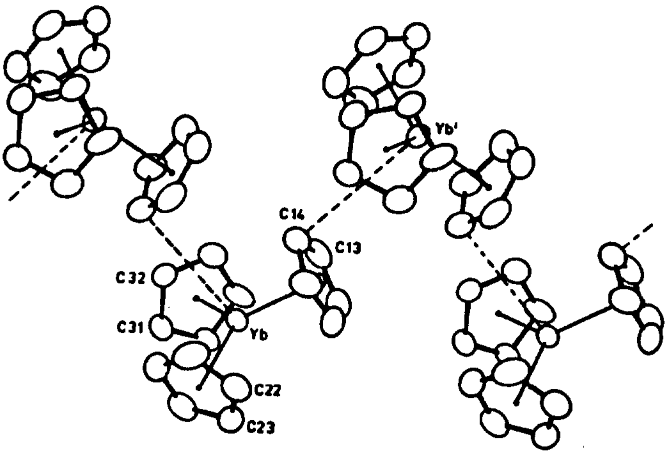

Fig. 20. Cp_3Yb. (Reprinted with permission from Acta Crystallographica.)

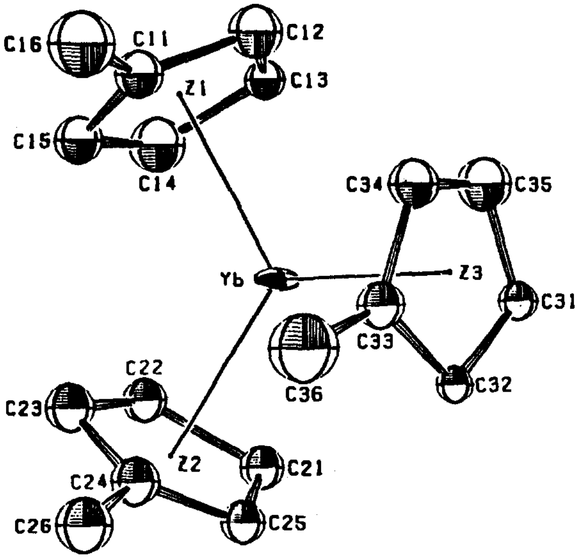

Fig. 21. $(CpMe)_3Yb$. (Reprinted with permission from Journal of Organometallic Chemistry.)

The mixed Cp compound Cp^*_2CpSm was prepared by Evans and Ulibarri[65] by reaction of Cp^*_2Sm with excess CpH. Its structure is shown in Figure 22 (Sm-C(Cp^*) = 2.770(3)Å; Sm-C(Cp) = 2.738(4)Å). The mixed valence $Cp^*_2Sm(\mu\text{-}Cp)SmCp^*_2$ was also prepared and crystallographically characterized (Figure 23). The Cp ligand was found to bridge in an $\eta^5:\eta^2$ fashion.

Borisov, et al.[66] studied the thermal decomposition of Cp_3Ln (Ln = Y, La, Nd) while Paolucci, Fischer, and Traldi, et al.[67] published a report detailing the mass spectral fragmentation pattern common to $(CpMe)_3Ln$ (Ln = La, Pr, Nd, Tm, Yb) compounds. Luminescence spectra were reported for some Cp_3Ln compounds.[58,68]

Qian, et al.[69] investigated the reduction of olefins with Cp_3Ln/NaH. A decrease in activity was observed to correlate with a decrease in ionic radius of the lanthanide. The compounds Cp_3Ln (Ln = La, Ce, Pr, Nd, Sm, Eu) were utilized with sodium naphthalene in THF to reduce N_2 to ammonia.[70] The organometallic $(CpMe)_3Yb$ was used as a source of Yb in the growth of highly doped InP:Yb layers by organometallic vapor phase epitaxy.[71]

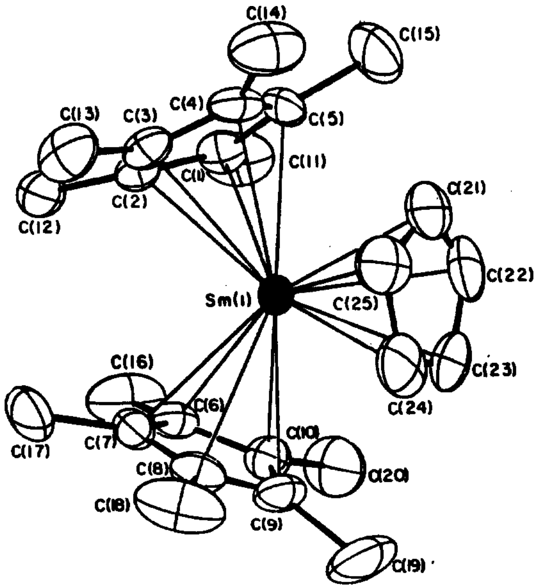

Fig. 22. Cp$^*_2$CpSm. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1987 American Chemical Society.)

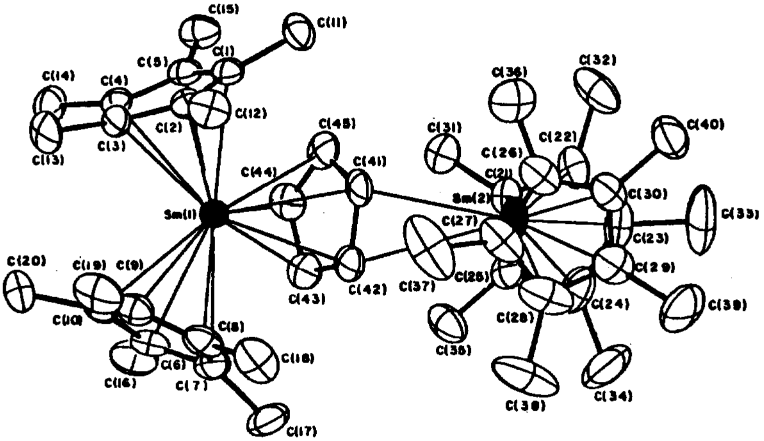

Fig. 23. Cp$^*_2$Sm(μ-Cp)SmCp$^*_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1987 American Chemical Society.)

Several contributions appeared investigating the chemistry of Cp_3Ln adducts, Cp_3LnL_n. Fischer, et al.[72] gave a detailed account of ^{139}La NMR studies of $[Cp_3LaL_n]^q$ (Cp = Cp or CpMe; L = monodentate ligand; n = 0-2; q = 0 or -1). Andersen, et al.[73] gave a brief summary of the relative strengths of Cp_3Ln-L interactions (L = THF, $N(CH_2CH_2)_3CH$, PMe_3, $P(OCH_2)_3Et$, CNEt). Amberger, et al.[74,75] studied the electronic structure of Cp_3Ln adducts. Vibronic coupling in $Cp_3NdMe(THF)$ was studied in order to separate the vibronic and electronic transitions in $Cp_3Yb(CNC_6H_{11})$ and $Cp_3YbMe(THF)$.[74] Magnetic susceptibility measurements and EPR spectra for Cp_3YbL (L = THF, γ-picoline) were used to determine the spin-orbit coupling constant and crystal field parameters.[75]

Deacon, et al.[76] studied transmetallation reactions in pyridine, acetonitrile, and ether. The salt TlCp was used to give Cp_3Ln(pyridine) (Ln = Nd, Sm, Eu, Yb) in pyridine and $Cp_3Ln(NCMe)$ (Ln = Nd, Sm, Yb) in acetonitrile. The complex Cp_3Sm(pyridine) was also prepared by ligand exchange, and $Cp_3Eu(THF)$ was synthesized from Eu and $HgCp_2$ in THF. The crystal structures of Cp_3Ln(pyridine) (M = Sm (Figure 24), Nd)[77] were determined. The two structures are reported to differ in pyridine coordination and cell packing. Average bonding parameters reported include Sm-C(Cp) = 2.77(1)Å and Nd-C(Cp) = 2.80(1)Å.

Spirlet, et al.[78,79] reported the crystal structures of $Cp_3La(NC_3H_5)_2$ (Figure 25, La-C(Cp) = 2.86(1)Å)[78] and $Cp_3Ln(NC_3H_5)$ (Ln = La, Figure 26, La-C(Cp) = 2.830(5)Å; Pr; Yb, Yb-C(Cp) = 2.677(6)Å).[79] The latter group of three complexes are isostructural. However, only Ln = La and Yb were fully characterized structurally.

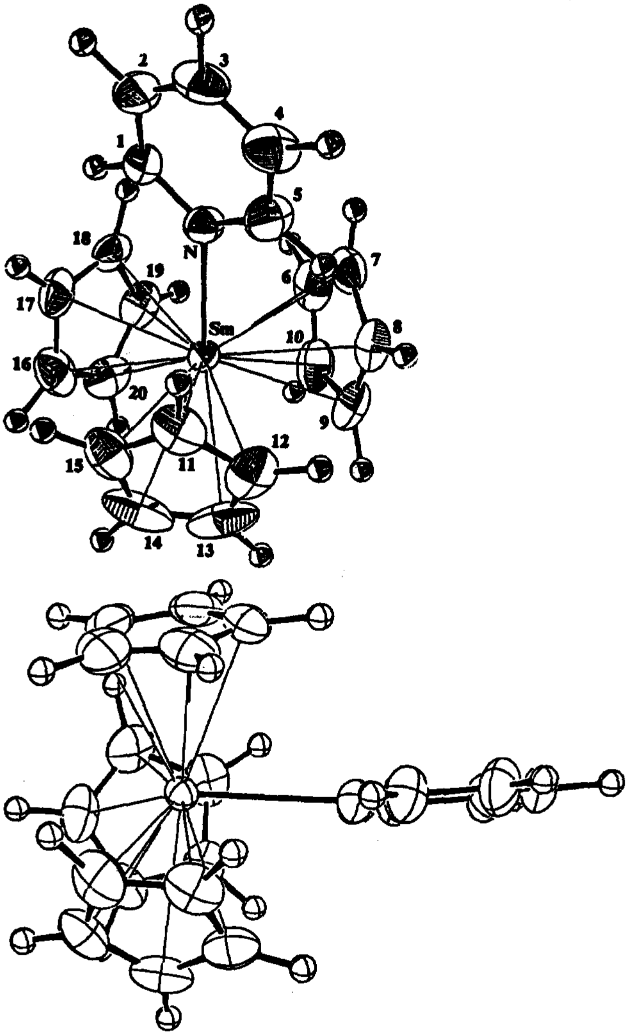

Fig. 24. Cp$_3$Sm(pyridine). (Reprinted with permission from *Australian Journal of Chemistry*.)

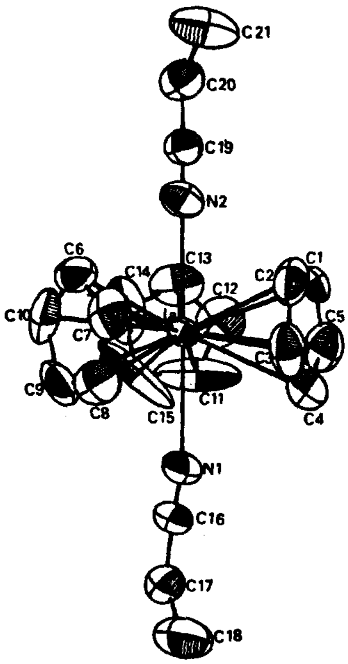

Fig. 25. $Cp_3La(NC_3H_5)_2$. (Reprinted with permission from *Acta Crystallographica*.)

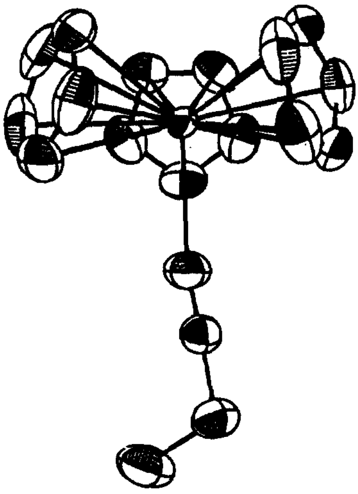

Fig. 26. $Cp_3Ln(NC_3H_5)$. (Reprinted with permission from *Inorganica Chimica Acta*.)

Schumann reported the reactions of $Cp_2Sm(\mu\text{-}Cl)_2Na(dme)$ with $LiGeMe_3$[27] or Cp_3Sm with NaCl[27] to give $[Cp_3Sm]_2Cl^-$. LiN_3 was reported to react with Cp_3Sm in dme to yield $[Li(dme)_3][(Cp_3Sm)_2(\mu\text{-}N_3)]$.[80] The crystal structures of these compounds are shown in Figure 27 (μ-Cl)[27] and Figure 28 (μ-N_3).[80]

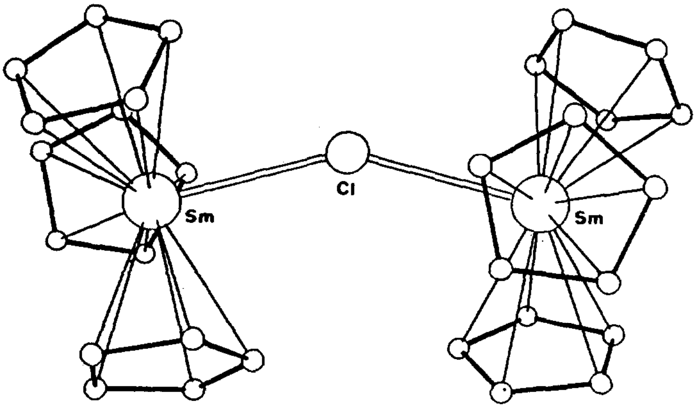

Fig. 27. The anion in $[Li(dme)_3]\{[Cp_3Sm]_2Cl\}$. (Reprinted with permission from Polyhedron. Copyright 1988 Pergamon Press plc.)

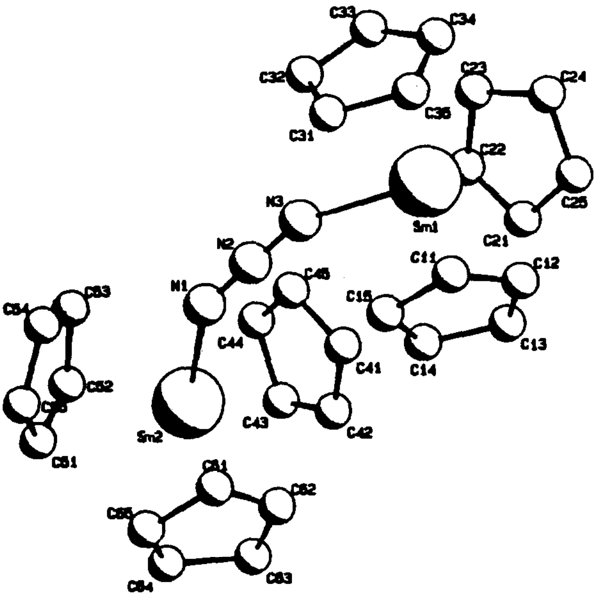

Fig. 28. The anion in [Li(dme)$_3$][(Cp$_3$Sm)$_2$(μ-N$_3$)]. (Reprinted with permission from Polyhedron. Copyright 1988 Pergamon Press plc.)

Stults and Zalkin[81] investigated the crystal structure of (CpMe)$_3$Ce(PMe$_3$) (Figure 29; Ce-C(Cp) = 2.82(4)Å, Ce-P = 3.072(4)Å). Another report with Andersen,[82] detailed the crystal structures of (CpMe)$_3$CeL (L = quinuclidine, P(OCH$_2$)$_3$CEt). These compounds are isostructural with their uranium analogs and are described further in the actinide section.

The triscyclopentadienyl alkoxide, Cp$_3$Ce(O^{i}Pr), was prepared by Marks and Fragala, et al.[83] from Ce(O^{i}Pr)$_4$ and CpSnMe$_3$. Its redox properties and electronic structure were discussed. Evans, et al.[84] prepared the alkoxide, Cp$_3$Ce(OCMe$_3$) from Ce(OCMe$_3$)(NO$_3$)$_3$-(THF)$_2$ with NaCp and determined its crystal structure (Figure 30, Ce-C(Cp) = 2.76(2)Å).

Bulgakov, et al.[85] studied the chemiluminescence resulting from the hydrolysis of Cp$_3$Sm. Gao, et al.[86] prepared [Li(dme)$_3$]-[Cp$_3$Nd(C$_6$H$_5$)].

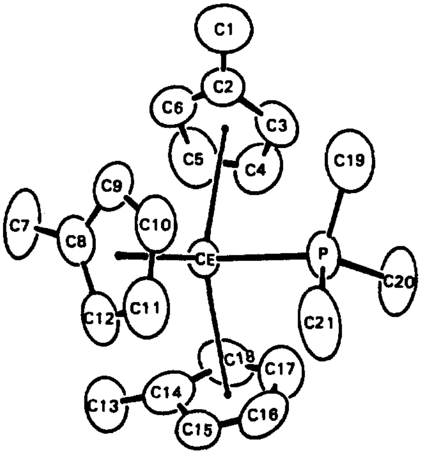

Fig. 29. $(CpMe)_3Ce(PMe_3)$. (Reprinted with permission from Acta Crystallographica.)

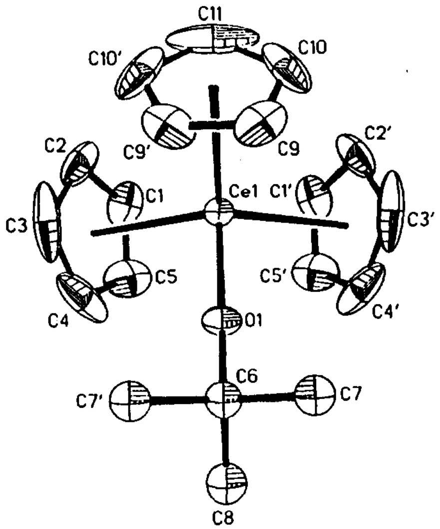

Fig. 30. $Cp_3Ce(OCMe_3)$. (Reprinted with permission from Organometallics. Copyright 1989 American Chemical Society.)

(iii) *Biscyclopentadienyl compounds with halide and oxygen ligands*. Evans[87] investigated the chemistry of Sm(II) including the synthesis and reactivity of $Cp^*_2Sm(THF)_2$. In a second paper[88] he reported the preparation and structural characterization of $Cp^*_2Sm(dihydropyran)_2$ (Figure 31, Sm-C(Cp^*) = 2.842(4)Å) and $Cp^*_2Sm(tetrahydropyran)$ (Figure 32, Sm-C(Cp^*) = 2.816(3)Å) by replacement of the solvent in $Cp^*_2Sm(THF)_2$. Schumann, *et al.*[89] published the crystal structure of $Cp^*_2Sm(dme)$ (Figure 33, Sm-C(Cp^*) = 2.82(3)Å). Deacon, *et al.*[90] prepared the pentadeutero derivative, $(\eta^5\text{-}C_5D_5)_2Yb(dme)$, while Weidlein, *et al.*[91] published a preparative route to $(CpMe)_2Yb(dme)$. Andersen, *et al.*[92] presented the thermal average molecular structure of Cp^*_2Yb by gas phase electron diffraction. A bent sandwich model was proposed.

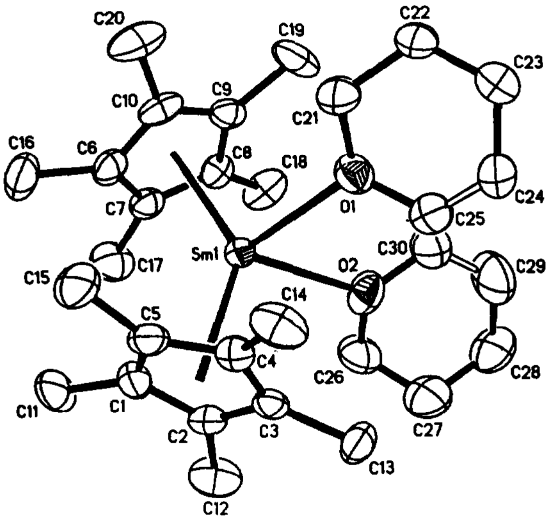

Fig. 31. $Cp^*_2Sm(dihydropyran)_2$. (Reprinted with permission from *Polyhedron*. Copyright 1989 Pergamon Press plc.)

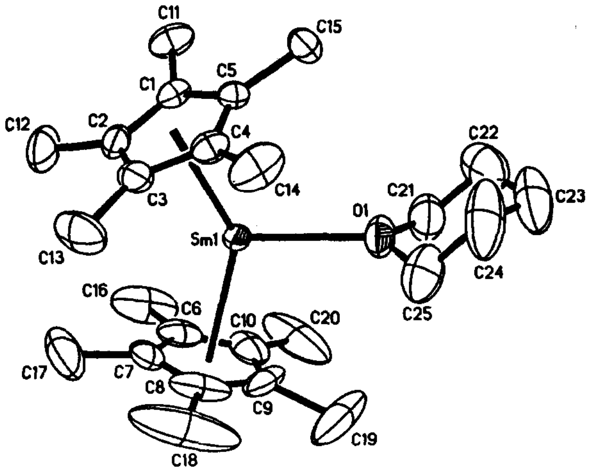

Fig. 32. Cp$^*_2$Sm(tetrahydropyran). (Reprinted with permission from <u>Polyhedron</u>. Copyright 1989 Pergamon Press plc.)

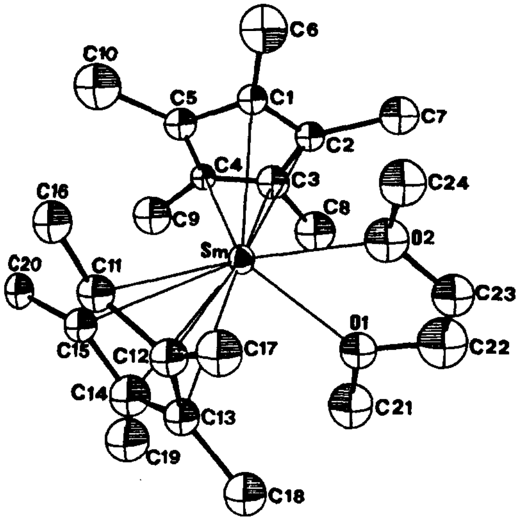

Fig. 33. Cp$^*_2$Sm(dme). (Reprinted with permission from <u>Journal of Organometallic Chemistry</u>.)

The formation and crystal structure of $[Cp^*_2Yb]_2(\mu\text{-}F)$ appeared (Figure 34).[93] The Yb^{+2}-F-Yb^{+3} bridge is asymmetric. Deacon, et al.[94] published the first crystal structure of a phosphine oxide complex of a divalent organolanthanide, $Cp_2Yb(OPPh_3)_2$ (Figure 35).

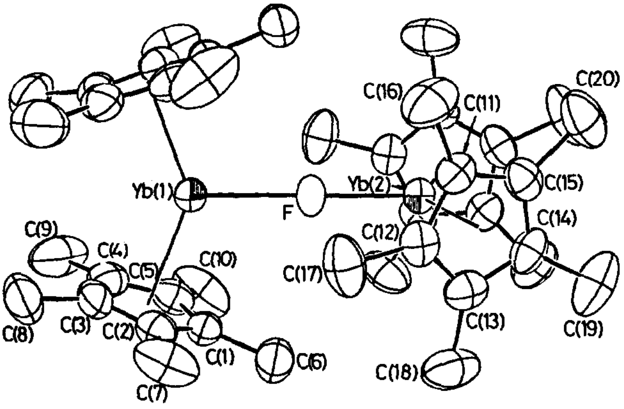

Fig. 34. $[Cp^*_2Yb]_2(\mu\text{-}F)$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

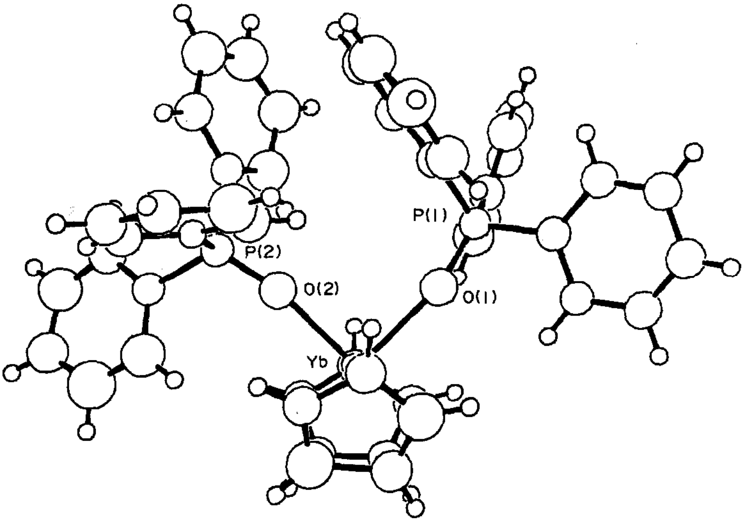

Fig. 35. $Cp_2Yb(OPPh_3)_2$. (Reprinted with permission from Polyhedron. Copyright 1989 Pergamon Press plc.)

In three contributions Lueken, et al. presented the crystal structures of the isostructural dimers $[Cp_2LnBr]_2$ (Ln = Dy,[95] Er,[95] Yb[96] Figure 36; Dy-C(Cp) = 2.61(2)Å, Er-C(Cp) = 2.58(2)Å, Yb-C(Cp) = 2.55(4)Å); and the isostructural dimers $[Cp_2LnCl]_2$ (Ln = Er,[97] Yb;[96] Er-C(Cp) = 2.59(2)Å, Yb-C(Cp) = 2.58(1)Å). The Cl and Br derivatives differ in cell packing. Lueken also reported two other structural types for these compounds: $[Cp_2DyCl]_n$[98] (Figure 37; Dy-C(Cp) = 2.63(1)Å) and the tetrametallic $[Cp_2GdCl]_4$[99] (Figure 38; Gd-C(Cp) = 2.67(4)Å). The magnetic properties of several of these compounds were also presented.

Suleimanov[100] reasserted his claim to the synthesis of Cp_2Sm from the reaction of $HgCp_2$ and excess activated samarium.

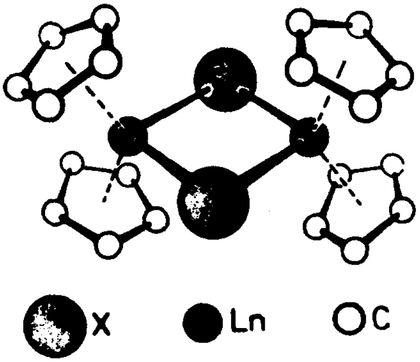

Fig. 36. $[Cp_2LnBr]_2$ (Ln = Dy, Er, Yb). (Reprinted with permission from Inorganica Chimica Acta.)

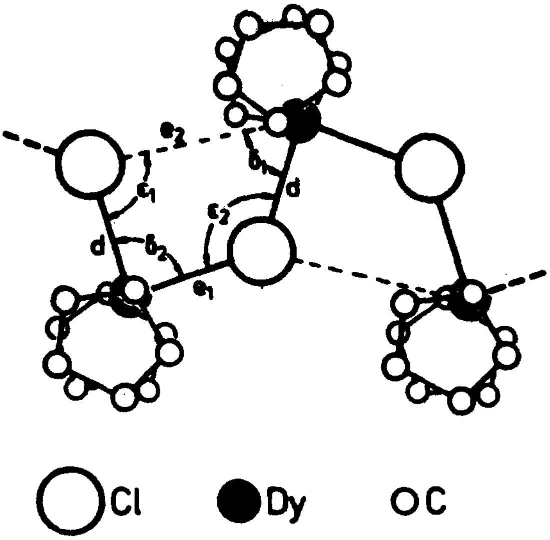

Fig. 37. $[Cp_2DyCl]_n$. (Reprinted with permission from *Inorganica Chimica Acta*.)

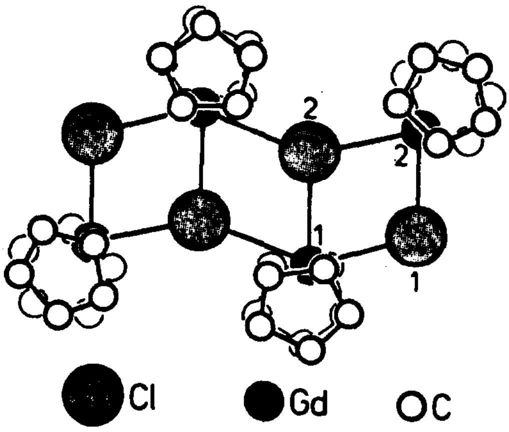

Fig. 38. $[Cp_2GdCl]_4$. (Reprinted with permission from *Inorganica Chimica Acta*.)

Evans and Atwood, *et al.*[101] discussed the structure of the trimetallic $[Cp^*_2SmCl]_3$ (Figure 39, Sm-C(Cp^*) = 2.73(4)Å). This compound was reported to crystallize in the presence of tetraglyme as the complicated structure {$Cp^*_2ClSm(\mu-Cl)SmCp^*_2[\mu,\eta^4-Me(OCH_2CH_2)_4OMe]SmCp^*_2$}{$[Cp^*_2ClSm]_2(\mu-Cl)$}} (Figures 40, 41).

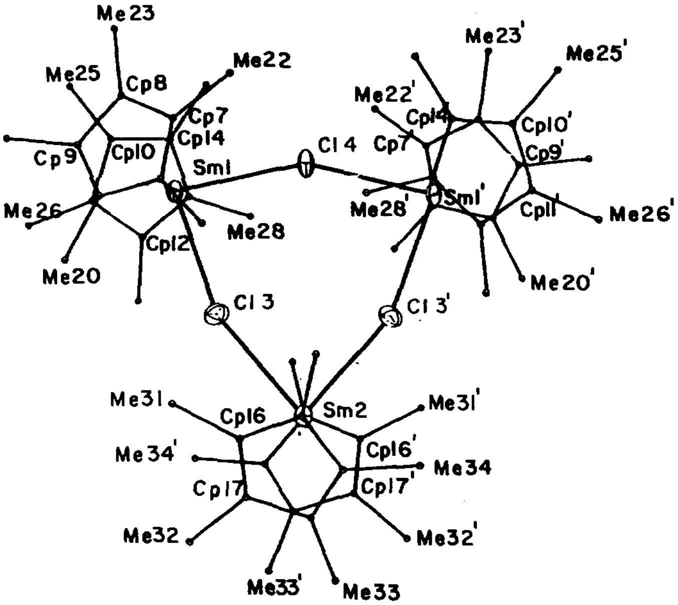

Fig. 39. $[Cp^*_2SmCl]_3$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1987 American Chemical Society.)

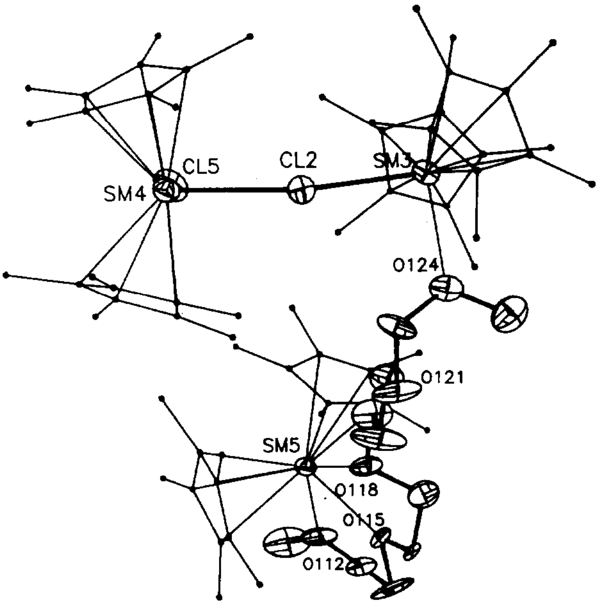

Fig. 40. The cation in {Cp$^*_2$ClSm(μ-Cl)SmCp$^*_2$[μ,η^4-Me(OCH$_2$CH$_2$)$_4$OMe]SmCp$^*_2$}{[Cp$^*_2$ClSm]$_2$(μ-Cl)} (Reprinted with permission from Journal of the American Chemical Society. Copyright 1987 American Chemical Society.)

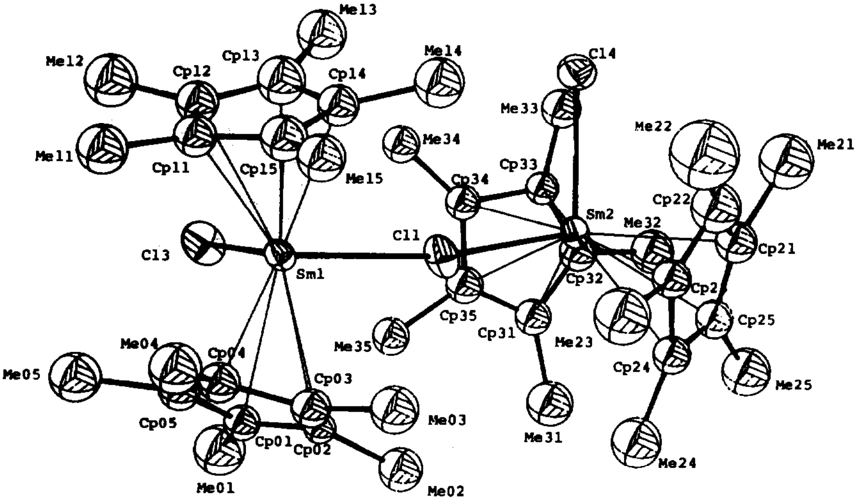

Fig. 41. The anion in {Cp$^*_2$ClSm(μ-Cl)SmCp$^*_2$[μ,η^4-Me(OCH$_2$CH$_2$)$_4$OMe]SmCp$^*_2$}{[Cp$^*_2$ClSm]$_2$(μ-Cl)}. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1987 American Chemical Society.)

Shen, et al.[102] reported the reaction of $Ce(PhEt_3)_2Cl_6$ or $CeCl_6$(pyridine) with $LiCp^*$ in THF to give $Li[Cp^*_2CeCl_2]\cdot 2THF$ or $Li[Cp^*_2CeCl_2]\cdot$2pyridine, respectively. Teuben and den Haan[103] reported the synthesis of $Cp^*_2Y(\mu\text{-}Cl)_2Li(OEt_2)_2$ and $Cp^*_2Y(\mu\text{-}Cl)_2Na(OEt_2)$ from the metal chloride and $LiCp^*$ or $NaCp^*$ in THF. Replacement of the solvent led to $Cp^*_2Y(\mu\text{-}Cl)_2Li$(tmeda), $Cp^*_2Y(\mu\text{-}Cl)_2Li$(dme), $Cp^*_2Y(\mu\text{-}Cl)_2Na$(tmeda), and Cp^*_2YCl(THF). The latter was reported to react with pyridine, acetone, and $Al_2Cl_2Et_4$ to yield $Cp^*_2YCl(NC_5H_5)$, $Cp^*_2YCl(OCMe_2)$, and $Cp^*_2Y(\mu\text{-}Cl)_2AlEt_2$. The dimer $[Cp^*_2YCl]_2$ was prepared by sublimation of the THF adduct.

Evans and Atwood, et al.[104] published the synthesis and crystal structure of the polymeric $[Cp^*_2Ce(\mu\text{-}Cl)_2K(THF)]_n$ (Figure 42, Ce-C(Cp^*) = 2.79(2)Å). Unit cell data for Cp^*_2CeCl(THF) were also given. The data agree with that found by Streitwieser, et al.[105] for Cp^*_2LuCl(THF) (Figure 43, Lu-C(Cp^*) = 2.63(1)Å) and Schumann, et al.[106] for Cp^*_2HoCl(THF) (Ho-C(Cp^*) = 2.67(1)Å). The crystal structure of $[Cp_2NdCl(THF)]_2$ was also reported.[107] The Nd atoms are reported to be asymmetrically bridged by the chloro anions. The structure of the Yb analog was published by Yasuda, et al.[108]

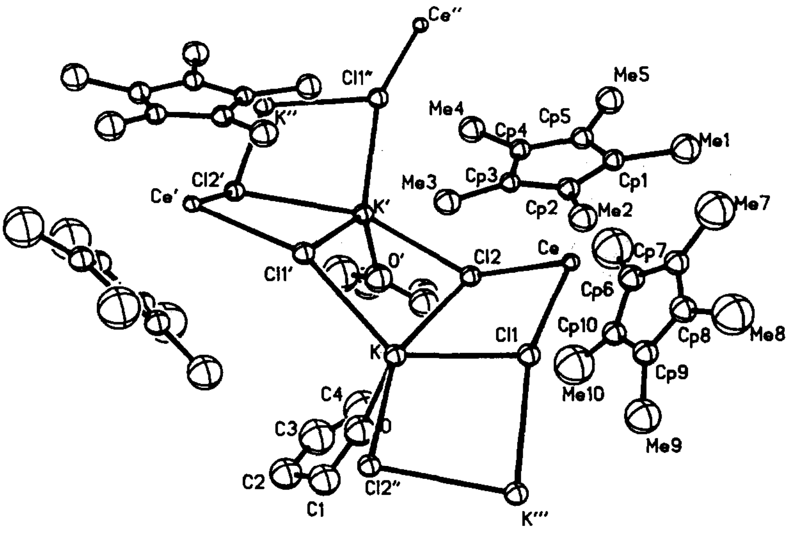

Fig. 42. $[Cp^*_2Ce(\mu\text{-}Cl)_2K(THF)]_n$. (Reprinted with permission from Organometallics. Copyright 1988 American Chemical Society.)

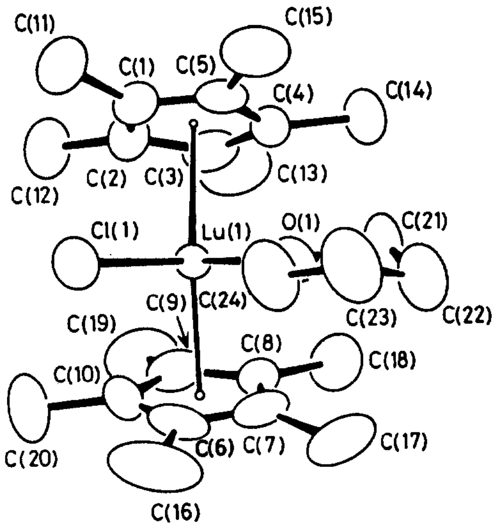

Fig. 43. $Cp^*_2LuCl(THF)$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

Wayda[36] prepared $(Cp^tBu)_2Ln$ (Ln = Sm, Lu). The crystal structure of $[(Cp^tBu_2)_2Lu(\mu\text{-}Cl)]_2$ was published by Bel'skii, et al.[109] and is depicted in Figure 44. The same authors prepared and structurally characterized $[(Cp^tBu_2)_2Ln(\mu\text{-}Cl)_2Li(tmeda)]$ (Ln = Ce,[110] Lu[111])

In a major publication, Marks, et al.[112] investigated bond disruption enthalpies in Cp^*_2Sm compounds. Ligands studied included hydrides, dialkyl amides, alkoxides, halides, thiolates, and phosphides.

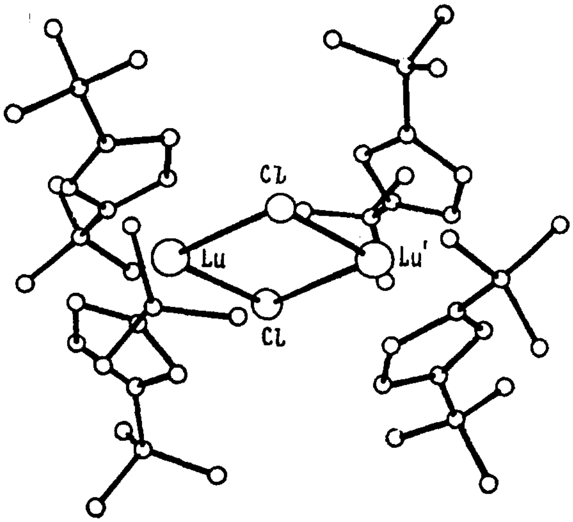

Fig. 44. [$(Cp^tBu_2)_2Lu(\mu\text{-}Cl)]_2$. (Reprinted with permission from Metalloorganicheskoi Khimiya.)

Evans, et al.[38] used $[NH_4]_2[Ce(NO_3)_6]$ with NaCp to prepare $Cp_2Ce(NO_3)_2Na(THF)_2$. Shi, et al.[113] prepared and structurally characterized $Cp_2Yb(acac)$ (Figure 45, Yb-C(Cp) = 2.61(1)Å). Other β-diketonate complexes of Cp_2Ln (Ln = Nd, Sm, Gd, Dy, Er, Yb) were prepared and studied.[39-43] The specific ligands used are the same as given in section (i) for $CpLnL_2$ β-diketonate complexes. Shen, et al.[114] reported the preparation of Cp_2Yb benzoates and Chen, et al.[115] studied heats of hydrolysis for Cp_2LnOAc (Ln = Sm, Gd, Tb, Lu) and Cp_2YbL (L = $CH(CO_2Me)_2$, $MeCOCHCO_2Et$, $MeCOCHCOCF_3$).

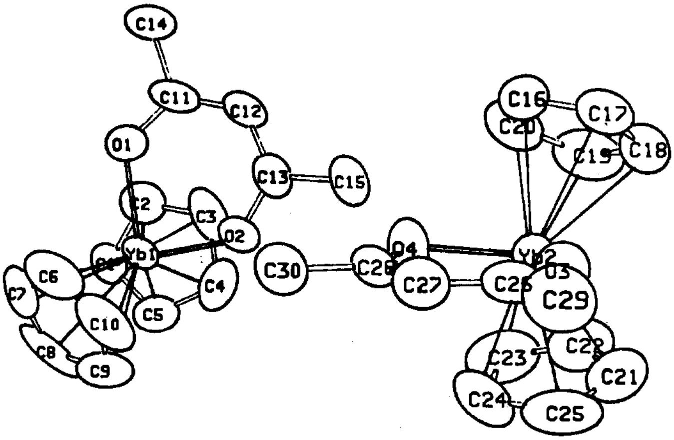

Fig. 45. $Cp_2Yb(acac)$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Evans and Atwood, et al.[116] published the preparation and crystal structures of $[Cp^*_2Sm(THF)]_2O_2C_{16}H_{10}$ (Figure 46, Sm-C(Cp*) = 2.75(2)Å), $[Cp^*_2Sm(CNCMe_3)]_2O$ (Figure 47, Sm-C(Cp*) = 2.80(1)Å), and $Cp^*_2SmI(C_6H_{10}N_4)$ (Figure 48, Sm-C(Cp*) = 2.73(2)Å). The same authors also published the μ-hydroxo species, $[Cp_2Y(\mu\text{-}OH)]_2 \cdot C_2Ph_2$ (Figure 49, Y-C(Cp) = 2.68(3)Å).[117] Deacon and Wilkinson[118] prepared several carboxylate compounds, $Cp_2Yb(O_2CR)$ (R = Me, CF_3, Ph, C_6F_5, C_6Br_5, o-$MeO_2CC_6F_4$, 2,4,6-$Me_3C_6H_2$, pyridin-2-yl, quinolin-2-yl), by oxidation of $Cp_2Yb(dme)$ with Tl^+ and Hg^{+2} carboxylates.

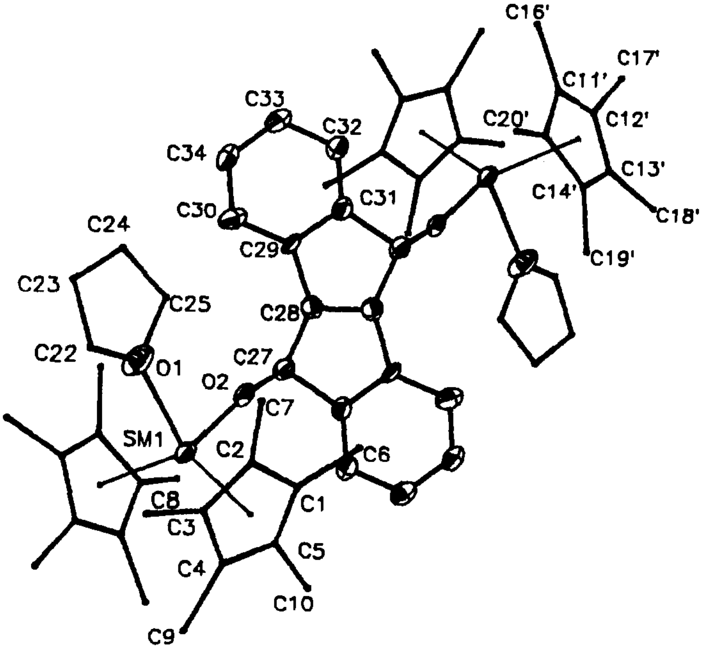

Fig. 46. [Cp$^*_2$Sm(THF)]$_2$O$_2$C$_{16}$H$_{10}$. (Reprinted with permission from Polyhedron. Copyright 1988 Pergamon Press plc.)

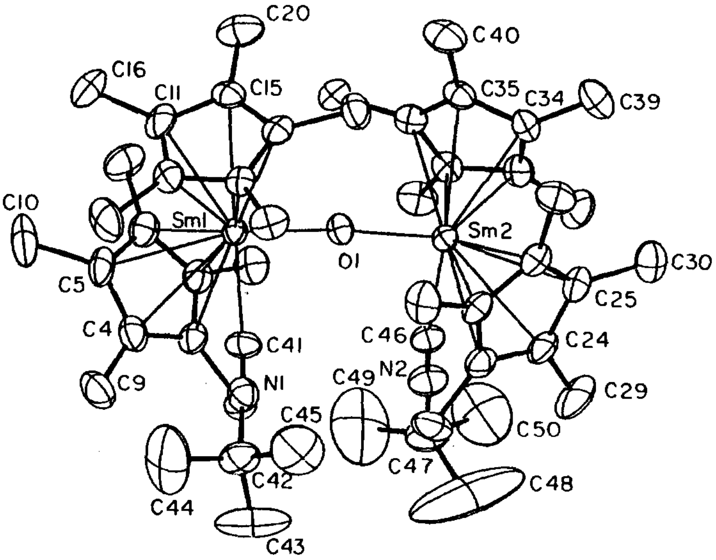

Fig. 47. [Cp$^*_2$Sm(CNCMe$_3$)]$_2$O. (Reprinted with permission from Polyhedron. Copyright 1988 Pergamon Press plc.)

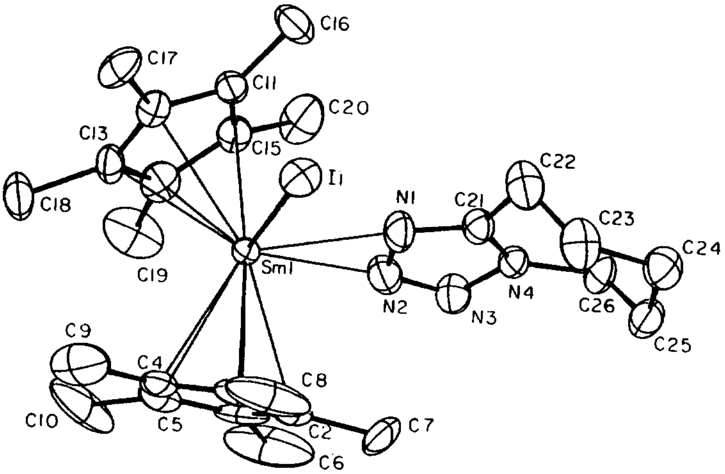

Fig. 48. $Cp^*_2SmI(C_6H_{10}N_4)$. (Reprinted with permission from Polyhedron. Copyright 1988 Pergamon Press plc.)

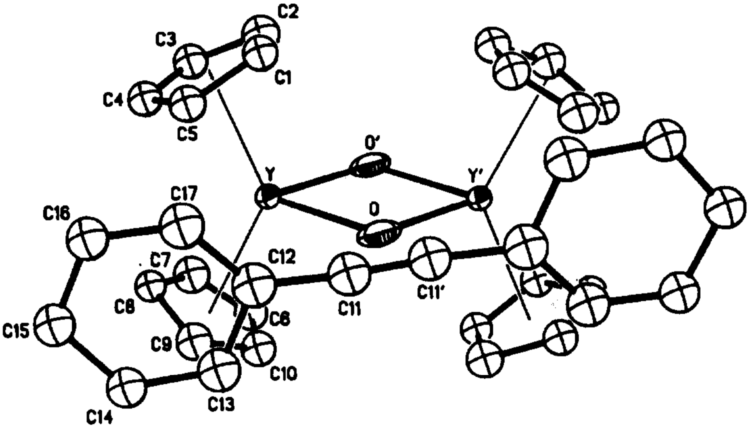

Fig. 49. $[Cp_2Y(\mu\text{-}OH)]_2{\cdot}C_2Ph_2$. (Reprinted with permission from Inorganic Chemistry. Copyright 1988 American Chemical Society.)

Kinetic studies were carried out by Finke and Watson, et al.[119] on the reactions of $Cp^*_2LnOEt_2$ (Ln = Sm^{+2}, Eu^{+2}) with alkyl and aryl halides. Samarium was reported to display enhanced reactivity while Eu underwent nonredox reactions. Kagan, et al.[120] evaluated Cp_2Sm in organic synthesis and Trifonov, et al.[121] studied Cp_2Yb in the activation of N_2 in sodium naphthalide systems.

Long, et al.[122] studied the ^{151}Eu Mössbauer spectra of Cp^*_2Eu, $Cp^*_2Eu(THF)$, $Cp^*_2Eu(THF)(OEt_2)$, and $[Cp^*Eu(THF)_2(\mu\text{-}I)]_2$. Mass spectral data for seven 1,1'-(3-oxa-pentamethylene)dicyclopentadienyl lanthanide chlorides and eleven Cp_2LnCl compounds were published by Fu, et al.[123]

(iv) Biscyclopentadienyl group 6,9,10,14-16 compounds. Andersen, et al.[124] published the crystal structure of $Cp^*_2Yb(SC_6H_5)(NH_3)$ (Figure 50, Yb-C(Cp*) = 2.64(2)Å, Yb-NH_3 = 2.428(5)Å, Yb-S = 2.674(5)Å). Deacon, et al.[76] prepared $Cp_2Ln(pyridine)_2$ (Ln = Eu, Yb) and $Cp_2Yb(NCMe)$. Knee and Bruno, et al.[125] included the crystal structure of $Cp^*_2CeI(NCMe)_2$ (Figure 51, Ce-C(Cp*) = 2.79(1)Å, Ce-N = 2.63(1)Å) in a paper discussing the luminescence spectra and lifetimes of Cp^*_2Ce compounds.

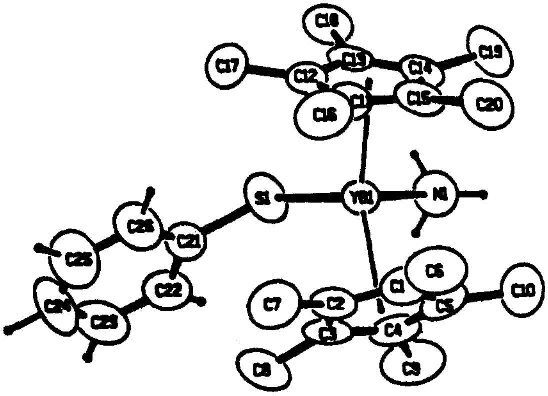

Fig. 50. $Cp^*_2Yb(SC_6H_5)(NH_3)$. (Reprinted with permission from Acta Crystallographica.)

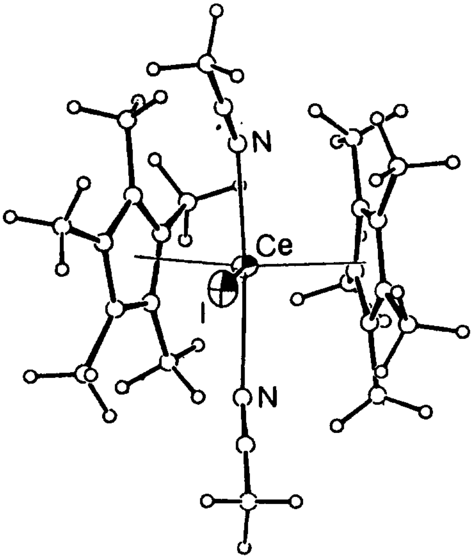

Fig. 51. $Cp^*_2CeI(NCMe)_2$. (Reprinted with permission from Inorganic Chemistry. Copyright 1988 American Chemical Society.)

Evans and Drummond[126] presented the reactions of $Cp^*_2Sm(THF)_2$ with pyridazine and benzaldehyde azine yielding reductively coupled products, and with bipyridine to give a Sm^{+3} bypyridyl complex. The crystal structures of all three products were described including $[Cp^*_2Sm(THF)]_2[\mu,\eta^4\text{-}(CH{=}NNCH{=}CHCH\text{-})_2]$ (Figure 52, Sm-C(Cp*) = 2.752(8)Å, Sm-N = 2.351(6), 2.430(6)Å), $[Cp^*_2Sm]_2[\mu,\eta^4\text{-}(PhHC{=}NNCHPh\text{-})_2]$ (Figure 53, Sm-C(Cp*) = 2.76(2)Å, Sm-N = 2.32(1), 2.43(1)Å), and $Cp^*_2Sm(\eta^2\text{-}N_2C_{10}H_8)$ (Figure 54, Sm-C(Cp*) = 2.724(3)Å, Sm-N = 2.427(2), 2.436(2)Å).

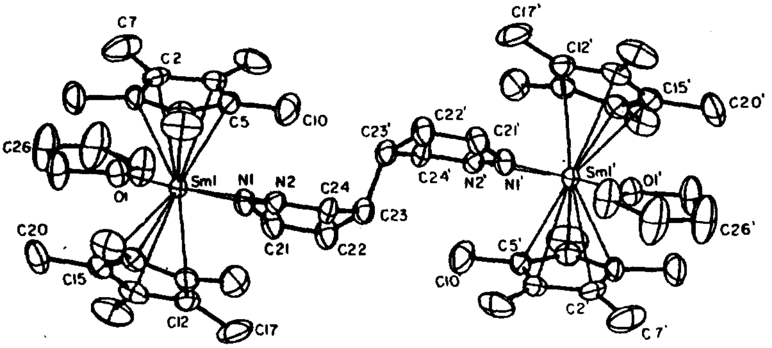

Fig. 52. $[Cp^*_2Sm(THF)]_2[\mu,\eta^4\text{-}(CH{=}NNCH{=}CHCH\text{-})_2]$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1989 American Chemical Society.)

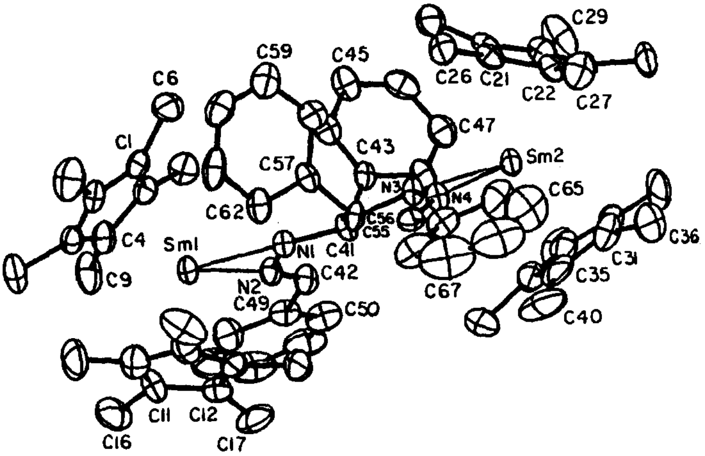

Fig. 53. $[Cp^*_2Sm]_2[\mu,\eta^4\text{-}(PhHC{=}NNCHPh\text{-})_2]$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1989 American Chemical Society.)

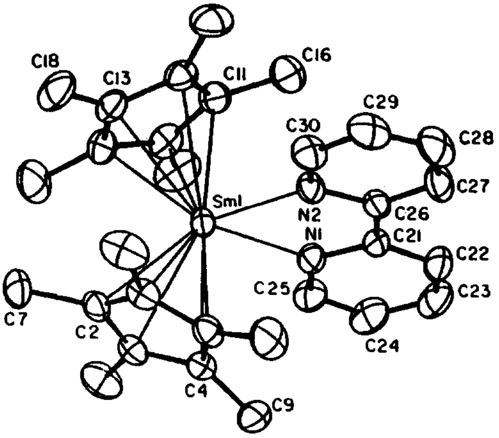

Fig. 54. $Cp^*_2Sm(\eta^2-N_2C_{10}H_8)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1989 American Chemical Society.)

Lawless, et al.[127] published high resolution ^{171}Yb NMR data for $Cp^*_2Yb(THF)_2$, $Cp^*_2Yb(OEt_2)$, and $Cp^*_2Yb(NC_5H_5)_2$. Evans, et al.[128] reported the crystal structure of the first dinitrogen complex of an f-element, $[Cp^*_2Sm]_2N_2$ (Figure 55, Sm-C(Cp*) = 2.73(2)Å, Sm-N = 2.36(1)Å).

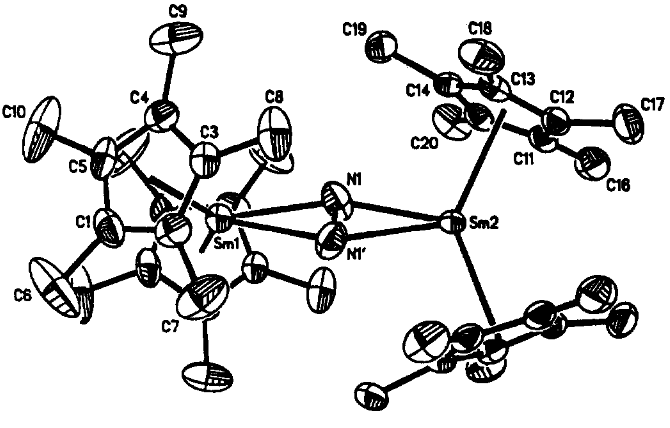

Fig. 55. $[Cp^*_2Sm]_2N_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

Evans, et al.[129] reported in depth on the synthesis, structure, and reactivity of reduction and CO derivatization of azobenzene mediated by divalent lanthanide compounds. The reactions of PhNNPh with $Cp^*_2Sm(THF)_2$ produced $Cp^*_2Sm(\eta^2\text{-}N_2Ph_2)(THF)\cdot 0.5(THF)$ (Figure 56, Sm-C(Cp^*) = 2.76(2)Å, Sm-N = 2.42(2)Å), $[Cp^*_2Sm]_2(N_2Ph_2)$ (Figure 57, Sm-C(Cp^*) = 2.74(3)Å, Sm-N = 2.40(1)Å), and $[Cp^*Sm(THF)]_2[\mu,\eta^2:\eta^2\text{-}N_2Ph_2]_2\cdot 2(THF)$ (Figure 58, Sm-C(Cp^*) = 2.76(1)Å, Sm-N = 2.323(8), 2.559(7)Å).

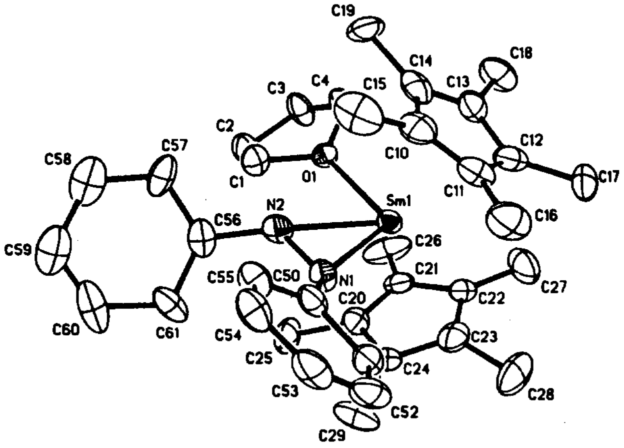

Fig. 56. $Cp^*_2Sm(\eta^2\text{-}N_2Ph_2)(THF)\cdot 0.5(THF)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

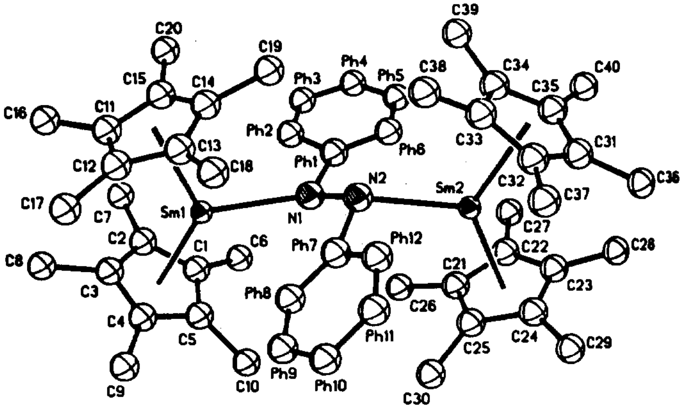

Fig. 57. $[Cp^*_2Sm]_2(N_2Ph_2)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

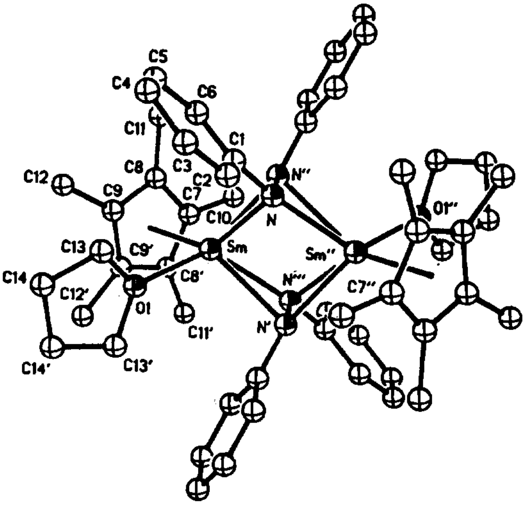

Fig. 58. $[Cp^*Sm(THF)]_2[\mu,\eta^2:\eta^2\text{-}N_2Ph_2]_2\cdot 2(THF)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

When $Cp_2Yb(THF)$ is utilized the compounds obtained included $[CpYb(THF)]_2[\mu,\eta^2:\eta^2\text{-}N_2Ph_2]_2\cdot C_7H_8$ (Figure 59, Yb-C(Cp) = 2.63(2)Å, Yb-N = 2.197(9), 2.53(4)Å). Reaction of the first Sm complex above with CO gave $[Cp^*_2Sm]_2[\mu,\eta^4\text{-}(PhN)OCCO(NPh)]\cdot 2C_7H_8$ (Figure 60, Sm-C(Cp^*) = 2.71(1)Å, Sm-N = 2.49(1)Å, Sm-O = 2.30(1)Å). Evans and Drummond[130] reported the reaction of RCHCHR (R = 2-pyridyl) with $Cp^*_2Sm(THF)_2$ followed by treatment with 80 psi of CO to produce $[Cp^*_2Sm]_2[\mu,\eta^4\text{-}RCH{=}C(O)C(O){=}CHR]\cdot 2C_7H_8$ (Figure 61, Sm-C(Cp^*) = 2.71(1)Å, Sm-N = 2.473(7)Å, Sm-O = 2.191(6)Å).

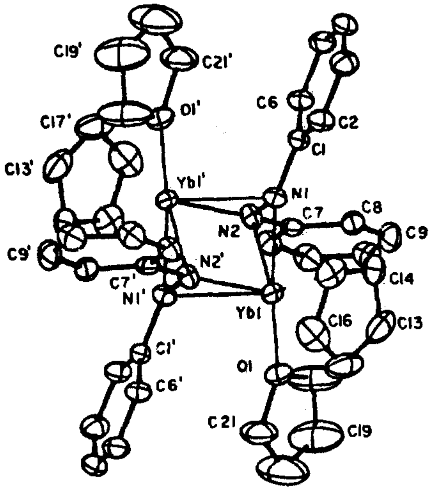

Fig. 59. [CpYb(THF)]$_2$[$\mu,\eta^2:\eta^2$-N$_2$Ph$_2$]$_2$·C$_7$H$_8$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

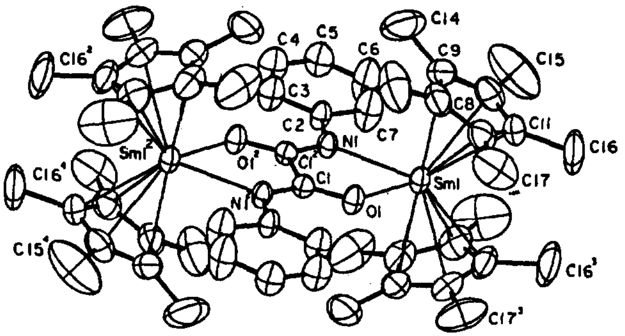

Fig. 60. [Cp$^*_2$Sm]$_2$[μ,η^4-(PhN)OCCO(NPh)]·2C$_7$H$_8$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

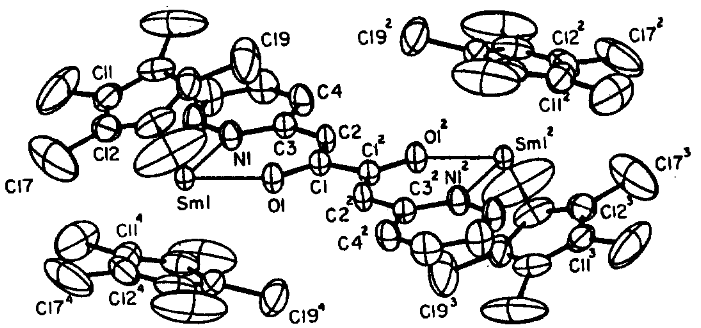

Fig. 61. [Cp$^*{}_2$Sm]$_2$[μ,η^4-RCH=C(O)C(O)=CHR]·2C$_7$H$_8$ (R = 2-pyridyl). (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

Isotope exchange in Cp$_2$LuN(D)CH$_2$Ph was investigated by Beletskaya, et al.[131] Heterobimetallic complexes of Cp$_2$Ln and metal carbonyls were the subject of three reports. Bruno, et al.[132] prepared and studied [Cp$''_2$Ce(μ-OC)W(CO)(Cp)(μ-CO)]$_2$ (Figure 62).

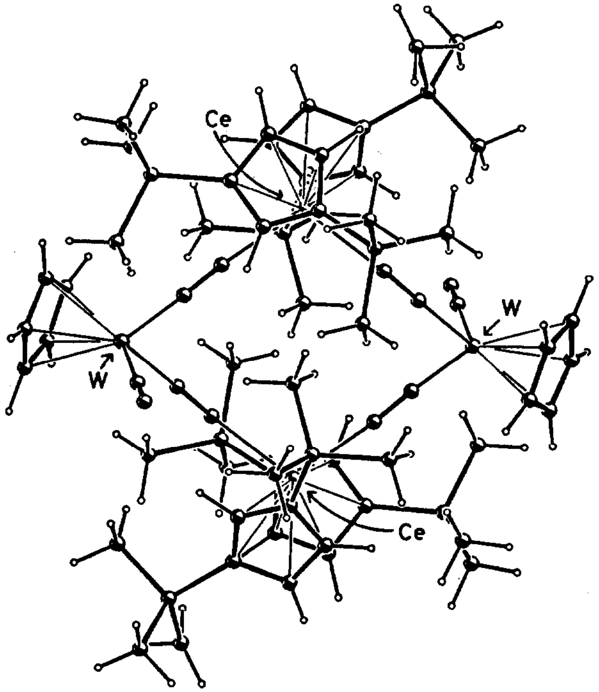

Fig. 62. [Cp$''_2$Ce(μ-OC)W(CO)(Cp)(μ-CO)]$_2$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

Beletskaya, *et al.*[133,134] made $[Cp_2Yb(THF)_2][Co(CO)_4]$ and $[Cp_2Yb(THF)(\mu\text{-}CO)Co(CO)_3]$ (which was structurally characterized). Magomedov, *et al.*[135] studied the photoinduced electron transfer in these complexes. Deacon, *et al.*[136] prepared $(CpPPh_2)_2Yb(THF)$ and utilized it in the synthesis of the heterometallic, $[Yb(THF)_2(CpPPh_2)_2PtMe_2]\cdot PhMe$. The crystal structure is depicted in Figure 63.

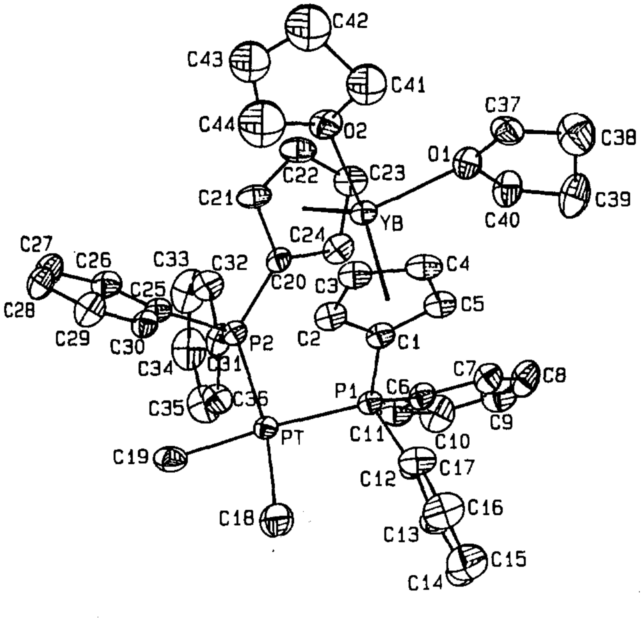

Fig. 63. $[Yb(THF)_2(CpPPh_2)_2PtMe_2]\cdot PhMe$. (Reprinted with permission from *Angewandte Chemie International*.)

Schumann, *et al.* synthesized and structurally characterized $Cp^*_2Lu(\mu\text{-}S^tBu)_2Li(THF)_2$ (Figure 64, Lu-C(Cp^*)= 2.66(2)Å, Lu-S = 2.716(7)Å),[27,137] $Cp_2Lu(\mu\text{-}SePh)_2Li(THF)_2$ (Figure 65, Lu-C(Cp) = 2.60(2)Å, Lu-Se = 2.799(1)Å),[27,137] $Cp_2Lu(\mu\text{-}PPh_2)_2Li(tmeda)$ (Figure 66),[27] $Cp_2Lu(\mu\text{-}AsPh_2)_2Li(tmeda)$ (Figure 67, Lu-C(Cp) = 2.59(1)Å, Lu-As = 2.88(1)Å),[27,138] and $[Li(dme)_3][Cp_2Ln(SiMe_3)_2]$ (Ln = Sm (Figure 68), Sm-Si = 2.88Å), Dy, Ho, Er, Tm, Lu).[27,139]

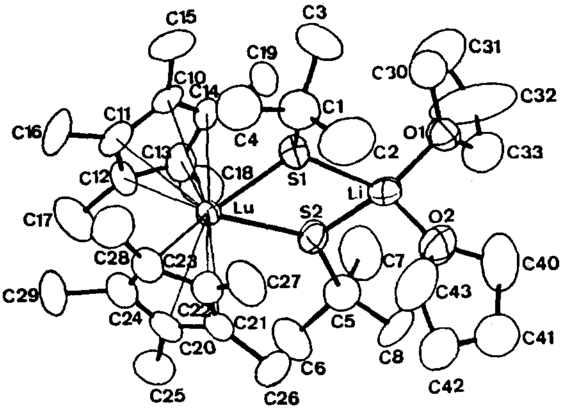

Fig. 64. $Cp^*_2Lu(\mu\text{-}S^tBu)_2Li(THF)_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

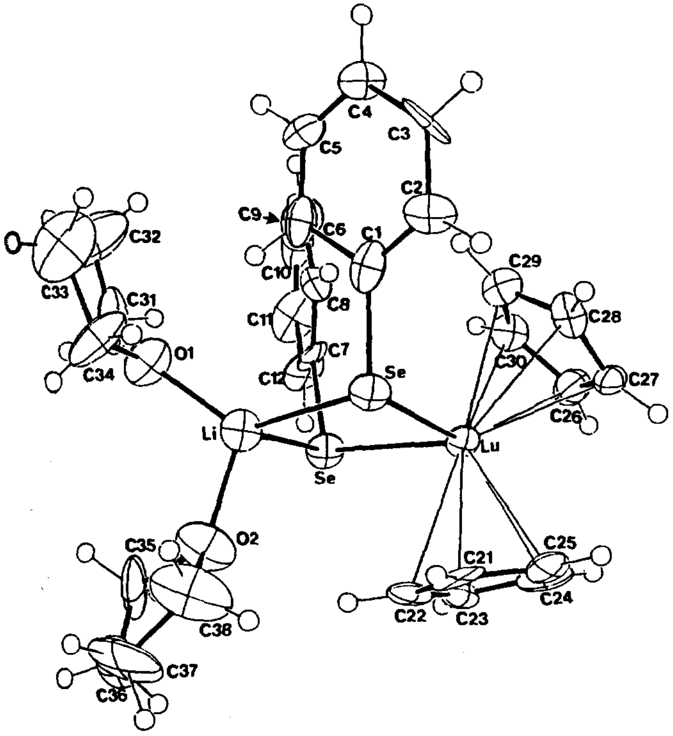

Fig. 65. $Cp_2Lu(\mu\text{-}SePh)_2Li(THF)_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

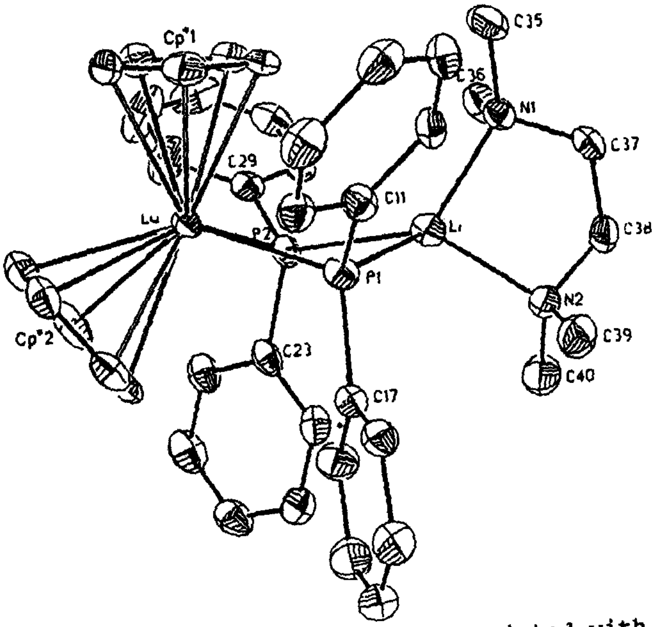

Fig. 66. $Cp_2Lu(\mu\text{-}PPh_2)_2Li(tmeda)$. (Reprinted with permission from *Polyhedron*. Copyright 1988 Pergamon Press plc.)

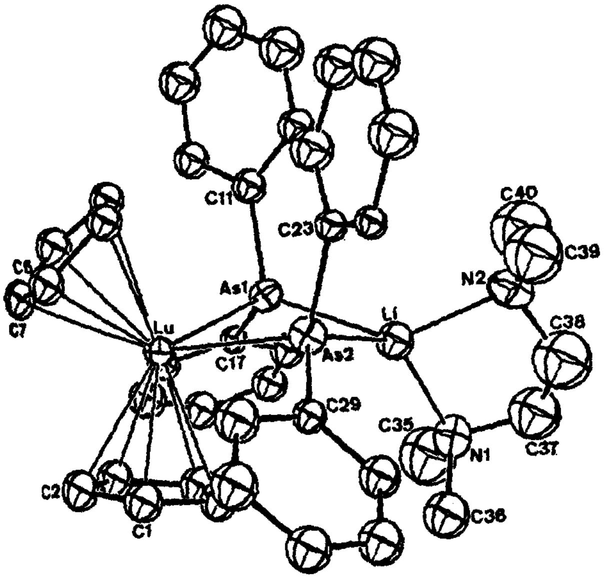

Fig. 67. $Cp_2Lu(\mu\text{-}AsPh_2)_2Li(tmeda)$. (Reprinted with permission from *Organometallics*. Copyright 1988 American Chemical Society.)

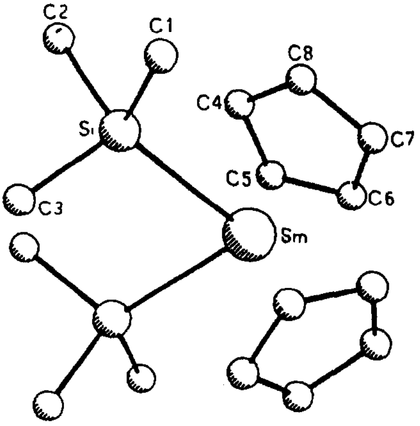

Fig. 68. The anion in $[Li(dme)_3][Cp_2Sm(SiMe_3)_2]$. (Reprinted with permission from Organometallics. Copyright 1988 American Chemical Society.)

Andersen, et al. published the chemistry of $[Cp^*_2Yb]_2E$[140] and $Cp^*_2Yb(ER)L$[141] (E = O, S, Se, Te; L = lewis base) derivatives. The crystal structures of $[Cp^*_2Yb]_2Se$ (Figure 69, Yb-C(Cp*) = 2.609(7)Å, Yb-Se = 2.621(1)Å),[140] $Cp^*_2Yb(TePh)(NH_3)$ (Figure 70, Yb-C(Cp*) = 2.63(3)Å, Yb-Te = 3.039(1)Å, $Yb\text{-}NH_3$ = 2.50(1)Å),[141] and $[Cp^*_2Yb]_2Te_2$ (Figure 71, Yb-C(Cp*) = 2.63(2)Å, Yb-Te = 3.156(4)Å)[142] were determined.

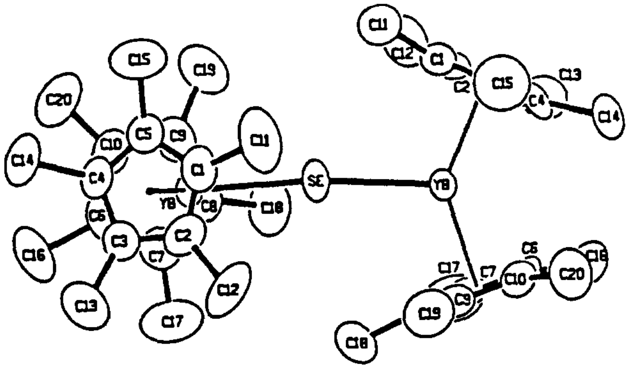

Fig. 69. $[Cp^*_2Yb]_2Se$. (Reprinted with permission from Organometallics. Copyright 1989 American Chemical Society.)

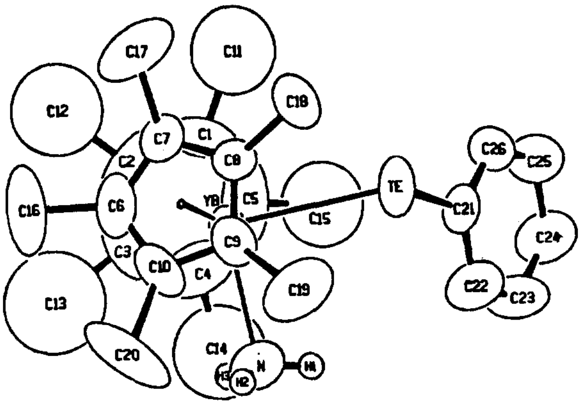

Fig. 70. Cp$^*_2$Yb(TePh)(NH$_3$). (Reprinted with permission from *Organometallics*. Copyright 1988 American Chemical Society.)

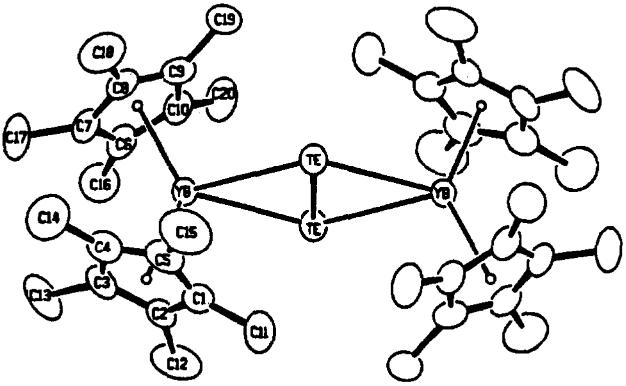

Fig. 71. [Cp$^*_2$Yb]$_2$Te$_2$. (Reprinted with permission from *Acta Crystallographica*.)

Samarium is directly coordinated to phosphorous and carbon in [Cp$^*_2$Sm(PC^{t}Bu)]$_2$.[143] The crystal structure (Figure 72) reveals Sm-P distances of 2.945(2) and 2.952(2)Å and Sm-C(σ) separations of 2.557(6) and 2.556(6)Å. The compound was prepared by reductive dimerization of the phosphaalkyne.

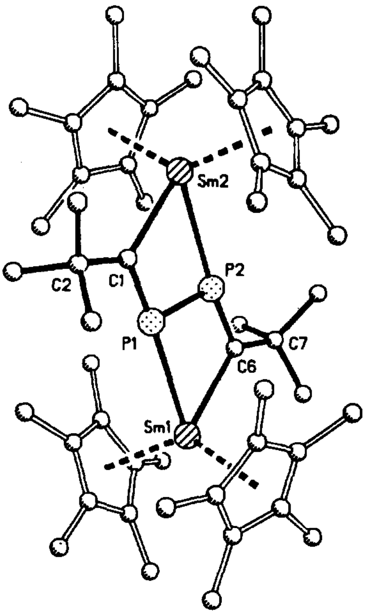

Fig. 72. $[Cp^*_2Sm(PC^tBu)]_2$. (Reprinted with permission from Angewandte Chemie International.)

(v) Biscyclopentadienyl hydrides. Marks[144] published the text of his address at the Second International Conference on the Basic and Applied Chemistry of f-Transition and Related Elements (Lisbon). The paper dealt with catalysis at actinide centers via cleavage of H-H bonds. In a later report,[145] he provided the first spectroscopic detection of an organolanthanide dihydrogen complex, $Cp^*_2EuH_2$. Ethylene coordination was also detected.

Teuben, et al.[146] prepared $[Cp^*_2YH]_2$ and $Cp^*_2YH(THF)$ by hydrogenolysis of $Cp^*_2YCH(SiMe_3)_2$ and $Cp^*_2YMe(THF)$, respectively. The latter was reported to be a catalyst in H/D exchange reactions between sp^3-CH and sp^2-CD bonds. Qian, et al.[147] reported the preparation, crystal structure, and reactivity with 1-hexane, 1-hexene, phenylacetylene, and diphenylethyne of $[Cp_2LuH(THF)]_2$ (Figure 73, Lu-C(Cp) = 2.63(2)Å, Lu-H = 2.04(6)Å).

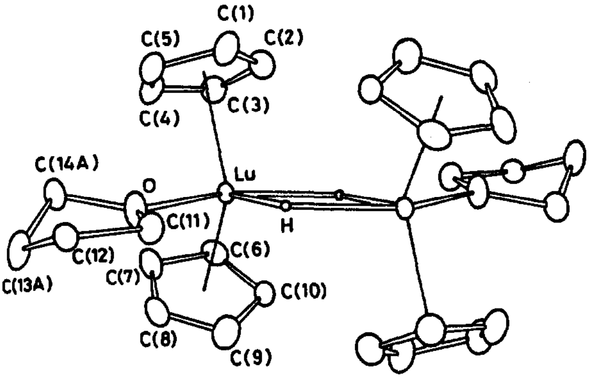

Fig. 73. $[Cp_2LuH(THF)]_2$. (Reprinted with permission from Inorganica Chimica Acta.)

Evans and Bau, et al.[148] published the synthesis of alkoxy hydride anions, $\{[Cp_2Y(\mu\text{-}H)]_x[Cp_2Y(\mu\text{-}OMe)_3]_{3-x}(\mu_3\text{-}H)]\}^-$ (x = 0-2) and the crystal structure of the $[Li(THF)_3]^+$ salt of x = 0 (Figure 74, Y-C(Cp) = 2.73(2)Å). The triply bridging central H atom was not located. The compounds were prepared by reaction of $[Li(THF)_4]\{[Cp_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}$ with CH_3OH at 0°C. Evans, et al.[149] also reported the hydrogenolysis of $[(CpMe_2)_2YMe]_2$ to yield $[(CpMe_2)_2YH]_3$ or if crystallized from THF, $[(CpMe_2)_2YH(THF)]_2$. Both were crystallographically characterized (Figure 75, Y-C($CpMe_2$) = 2.63(1)Å; Figure 76 (THF solvate), Y-C($CpMe_2$) = 2.69(1)Å, Y-H = 2.15Å).

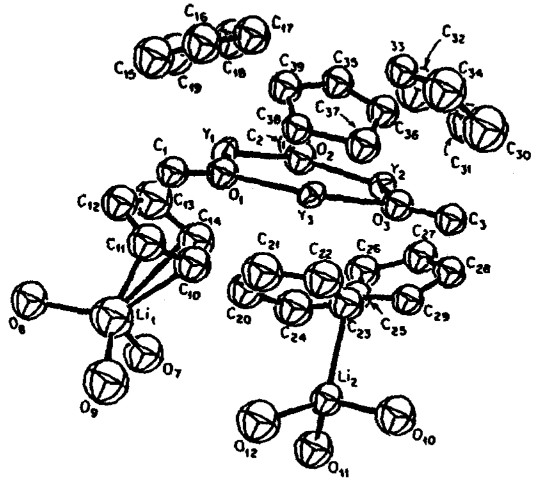

Fig. 74. The {[(THF)$_3$Li]$_2$[Cp$_2$Y(μ-OCH$_3$)]$_3$(μ_3-H)}$^+$ cation in {[Li(THF)$_3$]}$_2${[Cp$_2$Y(μ-OCH$_3$)]$_3$(μ_3-H)}$_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

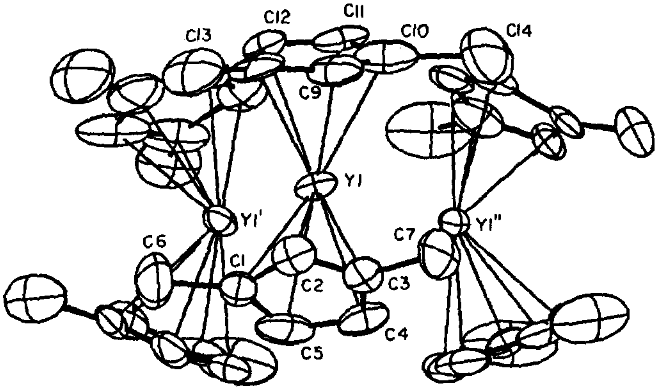

Fig. 75. [(CpMe$_2$)$_2$YH]$_3$. (Reprinted with permission from Organometallics. Copyright 1987 American Chemical Society.)

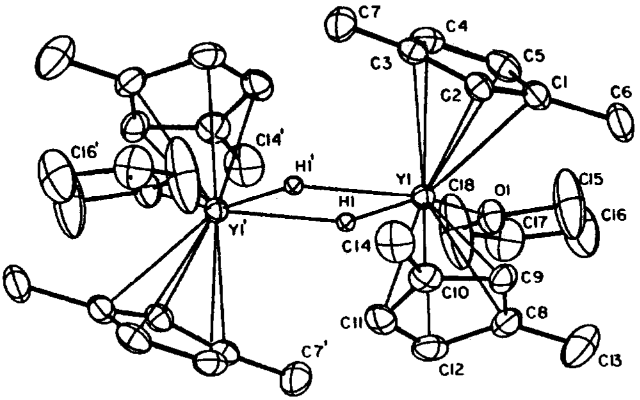

Fig. 76. $[(CpMe_2)_2YH(THF)]_2$. (Reprinted with permission from Organometallics. Copyright 1987 American Chemical Society.)

Bulychev, et al. studied the reactions of $[Cp_2YCl]_2$[150] and $[Cp_2LuCl]_2$[151] with $LiAlH_4$ in benzene and in the presence of Lewis bases. The structurally characterized complexes reported include $[Cp_2Y]_2AlH_4(NEt_3)\cdot C_6H_6$ (Figure 77),[150] $[Cp_2Lu(\mu_2\text{-}H)AlH_3(NEt_3)]_2$ (Figure 78),[151] $Cp_2Lu(\mu_2\text{-}H)_2AlH_3(NEt_3)$ (Figure 79),[151] and $[(Cp^tBu_2)_2LuH]_2$ (Figure 80)[152] IR data was reported for $Cp_2Y(THF)(\mu_2\text{-}H)_2AlCl(\mu_2\text{-}H)_2(THF)YCp_2$.[150]

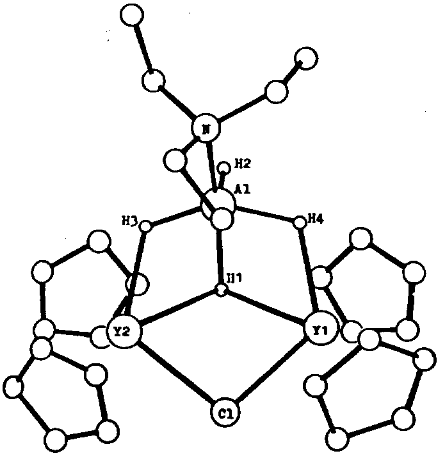

Fig. 77. $[Cp_2Y]_2AlH_4(NEt_3)\cdot C_6H_6$. (Reprinted with permission from Journal of Organometallic Chemistry.)

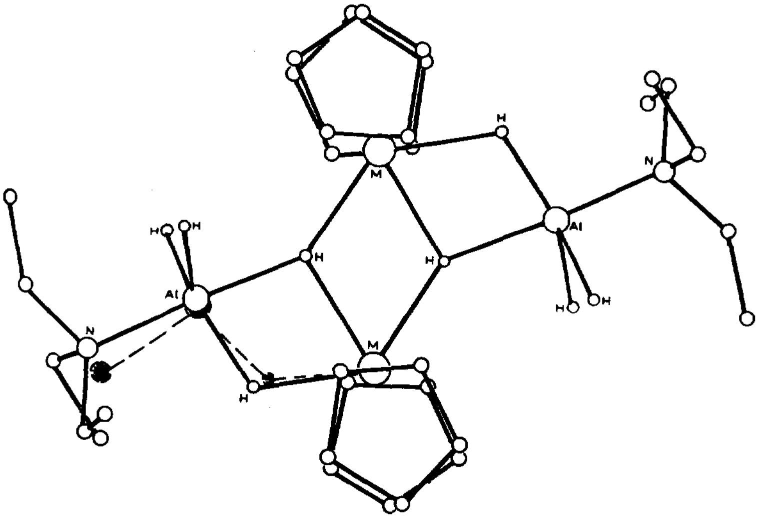

Fig. 78. $[Cp_2Lu(\mu_2\text{-}H)AlH_3(NEt_3)]_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

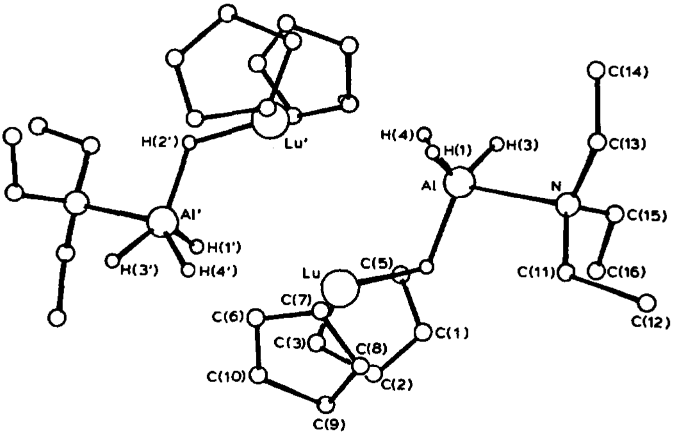

Fig. 79. $Cp_2Lu(\mu_2\text{-}H)_2AlH_3(NEt_3)$. (Reprinted with permission from Journal of Organometallic Chemistry.)

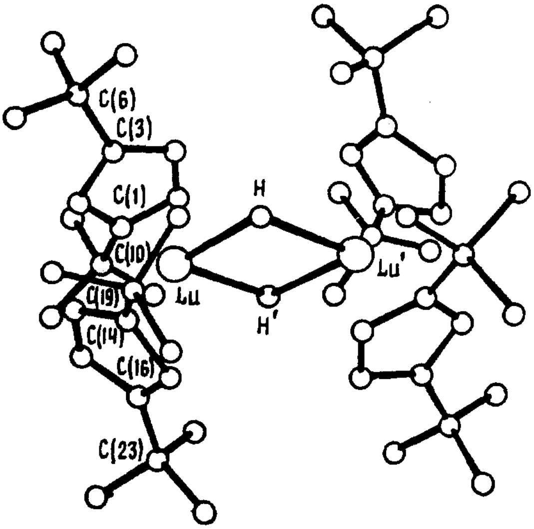

Fig. 80. $[(Cp^tBu_2)_2LuH]_2$. (Reprinted with permission from Organometallic Chemistry in the USSR.)

Hydrogenolysis of $Cp_2LuPh(THF)$ was reported[153] to give $[Cp_2Lu(\mu\text{-}H)(THF)]_2$. This compound was further utilized to prepare $Cp_2LuOCH_2Ph(THF)$ by reaction with PhCHO and $Cp_2Lu[Re(CO)_5](THF)$ by reaction with $PhCHORe(CO)_5$. The reactivity of $[Cp_2LuCl]_2$ with aluminum hydrides was investigated by Knyazhanskii, et al.[154] The complexes $[Cp_2LuAlH_4(L)]_2$ (L = NEt_3, OEt_2, THF), $[Cp_2LuAlH_4]_2$, $[Cp_2LuAlH_3R]_2$ (R = hexyl), and $[CpLuAlH_2R_2]_2$ (R = hexyl, Et) were prepared.

(vi) Biscyclopentadienyl alkyl, aryl, and allyl compounds. Evans, et al.[149] published the reactions of $(CpMe_2)_2YCl(THF)$ with LiMe to form $[(CpMe_2)_2YMe]_2$. The crystal structure revealed Y-C($CpMe_2$) = 2.65(2)Å, Y-C(Me) = 2.61(2)Å.

Several contributions detailed the synthesis, structures, and reactivities of compounds with linear bridges between Cp_2Ln and Be, Al, or Ga. Andersen and Burns[155] published the structure of $Cp^*_2YbMeBeCp^*$ (Figure 81, Yb-C(Cp^*) = 2.68(1)Å, Yb-Me = 2.766(4)Å, Yb-Me-Be = 177.2(3)°) prepared by addition of Cp^*_2Yb to Cp^*BeMe. Linearly bridging methyl groups were also observed in $[Cp^*_2Ln(\mu\text{-}Me)_2MMe_2]_2$ (Ln = Y, Lu; M = Al, Ga;[156] Ln = Sm, M = Al[157]). The crystal structures of the isostructural $[Cp^*_2Ln(\mu\text{-}Me)_2AlMe_2]_2$ (Ln = Y,[156] Figure 82, Y-Me = 2.66(2)Å, Y-Me-Al =

176(1)°; Ln = Sm,[157] Sm-Me = 2.75(2)Å, Sm-Me-Al = 176(1)°), appeared.

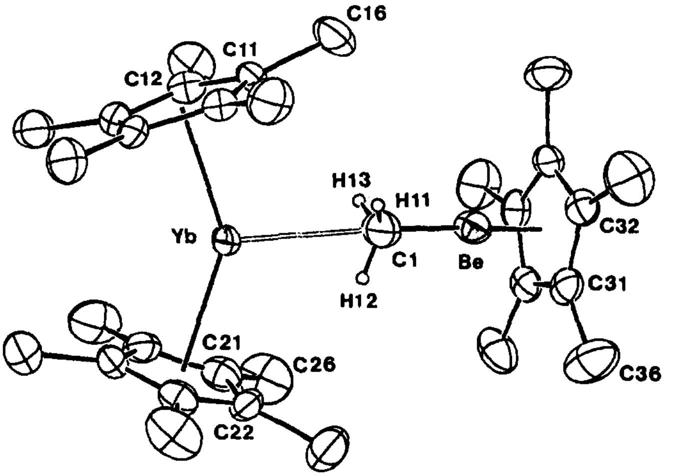

Fig. 81. $Cp^*_2YbMeBeCp^*$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1987 American Chemical Society.)

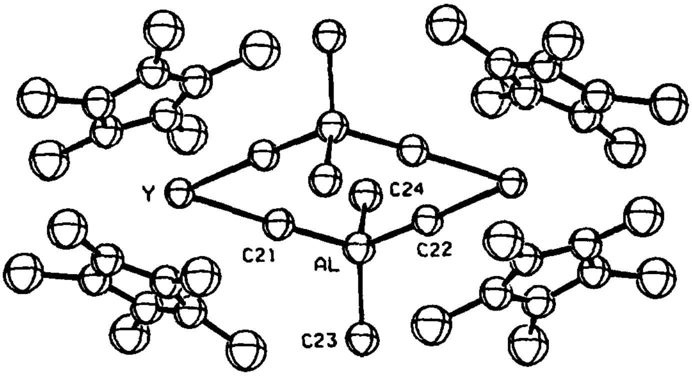

Fig. 82. $[Cp^*_2Y(\mu\text{-}Me)_2AlMe_2]_2$. (Reprinted with permission from Inorganica Chimica Acta.)

Two crystal structures were reported with terminal Ln-Me interactions. Evans, et al.[157] published $Cp^*_2SmMe(THF)$ (Figure 83, Sm-C(Cp*) = 2.711(6)Å, Sm-Me = 2.48(1)Å). The isostructural Y analog was published by Teuben, et al.[158] (Y-C(Cp*) = 2.66(2)Å, Y-Me = 2.44(2)Å). The Sm compound was reported to react with benzene and toluene to form Cp$^*_2$Sm(C$_6$H$_5$)(THF) and Cp$^*_2$Sm(CH$_2$C$_6$H$_5$)-(THF), respectively.[157]

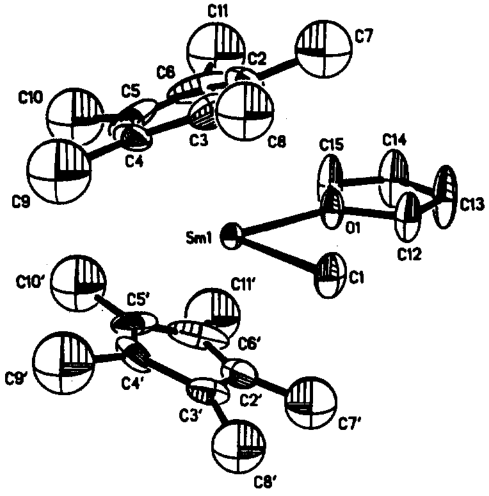

Fig. 83. Cp$^*_2$SmMe(THF). (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

Arnaudet and Ban[159] obtained [Li(THF)$_n$][Cp$_2$EuMe] by the reaction of Cp$_2$Eu(THF)$_n$ with LiMe. A variable temperature ^{1}H NMR study was reported.

Teuben, et al.[160] investigated the reactivity of Cp$^*_2$Y chlorides in OEt$_2$ and THF with LiMe and LiAlMe$_4$. The new compounds prepared include Cp$^*_2$Y(μ-Me)(μ-Cl)Li(OEt$_2$)$_2$, Cp$^*_2$Y(μ-Me)$_2$LiOEt$_2$, Cp$^*_2$YMe(THF), Cp$^*_2$YMe, [Cp$^*_2$Y(μ-Me)$_2$AlMe$_2$]$_2$, and the MgCl$_2$(THF)$_2$ salts of Cp$^*_2$YMe, Cp$^*_2$YCH$_2$Ph, and Cp$^*_2$Y(η^1-CH$_2$CMeCH$_2$).

Ethyl bridged Cp$^*_2$Ln complexes were reported. Evans, et al.[161] synthesized Cp$^*_2$Sm(μ-Et)$_2$AlEt$_2$ by reaction of Cp$^*_2$Sm and AlEt$_3$ in toluene. The crystal structure revealed the bridging ethyl groups (Figure 84, Sm-C(Cp*) = 2.712(2)Å, Sm-C(σ) = 2.662(4)Å). Yamamoto, et al.[162] prepared Cp$^*_2$Yb(AlR$_3$)(THF) (R = Et, Me, ^{i}Bu) by similar reactions starting with Cp$^*_2$Yb(THF). The R = Et derivative was crystallographically characterized and is presented in Figure 85 (Yb-C(Cp*) = 2.68(2)Å, Yb-C(1) = 2.85(2)Å, Yb-C(2) = 2.94(2)Å).

Teuben, et al.[163] published an extensive study of $Cp^*_2Ce^+$ complexes highlighted by the crystal structure of $Cp^*_2CeCH(SiMe_3)_2$ (Figure 86). An agostic interaction was justified on the basis of the unsymmetrical bonding of the alkyl ligand (Ce-C(σ) = 2.536(5)Å). Other compounds prepared and characterized in this paper included $Cp^*_2CeCl_2Li(THF)_{2.5}$, $Cp^*_2CeCl_2Li(dme)$, $(Cp^*_2CeCl)_n$, $Cp^*_2CeN(SiMe_3)_2$, $Cp^*_2CeCl_2Li(tmeda)_2$, $Cp^*_2CeNH^tBu{\cdot}NH_2{}^tBu$, $[Cp^*_2CeH]_2$, and $Cp^*CeCH(SiMe_3)_2{\cdot}{}^tBuCN$.

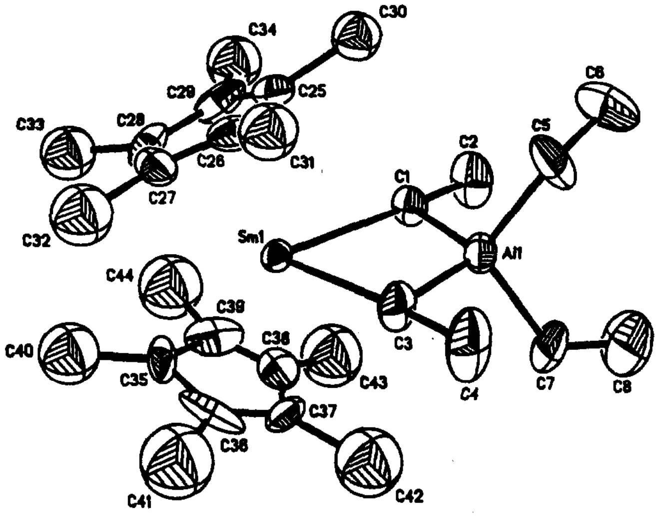

Fig. 84. $Cp^*_2Sm(\mu\text{-}Et)_2AlEt_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1987 American Chemical Society.)

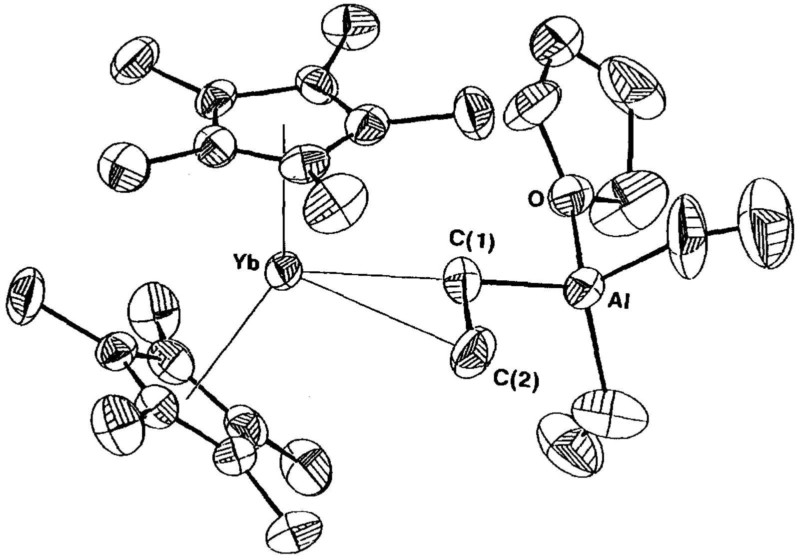

Fig. 85. $Cp^*_2Yb(\mu\text{-}Et)AlEt_2(THF)$. (Reprinted with permission from Chemistry Letters.)

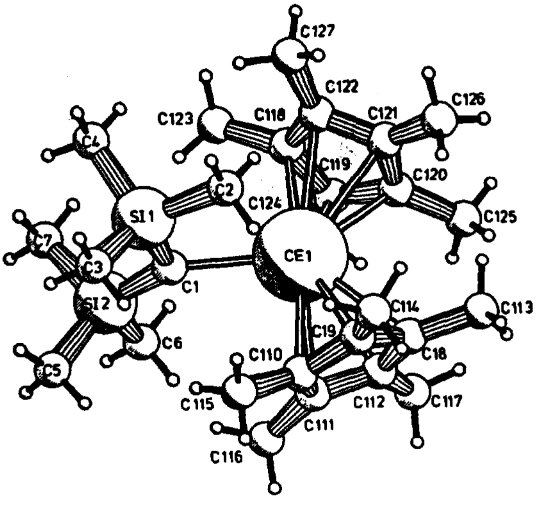

Fig. 86. $Cp^*_2CeCH(SiMe_3)_2$. (Reprinted with permission from Organometallics. Copyright 1988 American Chemical Society.)

Finke, Keenan, and Watson[164] published stoichiometric, kinetic, and mechanistic studies of $Cp^*_2YbOEt_2$ oxidative addition reactions and reactions of alkyl and aryl halides with Cp^*_2YbR.

The first η^2-olefin complex of a lanthanide was prepared and characterized by Andersen and Burns.[165] Addition of $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ to Cp^*_2Yb in toluene produced $Cp^*_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)_2$. The crystal structure was determined (Figure 87, Yb-C(Cp*) = 2.67(2)Å, Yb-C(η^2) = 2.781(6)Å).

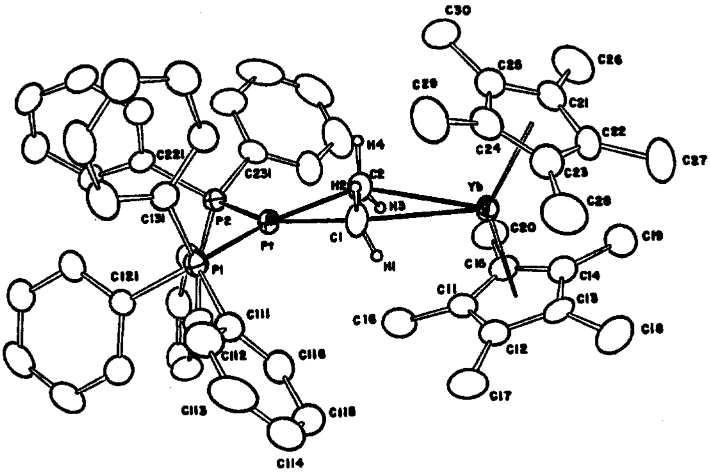

Fig. 87. $Cp^*_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1987 American Chemical Society.)

Evans, et al.[166] synthesized μ,η^2-N-alkylformimidoyl complexes of Er and Y by reaction of $[(CpR)_2Ln(\mu\text{-}H)(THF)]_2$ with ^tBuCN. The compounds $[(CpR)_2Ln(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$ (Ln = Er, Y; R = H, Me) were prepared. The two R = H complexes were structurally characterized (Ln = Y, Y-C(Cp) = 2.68(1)Å, Y-C(σ) = 2.553(8)Å, Y-N = 2.325(4)Å; Ln = Er, Figure 88, Er-C(Cp) = 2.64(1)Å, Er-C(σ) = 2.52(2)Å; Er-N = 2.304(8)Å). The two compounds are reported not to be isostructural. Teuben, et al.[146] prepared $Cp^*_2Y(\eta^2\text{-}NC_5H_4)$, $Cp^*_2Y(\eta^2\text{-}NC_5H_4)(THF)$, and $Cp^*_2Y(\eta^2\text{-}NC_5H_3,6\text{-}Me)$.

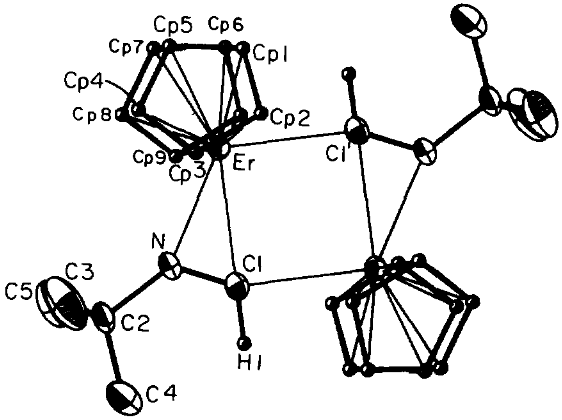

Fig. 88. $[Cp_2Er(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$. (Reprinted with permission from Organometallics. Copyright 1987 American Chemical Society.)

Teuben, et al.[167] investigated the reactions of $Cp^*_2YCH(SiMe_3)_2$ with CO_2, ${}^tBuCN$, and ${}^tBuNC$ which gave $Cp^*_2Y(\eta^2\text{-}O_2CCH(SiMe_3)_2)$, $Cp^*_2YNC({}^tBu)CH(SiMe_3)_2\cdot NC{}^tBu$, and $Cp^*_2YCH(SiMe_3)_2\cdot CN{}^tBu$. No reaction was observed with CS_2 and (2,6-xylyl)NC. Reactions of Cp^*_2YDMB (DMB = 3,5-dimethylbenzyl)[146] with the same ligands yielded $Cp^*_2Y(\eta^2\text{-}O_2C(DMB))$, $Cp^*_2Y(\eta^2\text{-}S_2C(DMB))$, $Cp^*_2YNC(DMB){}^tBu\cdot NC{}^tBu$, $Cp^*_2Y(\eta^2\text{-}C(DMB)N{}^tBu)\cdot CN{}^tBu$, and $Cp^*_2Y(\eta^2\text{-}C(DMB)N(2,6\text{-xylyl})$. The last compound reacted with THF to give $Cp^*_2Y(\eta^2\text{-}C(DMB)N(2,6\text{-xylyl}))(THF)$ and the crystal structure of this complex was determined (Figure 89, Y-C(Cp^*) = 2.728(4)Å, Y-C(η^2) = 2.392(3)Å, Y-N(η^2) = 2.407(3)Å.

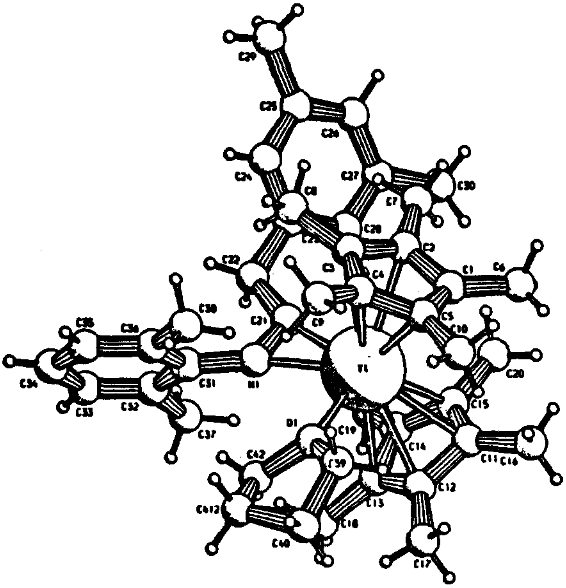

Fig. 89. $Cp^*_2Y(\eta^2\text{-}C(DMB)N(2,6\text{-xylyl}))(THF)$. (Reprinted with permission from <u>Organometallics</u>. Copyright 1987 American Chemical Society.)

Andersen and Burns[168] prepared and structurally characterized the first η^2-acetylene complex of a lanthanide. Addition of 2-butyne to Cp^*_2Yb in pentane produced $Cp^*_2Yb(\eta^2\text{-}MeCCMe)$ (Figure 90, Yb-C(Cp*) = 2.659(9)Å, Yb-C(η^2) = 2.85(1)Å). Evans and Atwood, <u>et al</u>.[169] also published an η^2 complex, $[Cp^*_2Sm]_2C_4Ph_2$, prepared by the reaction of $Cp^*_2Sm(THF)_2$ with PhC≡CC≡CPh. The crystal structure is shown in Figure 91 (Sm-C(Cp) = 2.71(2)Å, Sm-C(η^2) = 2.48(1)Å (C(1)), 2.76(1)Å (C(2)).

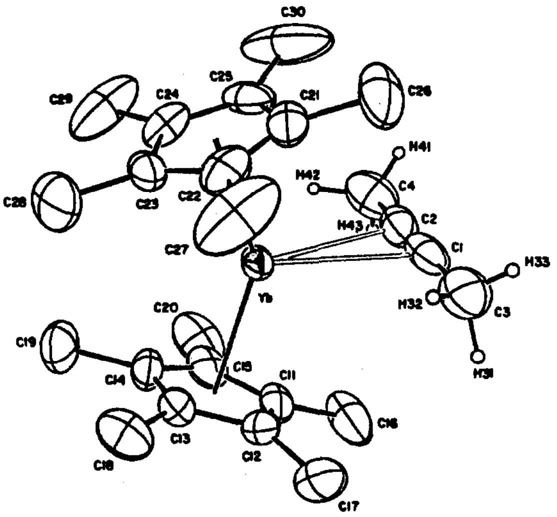

Fig. 90. Cp$^*_2$Yb(η^2-MeCCMe). (Reprinted with permission from Journal of the American Chemical Society. Copyright 1987 American Chemical Society.)

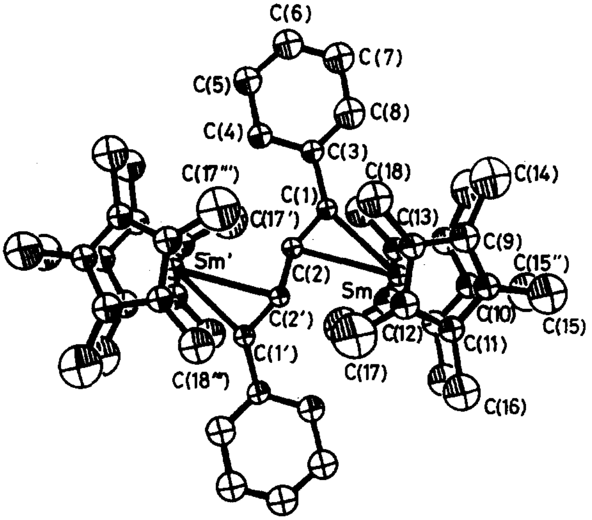

Fig. 91. [Cp$^*_2$Sm]$_2$C$_4$Ph$_2$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

Terminal alkynes $Cp^*_2YC\equiv CR\cdot 2(OEt)$ and $Cp^*_2YC\equiv CR\cdot 2(THF)$ (R = Me, Ph, $SiMe_3$) were isolated by Teuben, et al.[146] The isocyanide $[Cp^*_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3$ was prepared and structurally characterized by Evans and Drummond[170,171] (Figure 92, Sm-C(Cp*) = 2.75(2)Å, Sm-CNR = 2.58(2)Å).

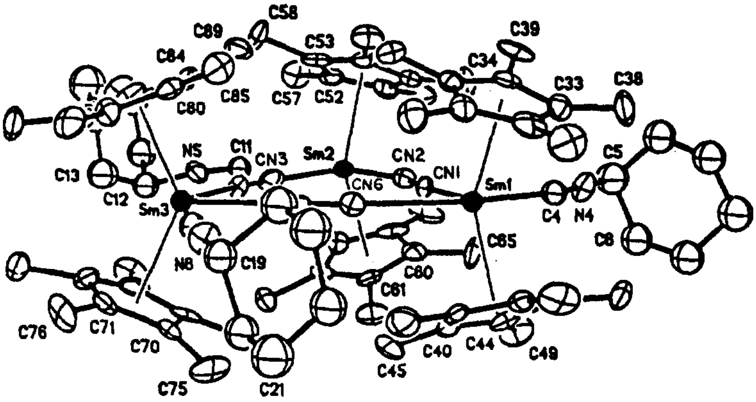

Fig. 92. $[Cp^*_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3$. (Reprinted with permission from Organometallics. Copyright 1988 American Chemical Society.)

Evans, et al.[172] prepared and structurally characterized the bridged alkynide $Cp^*_2Y(\mu\text{-}C\equiv CCMe_3)_2Li(THF)$ (Figure 93). This compound was prepared either by reaction of $Cp^*_2YCl(THF)$ and $LiC\equiv CCMe_3$ or by first preparing $Y(^tBu)_4Li(THF)_4$ and further reacting it with KCp^*. The ^tBu groups block all but one THF from coordinating Li^+.

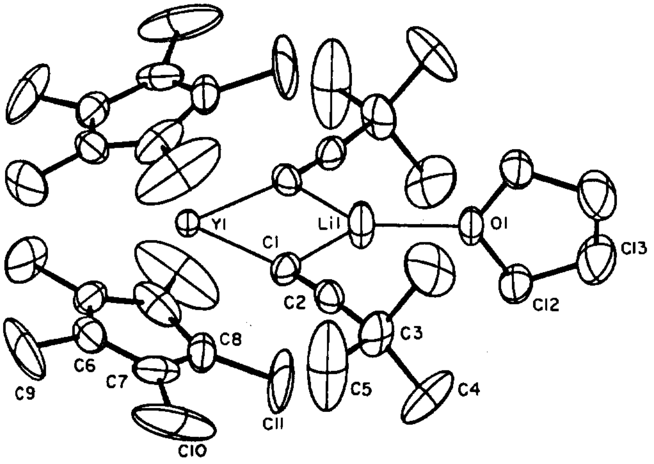

Fig. 93. $Cp^*_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Deacon and Wilkinson[173] prepared Cp_2YbR (R = C_6F_5, C_6Cl_5, PhC≡C) by reaction of $Cp_2Yb(dme)$ with HgR_2. Allyl compounds, $Cp_2NdC_3H_5$, $Cp_2Nd(C_3H_5)_2(THF)$, and $Li[CpNd(C_3H_5)_3]\cdot$dioxane were reported by Li, et al.[174] Benzyl samarium compounds Cp_2SmCH_2Ar (Ar = Ph, o-^{t}BuPh, 2,5-Me_2Ph) were prepared by Kagan, et al.[175] and their reactivity discussed.

The mixed ligand complexes $Cp_2LnInd(THF)$ (Ln = Sm, Dy, Ho, Er, Yb) were prepared by Zhennan, et al.[176] The complexes were characterized by analytical and spectral data.

(vii) Bridged biscyclopentadienyl compounds. Seven new solvated compounds of 1,1'-pentamethylenecyclopentadienyl ($Cp_2(CH_2)_5^-$) were reported by Qian, et al.[177] These include $(Cp_2(CH_2)_5)LnCl(THF)$ (Ln = Sm, Gd, Dy, Er, Lu, Y) and $(Cp_2(CH_2)_5)$-$CpY(THF)$. These authors also prepared the corresponding 1,1'-(3-oxa-pentamethylene)biscyclopentadienyl complexes, $(Cp_2(CH_2CH_2)_2O)$-LnCl (Ln = Nd, Gd, Ho, Er, Yb, Lu, Y).[178] ^{1}H and ^{13}C NMR spectra of some of their ring bridged Y and Lu chlorides were discussed in a third contribution.[179]

Swamy and Schumann[180] prepared $(Cp_2(CH_2)_3)Ln(THF)_2$ (Ln = Sm, Yb) by reaction of the sodium salt of the bridged cyclopentadienyl ligand with $LnCl_2$ in THF. The crystal structure of the Yb complex was determined (Figure 94). The centroid-Yb-centroid angle is contracted at 127(1)°, however, the Yb-C distances of 2.67(2) to 2.73(2)Å are within the range observed for Cp_2Yb derivatives.

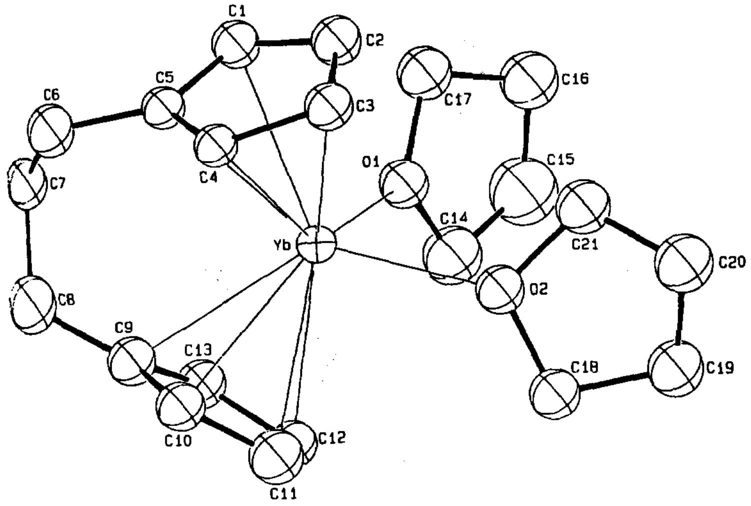

Fig. 94. $(Cp_2(CH_2)_3)Yb(THF)_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

(viii) Cyclooctatetraene compounds. Wayda, et al.[181] reported a facile route to $SmI_2(THF)_2$ and its use in the synthesis of Sm(COT) and $K_2Sm(COT)_2$. Qi, et al.[182] published the reactions of $SmCl_2$ and $NdCl_2$ with COT in THF leading to $Ln(COT)Cl(THF)_2$ (Ln = Sm, Nd). A similar reaction with Yb was unsuccessful. Luminescence studies of COT compounds[55] and the preparation of CpLnCOT compounds were discussed in earlier sections.

Streitwieser, et al.[183] studied the electron exchange between $K_2[Yb(COT^tBu)_2]$ and $K[Yb(COT^tBu)_2]$ in THF and THF/diglyme. A mechanism involving change in coordination of solvating diglyme was proposed. Wayda and Rogers, et al.[184] reported the synthesis and crystal structure of $Yb(COT)(NC_5H_5)_3 \cdot 0.5(NC_5H_5)$ (Figure 95 Yb-C = 2.64(3)Å, Yb-N = 2.58(2)Å). The COT^tBu derivative was also prepared.

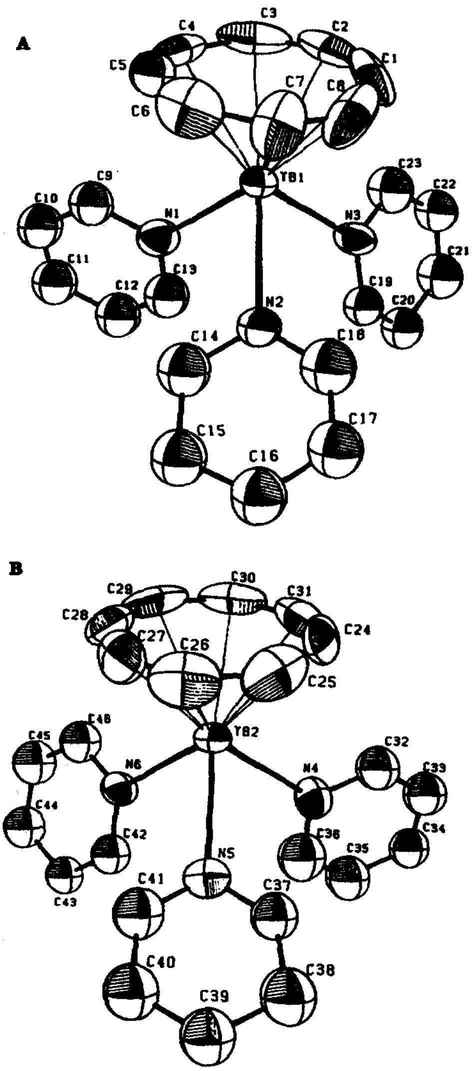

Fig. 95. $Yb(COT)(NC_5H_5)_3 \cdot 0.5(NC_5H_5)$. (Reprinted with permission from Organometallics. Copyright 1987 American Chemical Society.)

Cloke, et al.[185] prepared $[Y(COT(SiMe_3)_2)(THF)(\mu\text{-}Cl)]_2$. Reaction of $[YCl_3(THF)_3]$ with the 1,4-bis(trimethylsilyl)cyclooctatetraene dianion (via deprotonation) afforded the compound. Takaya and Mashima[186] used iodine to prepare $LnI(COT)(THF)_n$ (Ln = La, Ce, Pr, Nd, Sm; n = 1, 2, 3). The crystal structure of $CeI(COT)(THF)_3$ was determined (Figure 96, Ce-I = 3.299(1)Å, Ce-centroid = 2.010Å). Schumann, et al.[187] prepared $Li[Lu(COT^nBu)(tmeda)_2]$.

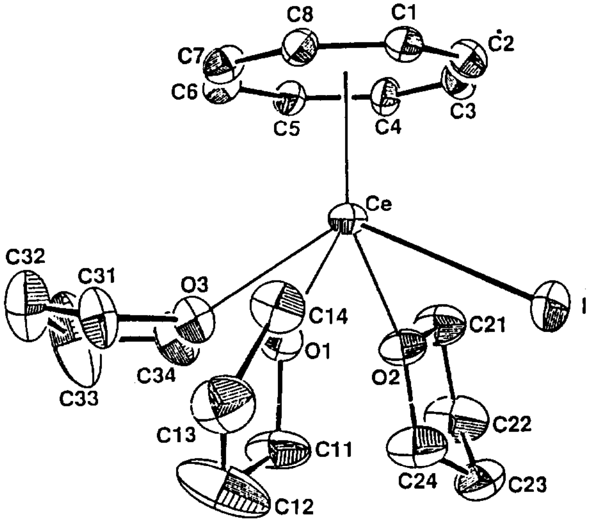

Fig. 96. $CeI(COT)(THF)_3$. (Reprinted with permission from Tetrahedron Letters. Copyright 1989 Pergamon Press plc.)

(ix) Carbollide compounds. Hawthorne, et al.[188,189] prepared and structurally characterized the first closo-lanthanacarboranes. Reaction of $Na_2[nido\text{-}7,8\text{-}C_2B_9H_{11}]$ with LnI_2 (Ln = Sm, Yb) in THF produced $Ln(C_2B_9H_{11})(THF)_4$. The Yb complex undergoes solvent replacement and the CH_3CN and dmf solvates were isolated. The crystal structure of the Yb-dmf adduct was determined (Figure 97). Further reaction of $Sm(C_2B_9H_{11})(THF)_4$ with $[PPN][closo\text{-}3,1,2\text{-}TlC_2B_9H_{11}]$ produced $[PPN][3,3\text{-}(THF)_2\text{-}commo\text{-}3,3'\text{-}Sm(3,1,2\text{-}SmC_2B_9H_{11})_2]$ (Figure 98).

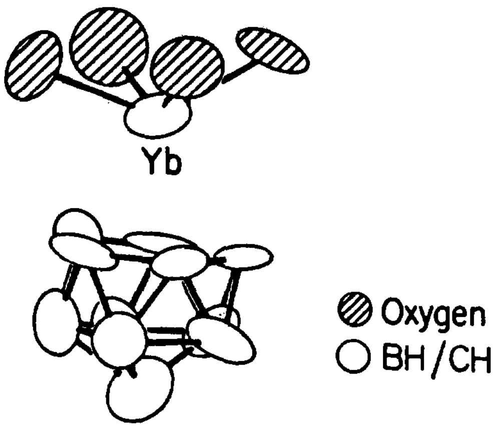

Fig. 97. $Yb(C_2B_9H_{11})(dmf)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

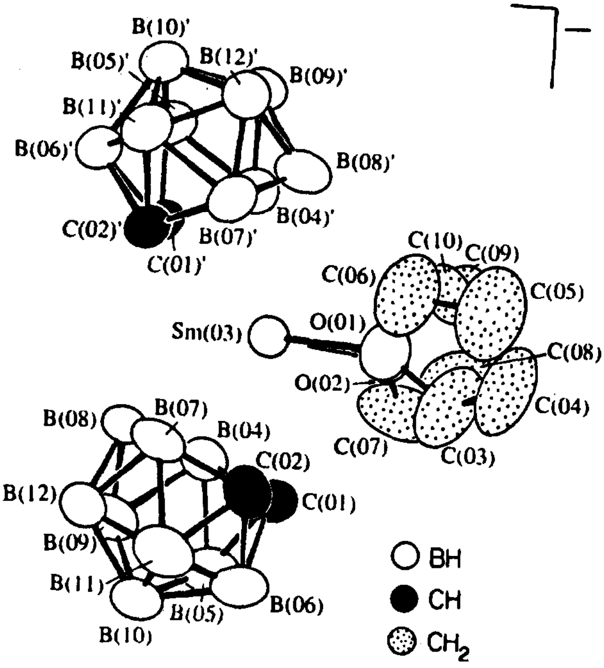

Fig. 98. The anion in $[PPN][3,3-(THF)_2$-commo-3,3'-Sm(3,1,2-$SmC_2B_9H_{11})_2]$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

Khikmatov, et al.[190] reported the synthesis of $Er(C_2B_9H_{11})_3$-$(THF)_7$, and $[La(BH_4)_2]_2C_2B_9H_{11}\cdot n(THF)$ (n = 4, 6, 7, 10) by reactions of $Na_2[C_2B_9H_{11}]$ with $ErCl_3$, $La(BH_4)Cl$, or $La(BH_4)_3$ in THF. Lebedev, et al.[191] published the synthesis of $Na[Gd(C_2B_9H_{11})_2]$ by a similar reaction with $GdCl_3$ in THF.

Afonin, et al.[192] published a study of the complexation of chlorinated cobalt dicarbollide with Sr^{+3} and Ce^{+3}.

(x) Indenyl compounds. R_3Ln (Ln = Y, Ce, Pr, Nd, La, Gd, Dy, Sm; R = indenyl, fluorenyl) were reported by Sharma and Sharma[193] by treatment of $LnCl_3$ with KR. Wu, et al.[194] prepared $[Na(THF)_6]\{[Ind_3Nd]_2Cl\}$ by reaction of $LnCl_3(THF)_n$ with NaInd in THF. The crystal structure was determined (Figure 99).

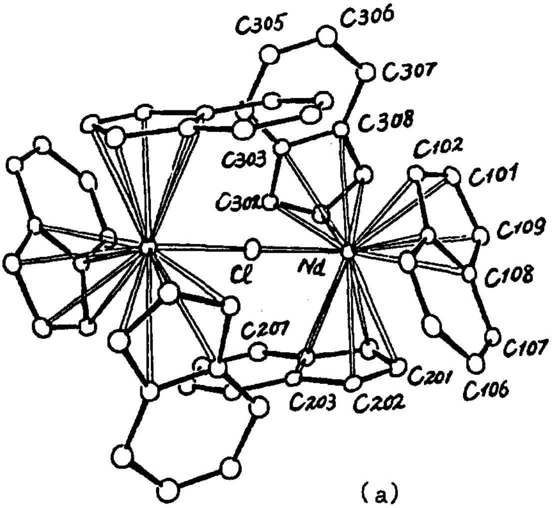

Fig. 99. The anion in $[Na(THF)_6]\{[Ind_3Nd]_2Cl\}$. (Reprinted with permission from Organometallics. Copyright 1988 American Chemical Society.)

Zhou, et al.[195] prepared seven complexes of the type Ind_nLnL_{3-n} (n = 1, 2; Ln = Nd, Sm; L = chelating 8-hydroxyquinoline, o-aminophenol) by reaction of the trisindenyl lanthanide with the chelating acid.

(xi) Phospholyl compound. Nief and Mathey[196] reported the syntheses of the first pi-heterocyclopentadienyl rare earth compounds. Reaction of Li[2,3,4,5-tetramethylphospholide] with

$LnCl_3$ produced (η^5-$C_4Me_4P)_2Ln(\mu$-$Cl)_2Li(solv)_2$ (Ln = Y, Lu; solv = OEt_2 or dme).

(xii) Electronic structure and theory. Green, Hohl and Rösch[197] studied the photoelectron spectra and molecular orbital calculations of Cp^*_2Ln (Ln = Sm, Eu, Yb). Predominantly ionic character was found. Li, et al.[198] investigated the electronic structure of $Cp_2NdCl(THF)$ using INDO. The authors report the compound to be covalent with some ionic character. Li, et al.[199] studied cyclopentadienyl compounds of the lanthanides in terms of the cone packing model. Calculations and predictions of structural patterns were presented.

Bauschlicher, et al.[200] reported on theoretical studies of first and second row transition metal methyl derivatives and their positive ions. Yttrium was included in this study.

Arene, aryl, alkyl, alkene, and allyl compounds not containing cyclopentadienyl ligands

(i) Arene and aryl compounds. Cotton and Schwotzer[201] prepared and structurally characterized the η^6-arene, (η^6-C_6Me_6)Sm-$(AlCl_4)_3$ (Figure 100, Sm-C(η^6) = 2.89(5)Å). The samarium derivative was prepared and structurally characterized by Fan, et al.[202] Cloke, et al.[203,204] prepared the Y^0 and Gd^0 complexes (η^6-$C_6H_3{}^tBu_3)_2Ln$ via metal vapor reaction with 1,3,5-tri-t-butylbenzene. The crystal structure of Ln = Gd (Figure 101) revealed eclipsed benzenes with staggered t-butyl groups and Gd-C(η^6) = 2.630(4)Å. In another contribution[205] this work was extended to Ln = Nd, Tb, Dy, Ho, Er, and Lu. Thermally unstable complexes were prepared for Ln = La, Pr, Sm. For Ln = Ce, Eu, Tm, and Yb no isolatable products could be prepared.

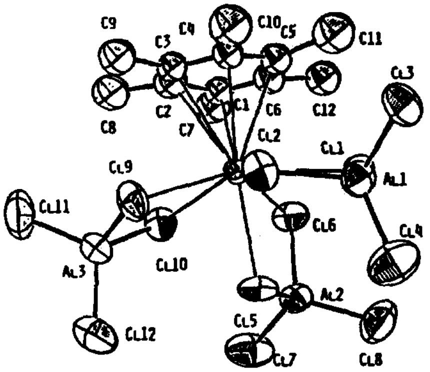

Fig. 100. (η^6-C_6Me_6)Sm($AlCl_4$)$_3$. (Reprinted with permission from *Organometallics*. Copyright 1987 American Chemical Society.)

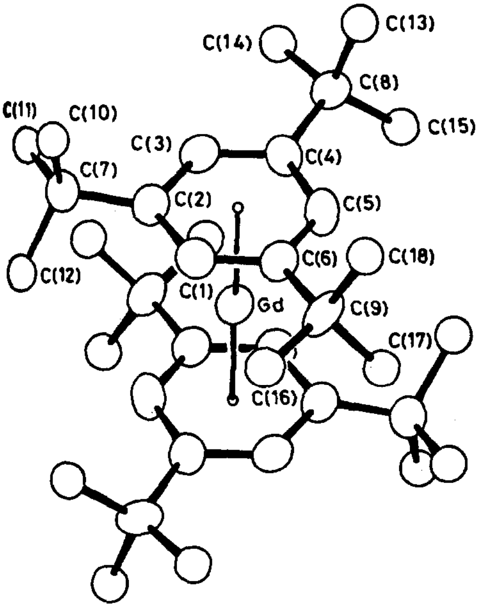

Fig. 101. (η^6-$C_6H_3{}^tBu_3$)$_2$Gd. (Reprinted with permission from *Journal of the Chemical Society, Chemical Communications*.)

Reaction of $LnCl_3$ with activated $AlCl_3$ in benzene produced (η^6-C_6H_6)Ln($AlCl_4$)$_3$·C_6H_6 (Ln = La, Nd, Sm; Shen, *et al.*[206]). The crystal structures of Ln = Nd and Sm were determined (Figure 102) and found to be isostructural. These same authors[207] determined the structure of the m-xylene derivative (η^6-$C_6H_4Me_2$)Sm($AlCl_4$)$_3$ (Figure 103).

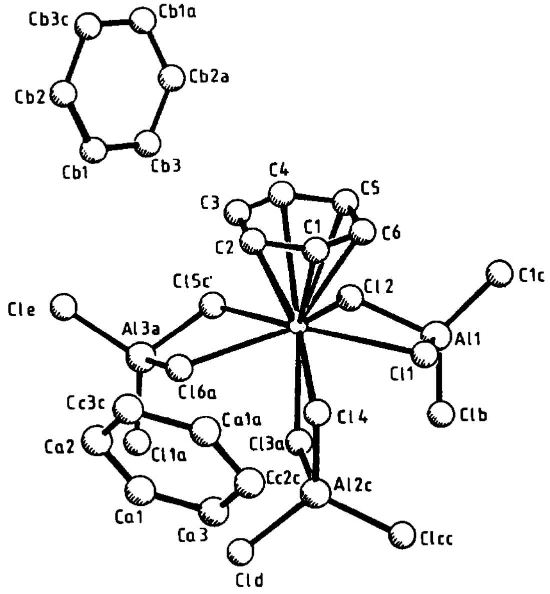

Fig. 102. (η^6-C_6H_6)Ln($AlCl_4$)$_3$·C_6H_6 (Ln = Nd, Sm). (Reprinted with permission from Journal of Organometallic Chemistry.)

Naphthalene complexes of Sm, Eu and Yb were investigated by Bochkarev, et al.[208-217] Arakawa, et al.[218] studied naphthalene and anthracene reactions with Ce, Eu, Pr, Nd, Dy, Ho, Er, and Sm. The UV spectra of Ln/naphthalene/OEt_2 (Ln = Ce, Eu) solutions were discussed.

The use of PhYbI in C-C bond formation and cleavage, and C-C double bond reduction was investigated by Fujiwara, et al.[219] Deacon, et al.[220] utilized Ln(C_6F_5)$_2$ (Ln = Yb, Eu) to prepare Ln(OR)$_2$(THF)$_3$ (Ln = Yb, Eu, R = 2-6-^{t}Bu$_2$-4-MeC$_6$H$_2$; Ln = Yb, R = 2,4,6-^{t}Bu$_3$C$_6$H$_2$, 2,6-^{t}Bu$_2$C$_6$H$_3$) and Ln(NR_2)$_2$(THF)$_4$ (Ln = Yb, Eu; NR_2 = carbazo-9-yl; Ln = Yb, NR_2 = 2-phenylindol-1-yl).

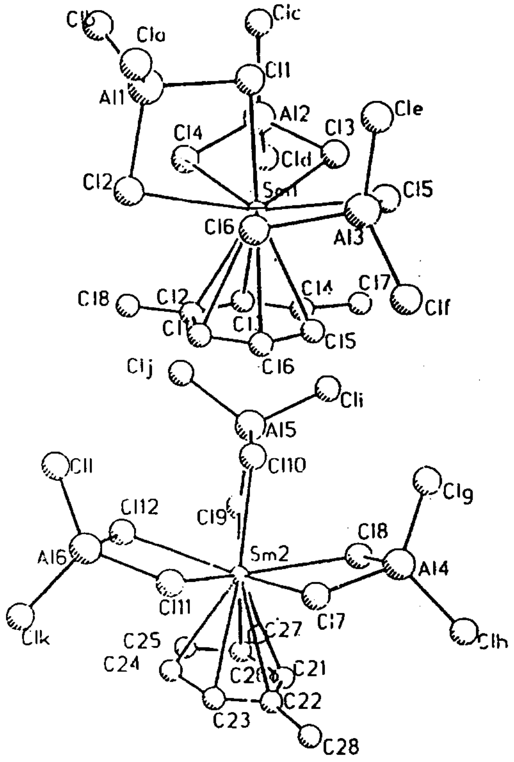

Fig. 103. (η^6-$C_6H_4Me_2$)Sm($AlCl_4$)$_3$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Rybakova, et al.[221,222] studied the reaction of PhYbI with aryl halides. Ph_2Yb was prepared by reaction of $HgPh_2$ with Yb^0 by activation with CH_2I_2.[223] Sigalov and Beletskaya[224] studied the reactions of PhLnI (Ln = Ce, Sm, Eu, Yb) with fluoroolefins. Suleimanov, et al.[225,226] studied the interaction of lanthanides in lanthanide-containing metallocene derivatives of Fe, Mg, Rh, and Mo. A Ln-C_5H_4 sigma interaction was proposed. Cai, et al.[227] reported the preparation of Er and Yb phenyl compounds.

Hu, et al.[228] carried out the structural determination of tris(2,4-dimethylpentadiene)gadolinium. The 1, 3, and 5 carbons bend toward Gd^{+3}, while the 2,4 carbons bend away from the metal ion. The average Gd-C separations range from 2.738Å (C(1), C(5) positions) to 2.821Å (C(2), C(4) positions). The tris derivative of Nd was utilized by Taube, et al.[229] to prepare (2,4-C_7H_{11})-

$NdCl_2 \cdot 1/3(THF)$ via reaction with $NdCl_3 \cdot 2(THF)$. The crystal structure of this compound (Figure 104) revealed a hexameric $Nd_6Cl_{12}(2,4\text{-}C_7H_{11})_6(THF)_2$ structure.

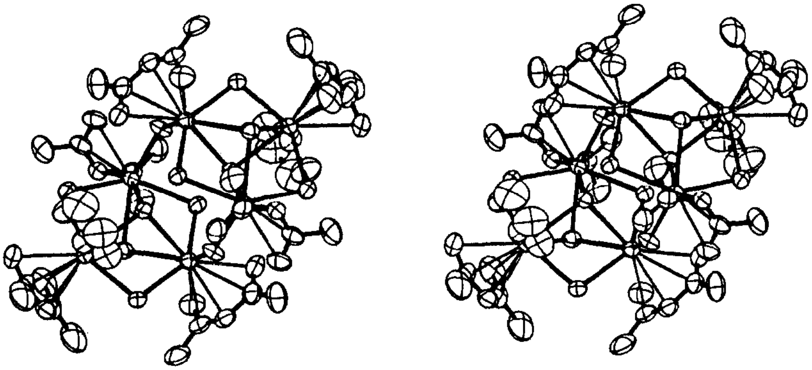

Fig. 104. $Nd_6Cl_{12}(2,4\text{-}C_7H_{11})_6(THF)_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

(ii) Alkyne, alkene, and alkyl compounds. The tris-alkynes $Ln(C_2Ph)_3$ (Ln = Eu, Er, Yb) were isolated by Bochkarev, *et al.*[230] The Yb derivative was used in sodium naphthalide solutions to activate N_2.[121] YbMeI was utilized in C-C bond formation and cleavage, and C-C bond reduction reactions.[219] The reactions of this same compound with alkyl halides were investigated.[221] Decomposition reactions of alkyllanthanides were studied by Yakovlev, *et al.*,[231-233] and gave stable hydrides.

Several contributions to the area of gas phase reactions of Ln^+ with alkanes and alkenes appeared. Schilling and Beauchamp[234] studied the reaction of Pr^+, Eu^+, and Gd^+ with several alkanes, cycloalkanes, and alkenes. The Gd^+ ion was observed to activate C-H and C-C bonds of alkanes while Pr^+ and Eu^+ did not. Both Gd^+ and Pr^+ were reported to react with alkenes to give dehydrogenation products and small amounts of C-C bond cleavage products. Reaction with oxygen-containing molecules (nitric oxide, formaldehyde, etc.) gave metal oxides. Sunderlin and Armentrout[235] studied the reactions of Y^+, La^+ and Lu^+ with methane and ethane using guided ion beam mass spectroscopy. Major products with methane at low energy were reported to be MCH_2^+ and at high energy MH^+. Haung and Freiser[236] investigated reactions of $LaFe^+$ with saturated hydrocarbons. The $LaFe^+$ ion was obtained by reaction of laser-generated La^+ with $Fe(CO)_5$. Observed results are different from those seen with either La^+ or Fe^+ alone. Hettich and Freiser[237] determined carbide, carbyne, and carbene bond energies by gas phase photodissociation of $LaCH_2^+$.

Andrews and Wayda[238] prepared $Eu(C_2H_4)_n$ by codepositing Eu atoms with ethylene at 12K. UV-VIS, IR, and thermal data were obtained. MO calculations revealed weak bonding by Eu f-orbitals into the π^* system of ethylene. Saussine, et al.[239] reacted metallic Sm and Yb with unsaturated hydrocarbons in ether to give organometallic adducts. The Sm derivatives were reported to catalyze hydrogenation of monoolefins and to polymerize ethylene.

Linear and cyclic dienes $LnCl_{3-x}R_xM \cdot nL$ (Ln = La, Pr, Nd, Sm, Gd, Dy; M = MgCl, LiCl; x, n = 0-3; L = THF, dmso) were prepared by Sun and Chen.[240] Shan, et al.[241] published the crystal structure of $[Al_3Nd_6(\mu_2\text{-Cl})_6(\mu_3\text{-Cl})_6(\mu_2\text{-Et})_9O^iPr]_2$. Hu, et al.[242] reported $Nd(OMe)_3$ and Li^nBu react in pentane at room temperature to yield $Nd(^nBu)H_2 \cdot 3LiOMe$.

Thiele, et al.[243] prepared a La benzyl bond by reaction of $HgBz_2$ in THF with La to give $La(CH_2C_6H_5)(H)(OCHCH_2)(THF)_2$. Li, et al.[244] reported the preparation of the binuclear complexes $[(C_6H_5CO)_2CH]_2LnM(CO)_2Cp$ (M = Fe, Mo), $[(C_6H_5CO)_2CH]_2LnSnPh_3$, and $[(C_6H_5CO)_2CH]_2LnPPh_3$.

$Yb(CH_2SiMe_3)_3$ was used with sodium naphthalide to activate N_2.[121] Hitchcock, et al.[245] structurally characterized similar homoleptic lanthanide alkyls, $Ln[CH(SiMe_3)_2]_3$ (Ln = La, Sm). The complexes were prepared by reaction of $Ln(OC_6H_3{}^tBu_2\text{-}2,6)_3$ with $Li[CH(SiMe_3)_2]$. The structure of Ln = La is shown in Figure 105 (La-C = 2.515(9)Å, Sm-C = 2.33(2)Å). Agostic interactions are probable. When $LaCl_3$ was used as the starting material, the complex $La[CH(SiMe_3)_2]_3(\mu\text{-Cl})Li(pmdeta)$ (pmdeta = $MeN(CH_2CH_2NMe_2)_2$) was isolated (Atwood and Lappert, et al.[246]). The crystal structure (Figure 106) revealed a La-C distance of 2.60(3)Å. The Sm analog with a bridging methyl group, $Sm[CH(SiMe_3)_2]_3(\mu\text{-Me})Li(pmdeta)$, was also isolated and structurally characterized (Figure 107, $Sm\text{-}CH(SiMe_3)_2$ = 2.51(2)Å, Sm-Me = 2.33(3)Å).[247]

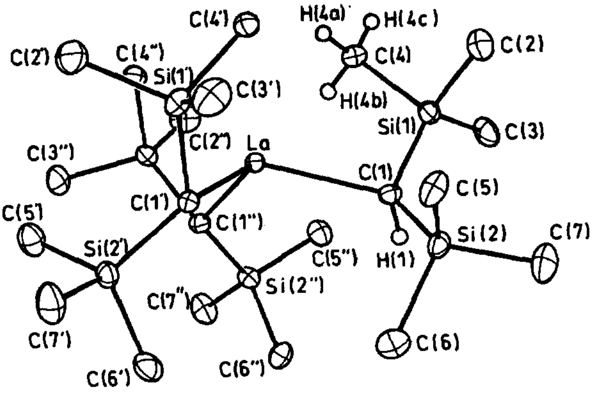

Fig. 105. La[CH(SiMe$_3$)$_2$]$_3$. (Reprinted with permission from *Journal of the Chemical Society, Chemical Communications*.)

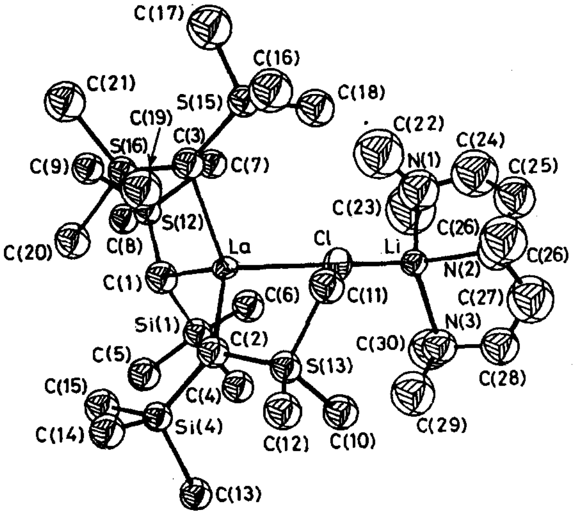

Fig. 106. La[CH(SiMe$_3$)$_2$]$_3$(μ-Cl)Li(pmdeta). (Reprinted with permission from *Journal of the Chemical Society, Chemical Communications*.)

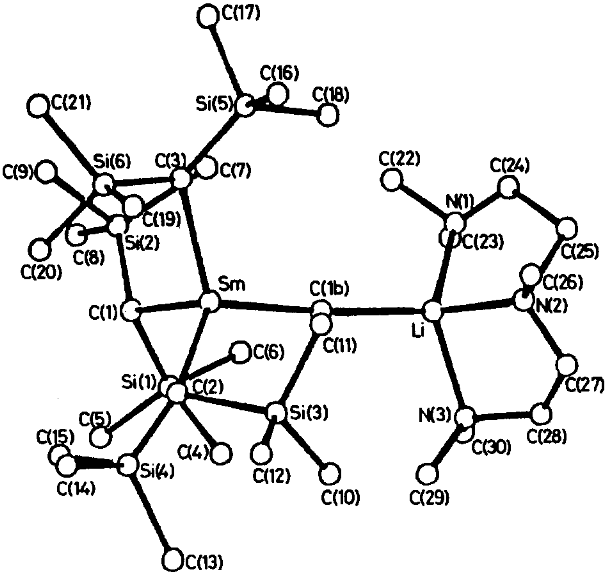

Fig. 107. $Sm[CH(SiMe_3)_2]_3(\mu\text{-}Me)Li(pmdeta)$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

The tetraphenylbutadiene lanthanide metallacycles $LLn(\mu\text{-}Cl)_2Li(THF)_n$ (Ln = Nd, Gd) were prepared by Bao and Chen.[248]

(iii) Allyl compounds. The crystal structure of $[Li_2(\mu\text{-}C_3H_5)(THF)_3][Ce(\eta^3\text{-}C_3H_5)_4]$ was reported by Huang, et al.[249] (Figure 108). The Ce-C(η^3) bonds reported ranged from 2.712(8) to 2.858(7)Å. The same authors reported the synthesis of the allyls, $Li_2Ln(C_6H_5)_5 \cdot 2.5$dioxane (Ln = Dy, Ho, Er).[250] Brunelli, et al.[251] investigated $LiLn(C_3H_5)_4 \cdot$dioxane complexes of Ce, Nd, Sm, Gd, and Dy.

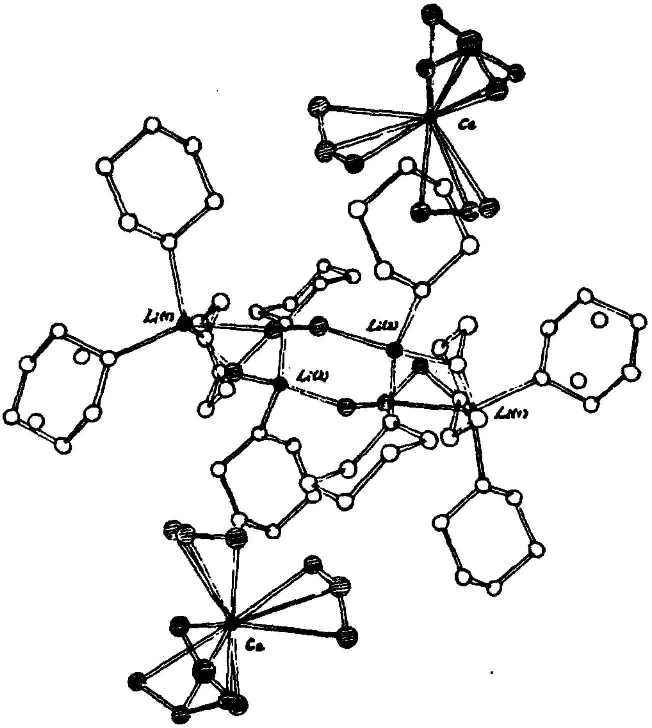

Fig. 108. $[Li_2(\mu-C_3H_5)(THF)_3][Ce(\eta^3-C_3H_5)_4]$. (Reprinted with permission from <u>Inorganica Chimica Acta</u>.)

ACTINIDES

<u>Cyclopentadienyl and cyclopentadienyl-like compounds</u>

(i) <u>Tetrakiscyclopentadienyl compounds</u>. Kuleshov, <u>et</u> <u>al</u>.[252] discussed the chemiluminescence of the autooxidation of Cp_4U and the photoluminescence of the oxidation products. Leonov, <u>et</u> <u>al</u>.[253] studied the mechanism of the reaction of Cp_4U with O_2.

Sonnenberger and Gaudiello[254] carried out a cyclic voltammetric study of Cp_4U and Cp_4Np to investigate the effect of ligand on the An(IV)/An(III) couple. The compounds exhibited a single reduction wave indicating a one electron reversible process. Adrian, <u>et</u> <u>al</u>.[255,256] studied the ^{237}Np Mössbauer spectra of Cp_4Np and began to develop a model which describes the splitting of the nuclear states by an asymmetric quadrapole splitting and an anisotropic paramagnetic hyperfine coupling. Conclusions on distribution of charge density and on molecular structure were drawn. Pyykkö, Laakkonen, and Tatsumi[257] presented interactive relativistic extended Hückel energy parameters for An = Th-Np which gave realistic metal orbital populations for Cp_4Th and Cp_4U.

(ii) Triscyclopentadienyl compounds. Zalkin and Andersen[258] published the crystal structure of Cp'_3U (Figure 109, U-C(Cp') = 2.78(4)Å). Edelstein, et al. and Lappert, et al. published the synthesis and crystal structure of Cp''_3Th (Figure 110, Th-C(Cp") = 2.80(2)Å)[259] and obtained its EPR spectrum.[260] In this compound Th(III) has a $6d^1$ ground state. Bursten, et al.[261] carried out quasi-relativistic Xα-scattered wave calculations on Cp_3An (An = Th, U, Pa, Np, Pu). The An = Th compound was predicted to have a $6d^1$ ground state, while An = U was reported to probably be $6d^15f^2$. In a second contribution Bursten, et al.[262] studied Cp_3UL compounds for L = H, CO, NO, OH. Sigma bonding to the π-neutral, π-acidic, and π-basic ligands was reported to be essentially the same-donation of electron density from the sigma orbital of L into a uranium orbital that is primarily $6d_{z^2}$ in character. The authors reported that the 5f orbitals are responsible for back donation into the π^* orbitals of CO and NO. Acceptance of electron density from the π orbitals of OH reportedly involves the 6d orbitals. Andersen, et al.[73] studied the relative affinity of Lewis bases toward $(CpMe)_3U$ and found the trend $PMe_3 > P(OMe)_3 > NC_5H_5 > SC_4H_8 \sim THF \sim N(CH_2CH_2)_3CH > CO$.

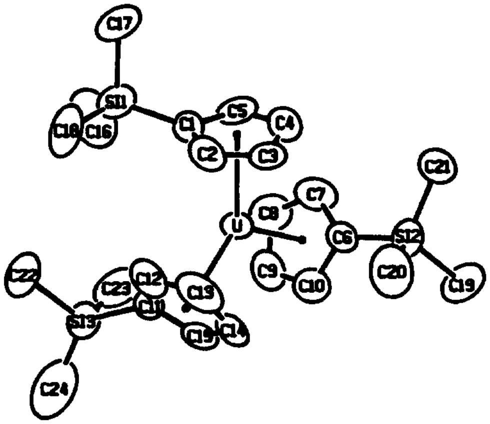

Fig. 109. Cp'$_3$U. (Reprinted with permission from Acta Crystallographica.)

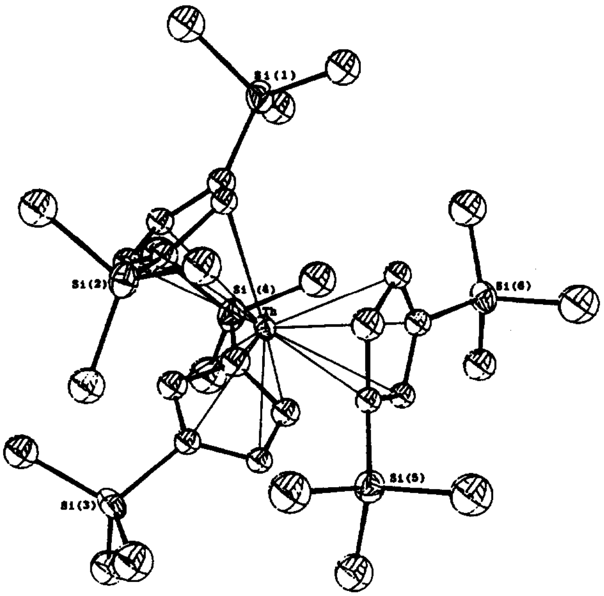

Fig. 110. Cp"$_3$Th. (Reprinted with permission from Inorganica Chimica Acta.)

(iii) Triscyclopentadienyl halide compounds. Deacon and Tuong[263] reported the preparation of Cp$_3$UCl from reaction of

$HgCp_2/HgCl_2$ or $TlCp/HgCl_2$ with excess uranium in THF. The neutron diffraction crystal structure of this compound was determined by Spirlet, et al.[264] Disorder of the Cp rings and a crystallographic phase transition between 80 and 100 K were observed. These authors also published the X-ray structure of Cp_3UBr[265] (Figure 111, U-C(Cp) = 2.72(1)Å). The chloro and bromo derivatives are reported to be geometrically similar but not isostructural. Chang, et al.[266] prepared the bridging complexes $Cp_3U(\mu\text{-}Cl)_2AlCl_2$ and $Cp_3U(\mu\text{-}Cl)_2AlCl_2(THF)$ by reaction of Cp_3UCl with $AlCl_3$.

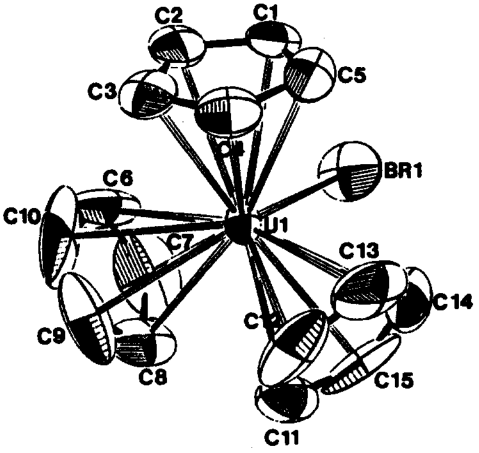

Fig. 111. Cp_3UBr. (Reprinted with permission from Acta Crystallographica.)

Amberger, et al.[267] determined the crystal field splitting pattern of $(\eta^5\text{-}C_5D_5)_3UCl$ from the absorption and magnetic circular dichroism spectra at room temperature. McGarvey and Nagy[268,269] measured the ^1H NMR spectra of solid powders of Cp_3UCl from 90 to 298K. Anisotropy in the line shape became more evident as the temperature was lowered. Below 140K rotation of the Cp rings appeared to cease. A case was made for different solution versus solid state structures.

Leonov, et al.[253] discussed the reaction of Cp_3UCl with O_2. Cyclic voltammetry on Cp_3UCl and Cp_3NpCl was carried out by Sonnenberger and Gaudiello.[254] ^{237}Np Mössbauer results were reported by Adrian, et al.[270] for $Cp_3Np(\mu\text{-}Cl)_2AlCl_2$ and by Spitsyn, et al.[271] for Cp_3NpCl. The U^{+3} compound $[Na(18\text{-crown-6})(THF)_2]$-$[(Cp_3U)_2Cl]$ was prepared by amalgam reductions of Cp_3UX ($X = Cl$, BH_4, Me, ^nBu).[272] The crystal structure (Figure 112) revealed a symmetrical, bent chloro bridge.

Tel'noi, et al.[273] determined the average heats of formation and U-Cl, U-C, and U-O bond cleavage for Cp_3UR compounds ($R = Cl$, CH_2CHMe_2, OBu).

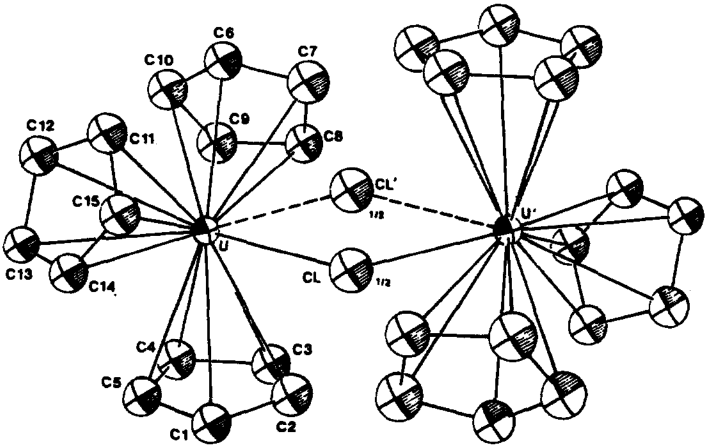

Fig. 112. The anion in $[Na(18\text{-crown-6})(THF)_2][(Cp_3U)_2Cl]$. (Reprinted with permission from Journal of Organometallic Chemistry.)

(iv) Triscyclopentadienyl hydrides. Zanella, et al.[274] prepared Cp_3U(9-borabicyclo(3.3.1)nonane) by the reaction of Cp_3UCl and the sodium salt of the ligand. The crystal structure was determined (Figure 113, U-C(Cp) = 2.76(1)Å, U···B = 2.78(4)Å). The borohydride Cp_3UBH_4 was obtained by Porchia, et al.[275] when reacting Cp_3UL (L = Me, Et, Ph, NEt_2, OMe, F, $CONEt_2$, COBu) with BH_3L' (L' = THF, BH_3, Me_2S). Cp_3UX (X = Cl, Br, I) compounds were not reactive. Zanella et al.[276] studied the chemical and physical properties of Cp_3UBH_4, $(CpMe)_3UBH_4$, Cp_3UBH_3Me, Cp_3UBH_3Et, and Cp_3UBH_3Ph. A partial structure determination of Cp_3UBH_4 indicated a trihapto coordination of BH_4^- to U (U···B = 2.48Å).

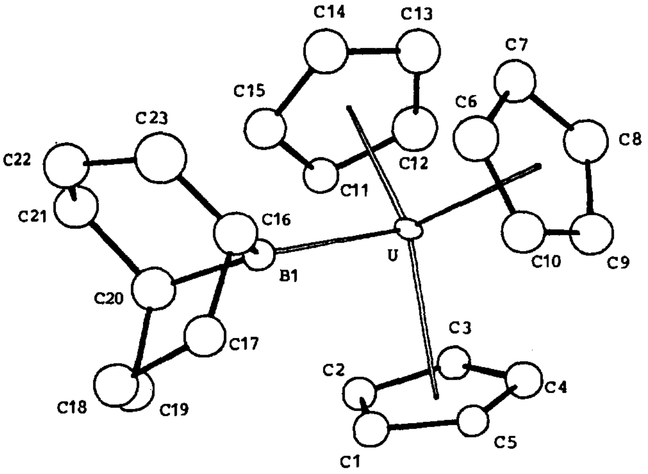

Fig. 113. Cp_3U(9-borabicyclo(3.3.1)nonane). (Reprinted with permission from Journal of Organometallic Chemistry.)

Ephritikhine, et al.[277] prepared the anionic U(III) compound [Na(18-crown-6)][Cp_3UBH_4] by Na/Hg reduction of Cp_3UBH_4. When Cp_3UCl was reduced in a similar fashion and in the presence of NaH, [$Na(THF)_2$][$(Cp_3U)_2(\mu$-H)][278] was prepared. The crystal structure is depicted in Figure 114 (U-C(Cp) = 2.82Å, U-H = 2, 2.4Å).

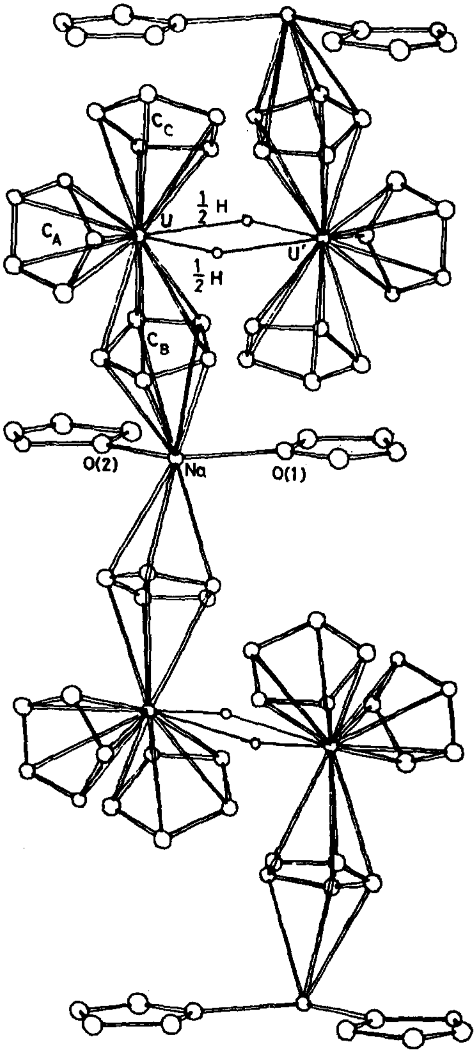

Fig. 114. [Na(THF)$_2$][(Cp$_3$U)$_2$(μ-H)]. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

(v) Triscyclopentadienyl compounds with bonds to N. The crystal structure of (CpMe)$_3$UNH$_3$ was published by Rosen and Zalkin[279] (Figure 115, U-C(CpMe) = 2.81(5)Å, U-NH$_3$ = 2.61(3)Å). Rebizant, *et al.*[280] reported the crystal structure of [Cp$_3$U-(NCMe)$_2$][CpThCl$_4$(NCMe)] (cation: Figure 116, U-C(Cp) = 2.73(3)Å, U-N = 2.54(4)Å). The crystal structure of (CpMe)$_3$U(NC$_5$H$_4$NMe$_2$) was carried out by Zalkin and Brennan[281] (Figure 117, U-C(CpMe) = 2.82(4)Å, U-N = 2.64(2)Å).

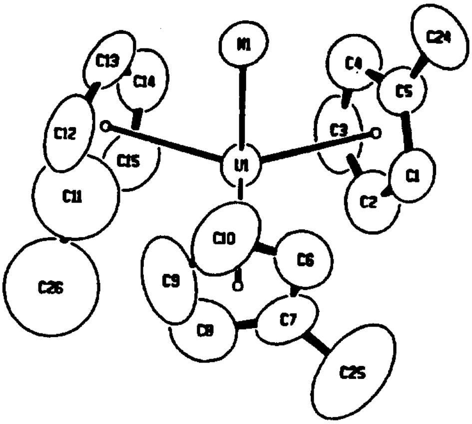

Fig. 115. (CpMe)$_3$UNH$_3$. (Reprinted with permission from Acta Crystallographica.)

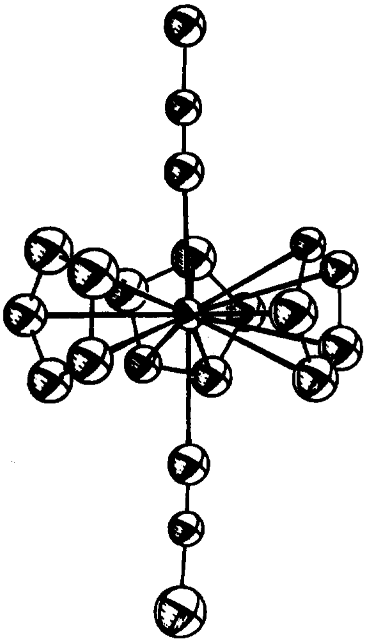

Fig. 116. The cation in [Cp$_3$U(NCMe)$_2$][CpThCl$_4$(NCMe)]. (Reprinted with permission from Inorganica Chimica Acta.)

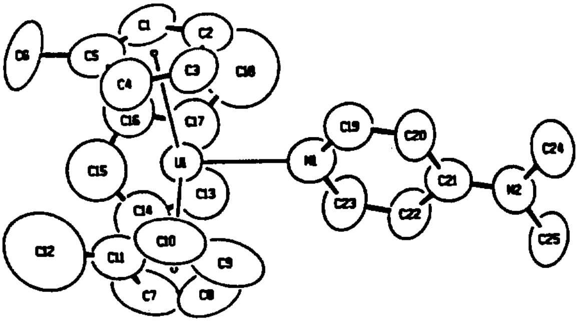

Fig. 117. $(CpMe)_3U(NC_5H_4NMe_2)$. (Reprinted with permission from Acta Crystallographica.)

Cramer, et al.[282] prepared $Cp_3AnNPPh_3$ by the reaction of Cp_3AnCl (An = U, Th) with $LiNPPh_3$ and determined the crystal structure of An = U (Figure 118, U-C(Cp) = 2.78(2)Å, U-N = 2.07(2)Å). The authors suggest a U-N triple bond and carried out molecular orbital calculations on several Cp_3U-N and Cp_3U-O compounds which support their claim. The crystal structure of Cp_3UNPh_2 was reported by the same authors[283] (Figure 119, U-C(Cp) = 2.79(3)Å, U-N = 2.29(1)Å). The compound was prepared by the reaction of $Cp_3UCHPMePh_2$ and $HNPh_2$. The authors suggest the presence of a U-N double bond.

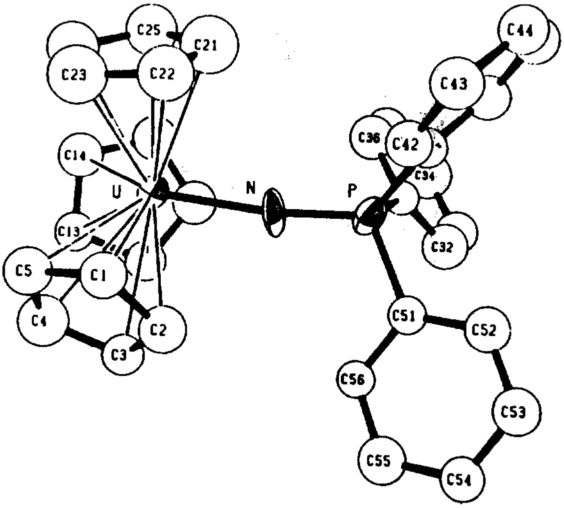

Fig. 118. Cp_3UNPPh_3. (Reprinted with permission from Organometallics. Copyright 1988 American Chemical Society.)

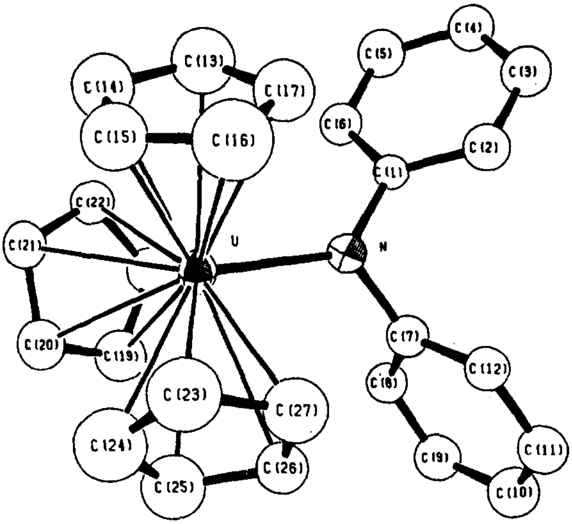

Fig. 119. Cp_3UNPh_2. (Reprinted with permission from Organometallics. Copyright 1987 American Chemical Society.)

Fischer, et al.[284] published the preparation of $[Cp_3U(NCR)_2]$-$[BPh_4]$ (R = Me, Et, ^nPr, Ph) by reaction of $[Cp_3U(OH_2)_2]$-$[BPh_4]\cdot n(H_2O)$ and nitrile in n-hexane or by reaction of Cp_3UCl and $Na[BPh_4]$ in NCR/H_2O mixtures. ^1H NMR, near-IR/VIS spectra and the crystal structures of $[Cp_3U(NCMe)_2][BPh_4]$ (Figure 120, U-C(Cp) = 2.73Å, U-N = 2.57(1)Å) and $Cp_3U(NCS)(NCMe)$ (Figure 121, U-C(Cp) = 2.74Å, U-N = 2.44(1)Å (S), 2.66(1)Å (Me)) were reported.

Andersen, et al.[82] published the synthesis and structure of $(CpMe)_3U[N(CH_2CH_2)_3CH]$ (Figure 122, U-C(CpMe) = 2.82(3)Å, U-N = 2.764(4)Å).

Rossetto, et al.[285] reacted Cp_3UL (L = Cl, Me, ^nBu, Ph) in toluene with tetracyanoethylene and 7,7,8,8-tetracyanoquinodimethane to yield Cp_3U keteniminates. Spectral data indicated trigonal bipyramidal metal coordination. Amberger, et al.[286] discussed the parameterization of the crystal field splitting patterns in $[Cp_3U(NCS)_2]^-$ and $[Cp_3U(NCBH_3)_2]^-$. ^{237}Np Mössbauer data were reported for $[Cp_3Np(NCMe)_2][AlCl_4]$,[255] Cp_3NpL (L = NCS, NCMe)[256] and $Cp_3Nd(NC_4H_4)$.[270]

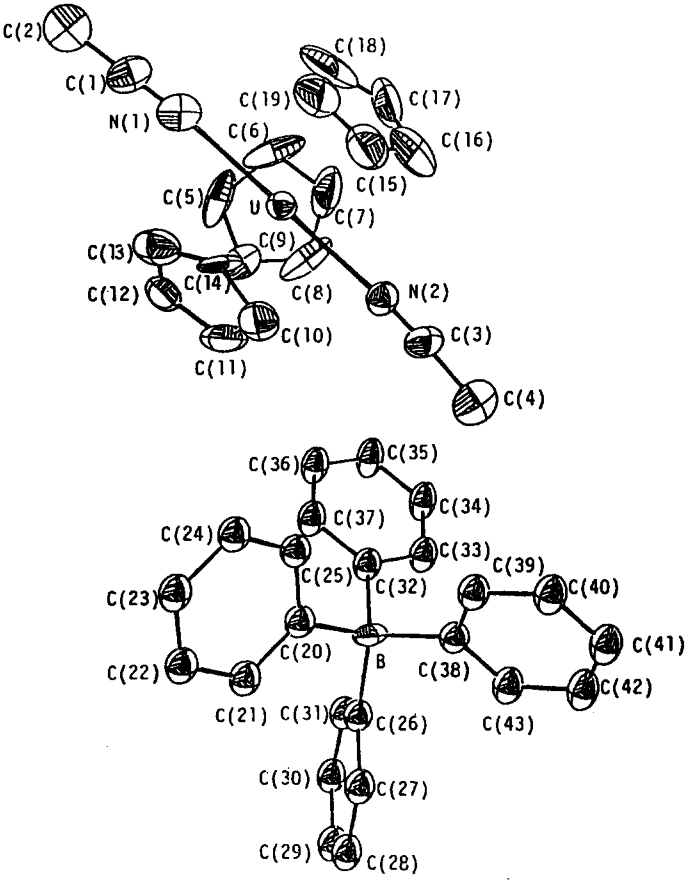

Fig. 120. [$Cp_3U(NCMe)_2$][BPh_4]. (Reprinted with permission from <u>Journal of Organometallic Chemistry</u>.)

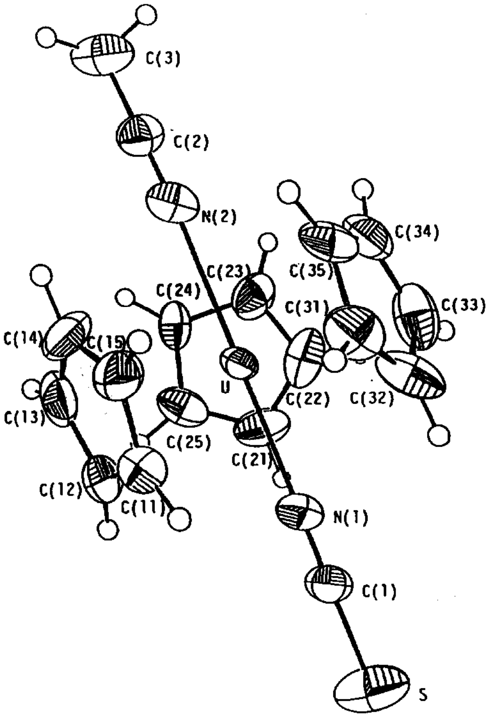

Fig. 121. $Cp_3U(NCS)(NCMe)$. (Reprinted with permission from Journal of Organometallic Chemistry.)

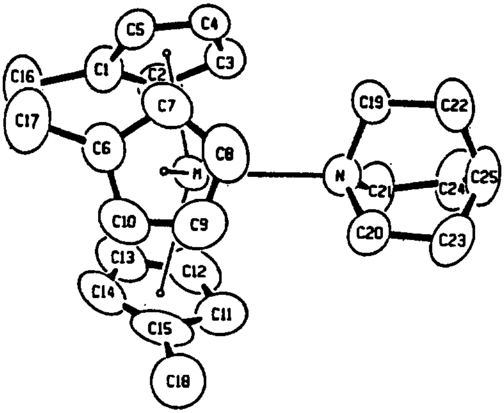

Fig. 122. $(CpMe)_3U[N(CH_2CH_2)_3CH]$. (Reprinted with permission from Organometallics. Copyright 1988 American Chemical Society.)

(vi) Triscyclopentadienyl compounds with bonds to O, P, Si, Fe, Ge, Ru. Edelmann, et al.[287] prepared Cp_3UOR (R = CH_2CF_3, $C(CF_3)_2CH_3$, $C(CF_3)_2CCl_3$, $C(CF_3)_2CF(CF_3)_2$, C_6F_5) by reaction of Cp_3UCl with NaOR in THF. The crystal structure of R = $C(CF_3)_2CCl_3$ is presented in Figure 123 (U-C(Cp) = 2.74(1)Å, U-O = 2.23(1)Å).

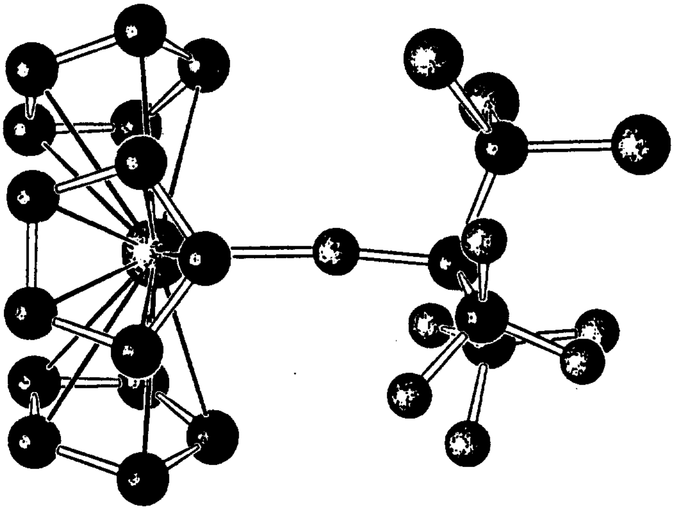

Fig. 123. $Cp_3UOC(CF_3)_2CCl_3$. (Reprinted with permission from Inorganica Chimica Acta.)

Cramer, et al.[288] reported the insertion of PhNCO into the U-C double bond in $Cp_3UCHP(Ph)(R)(Me)$ (R = Me, Ph) to yield Cp_3U-[(NPh)(O)CCHP(Ph)(R)(Me)]. The R = Me derivative was crystallographically characterized (Figure 124, U-C(Cp) = 2.84(2)Å, U-N = 2.45(1)Å, U-O = 2.34(1)Å).

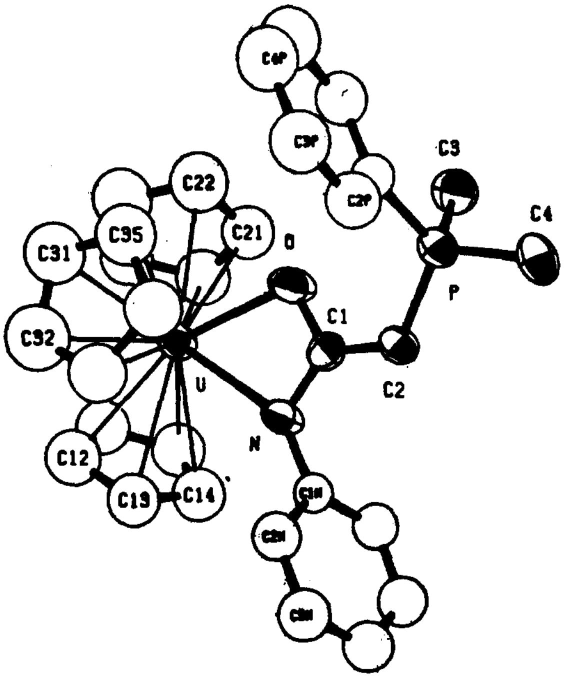

Fig. 124. $Cp_3U[(NPh)(O)CCHP(Ph)(Me)_2]$. (Reprinted with permission from Organometallics. Copyright 1987 American Chemical Society.)

Andersen, et al. prepared and structurally characterized two compounds with P bonded to Cp_3U fragments. Reaction of $Cp_3U(THF)$ with dmpe produced $(Cp_3U)_2$dmpe (Figure 125, U-C(Cp) = 2.77(3)Å, U-P = 3.022(2)Å).[289] The reaction of $(CpMe)_3U(THF)$ with $P(OCH_2)_3CEt$ in OEt_2 produced $(CpMe)_3U[P(OCH_2)_3CEt]$[82] (Figure 126, U-C(CpMe) = 2.80(5)Å, U-P = 2.998(6)Å). In the latter compound the authors rationalized the bond lengths in terms of U-P π-back bonding after comparison with the isostructural Ce compounds[82] (L = $N(CH_2CH_2)_3CH$, Ce-C(CpMe) = 2.85(3)Å, Ce-N = 2.789(3)Å; L = $P(OCH_2)_3CEt$, Ce-C(CpMe) = 2.82(3)Å, Ce-P = 3.086(3)Å).

Porchia, et al.[290] reported the synthesis of $Cp_3U(SiPh_3)$ from Cp_3UCl and $Li(SiPh_3)$, its 2,6-dimethylphenyl isocyanide insertion product, $Cp_3U[C(NC_6H_3Me_2\text{-}2,6)SiPh_3]$, and the crystal structure of $Cp_3U(OSiPh_3)$. The latter complex was prepared by reaction of $Cp_3U(NEt_2)$ and $SiPh_3OH$ and exhibits a nearly linear U-O-Si interaction (U-O = 2.135(8)Å, U-O-Si = 172.6(6)°).

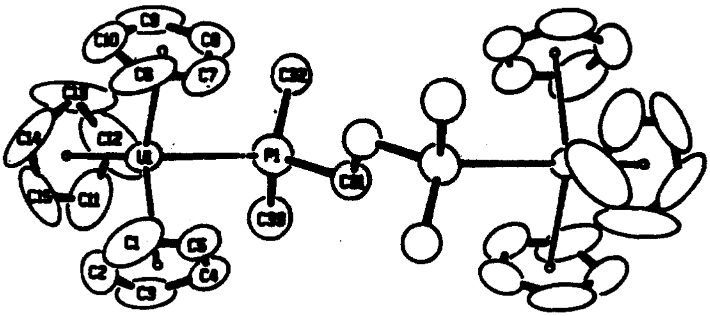

Fig. 125. (Cp$_3$U)$_2$dmpe. (Reprinted with permission from *Acta Crystallographica*.)

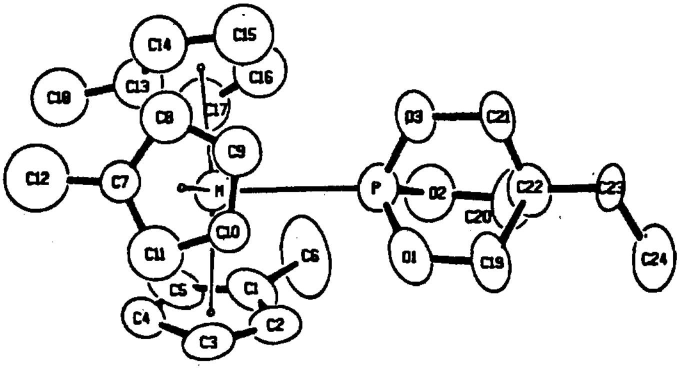

Fig. 126. (CpMe)$_3$U[P(OCH$_2$)$_3$CEt]. (Reprinted with permission from *Organometallics*. Copyright 1988 American Chemical Society.)

Marks and Sternal[291] reacted Cp$_3$AnCl (An = Th, U) and (CpMe)$_3$-ThCl with NaCpM(CO)$_2$ (M = Fe, Ru) to give the metal-metal bonded Cp$_3$An-MCp(CO)$_2$ and (CpMe)$_3$Th-MCp(CO)$_2$. The authors reported hindered rotation about the An-M bond and facile cleavage by alcohols and ketones. Porchia, *et al.*[292] prepared Cp$_3$UGePh$_3$ from Cp$_3$UCl and KGePh$_3$. Insertion of CN(xylyl) into the U-Ge bond was readily accomplished.

(vii) *Triscyclopentadienyl compounds with bonds to C*. Marks, *et al.*[293] measured the absolute bond disruption enthalpies in Cp'$_3$UR (R = I, 62.4(4); ^{n}Bu, 29(2); Bz, 26(3); CH$_2$SiMe$_3$, 39(2);

Me, 45(1); vinyl, 48(2); C≡CPh, 86.7) by halogenolytic isoperibol titration calorimetry of Cp'$_3$U/Cp'$_3$UI/Cp'$_3$UR. The crystal structure of Cp'$_3$U(vinyl) was included (Figure 127, U-C(Cp') = 2.759(4)Å, U-C(α-vinyl) = 2.436(4)Å).

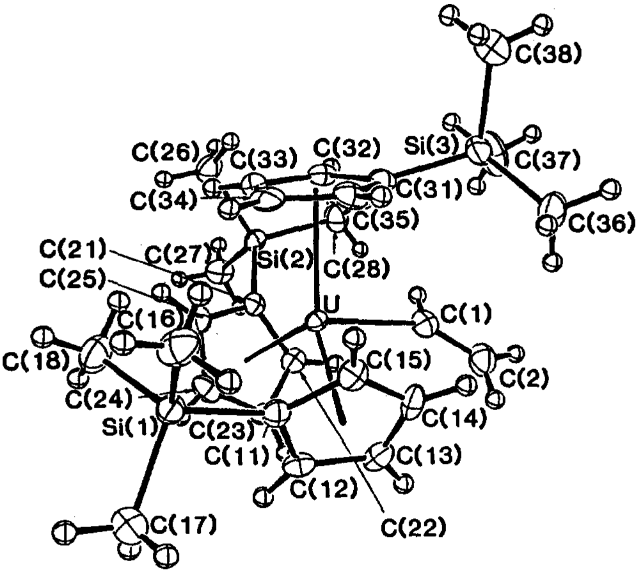

Fig. 127. Cp'$_3$U(vinyl). (Reprinted with permission from Polyhedron. Copyright 1988 Pergamon Press plc.)

Andersen, et al.[294] prepared Li(tmeda)$_2${[Li(tmeda)]$_2$CpMe}-{[(CpMe)$_3$U]$_2$Me} by reaction of (CpMe)$_3$U(THF) with LiMe in OEt$_2$ and 1 equivalent of tmeda. The crystal structure (Figure 128) reveals U-C(Cp) = 2.82(4)Å, U-Me = 2.72(1)Å and U-Me-U = 177(1)°.

The complexes Cp$_3$UBPh$_4$, Cp$_3$UMeBPh$_3$, and their CpMe derivatives were prepared (Fischer, et al.[295]) by dehydration of [Cp$_3$U(OH$_2$)$_2$]-[BPh$_4$]·n(H$_2$O) or addition of BPh$_3$ to Cp$_3$UMe. Spectroscopic and chemical evidence suggested cation/anion interactions such as U-Me-B bridges.

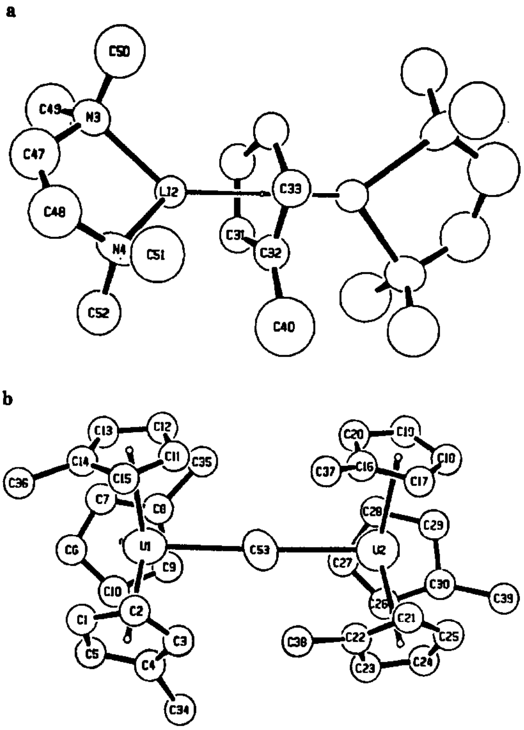

Fig. 128. Li(tmeda)$_2${[Li(tmeda)]$_2$CpMe}{[(CpMe)$_3$U]$_2$Me}. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1989 American Chemical Society.)

Alkyl complexes, Cp_3UR (R = Me, ^{n}Bu, ^{n}Pent), were purified by (Ephritikhine, et al.[296,297]) by reaction of $Cp_3U(THF)$ with LiR. Further reaction with LiR' or hydrogenolysis in the presence of a terminal olefin resulted in alkyl exchange. The alkyne complex $Cp_3U(C_2Ph_2)$ was obtained by reaction of $Cp_3U(THF)$ with C_2Ph_2. Anionic complexes [Na(18-crown-6)][Cp_3UR] (R = Me, ^{n}Bu) were obtained by Na/Hg reduction of Cp_3UR.[277]

Zanella, et al.[298] studied the insertion reactions of 2,6-dimethylphenyl isocyanide into the U-N bonds in Cp_3UNEt_2 and the U-P bonds in Cp_3UPPh_2. The crystal structure of $Cp_3U[C(NEt_2)=NC_6H_3Me_2\text{-}2,6]$ was also reported (Figure 129, U-C(Cp) = 2.808Å, U-C(η^2) = 2.35(2)Å, U-N(η^2) = 2.35(2)Å).

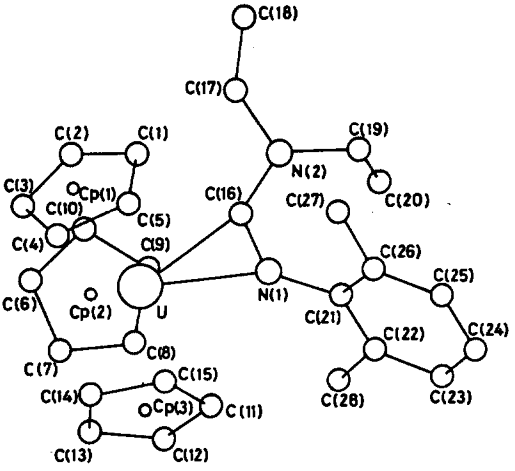

Fig. 129. $Cp_3U[C(NEt_2)=NC_6H_3Me_2\text{-}2,6]$. (Reprinted with permission from Journal of the Chemical Society, Dalton Transactions.)

Cramer, et al.[299] published the synthesis and structure of $Cp_3UCHPMe_3$. Reaction of Cp_3UCl with $Li[CH_2]_2PMe_2$ or CH_2PMe_3 gave the compound and its crystal structure was determined (Figure 130, U-C(Cp) = 2.80(1)Å, U-C(σ) = 2.274(8)Å). The short U-C bond was interpreted as a double bond. A second report[300] described the activation of CO by U-C double bonds in Cp_3UCHPR_3.

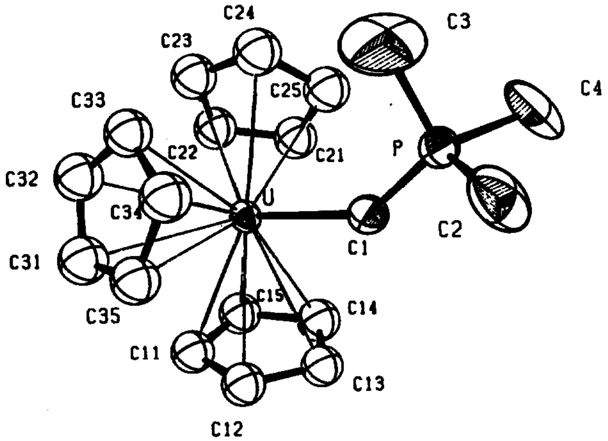

Fig. 130. $Cp_3UCHPMe_3$. (Reprinted with permission from Chemische Berichte.)

Leonov and Solov'eva[301] investigated the carbonylation and carboxylation of Cp_3UR (R = Bu, ^iBu). The reactions of $Cp_3UCH_2CHMe_2$ with N_2 and CO at 80K were studied by IR.[302] ^{237}Np Mössbauer results were reported for $(Cp_3Np)_2C_2$,[251,252,261] Cp_3NpBu,[262] and $Cp_3NpC_6H_4Et$.[262]

In a further contribution to his study of geometric control of organometallic f-element compounds, Xing-Fu[303] discussed the effect of steric hindrance on the structure and chemistry of Cp_3M compounds. The compound, Cp_3UMe, was used as an example. Gramoteeva[304] prepared Cp_3UR (R = Me, Bu, ^iBu) from the 1/30 reaction of Cp_4U and RCl.

(viii) Biscyclopentadienyl halide compounds. Zalkin, Stuart, and Andersen[305] published the synthesis (from $K(Cp^tBu_2)$ and UCl_3) and structure of $[(Cp^tBu_2)_2UCl]_2$ (Figure 131, $U\text{-}C(Cp^tBu_2)$ = 2.79(4)Å, U-Cl = 2.856(4)Å). Atwood and Lappert, et al.[306] reduced Cp''_2UCl_2 with Li^nBu or Na/Hg in the presence of THF, tmeda or pmdeta ($(Me_2NCH_2CH_2)_2NMe$) to produce $Cp''_2U(\mu\text{-}Cl)_2ML$ (M = Li, Na; L = $(THF)_2$, tmeda; M = Li, L = pmdeta). Reaction of the starting chloride with LiX (X = Cl, Br) in THF or $[PPh_4]X$ in toluene gave $Cp''_2U(\mu\text{-}Cl)(\mu\text{-}X)Li(THF)_2$ or $[PPh_4][Cp''_2UCl(X)]$. The crystal structures were reported for $Cp''_2U(\mu\text{-}Cl)_2Li(pmdeta)$ (Figure 132, U-Cl = 2.70(2)Å) and $[PPh_4][Cp''_2UCl_2]$ (Figure 133, U-Cl = 2.666(8)Å). In a separate publication[307] the crystal structure of the THF solvate, $Cp''_2U(\mu\text{-}Cl)_2Li(THF)_2$, was reported (Figure 134, U-C(Cp'') = 2.77(2)Å, U-Cl = 2.730(1)Å). This paper featured a different preparative route: Cp''_2UCl_2 was reacted with $[LiP(SiMe_3)_2(THF)_2]_2$ in THF.

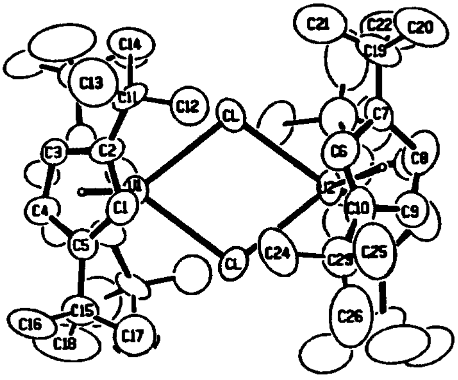

Fig. 131. $[(Cp^tBu_2)_2UCl]_2$. (Reprinted with permission from Acta Crystallographica.)

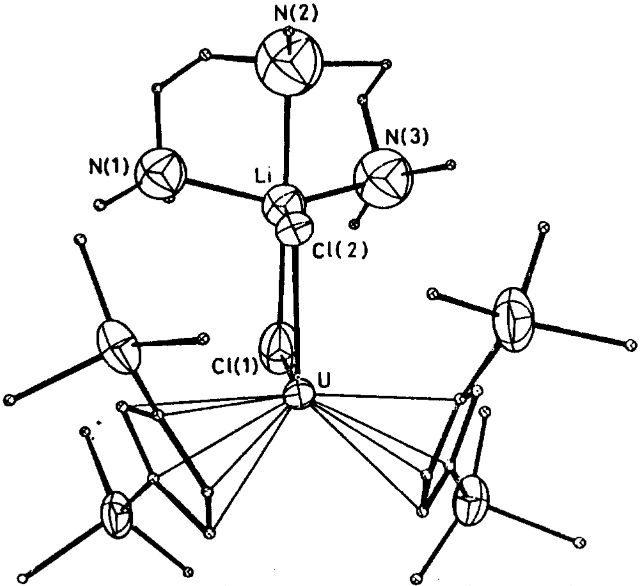

Fig. 132. $Cp''_2U(\mu\text{-}Cl)_2Li(pmdeta)$. (Reprinted with permission from <u>Journal of the Chemical Society, Chemical Communications</u>.)

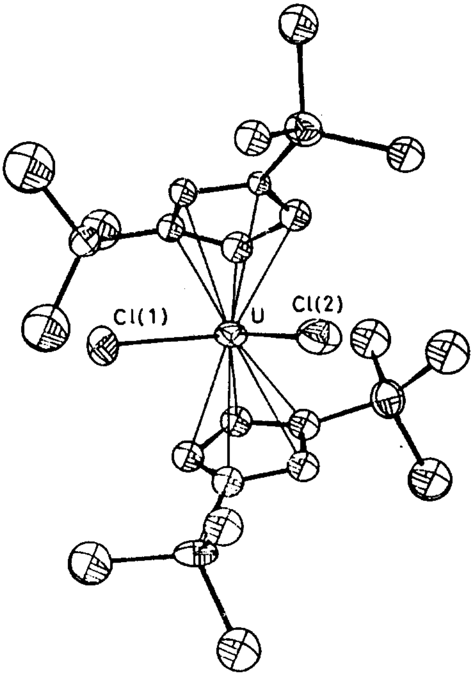

Fig. 133. The anion in $[PPh_4][Cp''_2UCl_2]$. (Reprinted with permission from <u>Journal of the Chemical Society, Chemical Communications</u>.)

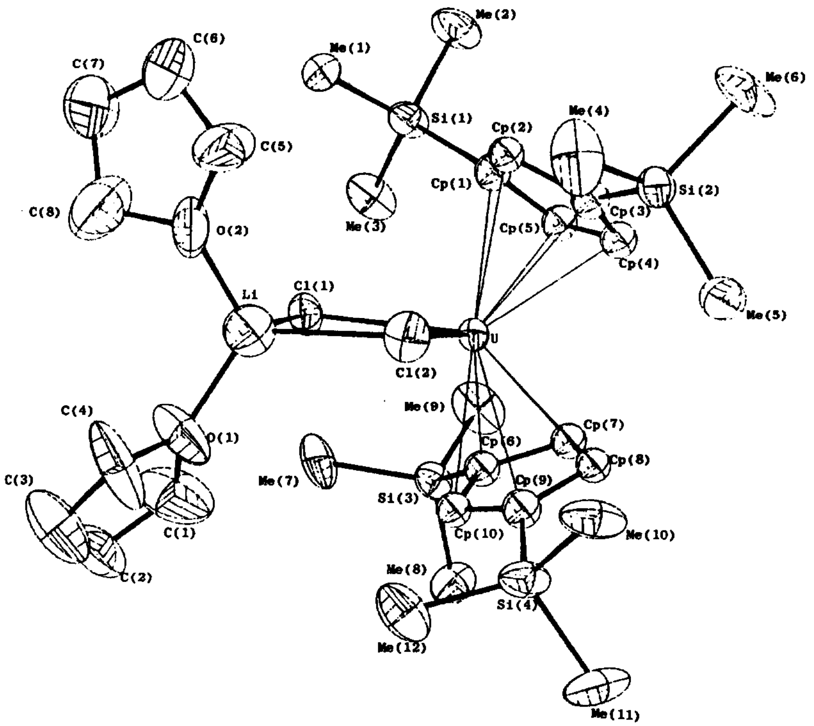

Fig. 134. Cp"$_2$U(μ-Cl)$_2$Li(THF)$_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Lappert[259] reviewed some of his work in this area in a paper derived from a presentation at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (Lisbon). The compounds discussed included [Cp"$_2$U(μ-F)(μ-BF$_4$)]$_2$, [Cp"$_2$UX]$_n$ (X = F, I), Cp"$_2$UCl(THF), [Cp"$_2$U(μ-X)]$_2$ (X = Cl, Br), and [PPh$_4$][Cp"$_2$UX$_2$] (X$_2$ = Cl$_2$ or ClBr).

Koulkès-Pujo, et al.[308] utilized pulse radiolysis to reduce Cp$^*_2$AnCl$_2$ (An = Th, U). The electronic spectra, reaction rates, and reaction order were discussed. Cyclic voltammetry studies mentioned earlier by Sonnenberger and Gaudiello[254] were carried out on Cp$^*_2$UCl$_2$ and Cp$^*_2$NpCl$_2$.

(ix) Biscyclopentadienyl hydrides. Takats and Fragala, et al.[309] studied the gas phase photoelectron spectra of Cp$_2$U(BH$_4$)$_2$. The first ionization corresponds to removal of a U 5f electron, while the next highest occupied ligand-based molecular orbital is π-ring in nature.

In a review of his work with the Cp" ligand, Lappert[259] discussed $[\mathrm{Cp''_2U(BH_4)}]_n$, $[\mathrm{Cp''_2U(BH_4)(THF)}]$, and $[\mathrm{Cp''_2U(BH_4)_2}]$. Le Marechal, et al.[277] reduced $\mathrm{Cp_2U(BH_4)_2}$ in the presence of 18-crown-6 to produce $[\mathrm{Na(18\text{-}crown\text{-}6)}][\mathrm{Cp_2U(BH_4)_2}]$. The compound was reported to be oxidized by $\mathrm{Tl(BH_4)}$. Zanella, et al.[273] published the synthesis, chemical, physical, and spectroscopic properties of $\mathrm{Cp_2An(BH_4)_2}$ (An = Th, U), $\mathrm{(CpMe)_2U(BH_4)_2}$, and $\mathrm{Cp'_2U(BH_4)_2}$. Marks[310] discussed H_2 and CH activation at $\mathrm{Cp^*_2Th}$ centers.

(x) Biscyclopentadienyl compounds with bonds to N. The photoelectron spectra of $\mathrm{Cp_2U(NEt_2)_2}$ revealed the first ionization potential to be U 5f and the second, N 2p lone pair in nature.[309] Lappert[259] discussed $\mathrm{Cp''_2An(Cl)NMe_2}$, $\mathrm{Cp''_2An(Cl)N(SiMe_3)_2}$ (An = U, Th), $\mathrm{Cp''_2UCl(tmeda)}$, and $\mathrm{Cp''_2UCl(pmdeta)}$ in a brief review of his Cp" actinide chemistry.

Marks, et al.[311] reported the reactions of $\mathrm{Cp^*_2Th(Cl)Ru(Cp)(CO)_2}$ with acetonitrile to produce the diazathoracyclobutene, $\mathrm{Cp^*_2ThCl(C_6H_8N_3)}$, and with acetone to give $\mathrm{Cp^*_2ThCl[O{=}C(Me)CH_2\text{-}C(Me)_2O]}$. The crystal structure of the acetonitrile oligomerization product was determined (Figure 135, Th-C(Cp*) = 2.80(2)Å, Th-N = 2.46(1)Å).

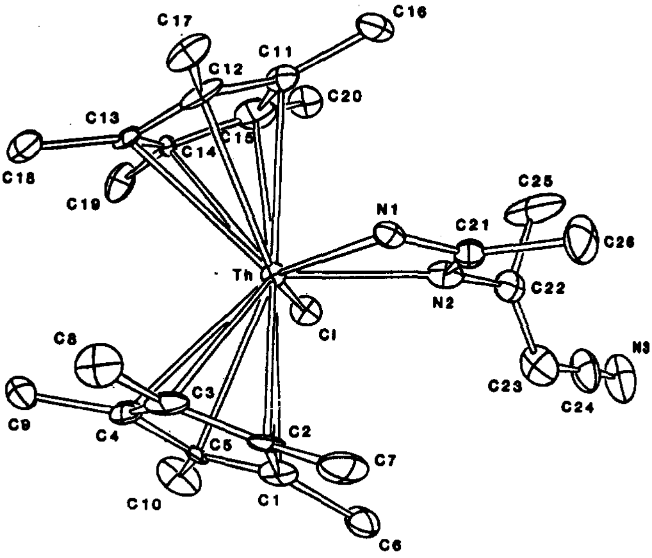

Fig. 135. $\mathrm{Cp^*_2ThCl(C_6H_8N_3)}$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1987 American Chemical Society.)

Cramer, Roth, and Gilje[312] prepared $Cp^{*}_{2}UCl_{2}(HNPPh_{3})$ from the reaction of $Cp^{*}_{2}UCl_{2}$ and $HNPPh_{3}$ in toluene. The crystal structure (Figure 136, U-C(Cp^{*}) = 2.773(1)Å, U-N = 2.43(1)Å) indicated U-H agostic interactions and N-H···Cl hydrogen bonding.

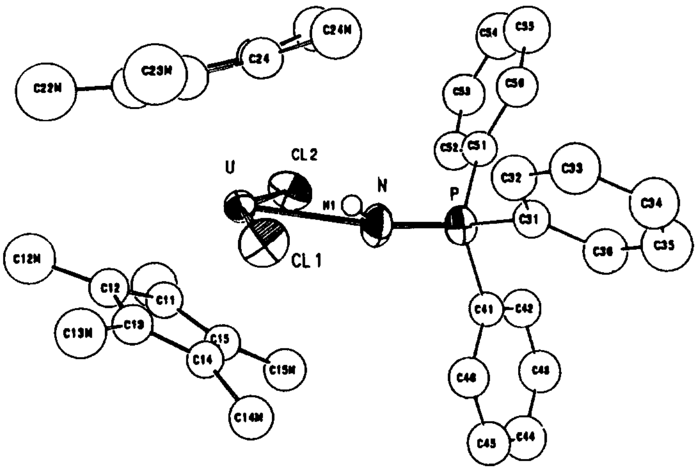

Fig. 136. $Cp^{*}_{2}UCl_{2}(HNPPh_{3})$. (Reprinted with permission from Organometallics. Copyright 1989 American Chemical Society.)

Andersen, et al.[313] published the crystal structures of $[(CpMe)_{2}U(\mu\text{-}NR)]_{2}$ (R = Ph, $SiMe_{3}$). The NPh ligand (Figure 137, U-C(CpMe) = 2.76(2)Å, U-N = 2.156(8), 2.315(8)Å) bridges asymmetrically, while the $N(SiMe_{3})$ ligand bridges symmetrically (Figure 138, U-C(CpMe) = 2.77(5)Å, U-N = 2.224(7)Å). Zalkin and Beshouri[314] published the crystal structure of $Cp''_{2}UCl(NCSiMe_{3})_{2}$ (Figure 139, U-C(Cp") = 2.79(2)Å, U-N = 2.61(1)Å, U-Cl = 2.698(3)Å).

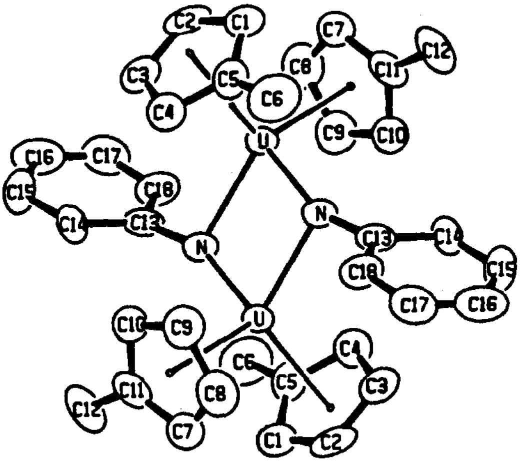

Fig. 137. [$(CpMe)_2U(\mu\text{-}NPh)]_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

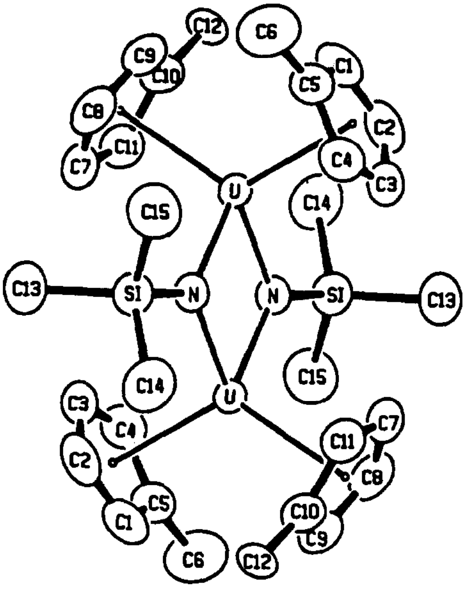

Fig. 138. [$(CpMe)_2U(\mu\text{-}NSiMe_3)]_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

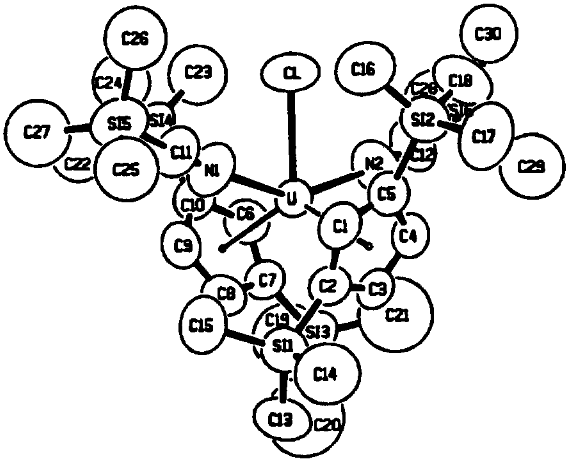

Fig. 139. $Cp''_2UCl(NCSiMe_3)_2$. (Reprinted with permission from Acta Crystallographica.)

Tatsumi and Nakamura[315] carried out a molecular orbital study based on the extended Huckel method on Cp^*_2An(bis-η^2-pyrazolates) and Cp^*_2An(bis-η^2-acyls).

(xi) Biscyclopentadienyl compounds with bonds to O, S, P. Zalkin and Beshouri[316] published the structure of $[Cp''_2U(\mu\text{-}O)]_2$ (Figure 140, U-C(Cp") = 2.77(3)Å, U-O = 2.11(2)Å). This compound was also among several discussed by Lappert.[259] Others included Cp''_2AnClL (An = Th, U; L = $OC_6H_3{}^iPr_2$-2,6, $OC_6H_3Ph_2$-2,6, $SC_6H_2{}^tBu_3$-2,4,6), $[Cp''_2U(OC_6H_3Ph_2\text{-}2,6)]_n$, and $[Cp''_2U(OC_6H_3{}^iPr_2\text{-}2,6)(THF)]$. The gas phase photoelectric spectral studies by Takats and Fragala, et al.[309] included $Cp_2U(O_2CCMe_3)$ and $Cp_2US_2CNEt_2$. Cramer, Bruck, and Gilje[317] reported the structural characterization of $\{Cp^*U[\mu\text{-}(CH_2)P(Ph)_2(CH_2)]\}_2Mg[CH_2PMePh_2]_2(\mu_3\text{-}O)(\mu_2\text{-}O)(\mu_2\text{-}Cl)_2$ (Figure 141, U-C(Cp^*) = 2.85(2)Å, U-C(σ) = 2.67(3), 2.60(3)Å, U-Cl = 2.93(1)Å, U-O(μ_2) = 2.13(2)Å, U-O(μ_3) = 2.18(2)Å).

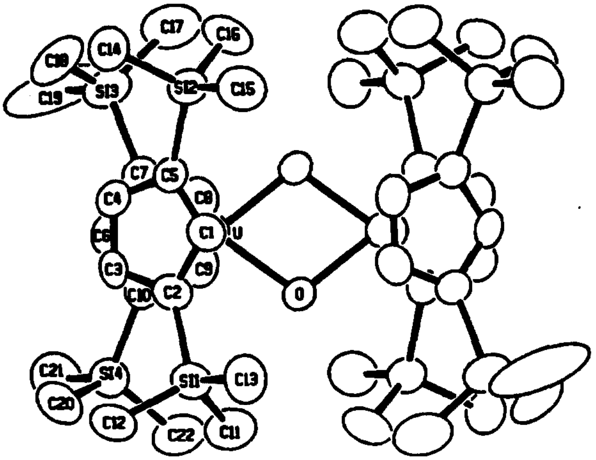

Fig. 140. [Cp"$_2$U(μ-O)]$_2$. (Reprinted with permission from <u>Acta Crystallographica</u>.)

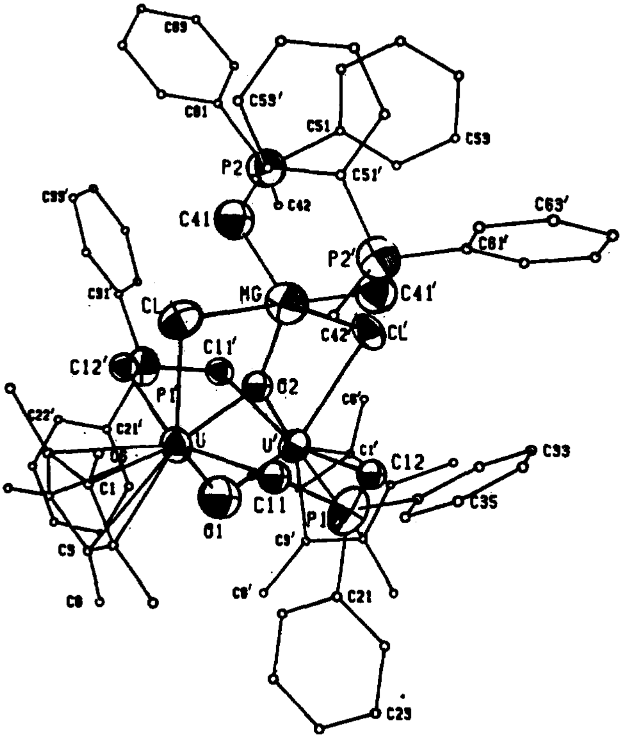

Fig. 141. {Cp*U[μ-(CH$_2$)P(Ph)$_2$(CH$_2$)]}$_2$Mg[CH$_2$PMePh$_2$]$_2$(μ_3-O)(μ_2-O)(μ_2-Cl)$_2$. (Reprinted with permission from <u>Organometallics</u>. Copyright 1988 American Chemical Society.)

Marks, *et al.*[318] prepared $Cp^*_2Th(SCH_2CH_2Me)_2$ by the reaction of $Cp^*_2ThMe_2$ and a ten-fold excess of $HSCH_2CH_2Me$ in toluene. The structure is depicted in Figure 142 (Th-C(Cp^*) = 2.799(8)Å, Th-S = 2.718(3)Å).

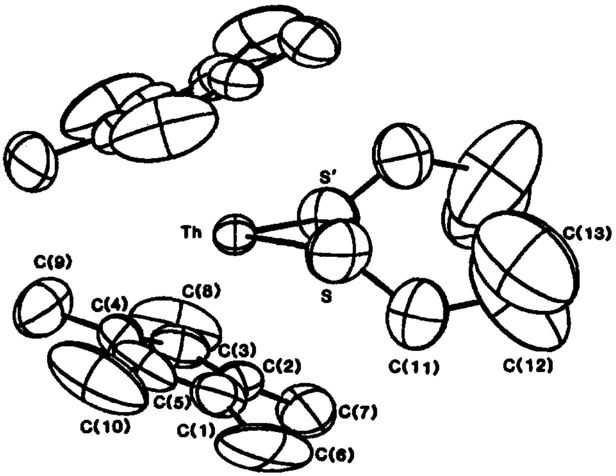

Fig. 142. $Cp^*_2Th(SCH_2CH_2Me)_2$. (Reprinted with permission from *Inorganica Chimica Acta*.)

Andersen, Brennan, and Zalkin published three crystal structures containing Cp_2Th-P bonds. The chelating dmpe was utilized to crystallize Cp_2ThMe_2(dmpe) (Figure 143, Th-C(Cp) = 2.84(3)Å, Th-C(σ) = 2.57(1)Å, Th-P = 3.146(2)Å),[319] the isostructural Cp_2ThCl_2(dmpe) (Th-C(Cp) = 2.80(2)Å, Th-Cl = 2.708(2)Å, Th-P = 3.122(2)Å),[319] and $Cp_2Th(Bz)_2$(dmpe) (Figure 144, Th-C(Cp) = 2.83(5)Å, Th-C(σ) = 2.657(9)Å, Th-P = 3.142(2), 3.237(2)Å).[320]

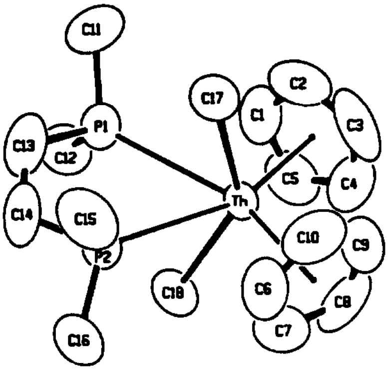

Fig. 143. Cp_2ThMe_2(dmpe). (Reprinted with permission from Acta Crystallographica.)

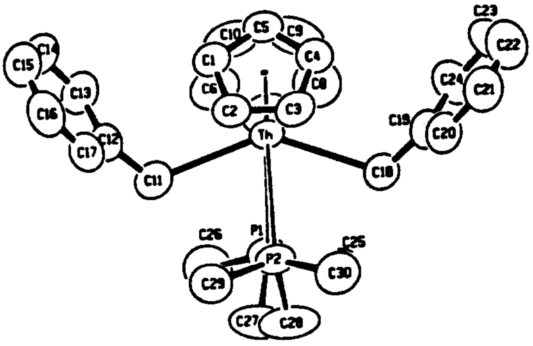

Fig. 144. $Cp_2Th(Bz)_2$(dmpe). (Reprinted with permission from Acta Crystallographica.)

Bursten and Novo-Gradac[321] carried out qualitative Xα-scattered wave molecular orbital calculations on the unsupported heterobimetallic, $Cp_2ThI\text{-}RuCp(CO)_2$. The bonding was found to be similar to other anionic ligands such as halides.

(xii) Biscyclopentadienyl compounds with bonds to C. Two crystal structures containing Th-Me and Th-CH_2Ph bonds were discussed in the preceding section.[319,320] In addition, the structure of a Cp^*_2U phosphoylide complex containing U-CH_2-P interactions was mentioned above.[317]

Tatsumi and Nakamura[322,323] examined the electronic structures of Cp_2AnL_2 (L = alkyl, butadiene, metallacyclopentadiene, cyclobutadiene). Among the features present, molecular orbital analysis pinpointed reasons for the observed deformation in Th-Cα-Cβ angles.

Marks and Lin[324] carried out a kinetic and mechanistic study of Cp^*_2An-carbon sigma bond hydrogenolysis. The rate law was determined to be first order in Cp^*_2AnR and first order in H_2. Relative rates determined included $Cp^*_2ThCH_2CMe_2CH_2$ ≈ $Cp^*_2U(CH_2{}^tBu)(O^tBu)$ > $Cp^*_2Th(CH_2{}^tBu)(OCH^tBu_2)$ = $Cp^*_2Th(CH_2{}^tBu)(O^tBu)$ > $Cp^*_2Th(CH_2{}^tBu)Cl$ > $(CpSiMe_2Cp)Th(^nBu)_2$ > $Cp^*_2Th(^nBu)_2$ ≈ $Cp^*_2ThMe_2$ > $Cp^*_2ThMe(O_3SCF_3)$ > $Cp^*_2Th(^nBu)(OCH^tBu_2)$ ≈ $Cp^*_2ThMe(OSiMe_2{}^tBu)$ > $Cp^*_2Th(p\text{-}C_6H_4NMe_2)(O^tBu)$ > $Cp^*_2Th(Ph)(O^tBu)$ > $Cp^*_2UMe(OCH^tBu_2)$ > $Cp^*_2ThMe(OCH^tBu_2)$.

Marks, et al.[325] studied C-H activation reactions of $Cp^*_2Th(CH_2CMe_2CH_2)$. Reaction with Cp_2MMe_2 (M = Zr, Hf) or $(CpMe_2)ZrMe_2$ in hexane produced m-methylene complexes with a metallated Cp ring. The crystal structure of $Cp^*_2Th(\mu\text{-}CH_2)(\mu\text{-}1\text{-}\eta^1{:}\eta^5\text{-}3,4\text{-}Me_2C_5H_2)Zr(1,2\text{-}Me_2C_5H_3)Me$ was determined (Figure 145, Th-C(Cp^*) = 2.837(8)Å, Th-C(μ-CH_2) = 2.377(8)Å, Th-C(m-$CpMe_2$) = 2.483(8)Å).

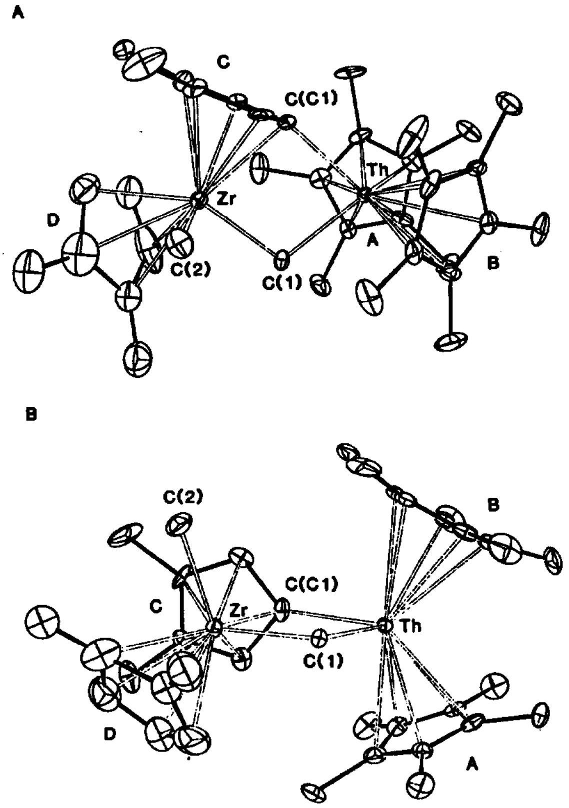

Fig. 145. $Cp^*_2Th(\mu\text{-}CH_2)(\mu\text{-}1\text{-}\eta^1:\eta^5\text{-}3,4\text{-}Me_2C_5H_2)Zr(1,2\text{-}Me_2C_5H_3)Me$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1987 American Chemical Society.)

Marks and Hedden[326] carried out ^{13}C CPMAS solid-state NMR studies of $Cp^*_2ThMe_2$ on $MgCl_2$ and observed surface alkylation and ethylene insertion polymerization. These studies supported transfer of a methyl group to the solid surface and formation of $Cp^*_2ThMe^+$. A second contribution by Marks, et al.[327] discussed the isolation and characterization of the $Cp^*_2ThMe(THF)_2^+$ cation in $[Cp^*_2ThMe(THF)_2][BPh_4]$ (Figure 146, Th-C(Cp*) = 2.80(1)Å, Th-C(σ) = 2.49(1)Å). The compound was prepared by reaction of $Cp^*_2ThMe_2$ with $[R_3N][BPh_4]$ (R = Me, Et) in toluene. In a similar fashion,

$[Cp^*_2Th(o\text{-}C_6H_4CH_2NMe_2)][BPh_4]$ was prepared from $Cp^*_2Th(o\text{-}C_6H_4CH_2NMe_2)Me$.

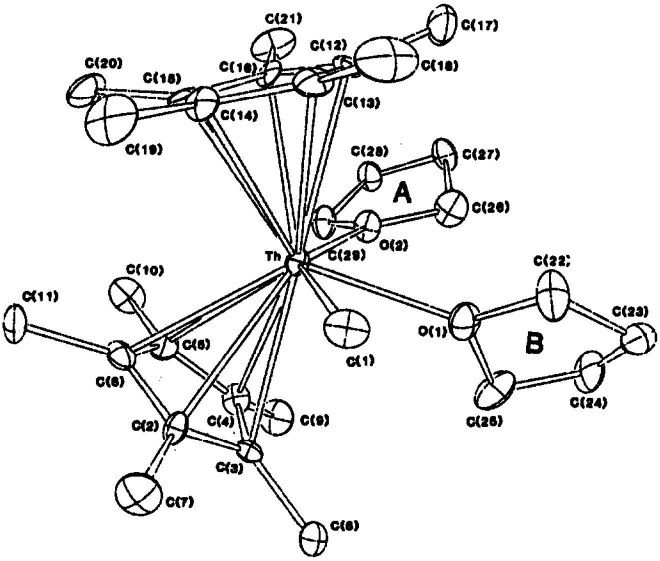

Fig. 146. The cation in $[Cp^*_2ThMe(THF)_2][BPh_4]$. (Reprinted with permission from <u>Journal of the American Chemical Society</u>. Copyright 1987 American Chemical Society.)

Cramer, <u>et al</u>.[328] produced the bridging phosphoylides, $Cp^*_2AnCl[(CH_2)(CH_2)PRR']$ (An = Th, U; RR' = MePh, Me_2, Ph_2) by reaction of Cp^*AnCl_2 with $Li(CH_2)(CH_2)PRR'$. The crystal structures of $Cp^*_2UCl[(CH_2)(CH_2)PPhR]$ (R = Me, Ph) were crystallographically determined. R = Me is shown in Figure 147 (U-C(Cp*) = 2.776(7)Å, U-Cl = 2.658(2)Å, U-C(σ) = 2.60(1)Å) and R = Ph in Figure 148 (U-C(Cp*) = 2.80(1)Å, U-Cl = 2.680(8)Å, U-C(σ) = 2.58(1)Å). The crystal structures of $Cp''_2UBr(CN^tBu)_2$ (U-C(σ) = 2.662(8), 2.697(7)Å, Figure 149)[329] and $Cp''_2UCl(CN\text{-}2,6\text{-dimethylphenyl})_2$ (U-C(σ) = 2.654(9), 2.681(9)Å, Figure 150)[330] appeared.

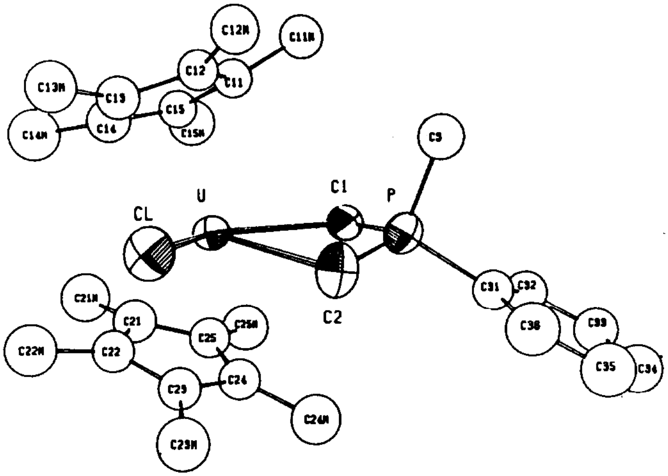

Fig. 147. $Cp^*_2UCl[(CH_2)(CH_2)PPhMe]$. (Reprinted with permission from <u>Organometallics</u>. Copyright 1989 American Chemical Society.)

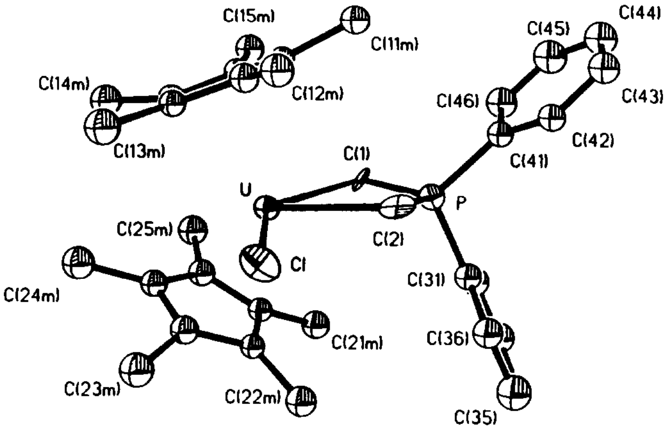

Fig. 148. $Cp^*_2UCl[(CH_2)(CH_2)PPh_2]$. (Reprinted with permission from <u>Organometallics</u>. Copyright 1989 American Chemical Society.)

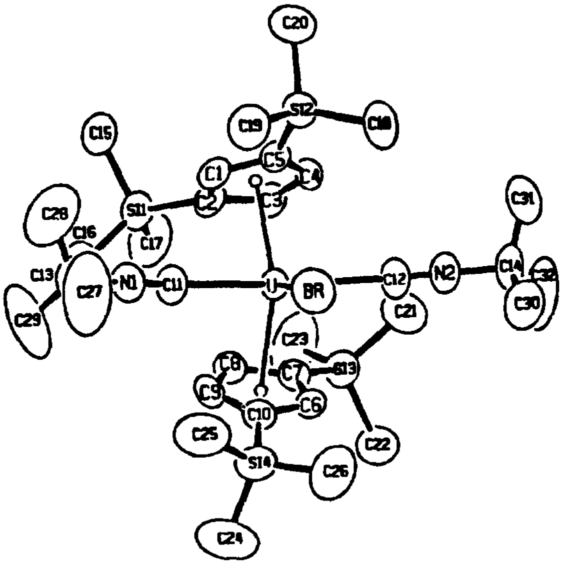

Fig. 149. $Cp''_2UBr(CN^tBu)_2$. (Reprinted with permission from *Acta Crystallographica*.)

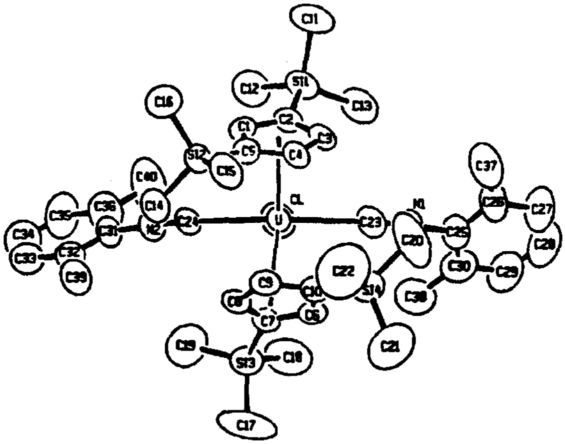

Fig. 150. $Cp''_2UCl(CN\text{-}2,6\text{-dimethylphenyl})_2$. (Reprinted with permission from *Acta Crystallographica*.)

$Cp^*_2UMe_2$ and $Cp^*_2ThMe_2$ were utilized by Harrod, *et al.*[331] as catalysts for the dehydrocoupling of phenylsilane. These compounds were ruled out as practical catalysts.

(xiii) *Bridged-biscyclopentadienyl compounds*. Marks, *et al.*[332] published a detailed account of the synthesis, structures, and reactivity of thorium hydrocarbyls and hydrides with the bridging-Cp ligand $C_5Me_4SiMe_2C_5Me_4^{2-}$ ($Cp_2^{\ddagger}$). $Li_2(Cp_2^{\ddagger})(dme)_2$ was reacted with $ThCl_4$ to give $(Cp_2^{\ddagger})ThCl_2 \cdot 2LiCl(dme)$. This complex was alkylated to yield $Cp_2^{\ddagger}ThR_2$ (R = CH_2SiMe_3, CH_2CMe_3, C_6H_5, ^nBu, Bz). The R = CH_2SiMe_3 compound was crystallographically characterized (Figure 151, Th-C($Cp_2^{\ddagger}$) = 2.79(2)Å, Th-C(σ) = 2.54(2), 2.48(2)Å). Hydrogenolysis of this compound led to $[Cp_2^{\ddagger}Th]_2(\mu\text{-}H)_4$ which was also crystallographically characterized (Figure 152, Th-C($Cp_2^{\ddagger}$) = 2.81(7)Å, Th$\cdots$Th = 3.632(2)Å).

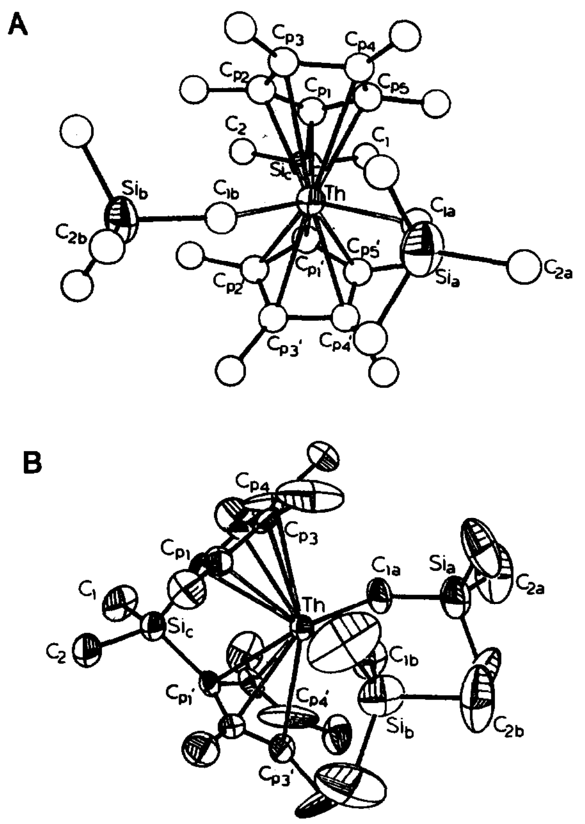

Fig. 151. $Cp_2^{\ddagger}Th(CH_2SiMe_3)_2$. (Reprinted with permission from *Organometallics*. Copyright 1988 American Chemical Society.)

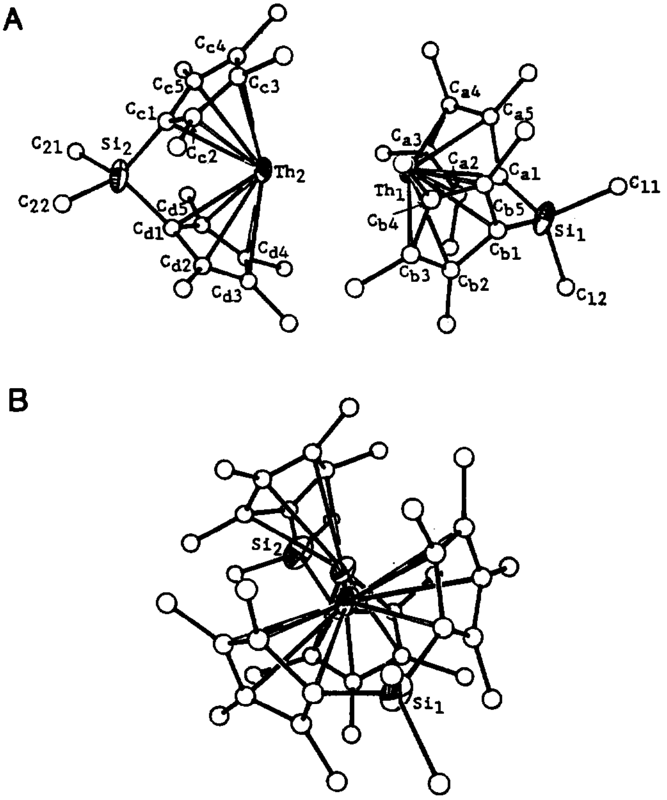

Fig. 152. $[Cp_2^{\ddagger}Th]_2(\mu\text{-}H)_4$. (Reprinted with permission from Organometallics. Copyright 1988 American Chemical Society.)

(xiv) Monocyclopentadienyl compounds. Leonov, et al.[253] studied the mechanism of reaction of $CpUCl_3$ with O_2. ^{237}Np Mössbauer data was presented for $(CpMe)NpCl_3$ by Spitsyn, et al.[271] Dormond, et al.[333] investigated $CpUCl_2R$ (R = Me, Et, ^nBu) in alkylation reactions of carbonyl compounds. Lappert, et al.[259] included $Cp''AnL_2$ (L = Cl, Br, I, BH_4, CH_2SiMe_3, CH_2Ph, $OC_6H_3Me_2$-2,6) in his account of the Cp''^- chemistry of U and Th. Atwood and Lappert, et al.[334] published the crystal structure of $Cp'''UCl_2(THF)(\mu\text{-}Cl)_2Li(THF)_2$ ($Cp''' = 1,2,4\text{-}(SiMe_3)_3C_5H_2^-$); Figure 153, U-C(Cp''') = 2.69-2.76Å, U-Cl(terminal) = 2.606(4)Å, U-Cl(μ-Cl) = 2.730(4)Å).

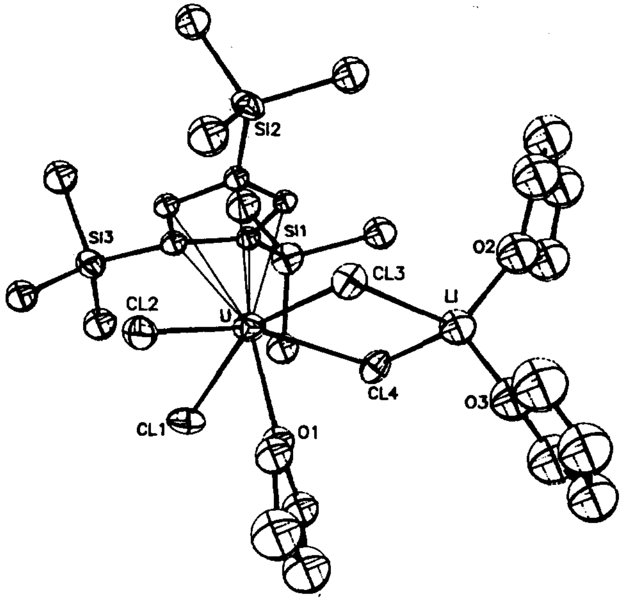

Fig. 153. Cp'''$UCl_2(THF)(\mu-Cl)_2Li(THF)_2$. (Reprinted with permission from Inorganica Chimica Acta.)

Sattelberger, et al.[335] discussed the preparation and use of $UI_3(THF)_4$ in organouranium chemistry. The compound $Cp^*UI_2(THF)_3$ was prepared by reaction of the reagent with KCp^* in THF.

Sattelberger, Gilbert, and Ryan[336] reacted $(COT)ThCl_2(THF)_2$ with $Cp^*MgCl(THF)$ in toluene to produce the mixed ring $Cp^*(COT)$-$ThCl(THF)_n$. Treatment with Me_3CCH_2MgCl in THF/OEt_2 produced $Cp^*(COT)Th(\mu-Cl)_2Mg(CH_2CMe_3)(THF)$ (Figure 154, Th-centroid(Cp^*) = 2.54Å, Th-centroid(COT) = 2.02Å, Th-Cl = 2.890(6)Å). Metathesis reactions of $Cp^*(COT)ThCl(THF)_n$ led to $Cp^*(COT)ThN(SiMe_3)_2$ and $Cp^*(COT)ThCH(SiMe_3)_2$. The latter was structurally characterized (Figure 155, Th-centroid(Cp^*) = 2.54Å, Th-centroid(COT) = 2.03Å, Th-C(σ) = 2.54(1)Å). An agostic Th···H-C interaction was proposed.

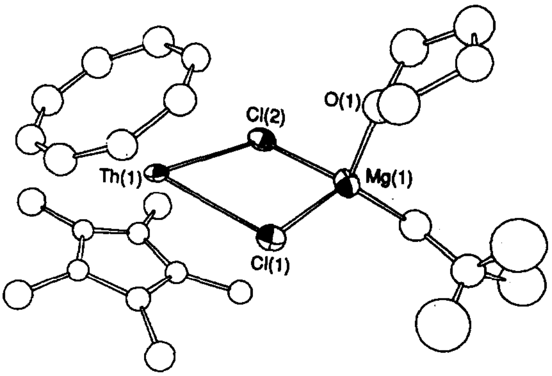

Fig. 154. $Cp^*(COT)Th(\mu-Cl)_2Mg(CH_2CMe_3)(THF)$. (Reprinted with permission from Organometallics. Copyright 1989 American Chemical Society.)

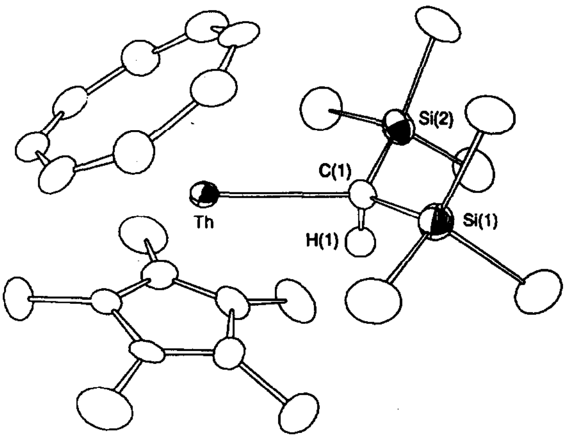

Fig. 155. $Cp^*(COT)ThCH(SiMe_3)_2$. (Reprinted with permission from Organometallics. Copyright 1989 American Chemical Society.)

Zanella, et al.[273] prepared and studied $CpU(BH_4)_3$ and $(CpMe)U(BH_4)_3$. Ryan et al.[337] prepared $[Na(THF)_6][Cp^*U(BH_4)_3]_2$ by reaction of $U(BH_4)_3(THF)_n$ with $Cp^*_2Th(PPh_2)_2$. The crystal structure is shown in Figure 156 ($U-C(Cp^*) = 2.74Å$, $U\cdots B = 2.61Å$). The BH_4^- ligands are tridentate.

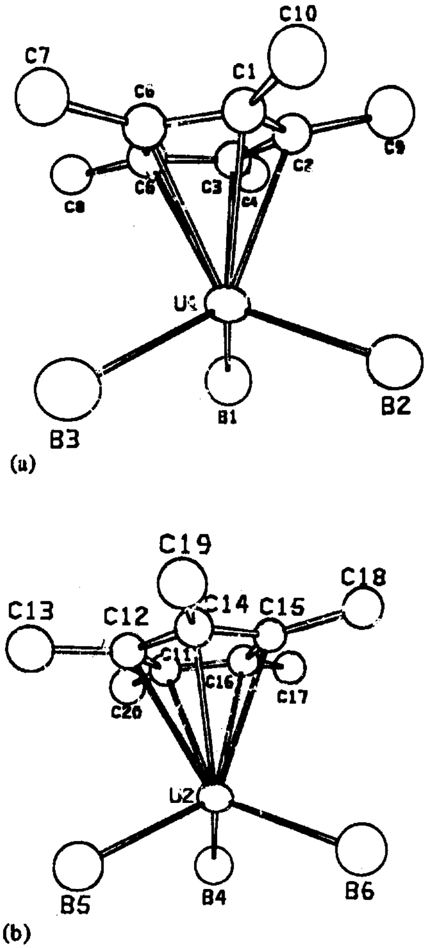

Fig. 156. The mixed valent anions in $[Na(THF)_6][Cp^*U(BH_4)_3]_2$. (Reprinted with permission from <u>Inorganica Chimica Acta</u>.)

Ephritikhine, <u>et</u> <u>al</u>. published two reports on derivatives of $U(BH_4)_4$. The synthesis and characterization of $CpU(BH_4)_3$ from the reaction of $U(BH_4)_4$ with TlCp was in one.[338] The second[339] focused on the structure and ligand exchange reactions of $CpU(BH_4)_3L_2$ (L = THF, dme, hexamethylphosphoramide, $OPPh_3$) in solution. A third contribution by these authors[340] reported the crystal structure of $CpUCl(acac)_2(OPPh_3)\cdot THF$ (Figure 157, U-C(Cp) = 2.79(1)Å, U-O(acac) = 2.35(1)Å, U-Cl = 2.662(8)Å, U-O($OPPh_3$) = 2.40(1)Å).

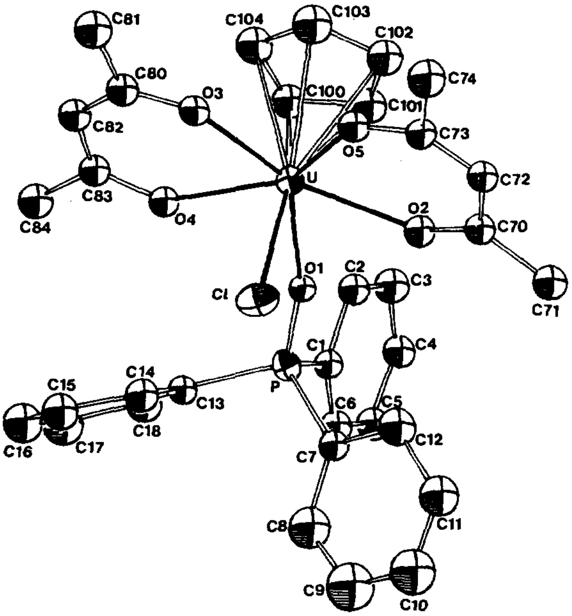

Fig. 157. CpUCl(acac)$_2$(OPPh$_3$)·THF. (Reprinted with permission from Journal of Organometallic Chemistry.)

The anion in [Cp$_3$U(NCMe)$_2$][CpThCl$_4$(NCMe)] published by Rebizant[280] (and discussed earlier) exhibited bonding parameters of Th-C(Cp) = 2.77(3)Å, Th-Cl = 2.658(8)Å, and Th-N = 2.58(3)Å (Figure 158).

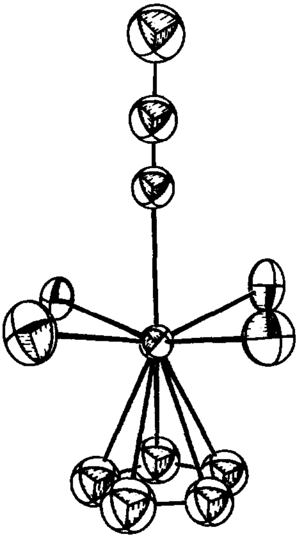

Fig. 158. The anion in $[Cp_3U(NCMe)_2][CpThCl_4(NCMe)]$. (Reprinted with permission from Inorganica Chimica Acta.)

Marques, et al.[341] briefly reviewed their work with pyrazolyl ligands and U^{4+}, Th^{4+}. The compounds discussed included $CpAnCl[HB(3,5\text{-}Me_2pyrazolyl)_3](OR)$ (An = Th, U; R = ^tBu, ^iPr, $C_6H_2\text{-}2,4,6\text{-}Me_3$). Brianese, et al.[342] reported the preparation of $[Cp(CH_3COO)_5U_2O]_2$ by reaction of $[Cp_2U(AlH_4)_2]\cdot nEt_2O$ with CH_3COOH. Its crystal structure (Figure 159) revealed both inorganic and organometallic uranium within the four metal cluster. Synthetic routes to $[Cp_2U(AlH_4)_2NEt_2]Li$ and $[Cp_2U(AlH_4)_2]\cdot nEt_2O$ from $Cp_2U(NEt_2)_2$ or $Cp_2U(BH_4)_2$ and $LiAlH_4$ were also detailed.

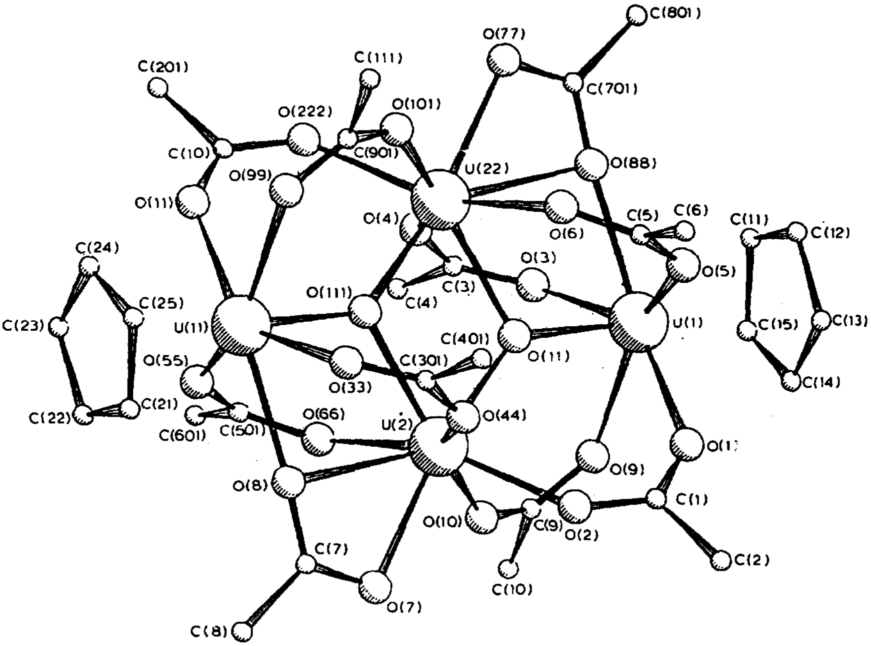

Fig. 159. [Cp(CH$_3$COO)$_5$U$_2$O]$_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Baudry, et al.[343] published the synthesis of [Na(18-crown-6)][Cp$_2$U(BH$_4$)$_2$] from the sodium amalgam reduction of Cp$_2$U(BH$_4$)$_2$. The crystal structure of CpU(BH$_4$)$_3$ (Figure 160) was also reported.

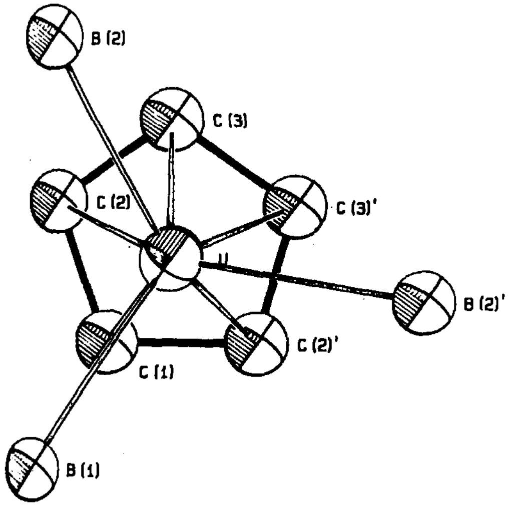

Fig. 160. $CpU(BH_4)_3$. (Reprinted with permission from <u>Journal of Organometallic Chemistry</u>.)

(xv) <u>Indenyl compounds</u>. The crystal structures of $(\eta^3$-Ind$)_3$UX (X = Br,[344] I[345]) and $(\eta^5$-Ind$)_2U(BH_4)_2$[346] were published by Goffart, <u>et al</u>. The two trisindenyl compounds are geometrically similar but not isostructural. The bromo analog is depicted in Figure 161 (X = Br: U-Br = 2.747(2)Å, U-C(η^3-Ind) = 2.68(6)-2.91(3)Å; X = I: U-I = 3.041(1)Å, U-C(η^3-Ind) = 2.57(7)-2.85(2)Å). The borohydride exhibits pentahapto indenyls (U-C = 2.62(2)-2.82(2)Å), and tridentate BH_4 coordination (Figure 162).

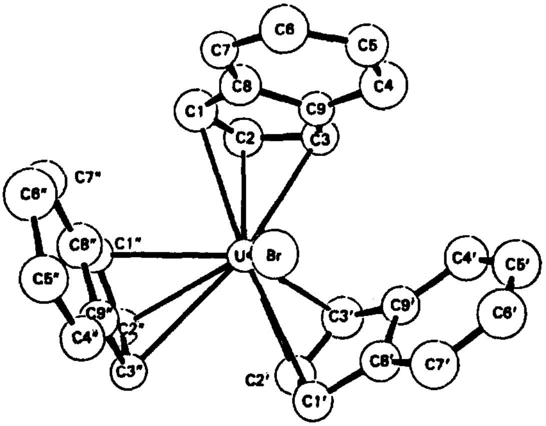

Fig. 161. $(\eta^3$-Ind$)_3$UBr. (Reprinted with permission from <u>Acta Crystallographica</u>.)

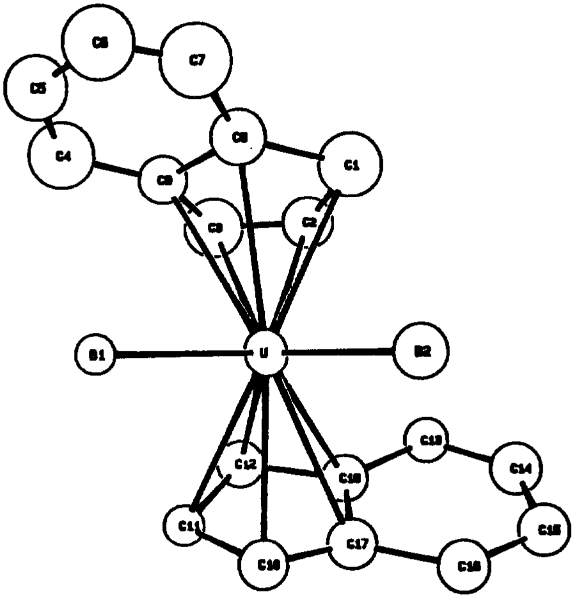

Fig. 162. $(\eta^5\text{-Ind})_2U(BH_4)_2$. (Reprinted with permission from <u>Acta Crystallographica</u>.)

Beeckman and Goffart[347] recorded the $N_2(\ell)$ and $He(\ell)$ temperature spectra of $(1\text{-EtInd})_3UCl$. The parameters obtained were used to calculate the temperature dependence of the paramagnetic susceptibility. Goffart, <u>et</u> <u>al</u>.[348] reported a new preparation of $(Ind)_4Th$ by treatment of $(Ind)_3ThCl$ with potassium metal in boiling benzene. They also published bond disruption enthalpies for $(Ind)_3AnR$ and $(1\text{-EtInd})_3AnR$ (An = U, Th; R = Me, $CH_2C_6H_5$, CH_2SiMe_3, $CHMe_2$, OCH_2CF_3).[349]

(xvi) <u>Cyclooctatetraene compounds</u>. The crystal structures and chemistry of mixed Cp*COT Th compounds including Cp*(COT)Th-CH$(SiMe_3)_2$ and Cp*(COT)Th$(\mu\text{-Cl})_2$Mg(CH_2CMe_3)(THF) were discussed in section (xiv).[336] REX calculations mentioned in section (i) for Cp_4An were also discussed for $(COT)_2An$.[257] ^{237}Np Mössbauer data were reported for $(COT)_2Np$[256,271] and K[$(COT)_2Np$].[271] ^1H NMR spectra of solid powders of $(COT)_2U$ were measured as discussed for Cp_3UCl in section (iii).[268,269]

Boerrigter, <u>et</u> <u>al</u>.[350] published the results of a relativistic LCAO Hartree-Fock-Slater investigation of the electronic structures of $(COT)_2An$ (An = Th, Pa, U, Np, Pu). Chang and Pitzer[351] computed the wave functions and energy levels for $(COT)_2U$ using ab initio techniques which included spin-orbit interaction and relativistic core potentials.

Leonov, et al.[302] studied complex formation of $(COT)_2U$ with N_2 and CO at 80K by IR. Kuznetsov, et al.[352] determined the heats of combustion, fusion, and evaporation of 1,1'-dibutyluranocene. Streitwieser, et al.[353] prepared 1,1',5,5'-tetra-tert-butyluranocene. Cloke, et al.[354,185] prepared the sandwich compounds $(1,4\text{-}(SiMe_3)_2C_8H_6)_2An$ (An = Th, U) and $(1,4\text{-}(SiMe_3)_2C_8H_6)U(\eta^3\text{-}BH_4)_2$.

Gilbert, Ryan, and Sattelberger[355] described an improved synthesis of $(COT)ThCl_2(THF)_2$. Reaction of $NaN(SiMe_3)_2$ with this compound or its U analog produced $(COT)An[N(SiMe_3)_2]_2$. The crystal structure of An = Th was determined (Th-C(COT) = 2.75(2)Å, Th-N = 2.34(1)Å). Agostic Th···HCSi interactions were noted.

(xvii) Arene and pentadienyl compounds. $(\eta^6\text{-}C_6Me_6)U(AlCl_4)_3$ was prepared.[201] The crystal structure is similar (but not isostructural) with the Sm analog shown in Figure 99[201] (U-C(η^6) = 2.94(3)Å). Sattelberger, et al.[356] crystallized $U(O\text{-}2,6\text{-}R_2C_6H_3)_3$ (R = ^{t}Bu, ^{i}Pr) from the reaction of $U[N(SiMe_3)_2]_3$ with the corresponding alcohol. The R = ^{i}Pr derivative was structurally characterized (Figure 163) and possesses an η^6-arene bridge (U-C(η^6) = 2.92(2)Å).

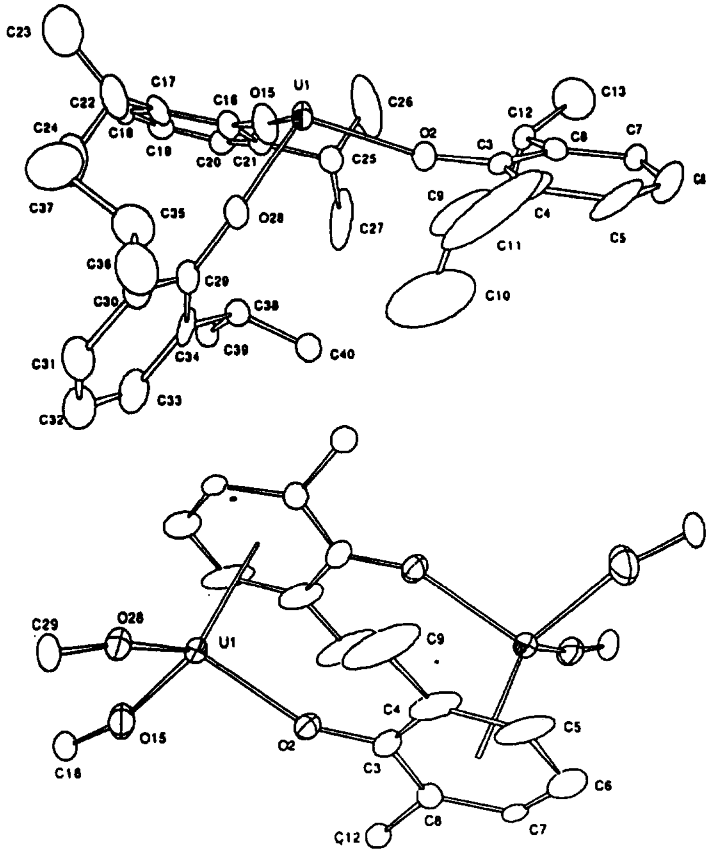

Fig. 163. U(O-2,6-$^{i}Pr_2C_6H_3)_3$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1988 American Chemical Society.)

Baudry, et al.[357,358,343] reported the preparation of (η^6-mesitylene)U$(BH_4)_3$ (Figure 164 by x-ray analysis) by thermal decomposition of U$(BH_4)_4$ in mesitylene. In toluene the reaction of U$(BH_4)_4$ with potassium dienylanions produced (η^5-2,4-dimethylpentadienyl)U$(BH_4)_3$ crystal structure - Figure 165 and (η^5-6,6-dimethylcyclohexadienyl)$_2$U$(BH_4)_2$.[343] Reactions of the homoleptic uranium pentadienyls with Tl(BH_4) produced (η^5-2,4-dimethylpentadienyl)$_2$U$(BH_4)_2$ and (η^5-6,6-dimethylcyclohexadienyl)U$(BH_4)_3$. In a second publication with Ephritikhine,[359] cationic and anionic forms of these compounds were isolated. Sattelberger, et al.[335]

prepared (η^5-2,4-dimethylpentadienyl)$_3$U by utilizing UI$_3$(THF)$_4$.

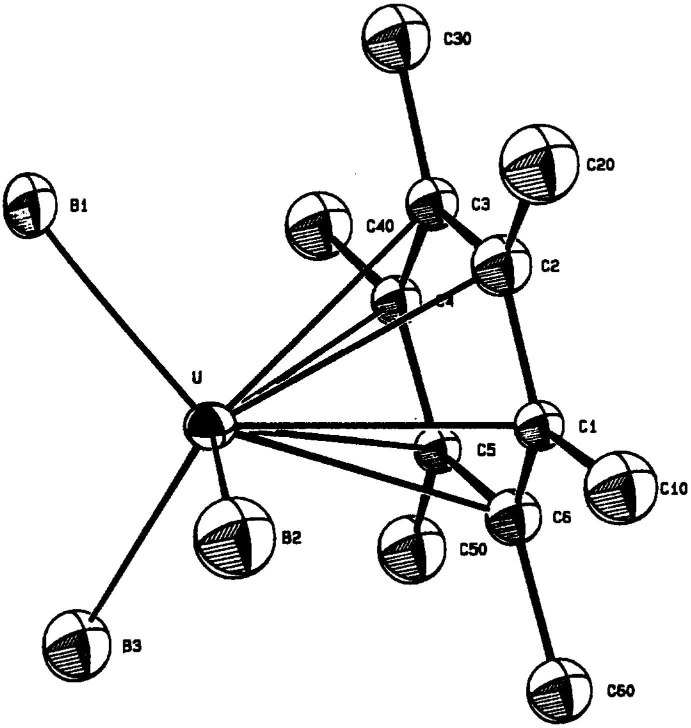

Fig. 164. (η^6-mesitylene)U(BH$_4$)$_3$. (Reprinted with permission from Journal of Organometallic Chemistry.)

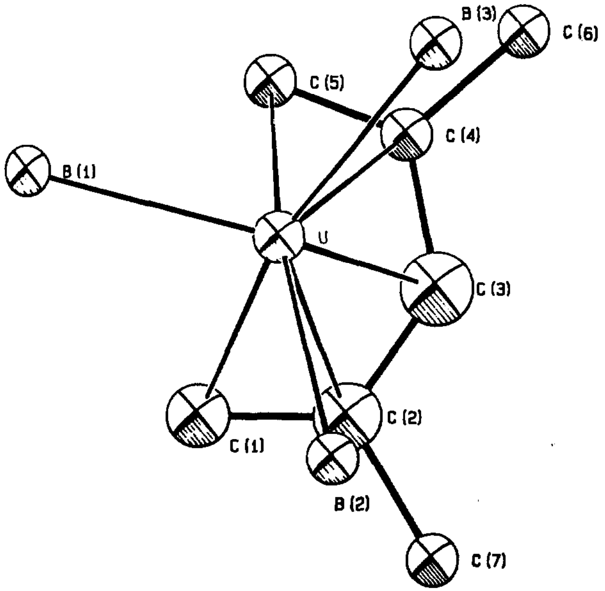

Fig. 165. (η^5-2,4-dimethylpentadienyl)U(BH_4)$_3$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Alkyl and allyl compounds without cyclopentadienyl ligands

Andersen and Stewart[360] published the reaction of LiMe and U[OCH(CMe_3)$_2$]$_4$ which yielded UMe[OCH(CMe_3)$_2$]$_2$[μ-OCH(CMe_3)$_2$]$_2$Li. The crystal structure revealed a square pyramidal geometry at U with U-Me = 2.465(7)Å (Figure 166, U-O(μ) = 2.262(4)Å, U-O(terminal) = 2.103(2)Å).

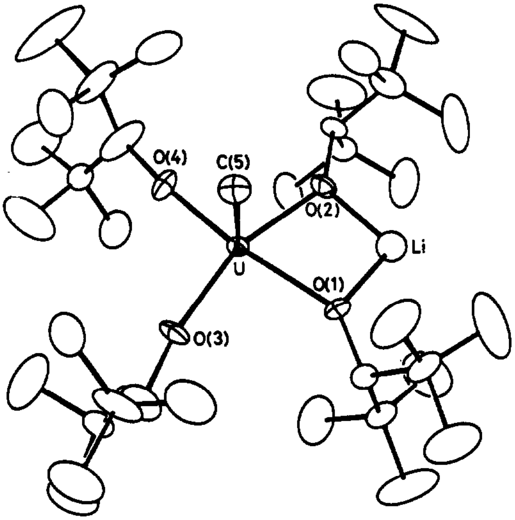

Fig. 166. $UMe[OCH(CMe_3)_2]_2[\mu\text{-}OCH(CMe_3)_2]_2Li$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

Sattelberger, et al.[361] studied the reaction of $U(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_3$ with $LiCH(SiMe_3)_2$ which produced the first homoleptic uranium alkyl, $U[CH(SiMe_3)_2]_3$. The crystal structure (Figure 167) revealed a U-C(σ) bond length of 2.48(2)Å and probable γ-agostic interactions with some of the methyl groups. The compound could not be prepared from $UCl_3(THF)_n$ and $LiCH(SiMe_3)_2$, however, $[Li(THF)_3][UCl(CH(SiMe_3)_2)_3]$ was isolated from this reaction.

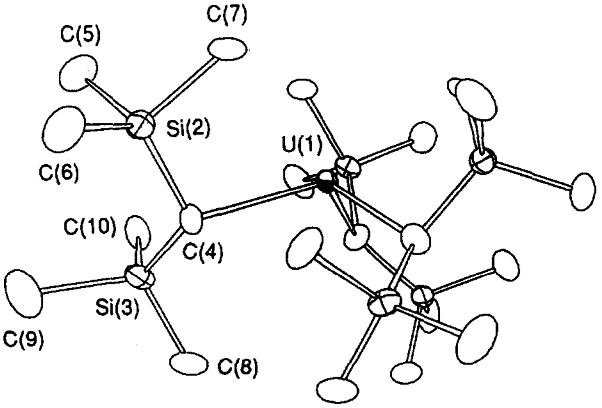

Fig. 167. $U[CH(SiMe_3)_2]_3$. (Reprinted with permission from <u>Organometallics</u>. Copyright 1989 American Chemical Society.)

Rothwell, <u>et</u> <u>al</u>.[362] prepared $ThCl_2(CH_2$-py-6Me$)_2$ from $ThCl_4$ and excess $LiCH_2$-py-6Me (CH_2-py-6Me = 2-(6-methylpyridyl)methyl). Further reaction with LiOAr' (OAr' = 2,6-di-<u>tert</u>-butylphenoxide) yielded Th(OAr'$)_2(CH_2$-py-6Me$)_2$. The crystal structure of this compound (Figure 168) revealed both pyridyl ligands to be chelating (Th-C = 2.55(1)Å, Th-N = 2.61(1)Å, Th-O = 2.190(9)Å).

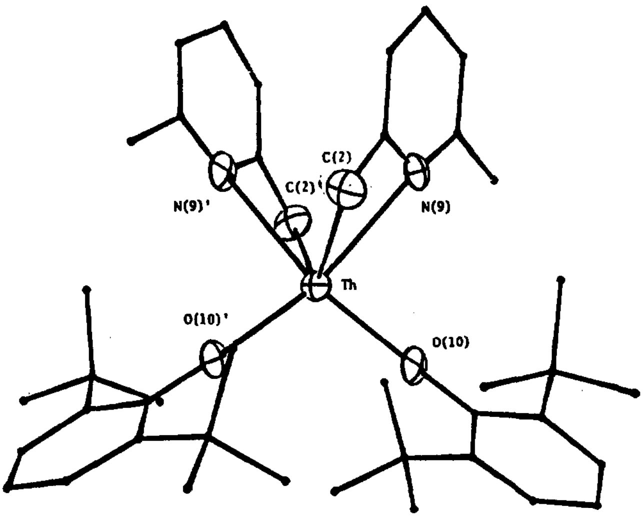

Fig. 168. Th(OAr'$)_2(CH_2$-py-6Me$)_2$. (Reprinted with permission from <u>Organometallics</u>. Copyright 1987 American Chemical Society.)

Ephritikhine and Baudin[363] prepared the compounds $U(^tBu_3CO)_2L_2$ ($L = CH_2Ph$, $\eta^3-C_3H_5$). Toropov, et al.[364] studied the reaction of $(\eta^3-C_3H_4)_4U$ with $OP(OBu)_3$.

Dormond, et al. published several accounts of the reactivity of the U-C sigma bond and its utility in organic reactions. A brief overview of this work with insertion reactions and nucleophilic substitution reactions in $UMe[N(SiMe_3)_2]_3$ and $UCH_2SiMe_2NSiMe_3[N(SiMe_3)_2]_2$ can be found in reference 365. The latter compound is the focus of four other publications, one[366] on its use as a mild reagent for the synthesis of methyl ketones from nitriles, another[367] on methylenation of carbonyl compounds, and two additional publications[368,369] on the insertion reactions of this metallocycle with polycyclic ketones and cyclohexanones. Two other publications[333,370] highlighted $UMe[N(SiMe_3)_2]_3$ as a highly selective nucleophile in chemo- and stereoselective alkylation reactions of carbonyl compounds.

REFERENCES

1. R.D. Ernst and T.J. Marks, J. Organomet. Chem., 318 (1987) 29.
2. J.D. Miller, Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem., 83 (1986) 357-379.
3. J.D. Miller, Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem., 84 (1987) 285-305.
4. M.J. Winter, Organomet. Chem., 15 (1987) 229-264.
5. M.J. Winter, Organomet. Chem., 18 (1989) 200-237.
6. M.J. Winter, Organomet. Chem., 17 (1989) 206-243.
7. W.J. Evans, Polyhedron, 6 (1987) 803-835.
8. W.J. Evans, ACS Symp. Ser., 333 (1987) 278-289.
9. I.P. Beletskaya, G.Z. Suleimanov, Metalloorg. Khim., 1 (1988) 10-24.
10. S.J. Swamy, Proc. Indian Natl. Sci. Acad., Part A, 55 (1989) 261-272.
11. G.-X. Xu, J. Ren, C.-H. Huang and J.-G. Wu, Pure & Appl. Chem., 60 (1988) 1145-1152.
12. Q. Shen, W. Chen, Y. Jin and C. Shan, Pure & Appl. Chem., 60 (1988) 1251-1256.
13. M.N. Bochkarev, Proc. Indian Natl. Sci. Acad., Part A, 55 (1989) 170-187.
14. V.M. Bulychev, G.L. Soloveichik, V.K. Bel'skii and A.I. Sizov, Metallorg. Khim., 2 (1989) 82-92.
15. W.J. Evans and M.A. Hozbor, J. Organomet. Chem., 326 (1987) 299-306.
16. H.B. Kagan, Inorg. Chim. Acta, 140 (1987) 3-6.
17. H.B. Kagan, M. Sasaki and J. Collin, Pure & Appl. Chem., 60 (1988) 1725-1730.
18. B.E. Kahn and R.D. Rieke, Chem. Rev., 88 (1988) 733-745.
19. M.N. Bochkarev, G.S. Kalinina, L.N. Zakharov and S. Ya, Organic Derivatives of Rare Earth Elements, Moscow, USSR, 1989.

20. I.P. Rothwell, Act. Funct. Alkanes, in: C.L. Hill (Ed.), New York, N.Y., 1989, pp. 151-194.
21. T.J. Marks, M.R. Gagne, S.P. Nolan, L.E. Schock, A.M. Seyam and D. Stern, Pure Appl. Chem. 61 (1989) 1665-1672.
22. A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson and R. Taylor, J.C.S., Dalton Trans., (1989) S1-S83.
23. J. Marcalo and A. Pires de Matos, Polyhedron, 8 (1989) 2431-2437.
24. C.J. Burns and B.E. Bursten, Comments Inorg. Chem., 9 (1989) 61-93.
25. G. Yang, Y. Fan, Z. Jin, Y. Xing and W. Chen, J. Organomet. Chem., 322 (1987) 57-63.
26. S.J. Swamy and H. Schumann, J. Organomet. Chem., 334 (1987) 1-7.
27. H. Schumann, I. Albrecht, M. Gallagher, E. Hahn, C. Janiak, C. Kolax, J. Loebel, S. Nickel and E. Palamidis, Polyhedron, 7 (1988) 2307-2315.
28. J. Zhongsheng, H. Ninghai, L. Yi, X. Xiaolong and L. Guozhe, Inorg. Chim. Acta, 142 (1988) 333-336.
29. Y. Li, X. Xu and G. Liu, Youji Huaxue, 8 (1988) 43-45.
30. X. Li, J. Liu and G. Liu, Yingyong Huaxue, 6 (1989) 62-64.
31. R. Zhang, G. Yu and T. Ye, Zhenkong Kexue Yu Jishu, 8 (1988) 89-90.
32. G. Nie, J. Wang and W. Chen, Yingong Huaxue, 6 (1989) 60-62.
33. Y. Wang, W. Chen and B. Zhang, Yingyong Huazue, 6 (1989) 37-41.
34. A. Zalkin and D. Berg, Acta Cryst., C45 (1989) 1630-1631.
35. C.J. Burns, D.J. Berg and R.A. Andersen, J.C.S., Chem. Comm., (1987) 272-273.
36. A.L. Wayda, J. Organomet. Chem., 361 (1989) 73-78.
37. P.N. Hazin, J.C. Huffman and J.W. Bruno, Organometallics, 6 (1987) 23-27.
38. P.S. Gradeff, K. Yunlu, T.J. Deming, J.M. Olofson, J.W. Ziller and W.J. Evans, Inorg. Chem., 28 (1989) 2600-2604.
39. H. Ma and X. Ye, J. Organomet. Chem., 326 (1987) 369-374.
40. L. Yang, L. Dai, H. Ma and Z. Ye, Organometallics, 8 (1989) 1129-1133.
41. Z. Ye, Y. Yu and H. Ma, Polyhedron, 7 (1988) 1095-1100.
42. Z. Ye and Z. Wu, Synth. React. Inorg. Met.-Org. Chem., 19 (1989) 157-168.
43. Z. Wu, Z. Ye and Z. Zhou, Polyhedron, 8 (1989) 2109-2113.
44. K. Jacob, M. Glanz, K. Tittes and K.-H. Thiele, Z. Anorg. Allg. Chem., 556 (1988) 170-178.
45. H.J. Heeres, A. Meetsma and J.H. Teuben, J.C.S., Chem. Comm., (1988) 962-963.
46. H.J. Heeres, A. Meetsma, J.H. Teuben and R.D. Rogers, Organometallics, 8 (1989) 2637-2646.
47. H.J. Heeres, J.H. Teuben and R.D. Rogers, J. Organomet. Chem., 364 (1989) 87-96.
48. M.Booij, N.H. Kiers, H.J. Heeres and J.H. Teuben, J. Organomet. Chem., 364 (1989) 79-86.
49. H. van der Heijden, C.J. Schaverien and A.G. Orpen, Organometallics, 8 (1989) 255-258.

50. C.J. Schaverien, H. van der Heijden and A.G. Orpen, Polyhedron, 8 (1989) 1850-1852.
51. H. van der Heijden, P. Pasman, E.J.M. de Boer, C.J. Schaverien and A.G. Orpen, Organometallics, 8 (1989) 1459-1467.
52. M. Booij, N.H. Kiers, A. Meetsma, J.H. Teuben, W.J.J. Smeets and A.L. Spek, Organometallics, 8 (1989) 2454-2461.
53. H. Schumann, R.D. Koehn, F.W. Reier, A. Dietrich and J. Pickardt, Organometallics, 8 (1989) 1388-1392.
54. H. Schumann, C. Janiak, R.D. Kohn, J. Loebel and A. Dietrich, J. Organomet. Chem., 365 (1989) 137-150.
55. P. Bruin, M. Booij, J. H. Teuben and A. Oskam, J. Organomet. Chem., 350 (1988) 17-23.
56. H. Schumann, J.A. Meese-Marktscheffel and A. Dietrich, J. Organomet. Chem., 377 (1989) C5-C8.
57. E.B. Lobkovskii, A.N. Chekhlov, S.Y. Knyazhanskii, B.M. Bulychev and G.L. Soloveichik, Metalloorg. Khim., 2 (1989) 1190-1191.
58. P.N. Hazin, J.W. Bruno and H.G. Brittain, Organometallics, 6 (1987) 913-918.
59. K. Jacob, J. Glanz, K. Tittes, K.-H. Thiele, I. Pavlik and A. Lycka, Z. Anorg. Allg, Chem., 577 (1989) 145-154.
60. Y.B. Zverev, I.V. Runovskaya, S.G. Chesnokova, N.P. Chernyaev and P.E. Gaivoronskii, Vysokochist. Veshchestva, 6 (1988) 141-143.
61. H.D. Kaesz (Ed.) Inorganic Synthesis, 29, John Wiley & Sons, Inc., New York, 1989, pp. 17-23.
62. J. Rebizant, C. Apostolidis, M.R. Spirlet and B. Kanellakopulos, Acta Cryst., C44 (1988) 614-616.
63. S.H. Eggers, J. Kopf and R.D. Fischer, Acta Cryst., C43 (1987) 2288-2290.
64. A Hammel, W. Schwarz and J. Weidlein, J. Organomet. Chem., 363 (1989) C29-C35.
65. W.J. Evans and T.A. Ulibarri, J. Am. Chem. Soc., 109 (1987) 4292-4297.
66. G.K. Borisov, A.I. Kuz'michev, N.N. Ryzhikova and V.N. Sinev, Zh. Obshch. Khim., 58 (1988) 71-76.
67. G. Paolucci, R.D. Fischer, H. Breitbach, B. Pelli and P. Traldi, Organometallics, 7 (1988) 1918-1923.
68. R.G. Bulgakov, S.P. Kuleshov, V.N. Khandozhko, I.P. Beletskaya, G.A. Tolstikov and V.P. Kazakov, Izv. Akad. Nauk SSSR, Ser. Khim., 8 (1988) 1937.
69. C. Qian, Y. Ge, D. Deng and Y. Gu, Huaxue Xuebao, 45 (1987) 210-212.
70. M.N. Bochkarev, A.A. Trifonov, G.A. Razuvaev, M.A. Ilatovskaya, V.B. Shur and M.E. Vol'pin, Dokl. Akad. Nauk SSSR, 295 (1987) 1381-1384.
71. J. Weber, A. Molassioti, M. Moser, A. Stapor, F. Scholz, G. Horcher, A. Forchel, A. Hammel, G. Laube and J. Weidlein, Appl. Phys. Lett, 53 (1988) 2525-2527.
72. S.H. Eggers, M. Adam, E.T.K. Haupt and R.D. Fischer, Inorg. Chim. Acta, 139 (1987) 315-318.
73. J.G. Brennan, S.D. Stults, R.A. Andersen and A. Zalkin, Inorg. Chim. Acta, 139 (1987) 201-202.
74. H.-D. Amberger and H. Schultze, Spectrochim. Acta, 43A (1987) 1301-1306.

75. H.-D. Amberger, H. Schultze, H. Reddmann, G.V. Shalimoff and N.M. Edelstein, J. Less-Common Met., 149 (1989) 249-253.
76. G.B. Deacon, C.M. Forsyth, R.H. Newnham and T.D. Tuong, Aust. J. Chem., 40 (1987) 895-906.
77. G.B. Deacon, B.M. Gatehouse, S.N. Platts and D.L. Wilkinson, Aust. J. Chem., 40 (1987) 907-914.
78. M.R. Spirlet, J. Rebizant, C. Apostolidis and B. Kanellakopulos, Acta Cryst., C43 (1987) 2322-2324.
79. M.R. Spirlet, J. Rebizant, C. Apostolidis and B. Kanellakopulos, Inorg. Chim. Acta, 139 (1987) 211-213.
80. H. Schumann, C. Janiak and J. Pickardt, J. Organomet. Chem., 349 (1988) 117-122.
81. S. Stults and A. Zalkin, Acta Cryst., C43 (1987) 430-432.
82. J.G. Brennan, S.D. Stults, R.A. Andersen and A. Zalkin, Organometallics, 7 (1988) 1329-1334.
83. A. Gulino, M. Casarin, V.P. Conticello, J.G. Gaudiello, H. Mauermann, I. Fragala and T.J. Marks, Organometallics, 7 (1988) 2360-2364.
84. W.J. Evans, T.J. Deming and J.W. Ziller, Organometallics, 8 (1989) 1581-1583.
85. R.G. Bulgakov, S.P. Kuleshov, V.N. Khandozhko, I.P. Beletskaya, G.A. Tolstikov and V.P. Kazakov, Izv. Akad. Nauk SSSR, Ser. Khim., 7 (1988) 1689-1690.
86. H. Gao, Q. Shen, J. Hu, S. Jin and Y. Lin, Chin. Sci. Bull., 34 (1989) 614.
87. W.J. Evans, Inorg. Chim. Acta, 139 (1987) 169-170.
88. W.J. Evans and T.A. Ulibarri, Polyhedron, 8 (1989) 1007-1014.
89. S.J. Swamy, J. Loebel, J. Pickardt and H. Schumann, J. Organomet. Chem., 353 (1988) 27-34.
90. G.B. Deacon, D.L. Wilkinson and R.L. Davis, Inorg. Chim. Acta, 142 (1988) 329-331.
91. A. Hammel, W. Schwarz and J. Weidlein, J. Organomet. Chem., 378 (1989) 347-361.
92. R.A. Andersen, R. Blom, J.M. Boncella, C.J. Burns and H.V. Volden, Acta Chem. Scand., A41 (1987) 24-35.
93. C.J. Burns and R.A. Andersen, J.C.S., Chem. Comm., (1989) 136-137.
94. G.B. Deacon, B.M. Gatehouse and P.A. White, Polyhedron, 8 (1989) 1983-1987.
95. H. Lueken, W. Lamberts and P. Hannibal, Inorg. Chim. Acta, 132 (1987) 111-118.
96. H. Lueken, J. Schmitz, W. Lamberts, P. Hannibal and K. Handrick, Inorg. Chim. Acta, 156 (1989) 119-124.
97. W. Lamberts, H. Lueken and B. Hessner, Inorg. Chim. Acta, 134 (1987) 155-157.
98. W. Lamberts and H. Lueken, Inorg. Chim. Acta, 132 (1987) 119-122.
99. W. Lamberts, B. Hessner and H. Lueken, Inorg. Chim. Acta, 139 (1987) 215-217.
100. G.Z. Suleimanov and I.P. Beletskaya, Metalloorg. Khim., 2 (1989) 704.
101. W.J. Evans, D.K. Drummond, J.W. Grate, H. Zhang and J.L. Atwood, J. Am. Chem. Soc., 109 (1987) 3928-3936.
102. Q. Shen and P. Zhou, Kexue Tongbao, 32 (1987) 28-30.
103. K.H. den Haan and J.H. Teuben, J. Organomet. Chem., 322 (1987) 321-329.

104. W.J. Evans, J.M. Olofson, H. Zhang and J.L. Atwood, Organometallics, 7 (1988) 629-633.
105. L. Gong, A. Streitwieser, Jr. and A. Zalkin, J.C.S., Chem. Comm., (1987) 460-461.
106. H. Schumann, J. Loebel, D. van der Helm and M.B. Hossain, Z. Naturforsch., (1988) 323-327.
107. Z. Jin, Y. Liu and W. Chen, Sci. Sin., Ser. B, 30 (1988) 1136-1143.
108. H. Yasuda, H. Yamamoto, K. Yokota and A. Nakamura, Chem. Lett., (1989) 1309-1312.
109. V.K. Bel'skii, S.U. Knyazhanskii, B.M. Bulychev and G.L. Soloveichik, Metalloorg. Khim., 2 (1989) 567-569.
110. Y.K. Gun'ko, V.K. Bel'skii, A.I. Sizov, B.M. Bulychev and G.L. Soloveichik, Metalloorg. Khim., 2 (1989) 1125-1128.
111. V.K. Bel'skii, S.Y. Knyazhanskii, B.M. Bulychev and G.L. Soloveichik, Metalloorg. Khim., 2 (1989) 754-756.
112. S.P. Nolan, D. Stern and T.J. Marks, J. Am. Chem. Soc., 111 (1989) 7844-7853.
113. L. Shi, H. Ma, Y. Yu and Z. Ye, J. Organomet. Chem., 339 (1988) 277-282.
114. F. Shen and Z. Ye, Youji Huaxue, (1987) 128-132.
115. R. Chen, Z. Gu, J. Zhu and Z. Ye, Zhongguo Xita Xuebao, 6 (1988) 85-87.
116. W.J. Evans, D.K. Drummond, L.A. Hughes, H. Zhang and J.L. Atwood, Polyhedron, 7 (1988) 1693-1703.
117. W.J. Evans, M.A. Hozbor, S.G. Bott, G.H. Robinson and J.L. Atwood, Inorg. Chem., 27 (1988) 1990-1993.
118. G.B. Deacon and D.L. Wilkinson, Aust. J. Chem., 42 (1989) 845-854.
119. R.G. Finke, S.R. Keenan, D.A. Schiraldi and P.L. Watson, Organometallics, 6 (1987) 1356-1358.
120. J.L. Namy, J. Collin, J. Zhang and H.B. Kagan, J. Organomet. Chem., 328 (1987) 81-86.
121. A.A. Trifonov, M.N. Bochkarev and G.A. Razuvaev, Zh. Obshch. Khim., 58 (1988) 931-932.
122. A.F. Williams, F. Grandjean, G.J. Long, T.A. Ulibarri and W.J. Evans, Inorg. Chem., 28 (1989) 4584-4588.
123. G. Fu, Y. Xu, Z. Xie and C. Qian, Acta Chim. Sin., (1989) 431-436.
124. A. Zalkin, T.J. Henly and R.A. Andersen, Acta Cryst., C43 (1987) 233-236.
125. P.N. Hazin, C. Lakshminarayan, L.S. Brinen, J.L. Knee, J.W. Bruno, W.E. Streib and K. Folting, Inorg. Chem., 27 (1988) 1393-1400.
126. W.J. Evans, D.K. Drummond, J. Am. Chem. Soc., 111 (1989) 3329-3335.
127. A.G. Avent, M.A. Edelman, M.F. Lappert and G.A. Lawless, J. Am. Chem. Soc., 111 (1989) 3423-3425.
128. W.J. Evans, T.A. Ulibarri and J.W. Ziller, J. Am. Chem. Soc., 110 (1988) 6877-6879.
129. W.J. Evans, D.K. Drummond, L.R. Chamberlain, R.J. Doedens, S.G. Bott, H. Zhang and J.L. Atwood, J. Am. Chem. Soc., 110 (1988) 4983-4994.
130. W.J. Evans and D.K. Drummond, J. Am. Chem. Soc., 110 (1988) 2772-2774.
131. I.P. Beletskaya, A.Z. Voskoboinikov and G.K. Magomedov, Metalloorg. Khim., 2 (1989) 808-809.
132. P.N. Hazin, J.C. Huffman and J.W. Bruno, J.C.S., Chem. Comm., (1988) 1473-1474.

133. I.P. Beletskaya, A.Z. Voskoboinikov, E.B. Chuklanova, A.I. Gusev and G.K. Magomedov, Metalloorg. Khim., 1 (1988) 1383-1390.
134. I.P. Beletskaya, A.Z. Voskoboinikov and G.K.-I. Magomedov, Dokl. Akad. Nauk SSSR, 306 (1989) 108-112.
135. G.K. Magomedov, A.Z. Voskoboinikov and I.P. Beletskaya, Metalloorg. Khim., 2 (1989) 823-825.
136. G.B. Deacon, A. Dietrich, C.M. Forsyth and H. Schumann, Angew. Chem., 101 (1989) 1374-1375.
137. H. Schumann, I. Albrecht, M. Gallagher, E. Hahn, C. Muchmore and J. Pickardt, J. Organomet. Chem., 349 (1988) 103-115.
138. H. Schumann, E. Palamidis, J. Loebel and J. Pickardt, Organometallics, 7 (1988) 1008-1010.
139. H. Schumann, S. Nickel, J. Loebel and J. Pickardt, Organometallics, 7 (1988) 2004-2009.
140. D.J. Berg, C.J. Burns, R.A. Andersen and A. Zalkin, Organometallics, 8 (1989) 1865-1870.
141. D.J. Berg, R.A. Andersen and A. Zalkin, Organometallics, 7 (1988) 1858-1863.
142. A. Zalkin and D.J. Berg, Acta Cryst., C44 (1988) 1488-1489.
143. A Recknagel, D. Stalke, H.W. Roesky and F.T. Edelmann, Angew. Chem. Int. Ed., 28 (1989) 445-446.
144. T.J. Marks, Inorg. Chim. Acta, 140 (1987) 1-2.
145. S.P. Nolan and T.J. Marks, J. Am. Chem. Soc., 111 (1989) 8538-8540.
146. K.H. den Haan, Y. Wielstra and J.H. Teuben, Organometallics, 6 (1987) 2053-2060.
147. C. Qian, D. Deng, C. Ni and Z. Zhang, Inorg. Chim. Acta, 146 (1988) 129-133.
148. W.J. Evans, M.S. Sollberger, S.I. Khan and R. Bau, J. Am. Chem. Soc., 110 (1988) 439-446.
149. W.J. Evans, D.K. Drummond, T.P. Hanusa and R.J. Doedens, Organometallics, 6 (1987) 2279-2285.
150. A.B. Erofeev, B.M. Bulychev, V.K. Bel'skii and G.L. Soloveichik, J. Organomet. Chem., 335 (1987) 189-199.
151. S.Y. Knjazhanski, B.M. Bulychev, V.K. Belsky and G.L. Soloveichik, J. Organomet. Chem., 327 (1987) 173-179.
152. S.Y. Knyazhanskii, V.K. Bel'skii, B.M. Bulychev and G.L. Soloveichik, Metalloorg. Khim., 2 (1989) 570-574.
153. I.P. Beletskaya, A.Z. Voskoboinikov and G.K. Magomedov, Metalloorg. Khim., 2 (1989) 810-813.
154. S.Y. Knyazhanskii, B.M. Bulychev and G.L. Soloveichik, Metalloorg. Khim., 2 (1989) 345-350.
155. C.J. Burns and R.A. Andersen, J. Am. Chem. Soc., 109 (1987) 5853-5855.
156. M.A. Busch, R. Harlow and P.L. Watson, Inorg. Chim. Acta., 140 (1987) 15-20.
157. W.J. Evans, L.R. Chamberlain, T.A. Ulibarri and J.W. Ziller, J. Am. Chem. Soc., 110 (1988) 6423-6432.
158. K.H. den Haan, J.L. de Boer, J.H. Teuben, W.J.J. Smeets and A.L. Spek, J. Organomet. Chem., 327 (1987) 31-38.
159. L. Arnaudet and B. Ban, New J. Chem., 12 (1988) 201-203.
160. K.H. den Haan, Y. Wielstra, J.J.W. Eshuis and J.H. Teuben, J. Organomet. Chem., 323 (1987) 181-192.
161. W.J. Evans, L.R. Chamberlain and J.W. Ziller, J. Am. Chem. Soc., 109 (1987) 7209-7211.
162. H. Yamamoto, H. Yasuda, K. Yokota, A. Nakamura, Y. Kai and N. Kasai, Chem. Let., (1988) 1963-1966.

163. H.J. Heeres, J. Renkema, M. Booij, A. Meetsma and J.H. Teuben, Organometallics, 7 (1988) 2495-2502.
164. R.G. Finke, S.R. Keenan and P.L. Watson, Organometallics, 8 (1989) 263-277.
165. C.J. Burns and R.A. Andersen, J. Am. Chem. Soc., 109 (1987) 915-917.
166. W.J. Evans, T.P. Hanusa, J.H. Meadows, W.E. Hunter and J.L. Atwood, Organometallics, 6 (1987) 295-301.
167. K.H. den Haan, G.A. Luinstra, A. Meetsma and J.H. Teuben, Organometallics, 6 (1987) 1509-1515.
168. C.J. Burns and R.A. Andersen, J. Am. Chem. Soc., 109 (1987) 941-942.
169. W.J. Evans, R.A. Keyer, H. Zhang and J.L. Atwood, J.C.S., Chem. Comm., (1987) 837-838.
170. W.J. Evans and D.K. Drummond, Organometallics, 7 (1988) 797-802.
171. W.J. Evans and D.K. Drummond, Organometallics, 8 (1988) 573.
172. W.J. Evans, D.K. Drummond, R.P. Hanusa and J.M. Olofson, J. Organomet. Chem., 376 (1989) 311-320.
173. G.B. Deacon and D.L. Wilkinson, Inorg. Chim. Acta, 142 (1988) 155-159.
174. Y. Li, X. Xu, L. Zhu and G. Liu, Yingyong Huaxue, 4 (1987) 82-85.
175. J. Collin, J.L. Namy, C. Beid and H.B. Kagan, Inorg. Chim. Acta, 140 (1987) 29-30.
176. Z. Zhennan, W. Zhongzhi, D. Baohu and Y. Zhongwen, Polyhedron, 8 (1989) 17-20.
177. C. Qian, Z. Xie and Y. Huang, Inorg. Chim. Acta, 139 (1987) 195-199.
178. C. Qian, Z. Xie and Y. Huang, J. Organomet. Chem., 323 (1987) 285-294.
179. C. Chen, X. Zhong, C. Qian, Z. Xie and Y. Huang, Youji Huaxue, 8 (1988) 235-237.
180. S.J. Swamy, J. Loebel and H. Schumann, J. Organomet. Chem., 379 (1989) 51-58.
181. A.L. Wayda, S. Cheng and I. Mukerji, J. Organomet. Chem., 330 (1987) C17-C19.
182. G. Qi and Q. Shen, Yingyong Huaxue, 5 (1988) 61-63.
183. D.C. Eisenberg, S.A. Kinsley and A. Streitwieser, J. Am. Chem. Soc., 111 (1989) 5769-5772.
184. A.L. Wayda, I. Mukerji, J.L. Dye and R.D. Rogers, Organometallics, 6 (1987) 1328-1332.
185. N.C. Burton, F.G.N. Cloke, P.B. Hitchcock, H.C. de Lemos and A.A. Sameh, J.C.S., Chem. Comm., (1989) 1462-1464.
186. K. Mashima and H. Takaya, Tetrahedron Lett., 30 (1989) 3697-3700.
187. H. Schumann, P.R. Lee and J. Loebel, Chem. Ber., 122 (1989) 1897-1900.
188. M.J. Manning, C.B. Knobler and M.F. Hawthorne, J. Am. Chem. Soc., 110 (1988) 4458-4459.
189. D.M. Schubert, M.J. Manning and M.F. Hawthorne, Phosphorus, Sulfur and Silica, 41 (1989) 253-266.
190. M. Khikmatov, V.V. Volkov, U. Mirsaidov and V.I. Budnikova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, (1988) 27-31.
191. V.N. Lebedev, N.F. Shemyakin, S.P. Solodovnikov and L.I. Zakharkin, Metalloorg. Khim., 1 (1988) 718.

192. M.A. Afonin, T.V. Dronova, A.A. Kopyrin, V.V. Korolev, A.V. Smirnov, L.N. Lazarev and V.N. Romanovskii, Radiokhim., 31 (1989) 79-83.
193. R.K. Sharma and C.P. Sharma, J. Indian Chem. Soc., 64 (1987) 506-507.
194. M. Chen, G. Wu, W. Wu, S. Zhuang and Z. Huang, Organometallics, 7 (1988) 802-806.
195. A. Zhou, Z. Wu, F. Zhao and X. Song, Youji Huaxue, 9 (1989) 230-232.
196. F. Nief and F. Mathey, J.C.S., Chem. Comm., (1989) 800-801.
197. J.C. Green, D. Hohl and N. Rösch, Organometallics, 6 (1987) 712-720.
198. Z. Li, W. Chen, G. Xu and J. Ren, Wuji Huaxue, 3 (1987) 111-114.
199. X. Li, X. Feng, Y. Xu, H. Wang, P. Sun and J. Shi, Kexue Tongbao, 32 (1987) 1259-1262.
200. C.W. Bauschlicher, Jr., S.R. Langhoff, H. Partridge and L.A. Barnes, J. Chem. Phys., 91 (1989) 2399-2411.
201. F.A. Cotton and W. Schwotzer, Organometallics, 6 (1987) 1275-1280.
202. B. Fan, Q. Shen and Y. Lin, Youji Huaxue, 9 (1989) 414-417.
203. J.G. Brennan, F.G.N. Cloke, A.A. Sameh and A. Zalkin, J.C.S., Chem. Comm., (1987) 1668-1669.
204. F.G.N. Cloke, K.A.E. Courtney, A.A. Sameh and A.C. Swain, Polyhedron, 8 (1989) 1641-1648.
205. D.M. Anderson, F.G.N. Cloke, P.A. Cox, N. Edelstein, J.C. Green, T. Pang, A.A. Sameh and G. Shalimoff, J.C.S., Chem. Comm., (1989) 53-55.
206. B. Fan, Q. Shen and Y. Lin, J. Organomet. Chem., 377 (1989) 51-58.
207. B. Fan, Q. Shen and Y. Lin, J. Organomet. Chem., 376 (1989) 61-66.
208. M.N. Bochkarev, A.A. Trifonov, V.K. Cherkasov and G.A. Razuvaev, Zh. Obshch. Khim., 58 (1988) 719-720.
209. M.N. Bochkarev, A.A. Trifonov, V.K. Cherkasov and G.A. Razuvaev, Metalloorg. Khim., 1 (1988) 392-396.
210. M.N. Bochkarev, E.A. Fedorov, I.M. Penyagina, O.A. Vasina, S.Y. Khorshev and A.V. Protchenko, Metalloorg. Khim., 2 (1989) 703.
211. E.A. Fedorova and O.A. Vasina, Metalloorg. Khim., 2 (1989) 392-394.
212. M.N. Bochkarev, I.M. Penyagina, L.N. Zakharov, Y.F. Rad'kov, E.A. Fedorova, S.Y. Khorshev and Y.T. Struchkov, J. Organomet. Chem., 378 (1989) 363-373.
213. M.N. Bochkarev, E.A. Fedorova, I.M. Penyagina, O.A. Vasina, A.V. Protchenko and S.Y. Khorshev, Metalloorg. Khim., 2 (1989) 1317-1319.
214. Y.F. Rad'kov, V.V. Khramenkov, L.N. Zakharov, Y.T. Struchkov, S.Y. Khorshev and M.N. Bochkarev, Metalloorg. Khim., 2 (1989) 1422-1427.
215. A.A. Trifonov, A.V. Protchenko, V.K. Gherkasov and M.N. Bochkarev, Metalloorg. Khim., 2 (1989) 471.
216. T.A. Basalgina, G.S. Kalinina and M.N. Bochkarev, Metalloorg. Khim., 2 (1989) 1142-1145.
217. M.N. Bochkarev, A.A. Trifonov, E.A. Fedorova, N.S. Emelyanova, T.A. Basalgina, G.S. Kalinina and G.A. Razuvaev, J. Organomet. Chem., 372 (1989) 217-224.
218. T. Arakawa, S. Shimada, G.-Y. Adachi and J. Shiokawa, Inorg. Chim. Acta, 145 (1988) 327-330.

219. Z. Hou, Y. Fujiwara, T. Jintoku, N. Mine, K. Yokoo and H. Taniguchi, J. Org. Chem., 52 (1987) 3524-3528.
220. G.B. Deacon, C.M. Forsyth and R.H. Newham, Polyhedron, 6 (1987) 1143-1145.
221. L.F. Rybakova, O.P. Syutkina, A.V. Garbar and E.S. Petrov, Zh. Obshch. Khim., 58 (1988) 1053-1056.
222. O.P. Syutkina, L.R. Rybakova and E.S. Petrov, Metalloorg. Khim., 2 (1989) 1146-1149.
223. T.A. Starostina, R.R. Shifrina, L.F. Rybakova and E.S. Petrov, Zh. Obshch. Khim., 57 (1987) 2402.
224. A.B. Sigalov and I.P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khich., 2 (1988) 445-450.
225. G.Z. Suleimanov, Y.S. Bogachev, P.V. Petrovskii, E.I. Kazimirchuk, I.L. Zhuravleva, R.Y. Mekhdiev, T.A. Agdamskii, N.E. Kolobova and I.P. Beletskaya, Zh. Organich. Khim., 25 (1989) 507-510.
226. N.E. Kolobova, E.I. Kazimirchuk, T.A. Agdamskii, Z.M. Umudova, V.N. Khandozhko, G.Z. Suleimanov, P.V. Petrovskii and I.P. Beletskaya, Zh. Organich. Khim., 23 (1987) 1699-1702.
227. R. Cai, J. Wei and S. He, Fudan Xuebao, Ziran Kexueban, 28 (1989) 111-112.
228. N. Hu, L.Gong, Z. Jin and W. Chen, Wuji Huaxue Xuebao, 5 (1989) 107-111.
229. J. Sieler, A. Simon, K. Peters, R. Taube and M. Geitner, J. Organomet. Chem., 362 (1989) 297-303.
230. L.N. Bochkarev, S.B. Shustov, T.V. Guseva and S.F. Shil'tsov, Zh. Obshch. Khim., 58 (1988) 923-924.
231. V.A. Yakovlev, I.A. Oreshkin and B.A. Dolgoplosk, Metalloorg. Khim., 2 (1989) 93-101.
232. S.B. Gol'shtein, V.A. Yakovlev, A.I. Mikaya and B.A. Dolgoplosk, Dokl. Akad. Nauk SSSR, 309 (1989) 1129-1131.
233. T.A. Starostina, L.F. Rybakova and E.S. Petrov, Metalloorg. Khim., 2 (1989) 915-918.
234. J.B. Schilling and J.L. Beauchamp, J. Am. Chem. Soc., 110 (1988) 15-24.
235. L.S. Sunderlin and P.B. Armentrout, J. Am. Chem. Soc., 111 (1989) 3845-3855.
236. Y. Huang and B.S. Freiser, J. Am. Chem. Soc., 110 (1988) 387-392.
237. R.L. Hettich and B.S. Freiser, J. Am. Chem. Soc., 109 (1987) 3543-3548.
238. M.P. Andrews and A.L. Wayda, Organometallics, 7 (1988) 743-749.
239. L. Saussine, H. Olivier, D. Commereuc and Y. Chauvin, New J. Chem., 12 (1988) 13-14.
240. S.Q. Sun and W.Q. Chen, Kidorui, 14 (1989) 170-171.
241. C. Shan, Y. Lin, S. Jin, J. Ouyang, Y. Fan, G. Yang and J. Yu, Huaxue Xuebao, 45 (1987) 949-954.
242. J. Hu, E. Pan, Y. Na and Q. Shen, Zhongguo Xitu Xuebao, 5 (1987) 75-76.
243. K.-H. Thiele, K. Unverhau, M. Geitner and K. Jacob, Z. Anorg. Allg. Chem., 548 (1987) 175-179.
244. S. Li, X. Yang, Y. Sun, P. Li, X. Wang and X. Zhou, Gaodeng Xuexiao Huaxue Xuebao, 9 (1988) 1242-1245.
245. P.B. Hitchcock, M.F. Lappert, R.G. Smith, R.A. Bartlett and P.P. Power, J.C.S., Chem. Comm., (1988) 1007-1008.
246. J.L. Atwood, M.F. Lappert, R.G. Smith and H. Zhang, J.C.S., Chem. Comm., (1988) 1308-1309.

247. P.B. Hitchcock, M.F. Lappert and R.G. Smith, J.C.S., Chem. Comm., (1989) 369-371.
248. X. Bao and W. Chen, Chin. Sci. Bull., 34 (1989) 207-211.
249. Z. Huang, M. Chen, W. Qiu and W. Wu, Inorg. Chim. Acta, 139 (1987) 203-207.
250. W. Qiu, S. Zhuang, Z. Huang and W. Wu, Fudan Xuebao Ziran Kexueban, 26 (1987) 113-117.
251. M. Brunelli, S. Poggio, U. Pedretti and G. Lugli, Inorg. Chim. Acta., 131 (1987) 281-285.
252. S.P. Kuleshov, R.G. Bulgakov, G.A. Tostikov and V.P. Kazakov, Izv. Akad. Nauk SSSR, Ser. Khim., (1989) 1207-1208.
253. M.R. Leonov, V.A. Il'yushenkova, V.M. Fomin and N.V. Il'yushenkova, Radiokhim., 30 (1988) 324-329.
254. D.C. Sonnenberger and J.G. Gaudiello, Inorg. Chem., 27 (1988) 2747-2748.
255. G. Adrian, Inorg. Chim. Acta, 139 (1987) 323-325.
256. G. Adrian, Kernf. Karls., (1988) 4356.
257. P. Pyykkö, L.J. Laakkonen and K. Tatsumi, Inorg. Chem., 28 (1989) 1801-1805.
258. A. Zalkin, J.G. Brennan and R.A. Andersen, Acta Cryst., C44 (1988) 2104-2106.
259. P.C. Blake, M.F. Lappert, R.G. Taylor, J.L. Atwood and H. Zhang, Inorg. Chim. Acta, 139 (1987) 13-20.
260. W.K. Kot, G.V. Shalimoff and N.M. Edelstein, J. Am. Chem. Soc., 110 (1988) 986-987.
261. B.E. Bursten, L.F. Rhodes and R.J. Strittmatter, J. Am. Chem. Soc., 111 (1989) 2756-2758.
262. B.E. Bursten, L.F. Rhodes and R.J. Strittmatter, J. Am. Chem. Soc., 111 (1989) 2758-2766.
263. G.B. Deacon and T.D. Tuong, Polyhedron, 7 (1988) 249-250.
264. A. Delapalme, P. Schweiss, M.R. Spirlet, J. Rebizant and B. Kanellakopulos, Mater. Sci. Forum, (1988) 27-28.
265. M.R. Spirlet, J. Rebizant, C. Apostolidis, G.D. Andreetti and B. Kanellakopulos, Acta Cryst., C45 (1989) 739-741.
266. C.C. Chang, N.K. Sung-Yu, C.W. Kang and C.T. Chang, Inorg. Chim. Acta, 129 (1987) 119-121.
267. H.-D. Amberger, H. Reddmann and N. Edelstein, Inorg. Chim. Acta, 141 (1988) 313-321.
268. B.R. McGarvey and S. Nagy, Inorg. Chem., 26 (1987) 4198-4203.
269. B.R. McGarvey and S. Nagy, Inorg. Chem., 139 (1987) 319-321.
270. G. Adrian, H. Appel, R. Bohlander, H. Haffner and B. Kanellakopulos, Hyperfine Interact., 40 (1988) 275-278.
271. V.I. Spitsyn and G.V. Ionova, Dokl. Akad. Nauk SSSR, 292 (1987) 921-923.
272. J.F. Le Marechal, C. Villiers, P. Charpin, M. Nierlich, M. Lance, J. Vigner and M. Ephritikhine, J. Organomet. Chem., 279 (1989) 259-269.
273. V.I. Tel'noi, I.B. Rabinovich, V.N. Larina, R.M. Leonov and G.V. Solov'eva, Radiokhim., 31 (1989) 38-40.
274. P. Zanella, F. Ossola, M. Porchia, G. Rossetto, A.C. Villa and C. Guastini, J. Organomet. Chem., 323 (1987) 295-303.
275. M. Porchia, N. Brianese, F. Ossola, G. Rossetto and P. Zanella, J.C.S., Dalton Trans., (1987) 691-694.
276. P. Zanella, N. Brianese, U. Casellato, F. Ossola, M. Porchia, G. Rossetto and R. Graziani, Inorg. Chim. Acta, 144 (1988) 129-134.

277. J.-F. Le Marechal, E. Bulot, D. Baudry, M. Ephritikhine, D. Hauchard and R. Godard, J. Organomet. Chem., 354 (1988) C17-C18.
278. J.-F. Le Marechal, C. Villiers, P. Charpin, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, J.C.S., Chem. Comm., (1989) 308-310.
279. R.K. Rosen and A. Zalkin, Acta Cryst., C45 (1989) 1139-1141.
280. J. Rebizant, C. Apostolidis, M.R. Spirlet and B. Kanellakopulos, Inorg. Chim. Acta, 139 (1987) 209-210.
281. A. Zalkin and J.G. Brennan, Acta Cryst., C43 (1987) 1919-1922.
282. R.E. Cramer, F. Edelmann, A.L. Mori, S. Roth, J.W. Gilje, K. Tatsumi and A. Nakamura, Organometallics, 7 (1988) 841-849.
283. R.E. Cramer, U. Engelhardt, K.T. Higa and J.W. Gilje, Organometallics, 6 (1987) 41-45.
284. H. Aslan, K. Yunlu, R.D. Fischer, G. Bombieri and F. Benetollo, J. Organomet. Chem., 254 (1988) 63-76.
285. G. Rossetto, N. Brianese, F. Ossola, M. Porchia, P. Zanella and S. Sostero, Inorg. Chim. Acta, 132 (1987) 275-278.
286. H.-D. Amberger, H. Reddmann, G. Shalimoff and N.M. Edelstein, Inorg. Chim. Acta, 139 (1987) 335-337.
287. F. Knosel, H.W. Roesky and F. Edelmann, Inorg. Chim. Acta, 139 (1987) 187-188.
288. R.E. Cramer, J.H. Jeong and J.W. Gilje, Organometallics, 6 (1987) 2010-2012.
289. A. Zalkin, J.G. Brennan and R.A. Andersen, Acta Cryst., C43 (1987) 1706-1708.
290. M. Porchia, N. Brianese, U. Casellato, F. Ossola, G. Rossetto, P. Zanella and R. Graziani, J.C.S., Dalton Trans., (1989) 677-681.
291. R.S. Sternal and T.J. Marks, Organometallics, 6 (1987) 2621-2623.
292. M. Porchia, F. Ossola, G. Rossetto, P. Zanella and N. Brianese, J.C.S., Chem. Comm., (1987) 550-551.
293. L.E. Schock, A.M. Seyam, M. Sabat and T.J. Marks, Polyhedron, 7 (1988) 1517-1529.
294. S.D. Stults, R.A. Andersen and A. Zalkin, J. Am. Chem. Soc., 111 (1989) 4507-4508.
295. H. Aslan, J. Forster, K. Yunlu and R.D. Fischer, J. Organomet. Chem., 355 (1988) 79-88.
296. M. Foyentin, G. Folcher and M. Ephritikhine, J.C.S., Chem. Comm., (1987) 494-495.
297. M. Foyentin, G. Folcher and M. Ephritikhine, J. Organomet. Chem., 335 (1987) 201-206.
298. P. Zanella, N. Brianese, U. Casellato, F. Ossola, M. Porchia, G. Rossetto and R. Graziani, J.C.S., Dalton Trans., (1987) 2039-2043.
299. R.E. Cramer, M.A. Bruck, F. Edelmann, D. Afzal, J.W. Gilje and H. Schmidbaur, Chem. Ber., 121 (1988) 417-420.
300. J.W. Gilje and R.E. Cramer, Inorg. Chim. Acta., 139 (1987) 177-181.
301. M.R. Leonov and G.V. Solov'eva, Zh. Obshch. Khim., 57 (1987) 2522-2529.
302. M.R. Leonov, I.I. Grinval'd, G.V. Solov'eva, V.A. Il'yushenkov and N.K. Rudnevskii, Radiokhim., 29 (1987) 107-109.

303. L. Xing-Fu and G. Ao-Ling, Inorg. Chim. Acta, 134 (1987) 143-153.
304. N.I. Gramoteeva and M.P. Leonov, Metalloorg. Khim., 2 (1989) 1430.
305. A. Zalkin, A.L. Stuart and R.A. Andersen, Acta Cryst., C44 (1988) 2106-2108.
306. P.C. Blake, M.F. Lappert, J.L. Atwood and H. Zhang, J.C.S., Chem. Comm., (1988) 1436-1438.
307. P.C. Blake, E. Hey, M.F. Lappert, J.L. Atwood and H. Zhang, J. Organomet. Chem., 353 (1988) 307-314.
308. A.M. Koulkès-Pujo, J.F. Le Marechal, A. Dormond and G. Folcher, Inorg. Chem., 26 (1987) 3171-3175.
309. A.L. Arduini, J. Maliot, J. Takats, E. Ciliberto, I. Fragala and P. Zanella, J. Organomet. Chem., 326 (1987) 49-58.
310. T.J. Marks, Inorg. Chim. Acta, 140 (1987) 1-2.
311. R.S. Sternal, M. Sabat and T.J. Marks, J. Am. Chem. Soc., 109 (1987) 7920-7921.
312. R.E. Cramer, S. Roth and J.W. Gilje, Organometallics, 8 (1989) 2327-2330.
313. J.G. Brennan, R.A. Andersen and A. Zalkin, J. Am. Chem. Soc., 110 (1988) 4554-4558.
314. A. Zalkin and S.M. Beshouri, Acta Cryst., C45 (1989) 1219-1221.
315. K. Tatsumi and A. Nakamura, Inorg. Chim. Acta, 139 (1987) 247-251.
316. A. Zalkin and S.M. Beshouri, Acta Cryst., C44 (1988) 1826-1827.
317. R.E. Cramer, M.A. Bruck and J.W. Gilje, Organometallics, 7 (1988) 1465-1469.
318. Z. Lin, C.P. Brock and T.J. Marks, Inorg. Chim. Acta, 141 (1988) 145-149.
319. A. Zalkin, J.G. Brennan and R.A. Andersen, Acta Cryst., C43 (1987) 418-420.
320. A. Zalkin, J.G. Brennan and R.A. Andersen, Acta Cryst., C43 (1987) 421-423.
321. B.E. Bursten and K.J. Novo-Gradac, J. Am. Chem. Soc., 109 (1987) 904-905.
322. K. Tatsumi and A. Nakamura, Organometallics, 6 (1987) 427-428.
323. K. Tatsumi and A. Nakamura, J. Am. Chem. Soc., 109 (1987) 3195-3206.
324. Z. Lin and T.J. Marks, J. Am. Chem. Soc., 109 (1987) 7979-7985.
325. G.M. Smith, M. Sabat and T.J. Marks, J. Am. Chem. Soc., 109 (1987) 1854-1856.
326. D. Hedden and T.J. Marks, J. Am. Chem. Soc., 110 (1988) 1647-1649.
327. Z. Lin, J-F. Le Marechal, M. Sabat and T.J. Marks, J. Am. Chem. Soc., 109 (1987) 4127-4129.
328. R.E. Cramer, S. Roth, F. Edelmann, M.A. Bruck, K.C. Cohn and J.W. Gilje, Organometallics, 8 (1989) 1192-1199.
329. S.M. Beshouri and A. Zalkin, Acta Cryst., C45 (1989) 1221-1222.
330. A. Zalkin and S.M. Beshouri, Acta Cryst., C45 (1989) 1080-1082.
331. C. Aitken, J.-P. Barry, F. Gauvin, J.F. Harrod, A. Malek and D. Rousseau, Organometallics, 8 (1989) 1732-1736.

332. C.M. Fendrick, L.D. Schertz, V.W. Day and T.J. Marks, Organometallics, 7 (1988) 1828-1838.
333. A. Dormond, A. Aaliti and C. Moise, J. Org. Chem., 53 (1988) 1034-1037.
334. M.A. Edelman, M.F. Lappert, J.L. Atwood and H. Zhang, Inorg. Chim. Acta, 139 (1987) 185-186.
335. D.L. Clark, A.P. Sattelberger, S.G. Bott and R.N. Vrtis, Inorg. Chem., 28 (1989) 1772-1773.
336. T.M. Gilbert, R.R. Ryan and A.P. Sattelberger, Organometallics, 8 (1989) 857-859.
337. R.R. Ryan, K.V. Salazar, N.N. Sauer and J.M. Ritchey, Inorg. Chim. Acta, 162 (1989) 221-225.
338. D. Baudry and M. Ephritikhine, J. Organomet. Chem., 349 (1988) 123-130.
339. D. Baudry, P. Dorion and M. Ephritikhine, J. Organomet. Chem., 356 (1988) 165-171.
340. C. Baudin, P. Charpin, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, J. Organomet. Chem., 345 (1988) 263-274.
341. N. Marques, J. Marcalo, T. Almeida, J.M. Carretas, A. Pires de Matos, K.W. Bagnall and J. Takats, Inorg. Chim. Acta, 139 (1987) 83-85.
342. N. Brianese, U. Casellato, F. Ossola, M. Porchia, G. Rossetto, P. Zanella and R. Graziani, J. Organomet. Chem., 365 (1989) 223-232.
343. D. Baudry, E. Bulot, P. Charpin, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, J. Organomet. Chem., 371 (1989) 163-174.
344. M.R. Spirlet, J. Rebizant and J. Goffart, Acta Cryst., C43 (1987) 354-355.
345. J. Rebizant, M.R. Spirlet, G. Van den Bossche and J. Goffart, Acta Cryst., C44 (1988) 1710-1712.
346. J. Rebizant, M.R. Spirlet, S. Bettonville and J. Goffart, Acta Cryst., C45 (1989) 1509-1511.
347. W. Beeckman and J. Goffart, Lanth. Act. Res., 2 (1988) 187-200.
348. J. Goffart and S. Bettonville, J. Organomet. Chem., 361 (1989) 17-19.
349. S. Bettonville, J.Goffart and J. Fuger, J. Organomet. Chem., 377 (1989) 59-67.
350. P.M. Boerrigter, E.J. Baerends and J.G. Snijders, Chem. Phys., 122 (1988) 357-374.
351. A.H.H. Chang and R.M. Pitzer, J. Am. Chem. Soc., 111 (1989) 2500-2507.
352. N.T. Kuznetsov, V.A. Mitin, K.V. Kir'yanov, V.G. Sevast'yanov and V.A. Bogdanov, Radiokhim., 29 (1987) 109-111.
353. M.H. Lyttle, A. Streitwieser and M.J. Miller, J. Org. Chem., 54 (1989) 2331-2335.
354. N.C. Burton, F.G.N. Cloke, P.B. Hitchcock, H.C. de Lemos and A.A. Sameh, J.C.S., Chem. Comm., (1989) 1462-1464.
355. T.M. Gilbert, R.R. Ryan and A.P. Sattelberger, Organometallics, 7 (1988) 2514-2518.
356. W.G. Van der Sluys, C.J. Burns, J.C. Huffman and A.P. Sattelberger, J. Am. Chem. Soc., 110 (1988) 5924-5925.
357. D. Baudry, E. Bulot and M. Ephritikhine, J.C.S., Chem. Comm., (1988) 1369-1370.

358. D. Baudry, E. Bulot, P. Charpin, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, J. Organomet. Chem., 371 (1989) 155-162.
359. D. Baudry, E. Bulot and M. Ephritikhine, J.C.S., Chem. Comm., (1989) 1316-1317.
360. J.L. Stewart and R.A. Andersen, J.C.S., Chem. Comm., (1987) 1846-1847.
361. W.G. Van der Sluys, C.J. Burns and A.P. Sattelberger, Organometallics, 8 (1989) 855-857.
362. S.M. Beshouri, P.E. Fanwick, I.P. Rothwell and J.C. Huffman, Organometallics, 6 (1987) 2498-2502.
363. C. Baudin and M. Ephritikhine, J. Organomet. Chem., 364 (1989) C1-C2.
364. S.A. Toropov, V.K. Vasil'ev and V.N. Sokolov, Radiokhim., 29 (1987) 150-154.
365. A. Dormond, A. Aaliti, A. El Bouadili and C. Moise, Inorg. Chim. Acta, 139 (1987) 171-176.
366. A. Dormond, A. El Bouadili and C. Moise, J. Org. Chem., 54 (1989) 3747-3748.
367. A. Dormond, A. El Bouadili and C. Moise, J. Org. Chem., 52 (1987) 688-689.
368. A. Dormond, C. Moise, A. El Bouadili and H. Bitar, J. Organomet. Chem., 371 (1989) 176-185.
369. A. Dormond, A. El Bouadili and C. Moise, J. Organomet. Chem., 369 (1989) 171-185.
370. A. Dormond, A. Aaliti, A. El Bouadili and C. Moise, J. Organomet. Chem., 329 (1987) 187-199.