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LANTHANIDES AND ACTINIDES
ANNUAL SURVEY COVERING THE YEAR 1990

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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. Abbreviations are defined after their first appearance in the text.

The Journal of Organometallic Chemistry annual surveys of lanthanides and actinides for the years 1982 (75 references)[1] and 1983 (75 references)[2] both appeared in 1990. The f-elements were included in Winter's review of complexes containing metal-carbon sigma bonds (418 total references).[3] Several organo-f-element compounds were discussed in Fryzuk, et al.'s review of metal complexes containing neutral phosphorous donor ligands (233 references of which 49 are related to the f-elements).[4] Organo-f-element carbonyl derivatives were reviewed by Beletskaya, et al. (81 references).[5]

Several reviews appeared in 1990 on specific synthetic aspects of organo-f-element compounds. Deacon, et al. reviewed chemical vapor deposition of rare earth compounds in superconductor synthesis (87 references).[6] Inanaga reviewed the preparation and reactions of organosamarium complexes (40 references)[7] while Kagan discussed organic reactions of divalent samarium in a review with 49 references.[8] Sattelberger reviewed the organo-f-element thermochemistry work of Nolan (6 references)[9] and cryosynthesis of organometallic compounds was reviewed by Zagorskii and Sergeev (8 references).[10]

***Lanthanides and Actinides, Annual Survey covering the years 1987-1989, see J. Organomet. Chem., 442 (1992) 83.**
Reprints for this Survey are not available.

Chapter 4 of Volume 27 of "Inorganic Syntheses"[11] was devoted to the synthesis of lanthanide and actinide complexes. The organometallic compounds discussed included $Yb(PhCC)_2$ (Ph = phenyl, C_6H_5), $Cp^*_2YbOEt_2$ (Cp^* = pentamethylcyclopentadienyl anion, $C_5(CH_3)_5^-$; Et = ethyl, C_2H_5), Lu(COT)Cl(THF) (COT = cyclooctatetraenyl dianion $C_8H_8^{2-}$; THF = tetrahydrofuran), $Lu(COT)[o\text{-}C_6H_4CH_2NMe_2](THF)$ (Me = methyl, CH_3), $Cp^*_2Sm(THF)_2$, $Cp_2Nd(^tBu)(THF)$ (Bu = butyl, C_4H_9), $Cp_2Lu[CH_2SiMe_3](THF)$, $Cp_2Lu(p\text{-}MeC_6H_4)(THF)$, $[Cp''_2Ln(\mu Cl)]_2$ (Ln = Y, La-Nd, Sm-Lu), $[Cp''_2Ln(\mu\text{-}Cl)_2Li(THF)_2]$ (Ln = Y, La, Ce, Pr, Nd, Yb; Cp" = bistrimethylsilylcyclopentadienyl anion, $C_5H_3(SiMe_3)_2^-$), Cp''_2AnCl_2 (An = Th, U), Cp''_2UX_2 (X = Br, I), and $Cp_3U[CHPMe_2Ph]$. There are 112 references in Chapter 4.

LANTHANIDES

(i) Tetrakiscyclopentadienyl compounds. The salt, $[Na(THF)][Cp_4Ce]$, was utilized to prepare $CpM(CH_2Ph)_3$ (M = Sn, Ti) by direct reaction with the tribenzyl metal chlorides.[12]

(ii) Monocyclopentadienyl compounds. Guan, et al.[13] reported the crystal structure of $[Li(THF)_4]_2[\{(CpMe)NdCl(\mu_2\text{-}Cl)NdCl_2\text{-}(CpMe)\}_2(\mu_4\text{-}O)]$ (CpMe = methylcyclopentadienyl anion, $C_5H_4Me^-$). The average Nd-C separation is 2.76(3)Å. Shen, et al.[14] published the crystal structure of another novel complex, $\{Na(\mu_2\text{-}THF)\text{-}[Cp^*Gd(THF)]_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2\}_2\cdot 6THF$ (Figure 1). This compound was isolated as a minor product in the reaction of $GdCl_3$ with $NaCp^*$.

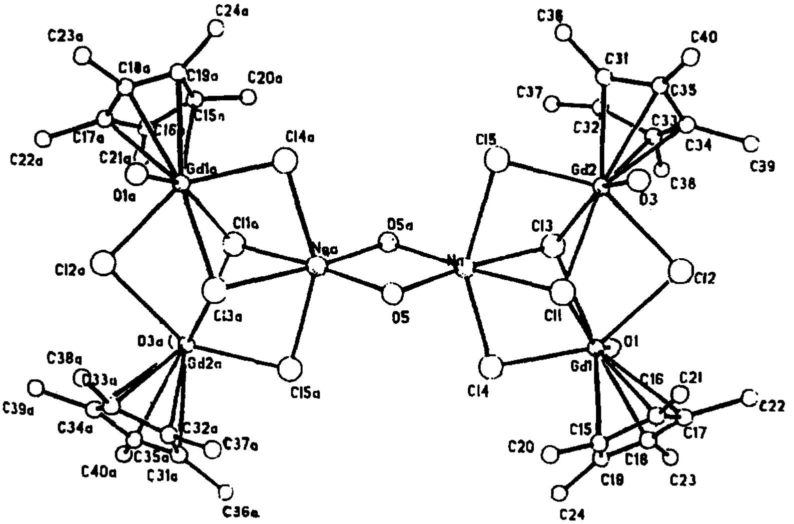


Fig. 1. $\{Na(\mu_2\text{-}THF)[Cp^*Gd(THF)]_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2\}_2\cdot 6THF$. (Reprinted with permission from Journal of Organometallic Chemistry.)

The benzylcyclopentadienyl compounds, $(CpCH_2Ph)LnCl_2 \cdot n(THF)$ (Ln = Nd, Sm, Gd; n = 1,2), were prepared by Zhang, et al.[15] Characterization was accomplished with combustion analysis, thermal analyses, IR, mass spectrometry, and NMR.

Schumann, et al.[16] reacted $GdCl_3$ with NaCp and 2NaOMe in THF to prepare $(CpGd)_5(\mu_2\text{-OMe})_4(\mu_3\text{-OMe})_4(\mu_5\text{-O})$. The crystal structure (Figure 2) reveals five CpGd moieties in a tetragonal pyramid with a μ_5-oxide ligand in the pyramid. The four Gd atoms in the base are each bridged by four μ_2-OMe's, while four more methoxide ligands bridge two basal and the apical Gd each.

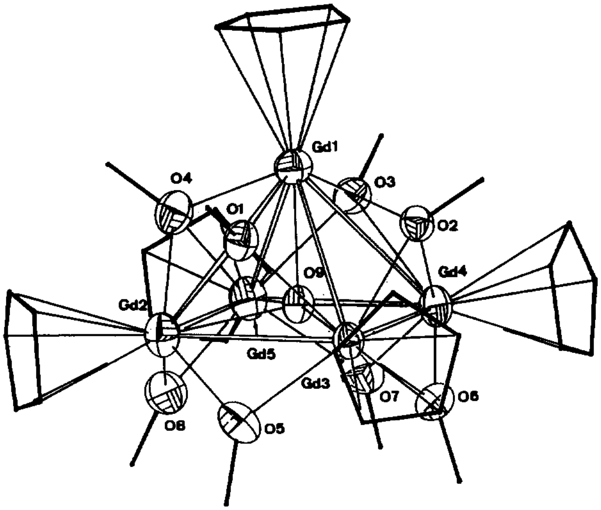


Fig. 2. $(CpGd)_5(\mu_2\text{-OMe})_4(\mu_3\text{-OMe})_4(\mu_5\text{-O})$. (Reprinted with permission from Zeitschrift für Anorganische und Allgemeine Chemie.)

Heeres and Teuben[17] studied the synthesis and ligand exchange reactions of $Cp^*La(OAr)_2$ (OAr = 2,6-di-^{t}butylphenoxide). The synthesis was accomplished by reaction of $La(OAr)_3$ with $LiCp^*$. Addition of THF gave $Cp^*La(OAr)_2(THF)_2$. Disproportionation in solution led to equal amounts of $Cp^*La(OAr)_2$, $La(OAr)_3$, and $Cp^*_2La(OAr)$.

Jin, et al.[18] reported the crystal structure of $[Li(DME)_3]_2[(CpNd)_4(\mu_2\text{-Me})(\mu_4\text{-O})(\mu_2\text{-Cl})_6]$ (DME = dimethoxy ethane) prepared by reaction of LiMe in Et_2O with $Cp_2NdCl \cdot 2LiCl \cdot nTHF$. The four Nd atoms form a distorted tetrahedron.

The mixed ring complex (CpMe)(COT)Y(THF) was prepared and structurally characterized (Figure 3) by Schumann, et al.[19]

Reaction of (COT)YCl(THF) with NaCpMe in THF led to the isolation of this compound. The centroid-Y-centroid angle is 149°. In a second contribution[20] similar mixed ring compounds (utilizing Cp^*) were used to deposit thin films of Y and other rare earths using chemical vapor deposition.

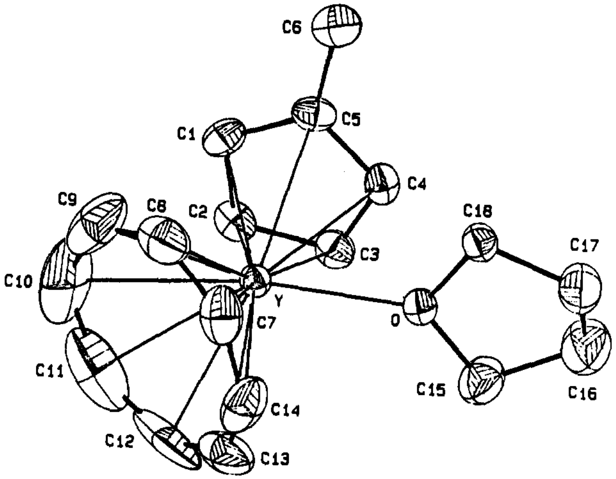


Fig. 3. (CpMe)(COT)Y(THF). (Reprinted with permission from Monatshefte für Chemie.)

(iii) Triscyclopentadienyl compounds. Fischer, et al.[21] published ^{139}La-NMR studies of oxygen adducts of Cp_3La. The compounds studied included $Cp_3LaDMSO$, Cp_3LaDMF, $Cp_3LaOP(OMe)_3$, and $Cp_3LaMeCOMe$.

Ye, et al.[22] published another structure in the $Cp_3Ln \cdot THF$ series with the Ln = Dy analog. The Dy-C separations average 2.74(8)Å.

Evans, et al.[23] prepared Cp''_3Sm by reaction of $SmCl_3$ and KCp" or from Cp''_2Sm under 90 psi of CO. The crystal structure of Cp''_3Sm is given in Figure 4. The Sm-C separations average 2.76(4)Å but have a large range due to the tilting of the carbon atoms bonded to silicons away from Sm.

Bel'sky, et al.[24] published the crystal structure of $[NaSm(\eta^5:\eta^2\text{-}Cp^tBu)_3 \cdot THF]_n$ (Figure 5). The compound was prepared by reaction of SmI_2 with $NaCp^tBu$. The average Sm-C distance is 2.89Å.

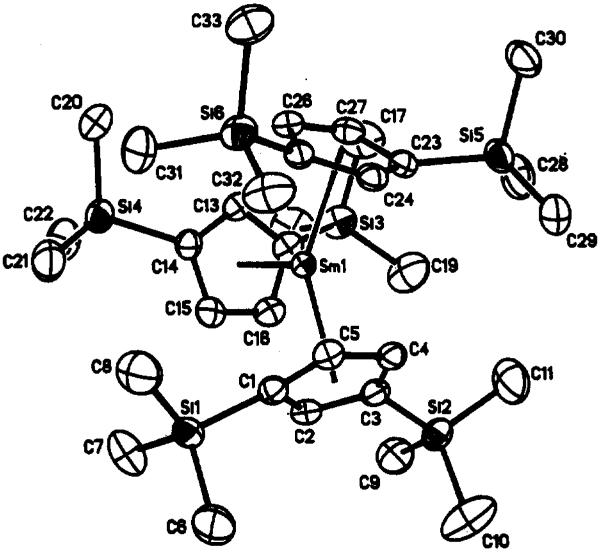


Fig. 4. Cp''$_3$Sm. (Reprinted with permission from Journal of Organometallic Chemistry.)

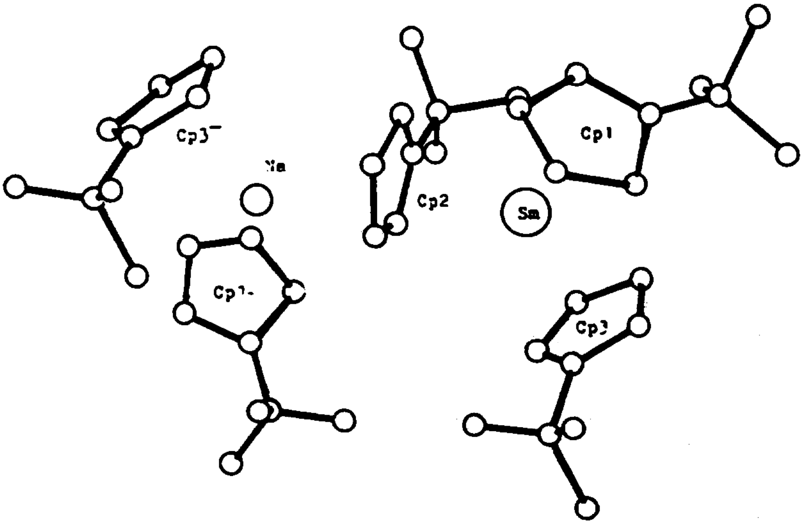


Fig. 5. [NaSm(η^5:η^2-Cp^{t}Bu)$_3$·THF]$_n$ without the THF molecules. (Reprinted with permission from Journal of Organometallic Chemistry.)

The crystal structure of $Cp_3Sm(NCCD_3)$ was published by Spirlet, et al.[25] (Figure 6). Bonding parameters include Sm-N = 2.53(1)Å and Sm-C = 2.74(1)Å average.

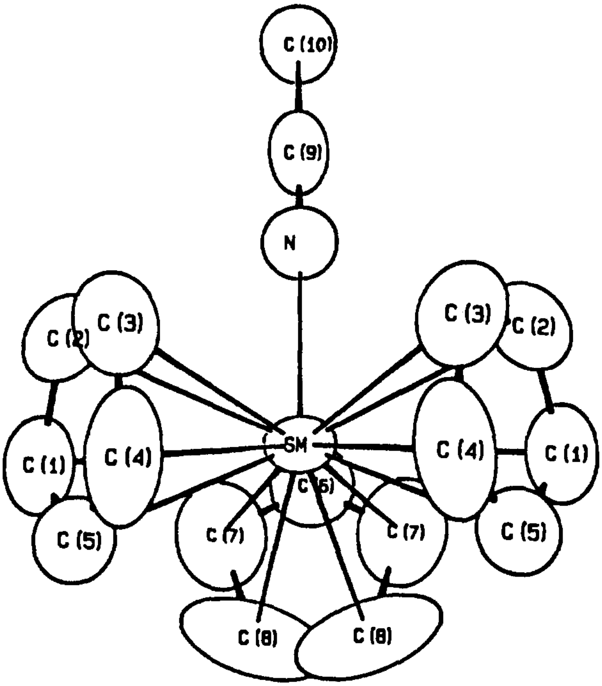


Fig. 6. $Cp_3Sm(NCCD_3)$. (Reprinted with permission from Acta Crystallographica.)

Andersen, et al.[26,27] published the crystal structures of several triscyclopentadienyl cerium(III) compounds and their complexes. $(CpMe_3)_3Ce$ (Figure 7) was found to be tetrameric in the solid state with average terminal Ce-C distances of 2.80(3)Å, and average bridging Ce-C(η^5) separations of 2.88(4)Å. One CpMe ligand bridges in an η^5:η^1 fashion. The structure of the adduct $(CpMe)_3Ce(CN^tBu)$ was also carried out (Figure 8). The Ce-C(η^5) separations are essentially the same at 2.79(3)Å. The bulkier Cp" ligand was observed to give a monomeric structure in the solid state structure of Cp''_3Ce (Figure 9) with a slightly longer average Ce-C separation of 2.83(4)Å. The crystal structure of the CN^tBu adduct of this compound was also carried out and is presented in Figure 10. The average Ce-C distance is 2.87(3)Å.

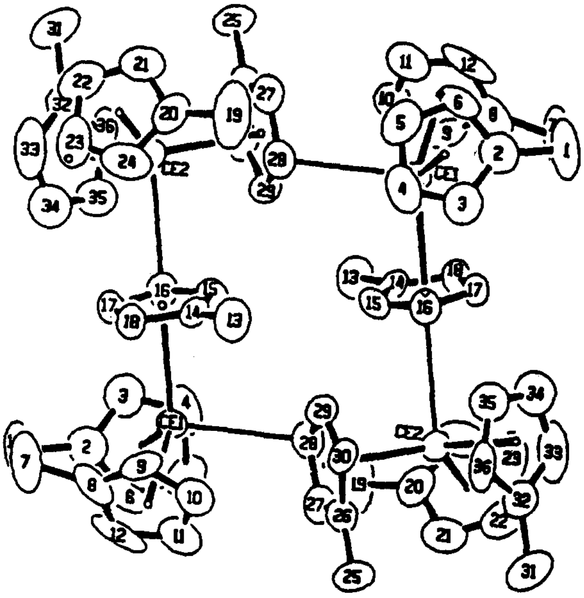


Fig. 7. $(CpMe_3)_3Ce$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

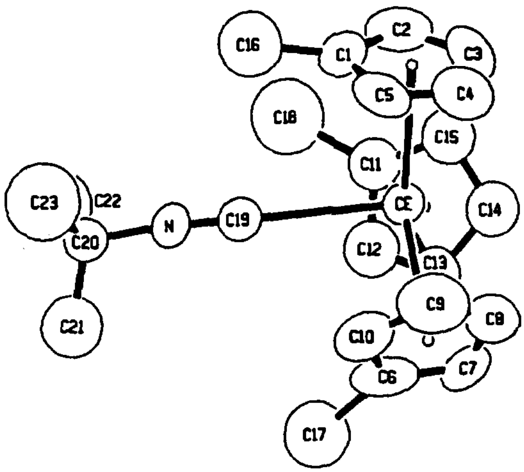


Fig. 8. $(CpMe_3)_3Ce(CN^tBu)$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

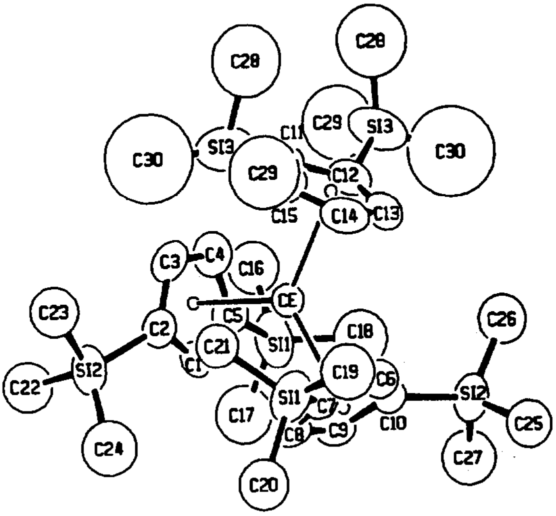


Fig. 9. Cp''_3Ce. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

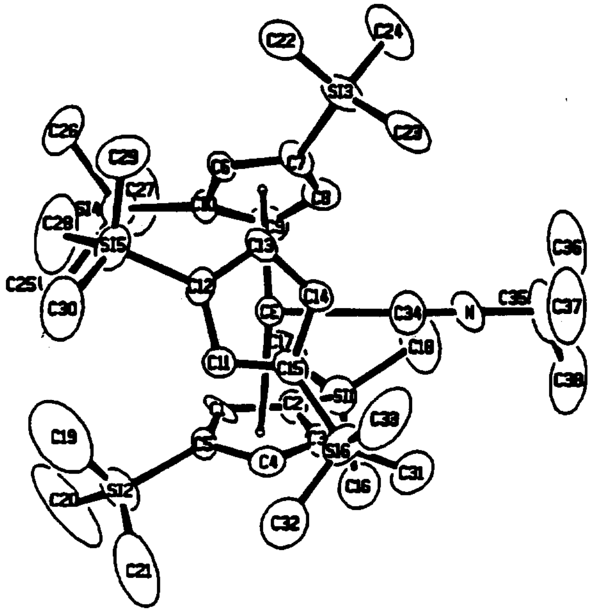


Fig. 10. $Cp''_3Ce(CN^tBu)$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

Makhaev, et al.[28] prepared $(Cp^iPr)_3Gd$ (Pr = propyl, C_3H_7) from $GdCl_3$ and the sodium salt of the ligand. The compound was used in the synthesis of high purity Gd_2O_3. The Er analog was used by Weber, et al.[29] to grow Er doped indium phosphide layers.

Sockwell and Hanusa[30] analyzed published crystal structures of over 200 Cp_2 and Cp_3 lanthanide and actinide derivatives in order to uncover evidence for covalent bonding. It was not possible to nail down one "effective ionic radius" for the Cp ligand.

(iv) Biscyclopentadienyl compounds. Streitwieser and Gong[31] studied the catalytic properties of Cp''_2YbCl in a Mukaiyama addition reaction. Marks, et al.[32] found Cp^*_2Sm and $Cp^*_2Sm(THF)_2$ catalyze hydroamination/cyclization of aminoolefins.

Evans, et al.[23] prepared Cp''_2Sm by desolvating $Cp''_2Sm(THF)$, which was itself prepared by the reaction of $SmI_2(THF)_2$ with two equivalents of KCp". The solvated compound polymerizes ethylene.

The dimeric compounds, $[(Cp(CH_2)_2OMe)_2Ln(\mu\text{-}Cl)]_2$ (Ln = La, Pr, Nd) were prepared by reaction of $LnCl_3$ and the sodium salt of the ligand in THF.[33] The crystal structure of Ln = La revealed a chelating $Cp(CH_2)_2OMe^-$ ligand η^5-coordinated through the ring carbon atoms and forming a Lewis acid/base adduct through the oxygen atom (Figure 11). X-ray photoelectron studies were conducted on the Ln = La, Nd, Gd, Ho, Er, Yb, and Y derivatives.[34]

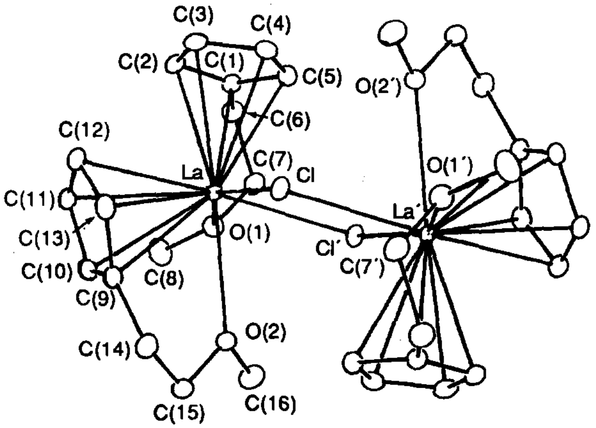


Fig. 11. $[(Cp(CH_2)_2OMe)_2La(\mu\text{-}Cl)]_2$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

Evans, et al.[35] studied the relative reactivity of $Cp^*{}_2Si$ and $Cp^*{}_2Sm$. The samarium compound proved to be the more strongly reducing of the two.

Gun'ko, et al.[36] prepared $(Cp^tBu_2)_2Ce(\mu_2\text{-}Cl)_2Li(Me_2NC_2H_4NMe_2)$ by reaction of $LiAlH_4$ with $[(Cp^tBu_2)_2CeCl_2]_2$. The crystal structure revealed the overall nature of the compound.

The crystal structure of the 20 electron hydride $\{[(Cp^tBu)_2\text{-}Sm(\mu_3\text{-}H)][(\mu_2\text{-}H)_2AlH(THF)]\}_2$ was determined by Gun'ko, et al.[37] (Figure 12). This compound was prepared by the reaction of $Na[(Cp^tBu)_3Sm]\cdot THF$ with $AlH_3\cdot THF$.

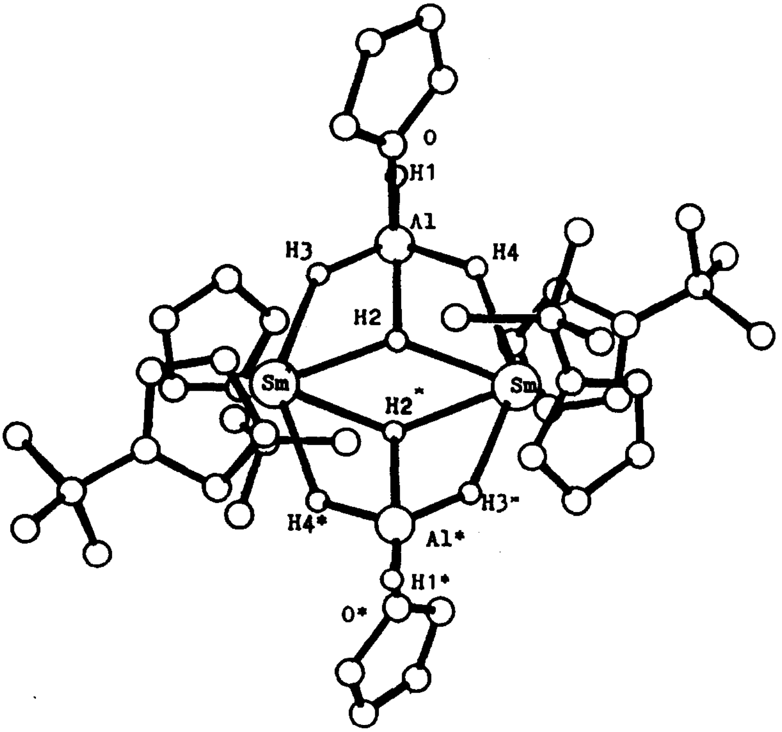


Fig. 12. $\{[(Cp^tBu)_2Sm(\mu_3\text{-}H)][(\mu_2\text{-}H)_2AlH(THF)]\}_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

The crystal structure of $(Cp^tBu)_2Yb(THF)_2$ was carried out by Shen, et al.[38] and is shown in Figure 13. The Yb-C distances average 2.72(2)Å. The bissubstituted cyclopentadienyl complex $(Cp^tBu_2)_2Sm(THF)$ was isolated as the monosolvate and its structure determined by Bel'sky, et al.[24] (Figure 14).

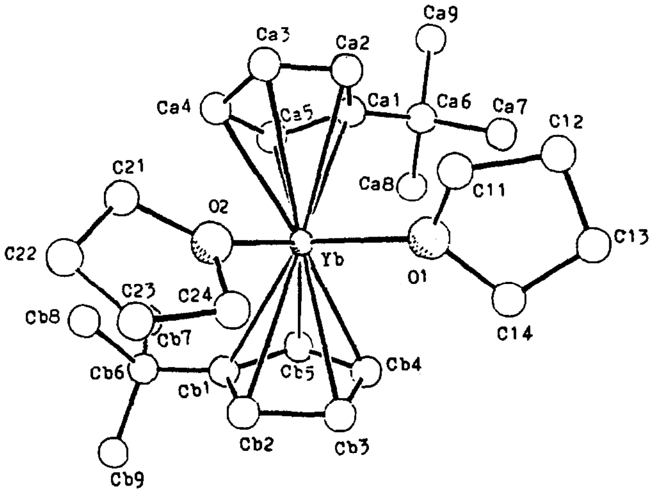


Fig. 13. (Cp^{t}Bu)$_2$Yb(THF)$_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

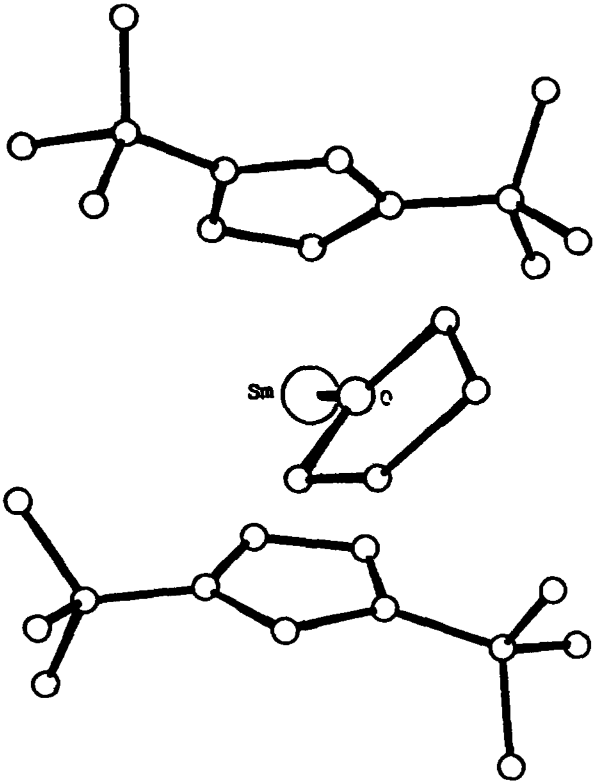


Fig. 14. (Cp^{t}Bu$_2$)$_2$Sm(THF). (Reprinted with permission from Journal of Organometallic Chemistry.)

Andersen, et al.[27] published the structures of the dimeric compounds $[(Cp^tBu)_2Ce(\mu\text{-}OCHMe_2)]_2$ (Figure 15) and $[(Cp^tBu)_2Ce(\mu\text{-}SCHMe_2)]_2$ (Figure 16). Both were prepared by reaction of $(Cp^tBu)_3Ce$ with the corresponding alcohol or thiol. In the isopropoxide derivative average bonding parameters of Ce-C = 2.83(4)Å and Ce-O = 2.373(3)Å were observed, while Ce-C = 2.78(2)Å and Ce-S = 2.870(2)Å were observed in the isopropylthiolate analog.

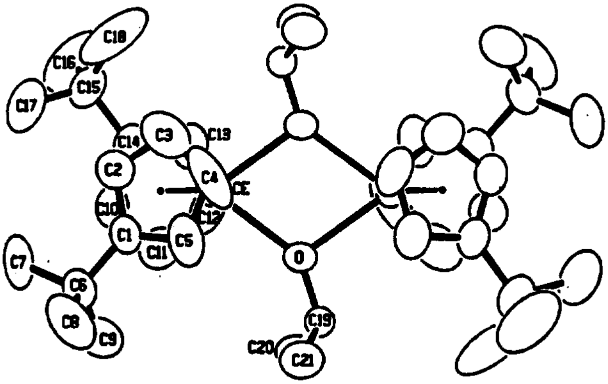


Fig. 15. $[(Cp^tBu)_2Ce(\mu\text{-}OCHMe_2)]_2$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

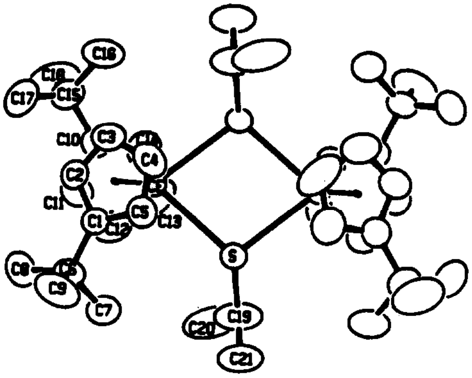


Fig. 16. $[(Cp^tBu)_2Ce(\mu\text{-}SCHMe_2)]_2$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

Li, et al.[39] published a thin-layer chromatographic and UV spectrum of Cp_2Yb o-substituted benzoic acid derivatives. Few other details are available.

Bruno, et al.[40] prepared $Cp''_2LnI(NCMe)_2$ (Ln = La, Ce) as precursors for complexes containing the $[Cp''_2Ln]^+$ moiety. The complexes prepared included $[Cp''_2Ce(\mu\text{-}\eta^2\text{-}OC)W(CO)(Cp)(\mu\text{-}\eta^2\text{-}CO)]_2$, $Cp''_2Ln(NCMe)_2(FBF_3)$, and $[Cp''_2Ln(NCMe)(DME)][BPh_4]\cdot 0.5DME$. The latter compound for Ln = La was structurally characterized (Figure 17).

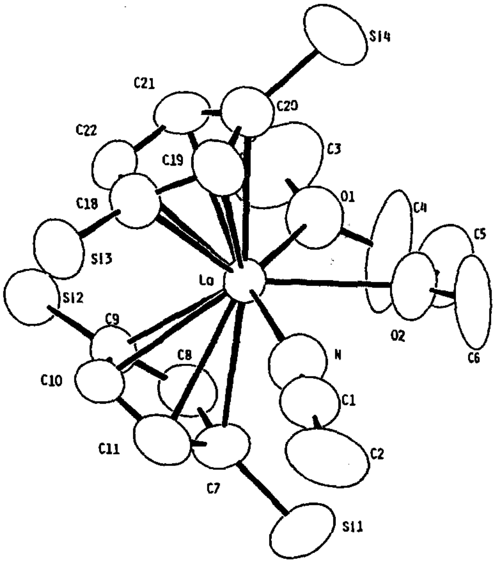


Fig. 17. The cation in $[Cp''_2La(NCMe)(DME)][BPh_4]\cdot 0.5DME$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

Weidlein and Hammel[41] structurally characterized $[(CpMe)_2YbNH_2]_2$ (Figure 18). The bridging Yb-N separations are 2.29(1) and 2.32(1)Å. The Yb-C distances range from 2.59(1) to 2.66(1)Å.

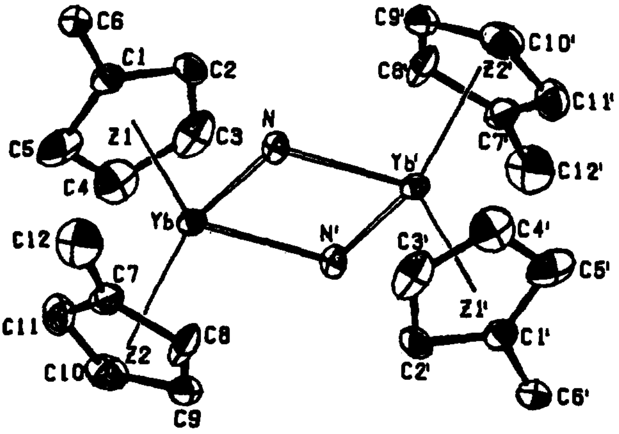


Fig. 18. $[(CpMe)_2YbNH_2]_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Schumann, et al.[42] utilized sodium pyrrolyls to prepare $Cp_2Lu(NC_4H_4)$, $Cp^*_2Y(NC_4H_4)(THF)$, and $Cp_2Lu(NC_4H_2Me_2)(THF)$ from the corresponding biscyclopentadienyl lanthanide chlorides. The crystal structure of the dimethylpyrrolyl complex was determined (Figure 19) and revealed a Lu-N separation of 2.289(4)Å and a Lu-N-centroid angle of 166.4(5)°.

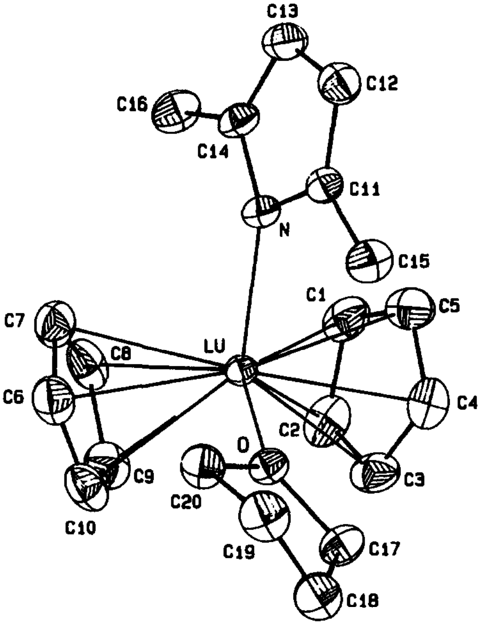


Fig. 19. $Cp_2Lu(NC_4H_2Me_2)(THF)$. Reprinted with permission from Chemische Berichte.)

Schumann, et al.[43] prepared $[Li(TMED)_2][Cp_2Sm(NPh_2)_2]$ (TMED = tetramethylethylenediamine) and $[Li(THF)_4][Cp_2Lu(NPh_2)_2]$ by utilizing $HNPh_2$ and the lithium salt of $[Cp_2LnMe_2]^-$. The crystal structure of the Lu compound is depicted in Figure 20. The Lu-N distances are 2.290(7) and 2.293(7)Å.

These same authors[44] also communicated their results on the reactions of $HPPh_2$ and $HAsPh_2$ with $Cp_2Lu(CH_2SiMe_3)(THF)$ to give $Cp_2LuPPh_2(THF)$ and $Cp_2LuAsPh_2(THF)$. Crystallization of the former led to the THF cleavage product, $[Cp_2Lu(\mu\text{-}O(CH_2)_4PPh_2)]_2$ (Figure 21) while the latter hydrolyzed to give $[Cp_2Lu(THF)]_2O$ (Figure 22).

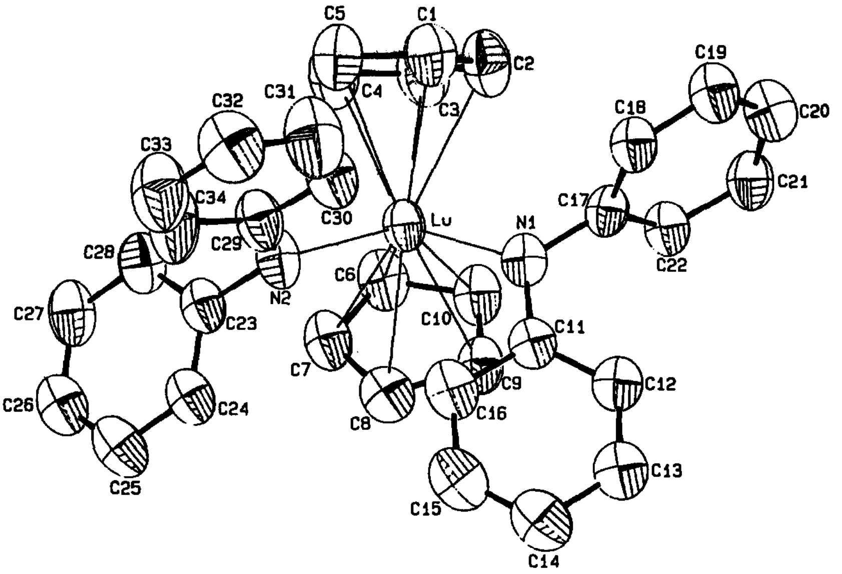


Fig. 20. The anion in $[Li(THF)_4][Cp_2Lu(NPh_2)_2]$. (Reprinted with permission from Journal of Organometallic Chemistry.)

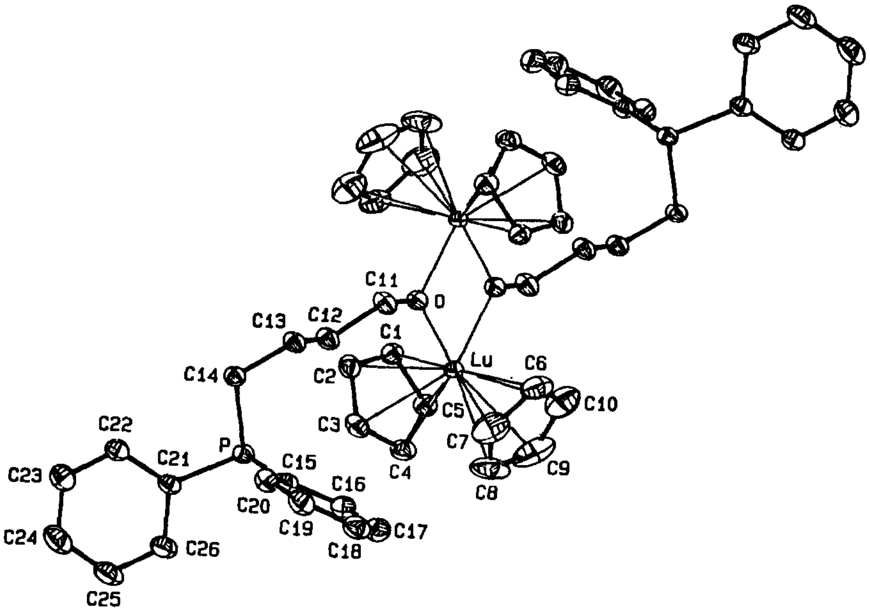


Fig. 21. $[Cp_2Lu(\mu\text{-}O(CH_2)_4PPh_2)]_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

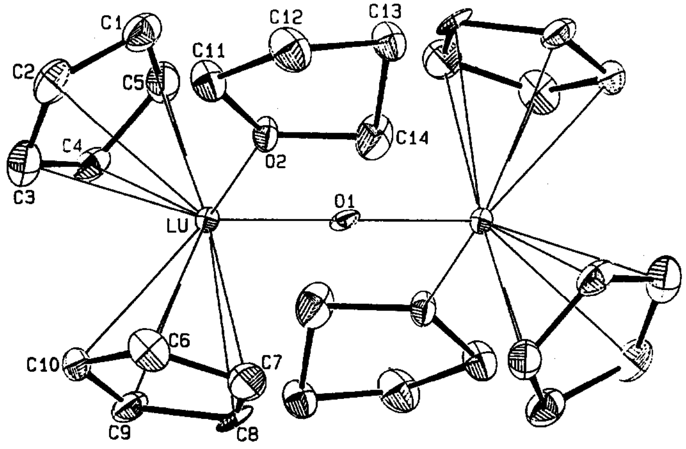


Fig. 22. $[Cp_2Lu(THF)]_2O$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Watson, et al.[45] reported the abstraction of fluorine atoms from perfluoroolefins by Cp^*_2LnL (Ln = Yb, Er, Sm; L = Et_2O, THF) and $(CpMe)_2Yb(THF)$. The crystal structures of $Cp^*_2YbF(OEt_2)$ (Figure 23) and $Cp^*_2YbF(THF)$ (Figure 24) gave the first values for terminal Ln-F bonds of Yb-F = 2.015(4)Å for the diethyl ether adduct and 2.026(2)Å for the THF complex. The cluster $[Cp^*_6Yb_5(\mu_4\text{-}F)(\mu_3\text{-}F)_2(\mu\text{-}F)_6]$ (Figure 25) was isolated from further reaction of Cp^*_2YbF with perfluoroolefins and was structurally characterized.

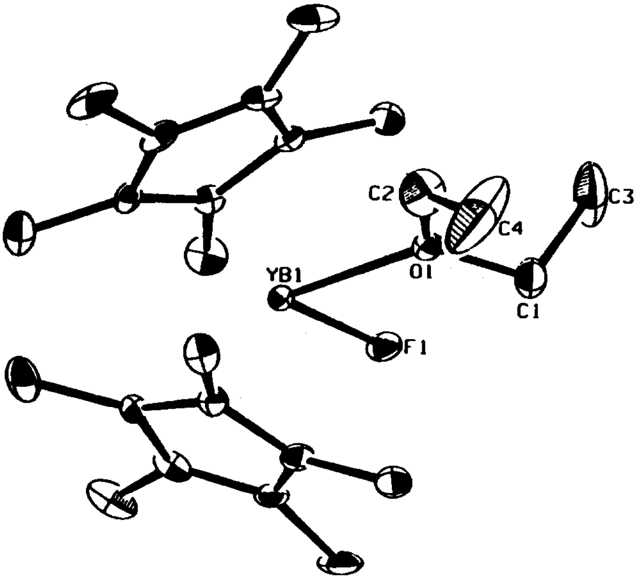


Fig. 23. $Cp^*_2YbF(OEt_2)$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

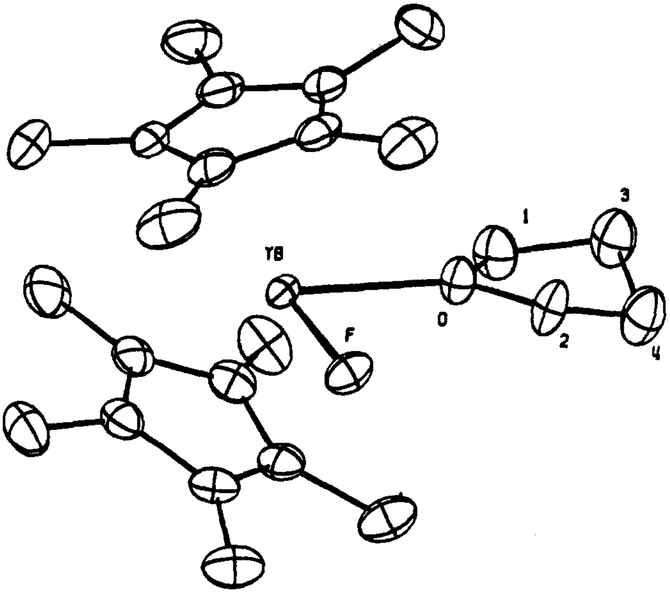


Fig. 24. $Cp^*_2YbF(THF)$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

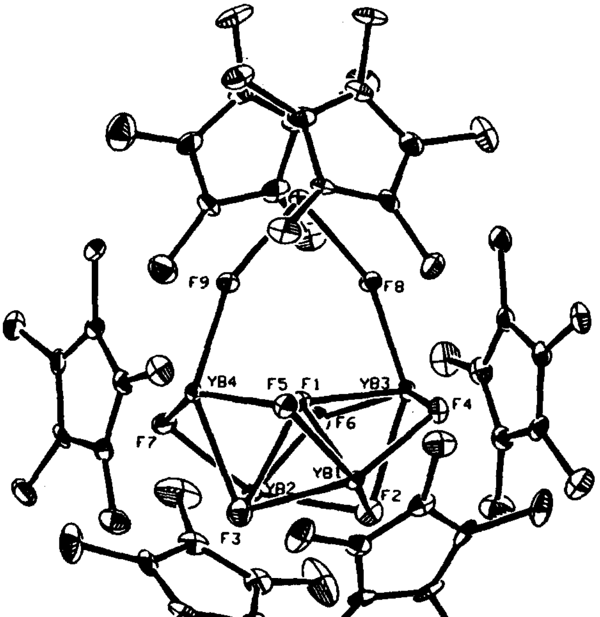


Fig. 25. $[Cp^*_6Yb_5(\mu_4\text{-}F)(\mu_3\text{-}F)_2(\mu\text{-}F)_6]$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

Edelmann, et al.[46] prepared the first divalent organoneodymium complex $[K(THF)_n]_2[Cp^*{}_2NdCl_2]$ by reaction of KCp^* with $NdCl_2(THF)_2$. Further reactions gave $Cp^*{}_2NdCl(THF)$, $Cp^*{}_2Nd(S_2CNMe_2)$, and $Cp^*{}_2NdSeMes(THF)$ (Mes = mesityl).

Schumann, et al.[47] synthesized and structurally characterized the ion pair $[Li(DME)_3][Cp_2Lu(SiMe_3)_2]$ (Figure 26) by reaction of $Cp_2Lu(\mu\text{-}Cl_2)Na(DME)_2$ with $LiSiMe_3$ in DME. The Lu-Si distance is 2.888(2)Å.

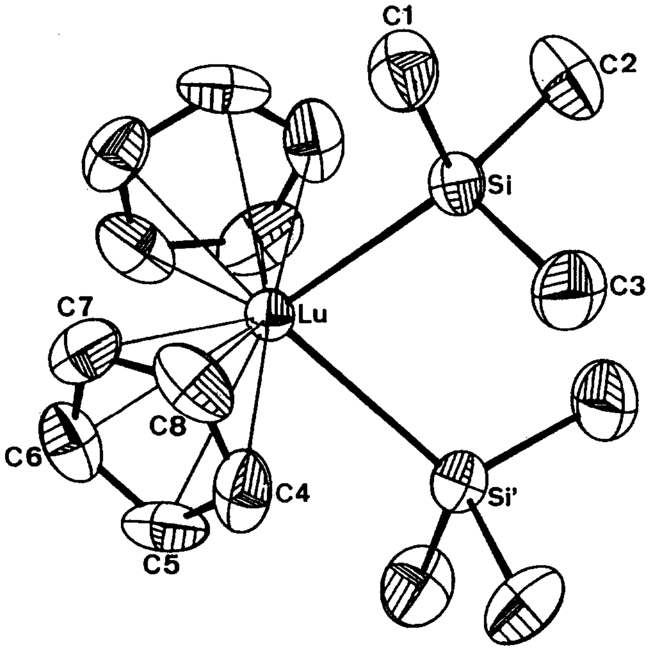


Fig. 26. The anion in $[Li(DME)_3][Cp_2Lu(SiMe_3)_2]$. (Reprinted with permission from Journal of Organometallic Chemistry.)

The mixed metal complexes, $Cp_2Y(THF)Re_2H_7(PMe_2Ph)_4$ and $Cp_2Lu\text{-}Re_2H_7(PMe_2Ph)_4$, were prepared and structurally characterized by Caulton, et al.[48] The Y complex (Figure 27) exhibits an Y-Re separation of 3.090(2)Å, while in the lutetium complex (Figure 28) Lu-Re = 3.068(1) and 3.025(1)Å.

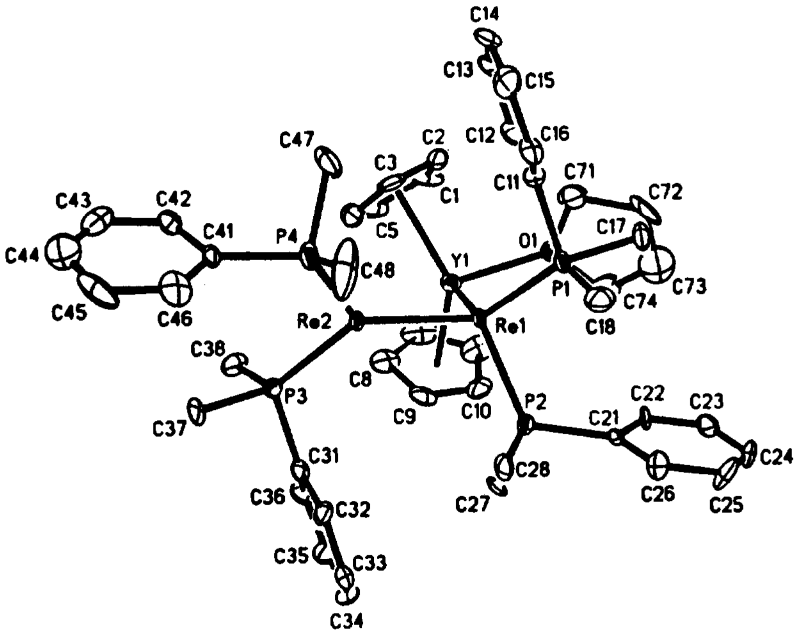


Fig. 27. $Cp_2Y(THF)Re_2H_7(PMe_2Ph)_4$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1990 American Chemical Society.)

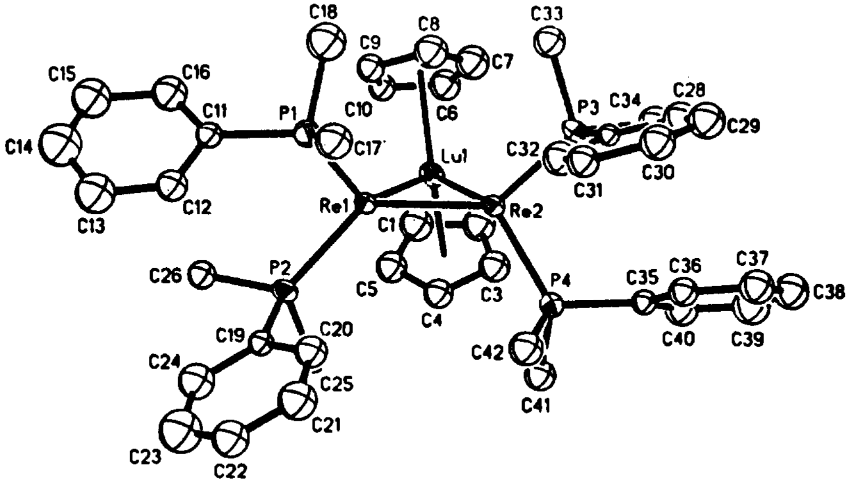


Fig. 28. $Cp_2LuRe_2H_7(PMe_2Ph)_4$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1990 American Chemical Society.)

Magomedov, et al.[49] observed a Lu-Ru bond length of 2.955(2)Å in the crystal structure of $Cp_2Lu(THF)Ru(CO)_2Cp$. There are no bridging carbonyl ligands.

Carbon-hydrogen activation of acetonitrile by $Cp^*_2LnCH(SiMe_3)_2$ (Ln = La, Ce) was observed by Teuben, et al.[50] The crystal structure of $[Cp^*_2LaCH_2CN]_2$ (Figure 29) revealed the CH_2CN ligand to be bridging through the nitrogen and terminal carbon ends with La-N = 2.537(4)Å and La-C = 2.748(4)Å.

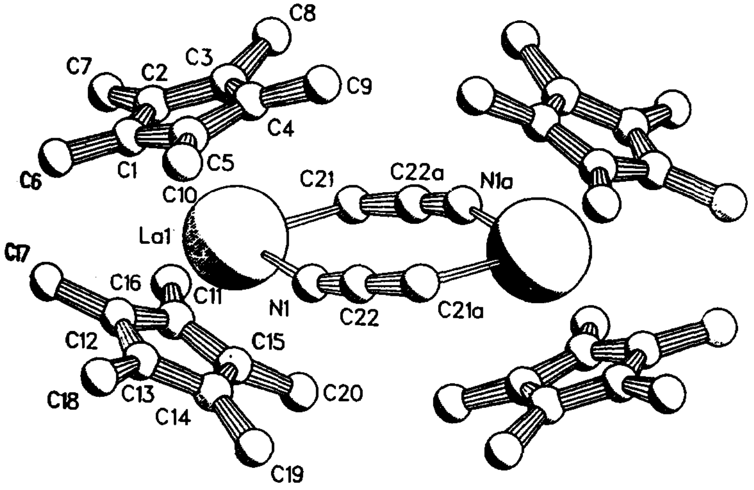


Fig. 29. $[Cp^*_2LaCH_2CN]_2$. (Reprinted with permission from Angewandte Chemie International.)

Yamamoto, et al.[51] studied the reactivity of Cp^*_2Yb with trialkylaluminum and metal halides. Reaction with metal halides led to Yb^{3+} moieties, $Cp^*_2YbCl(THF)$. Structural analysis of the $AlEt_3$ reaction product revealed a Yb-Al heterobimetallic complex with a mono-ethyl bridged structure.

Wong, et al.[52] studied the reaction of $[Li(OEt_2)_2][Cp^*_2LnCl_2]$ (Ln = Nd, Sm) with $Li(CH_2)(CH_2)PRR'$ (R = Me, R' = Ph; R = R' = Ph, Me, ^tBu). The compounds $Cp^*_2Ln[(CH_2)(CH_2)PRR'](LiCl)_2$ were prepared.

Evans, et al.[53] studied the reactivity of Cp^*_2Sm with aryl-substituted alkenes. Cis-stilbene was isomerized to trans-stilbene. Reaction with stilbene gave $[Cp^*_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^4\text{-}PhCHCHPh)$ while reaction with styrene afforded $[Cp^*_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^4\text{-}CH_2CHPh)$.

The connectivity in the former was established crystallographically although full details were not available due to poor crystal quality. The structure of the latter is depicted in Figure 30 and reveals an η^2-arene interaction.

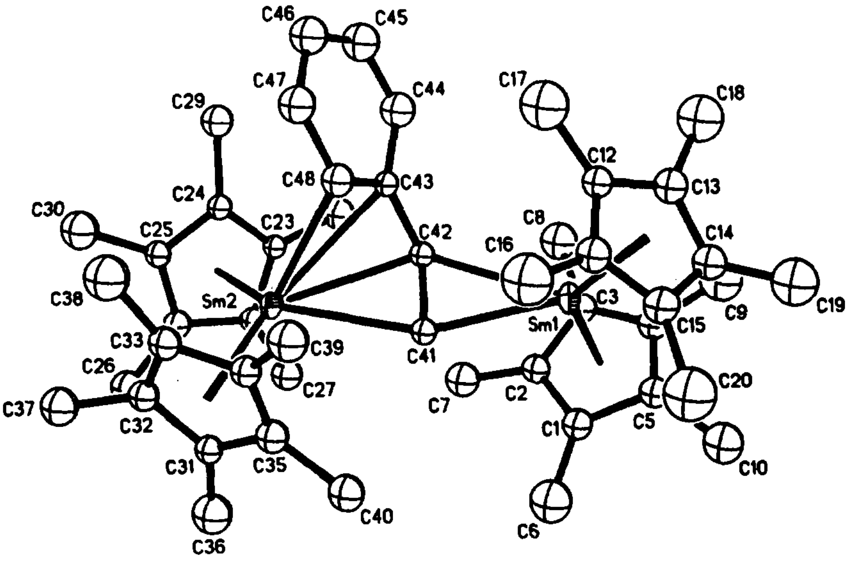


Fig. 30. $[Cp^*_2Sm]_2(\mu-\eta^2:\eta^4-CH_2CHPh)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1990 American Chemical Society.)

Roitershtein, et al.[54] treated Cp_2LuCl with the sodium salt of the anthracene dianion in THF and formed $Na[Cp_2Lu(R^{2\cdot})]$. Several chemical properties of the new compound were studied.

Evans, et al.[55] reacted $Cp^*_2Sm(THF)_2$ with $AgBPh_4$ in THF to form $[Cp^*_2Sm(THF)_2][BPh_4]$ (Figure 31). Further reactions with $KC{\equiv}CR$ led to $Cp^*_2Sm(C{\equiv}CR)(THF)$ (R = Ph (Figure 32), ${}^tBu$). The alkynide complex reacts with KCp, LiPh, and LiMe to form Cp^*_2CpSm, $Cp^*_2SmPh(THF)$, and $Cp^*_2SmMe(THF)$. Reaction with KCp^*, however, forms the alkoxy-tethered-Cp* complex $Cp^*_2Sm(O(CH_2)_4Cp^*)(THF)$ (Figure 33). The Sm-O(alkoxide) separation is 2.081(8)Å.

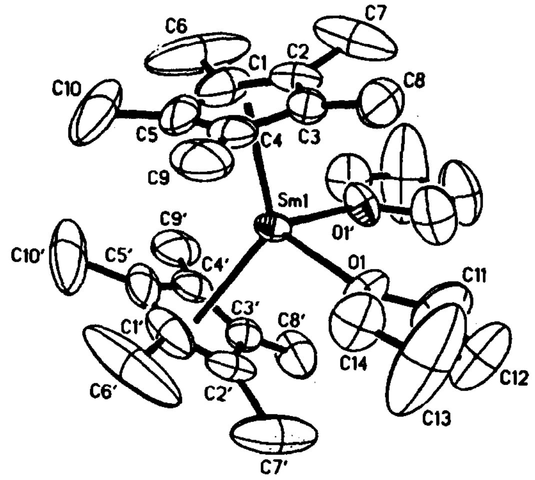


Fig. 31. The cation in $[\mathrm{Cp}^*_2\mathrm{Sm(THF)}_2][\mathrm{BPh}_4]$. (Reprinted with permission from *Organometallics*. Copyright 1990 American Chemical Society.)

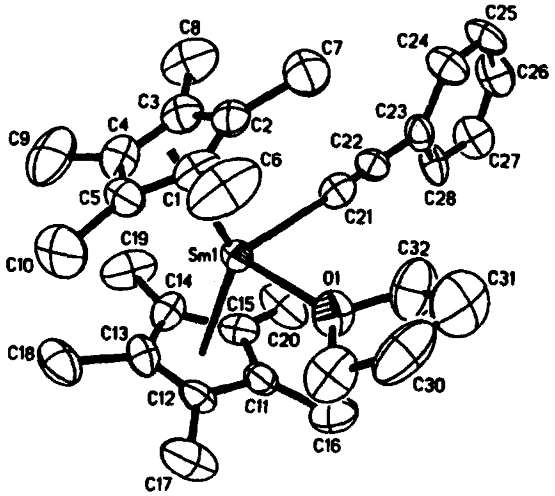


Fig. 32. $\mathrm{Cp}^*_2\mathrm{Sm(C{\equiv}CPh)(THF)}$. (Reprinted with permission from *Organometallics*. Copyright 1990 American Chemical Society.)

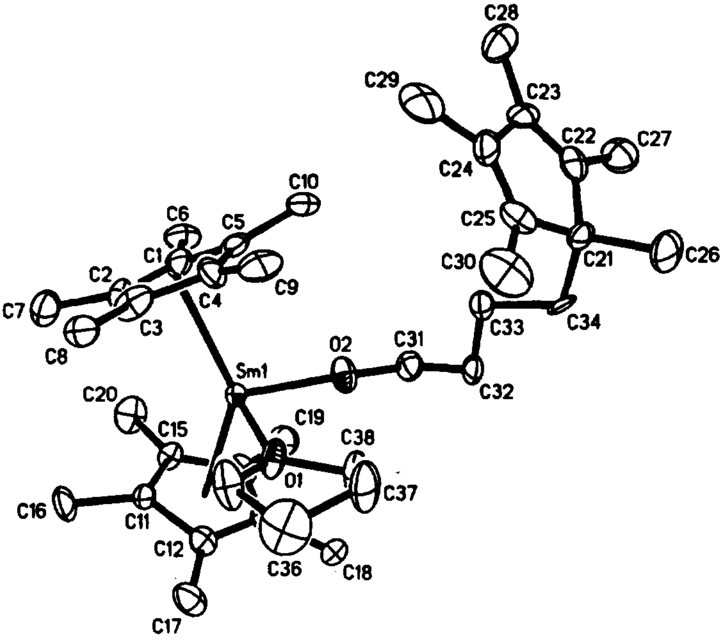


Fig. 33. $Cp^*_2Sm(O(CH_2)_4Cp^*)(THF)$. (Reprinted with permission from *Organometallics*. Copyright 1990 American Chemical Society.)

Shen, *et al.*[56] prepared $(Cp^tBu)_2Sm(DME)$ by reduction of the corresponding trivalent chloride. Reaction of this compound with phenylacetylene yielded $[(Cp^tBu)_2SmC{\equiv}CPh]_2$ (Figure 34). The Sm-C(σ) bond lengths are 2.56(1) and 2.62(1)Å.

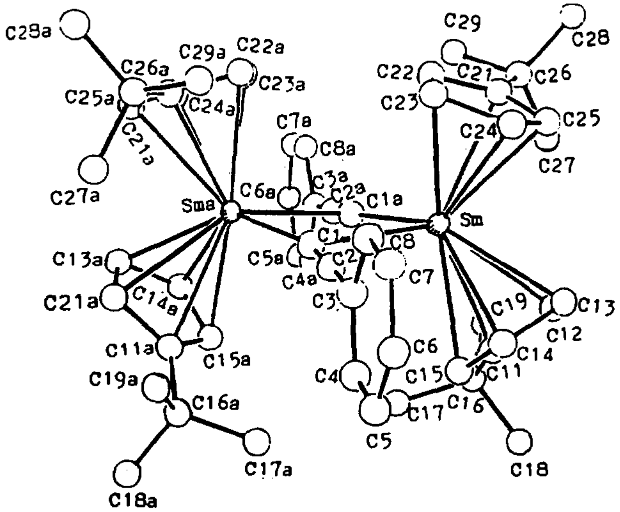


Fig. 34. $[(Cp^tBu)_2SmC{\equiv}CPh]_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

Coupling of phenylethyl ligands was observed by Evans, et al.[57] in the formation of $[Cp^*_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_4Ph)$ (Figure 35). This compound was prepared by reaction of $Cp^*_2Sm(THF)_2$ with PhC_4Ph, by reaction of $[Cp^*_2Sm(\mu\text{-}H)]_2$ with PhCCH, by thermolysis of $Cp^*_2Sm(CCPh)(THF)$, and by the reaction of $Cp^*_2SmCH(SiMe_3)_2$ with PhCCH.

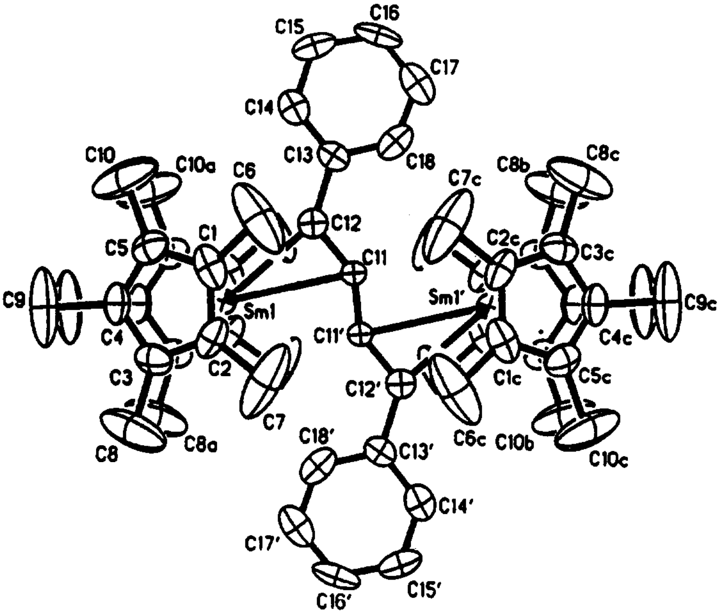


Fig. 35. $[Cp^*_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_4Ph)$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

Marks, et al.[58] published a symposium report on their investigation of absolute and relative metal-ligand bond enthalpies for L_2LnX, L_2LnR, and L_2LnL' (L = cyclopentadienyl type ligand; Ln = La, Nd, Sm, Eu, Yb; X = Cl, Br, I, alkoxide, dialkylamide; R = $CH(SiMe_3)_2$, η^3-allyl, H; L' = η^2-alkyne). The study was conducted using batch titration calorimetry.

Evans, et al.[59] structurally characterized a series of allyl compounds $Cp^*_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (Figure 36), $Cp^*_2Sm(\eta^3\text{-}CH_2CHCHMe)$ (Figure 37), $Cp^*_2Sm(\eta^3\text{-}CH_2CHCHPh)(OC_8H_8)$ (Figure 38), $[Cp^*_2Sm(\mu,\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$ (Figure 39), and $[Cp^*_2Sm(\mu,\eta^3\text{-}CH_2CHCH\text{-})]_2$ (Figure 40). The compounds were prepared by the reaction of Cp^*_2Sm with alkenes in hexane or toluene.

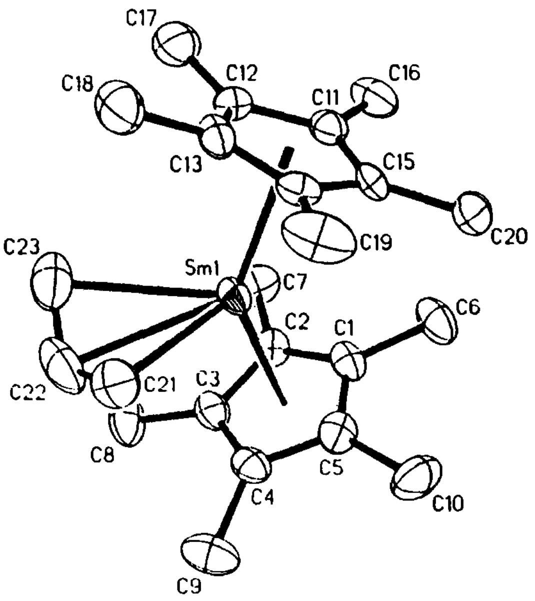


Fig. 36. $Cp^*_2Sm(\eta^3-CH_2CHCH_2)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1990 American Chemical Society.)

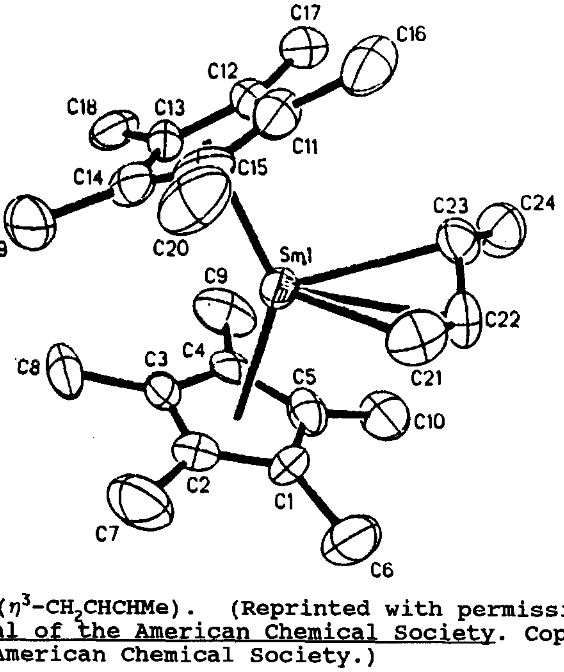


Fig. 37. $Cp^*_2Sm(\eta^3-CH_2CHCHMe)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1990 American Chemical Society.)

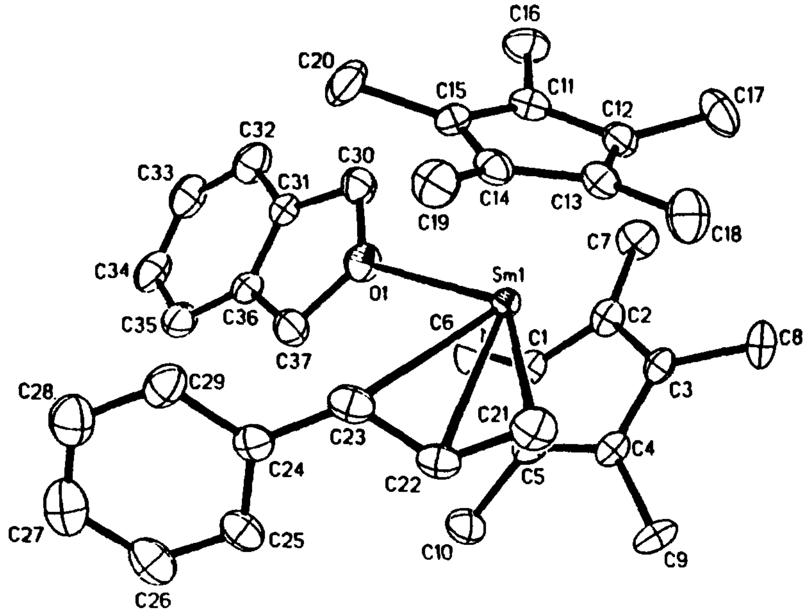


Fig. 38. $Cp^*_2Sm(\eta^3\text{-}CH_2CHCHPh)(OC_8H_8)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1990 American Chemical Society.)

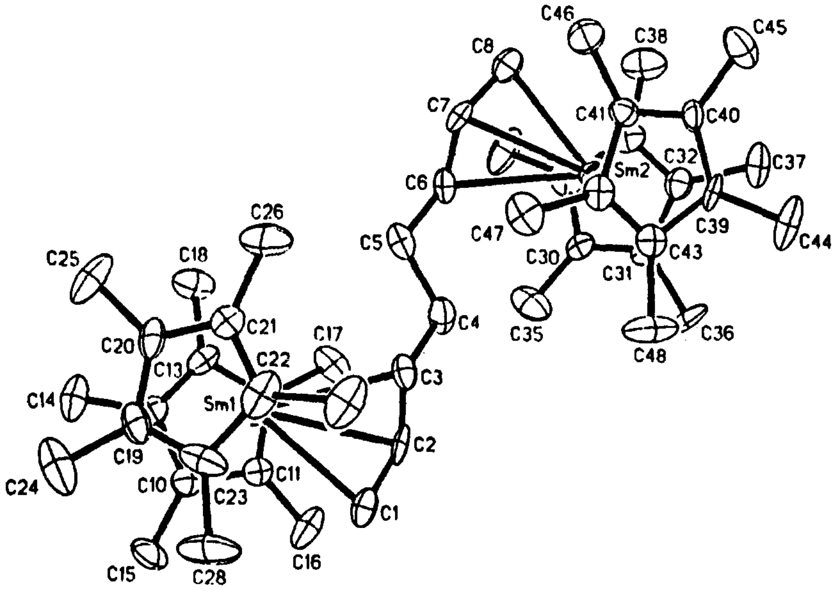


Fig. 39. $[Cp^*_2Sm(\mu,\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1990 American Chemical Society.)

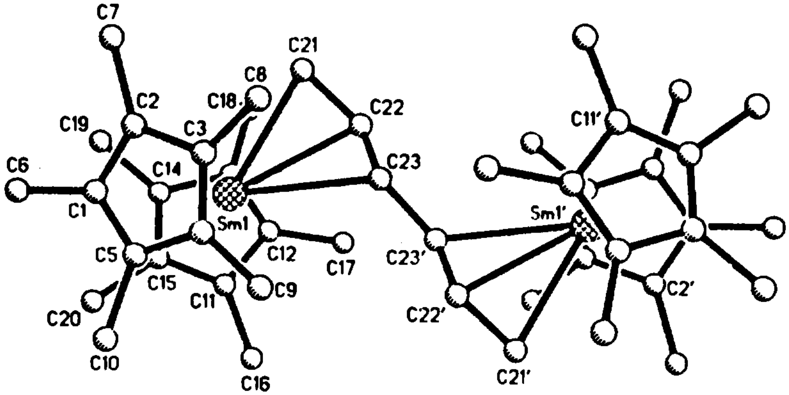


Fig. 40. $[Cp^*_2Sm(\mu,\eta^3\text{-}CH_2CHCH\text{-})]_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1990 American Chemical Society.)

(v) Bridged cyclopentadienyl compounds. Marks, et al.[60] published a massive report on Lu and Y hydrocarbyl and hydride chemistry using the bridged-Cp ligand, $[R_2Si(Me_4C_5)(C_5H_4)]^{2-}$ (R_2SiCp^*Cp, R = Me, Et). The ligand was prepared by reaction of NaCp with $R_2Si(Cp^*)Cl$ and then reacted with $LnCl_3(THF)_3$ to form $(R_2SiCp^*Cp)LnCl_2Li(OEt_2)$. Alkylation of these compounds led to $(R_2SiCp^*Cp)LnCH(SiMe_3)_2$ (R = Me, Ln = Lu - Figure 41). Hydrogenolysis gave $[(R_2SiCp^*Cp)LnH]_2$ (R = Et, Ln = Lu - Figure 42). Reaction of the hydrides with α-olefins led to bridged alkyls $[(R_2SiCp^*Cp)LnHR']_2$ (R' = ethyl, n-propyl, n-hexyl; R = ethyl, R' = ethyl, Ln = Lu - Figure 43). The latter two structures have R_2SiCp^*Cp ligands which bridge two different metal atoms. The thermochemistry of the new compounds was also discussed.

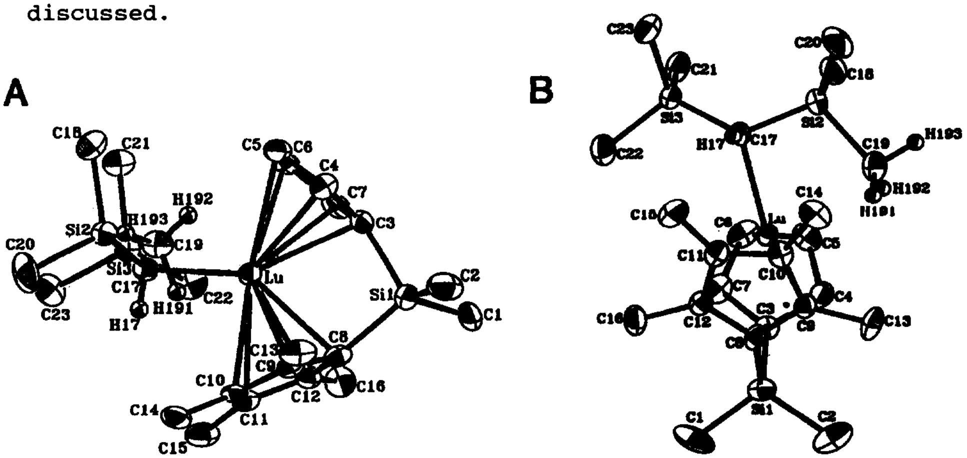


Fig. 41. $(Me_2SiCp^*Cp)LuCH(SiMe_3)_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1990 American Chemical Society.)

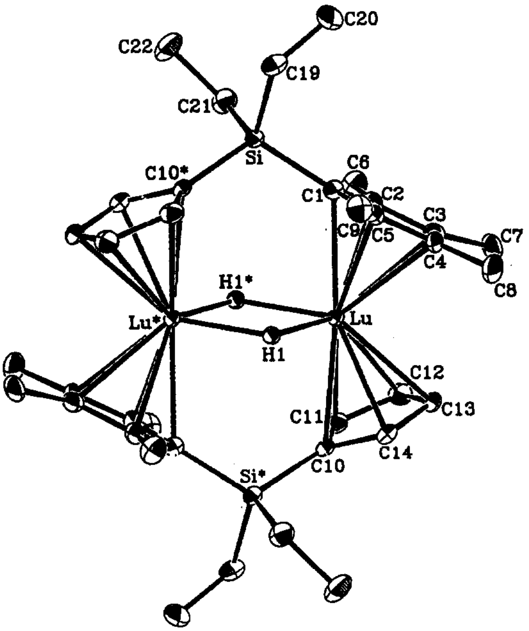


Fig. 42. [$(Et_2SiCp^*Cp)LuH]_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1990 American Chemical Society.)

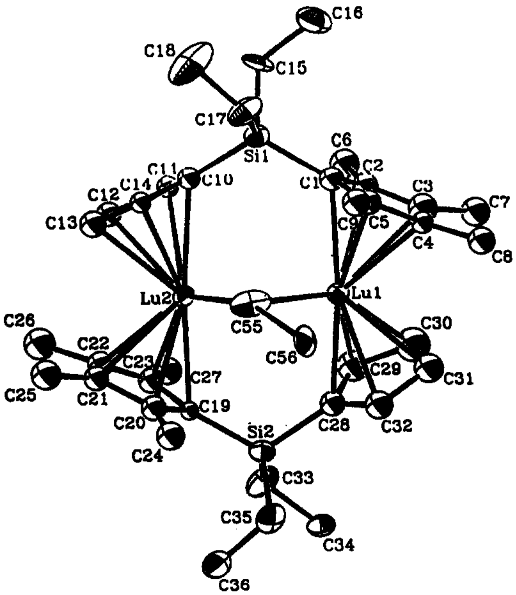


Fig. 43. [$(Et_2SiCp^*Cp)LuH(Et)]_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1990 American Chemical Society.)

Fischer, et al.[61] utilized mass spectrometry to determine the chelating or metal bridging nature of $Me_2SiCpCp$ in $[(Me_2SiCpCp)Yb(\mu\text{-}Cl)]_2$, $[(Me_2SiCpCp)Y(\mu\text{-}Cl)]_2$, and $(Me_2SiCpCp)Yb(\mu\text{-}Cl)_2\text{-}Y(CpCpSiMe_2)$. The first was observed to be metal bridging, while the latter two appear to be chelating.

Chen, et al.[62] prepared and structurally characterized $[Mg_2Cl_3(THF)_6][(Me_4C_2CpCp)YbCl_2]$ (Figure 44). The bridged Cp ligand is chelating.

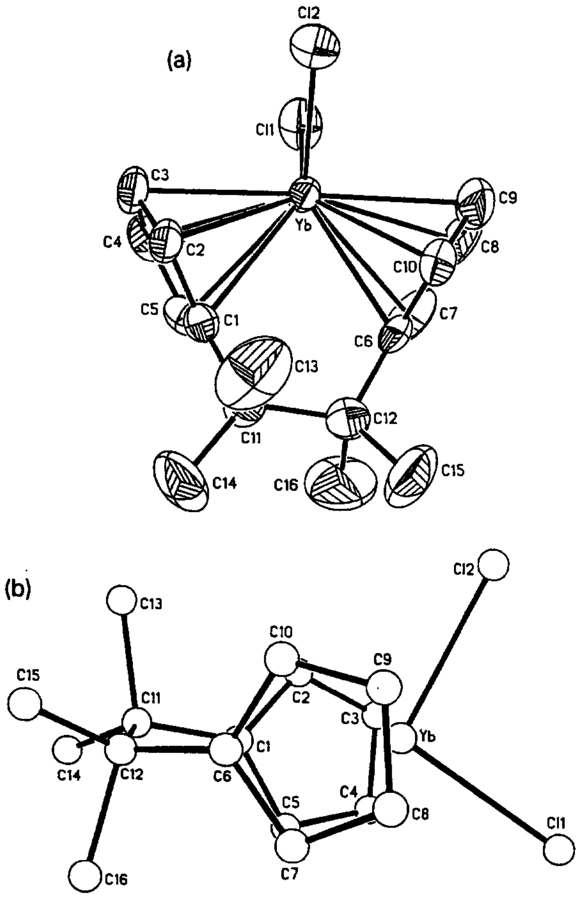


Fig. 44. The anion in $[Mg_2Cl_3(THF)_6][(Me_4C_2CpCp)YbCl_2]$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Qian, et al.[63] synthesized a bridging Cp ligand with a 3-oxapentamethylene bridge. Eight new compounds were prepared: $(Cp(CH_2)_2O(CH_2)_2Cp)(CpR)Ln$ (R = H, Ln = Nd, Gd, Er, Yb, Lu, Y; R = Me, Ln = Yb, Y). There is intramolecular coordination of the oxygen atom to the lanthanide.

Xylylene bridged-cyclopentadienyl ligands were also prepared by Qian, et al.[64] and used to make $(CpCH_2C_6H_4CH_2Cp)LnCl(THF)$ (Ln = La, Pr, Nd, Dy, Y, Er, Yb). Structures were characterized by elemental analysis, IR, ^1H NMR, mass spectroscopy, and XPS.

(vi) Indenyl and arene compounds. The synthesis and crystal structure of $[Na(THF)_6][(Ind_3Ln)_2Cl]$ (Ln = Sm, Nd; Ind = indenyl anion, $C_9H_7^-$) was reported by Su, et al.[65] A single chloride bridge joins two Sm centers.

Fan, et al.[66] prepared the η^6-arene complexes $Ln(C_6H_6)(AlCl_4)_3$-C_6H_6 (Ln = La, Nd) by reaction of activated $AlCl_3$ with $LnCl_3$ in benzene. The crystal structure of the Nd complex was reported.

Deacon, et al.[67] observed the formation of an intramolecular Yb···π-arene interaction in low coordinate bulky aryl oxide complexes. The crystal structure of $Yb(O\text{-}2,6\text{-}Ph_2C_6H_3)_3$ (Figure 45) revealed the π-arene interaction and an average Yb···C separation of 2.978(6)Å.

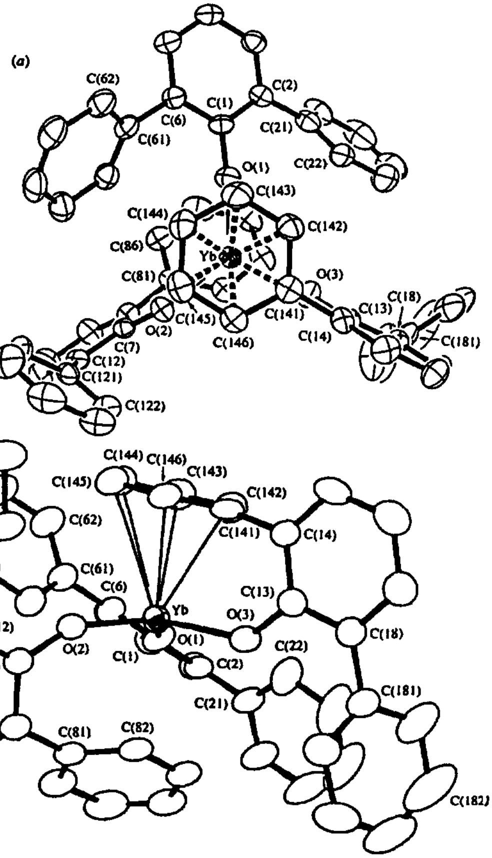


Fig. 45. $Yb(O\text{-}2,6\text{-}Ph_2C_6H_3)_3$. (Reprinted with permission from Australian Journal of Chemistry.)

(vii) Lanthanide carbon bonds without supporting cyclopentadienyl ligands. The crystal structure of $GdPhCl_2(THF)_4$ (Figure 46) was reported by Chen, et al.[68] It was prepared by reaction of $GdCl_3$ with LiPh in THF and exhibits a Gd-C distance of 2.42(2)Å.

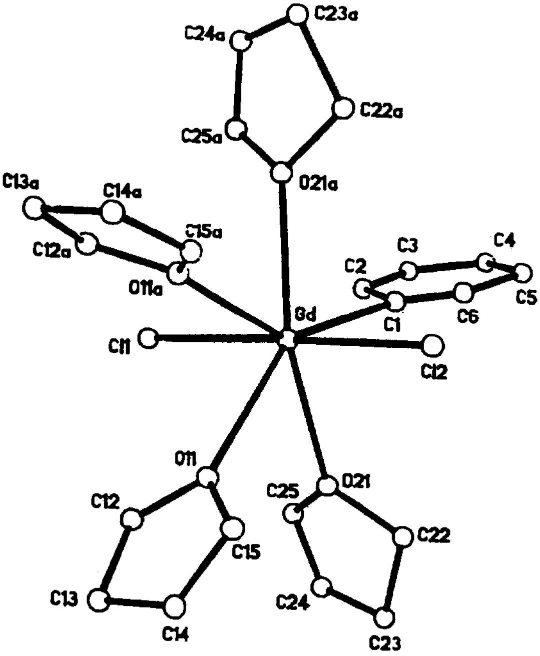


Fig. 46. $GdPhCl_2(THF)_4$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Huang, et al.[69] published the synthesis of $Ln(2\text{-}MePh)_3$ (Ln = Ce, Pr, Nd, Sm, Gd, Er). The compounds were prepared by reaction of $LnCl_3$ with Li(2-MePh) in benzene. The 2-methoxy derivatives, $Ln(2\text{-}MeOPh)_3$ (Ln = Ce, Pr, Nd) and $Gd(2\text{-}MeOPh)_2Cl$, were described in another publication.[70]

Bochkarev, et al.[71] reported that the reaction of napthalene-ytterbium and $HgPh_2$ or $BiPh_3$ in THF gave $Yb_2(Ph)_5(THF)_4$. Crystallographic and magnetic susceptibility studies indicated one divalent and one trivalent Yb atom. The reaction with $SnPh_4$ produced $Yb(Ph_3Sn)_2(THF)_4$.[72] Structural analysis revealed Yb-Sn bonds.

Roitershtein, et al.[73] studied the radical anion and dianion of anthracene as ligands for Ce, Sm, and Yb. The compounds were prepared by reaction of anthracene with Ln^0 in the presence of halide salts. The reactivities of the compounds with C-H acids were also investigated.

Rosi and Bauschlicher[74] carried out electronic structure calculations on the interaction of La^+ and La^{2+} with C_2H_2, C_2H_4, and C_3H_6. The bonding in the dication is electrostatic.

Collins, et al.[75] reported that the reaction of LiR (R = alkyl or aryl) with $La(OSO_2CF_3)_3$ led to $LaR(OSO_2CF_3)_2$. The alkyllanthanum triflates were used as organometallic nucleophiles and were found to convert hindered, tertiary amides to ketones.

$Yb(CN)_3$ was prepared by Utimoto, et al.[76] by reaction of YbR_3 with Me_3SiCN. The compound was found to catalyze regio- or stereoselective cleavage of an oxirane with Me_3SiCN to yield β-trimethylsiloxynitrile.

Ito, et al.[77] synthesized [2-(benzyloxy)-1-(N-2,6-xylylimino)ethyl]samarium and utilized it as a synthetic equivalent to the α-hydroxacetyl anion. It was prepared by the SmI_2 mediated coupling reaction of benzyl chloromethyl ether with 2,6-xylylisocyanide.

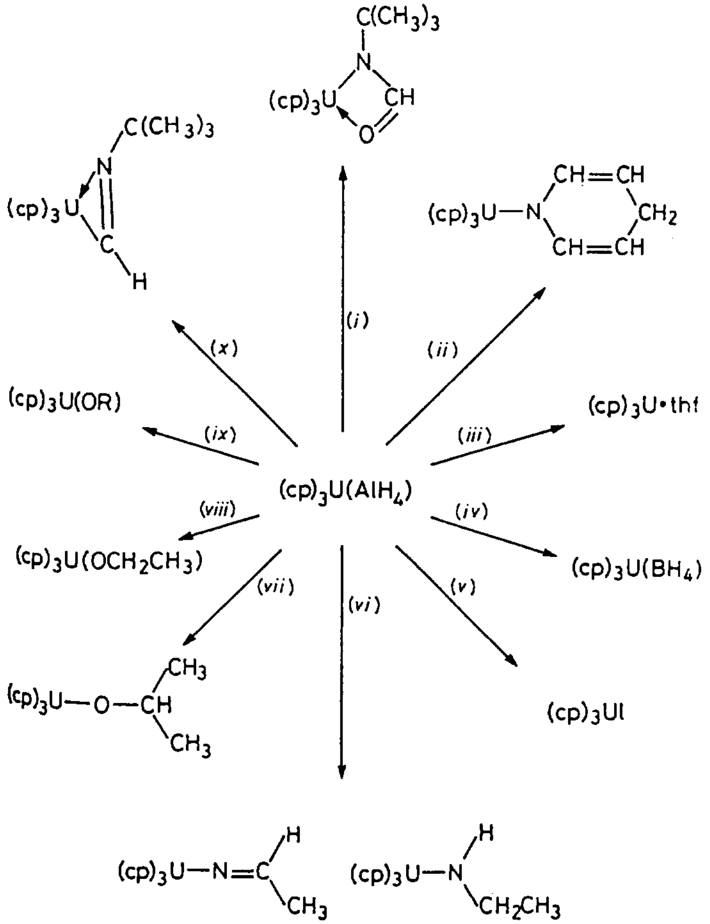
The phenylacetylide complexes $Ln(CCPh)_3$ (Ln = Pr, Sm, Eu, Gd, Tb, Er, Yb), $Ln(CCPh)_n(N(SiMe_3)_2)_{3-n}$, and $Ln(CCPh)_nX_{3-n}\cdot 0.5DME$ were prepared by Shustov, et al.[78] The catalytic behavior of the compounds was also investigated.

Fukuzawa, et al.[79] prepared the π-allyl compound $Li[Ln(C_3H_5)_4]$ (Ln = Ce, Nd, Sm) in situ from $Sn(C_3H_5)_4$, $LnCl_3$, and Li^nBu in THF. The complexes react with α,β-unsaturated carbonyl compounds to yield 3-hydroxy-1,5-dienes with 1,2-regioselectivity.

ACTINIDES

(i) Tetrakiscyclopentadienyl compounds. Leonov, et al.[80] reported the reaction of Cp_4U with CCl_4 or $CHCl_3$ which resulted in Cp_3UCl and $Cp_3U(C_5H_4CCl_3)$ or $Cp_3U(C_5H_4CHCl_2)$. Cp_3UBu was prepared by reaction of Cp_4U and BuCl, while $Me_2CHCH_2Cl_2$ gave $Cp_3UCH_2CHMe_2$ and Me_3CCl resulted in $Cp_3UCH_2CMe_2Cl$.

(ii) Triscyclopentadienyl compounds. The reactivity of the U-H bond in $Cp_3U(AlH_4)$ was investigated by Ossola, et al.[81] The specific reaction pathways discussed are depicted in Scheme 1.



Scheme 1. (i) $(CH_3)_3CNCO$; (ii)C_5H_5N; (iii) (THF); (iv) $BH_3 \cdot S(CH_3)_2$; (v) CH_3I; (vi) CH_3CN; (vii) CH_3COCH_3; (viii) CH_3CHO; (ix) ROH; (x) $(CH_3)_3CNC$. (Reprinted with permission from *Journal of the Chemical Society, Dalton Transactions*.)

Antiferromagnetic coupling between uranium centers was observed by Andersen, *et al.*[82] in the bimetallic $[(CpMe)_3U]_2[\mu\text{-}1,4\text{-}N_2C_6H_4]$. Coupling is not observed when the bridging ligand is $1,3\text{-}N_2C_6H_4$.

$Cp_3U(NCBH_3)(NCMe)$ was crystallized from concentrated solutions of $[^nBu_4N][Cp_3U(NCBH_3)_2]$ in acetonitrile. The crystal structure reported by Fischer, *et al.*[83] is presented in Figure 47. The $NCBH_3$ ligand is linear (172(1)°) and is coordinated to uranium through the nitrogen at a U-N separation of 2.54(1)Å. The U-NCMe separation is 2.70(1)Å.

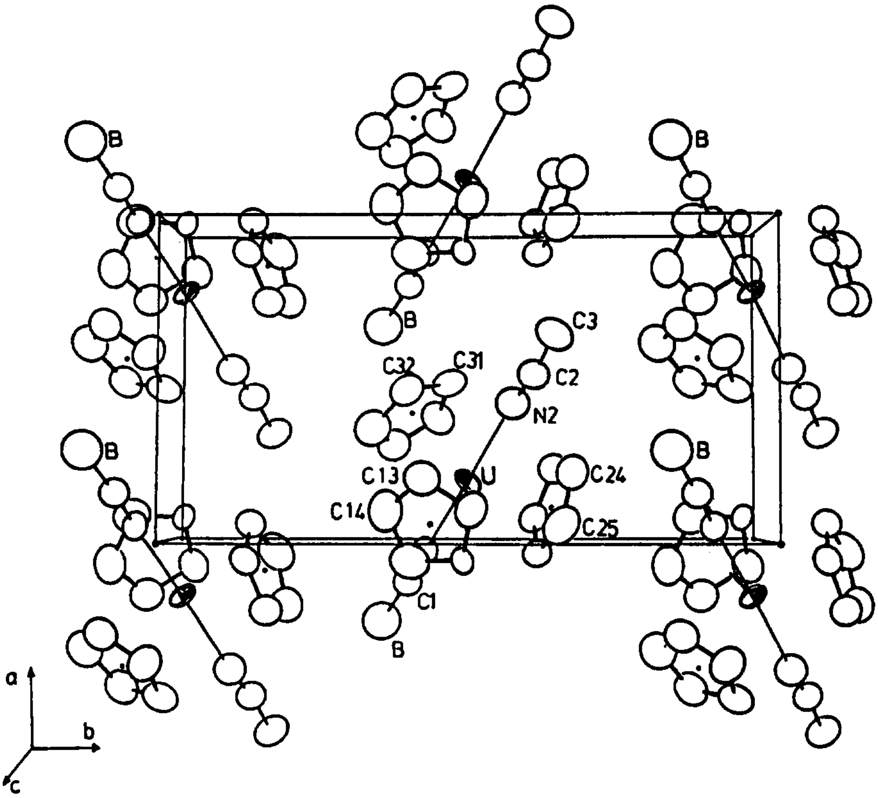


Fig. 47. The unit cell of $Cp_3U(NCBH_3)(NCMe)$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Villiers and Ephritikhine[84] studied the oxidative addition of organic halides to $Cp_3U(THF)$. Evidence for a halogen atom abstraction oxidative addition mechanism was obtained. The reaction in (1) was carried out

$$2Cp_3U(THF) + RX \longrightarrow Cp_3UX + Cp_3UR \qquad (1)$$

with R = MeI, ${}^{n}BuX$ (X = Cl, Br, I), ${}^{i}PrCl$, $PhCH_2Cl$, and $CH_2{=}CHCH_2Cl$. The alkyl derivatives were also prepared by reaction of Cp_3UCl with RX in the presence of Na/Hg.

Marks, et al.[85] carried out ${}^{13}C$ CPMAS NMR studies of the surface structures and reactivity of Cp^*_3ThMe, $Cp^*_2ThMe_2$, $Cp^*_2ThEt_2$, $Cp^*Th(CH_2Ph)_3$, and $Cp^*_2UMe_2$. Heterolytic Th-C scission was shown to occur transferring an alkyl anion to a Lewis acid surface. On more basic surfaces, μ-oxo moieties are formed either by Th-C protonolysis or transfer of an alkyl group to the surface.

Detailed information was given regarding the surface reactivity of these species.

Bau, et al.[86] published the first low temperature neutron diffraction analysis of an organometallic uranium complex, $Cp_3U{=}CHPMe_3$ (Figure 48). The α-hydrogen was shown to not be agostic, while the short U-C bond (2.293(1)Å) and large U-C-P angle (141.49(7)°) were taken as evidence of U=C multiple bond character.

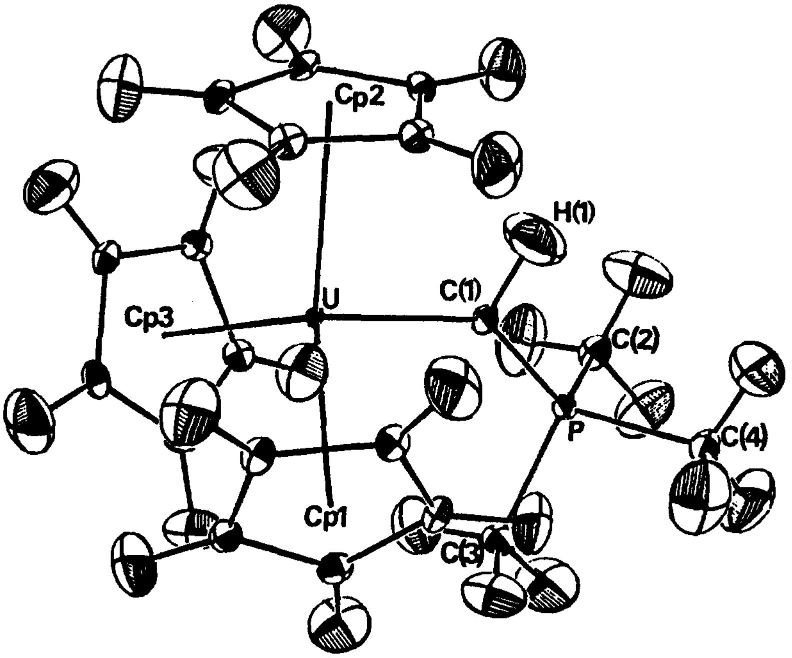


Fig. 48. $Cp_3U{=}CHPMe_3$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

Cramer, et al.[87] also reported on the reactivity of the U=C double bond in the reaction of $Cp_3U{=}CHPMeRPh$ (R = Ph, Me) with $CpCo(CO)_2$. Insertion into U=C produces $Cp(OC)CoC(OUCp_3){=}CHPMeRPh$. The R = Me derivative was crystallographically characterized (Figure 49). Further heating of this compound resulted in Cp(OC)CoPMeRPh.

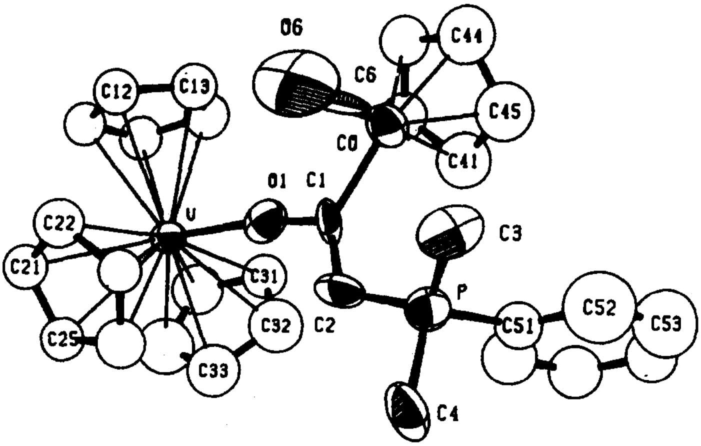


Fig. 49. Cp(OC)CoC(OUCp$_3$)=CHPMe$_2$Ph. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

Spirlet, et al.[88] published the crystal structure of Cp$_3$U(OPh) (Figure 50). Important parameters include U-O = 2.119(7)Å and U-O-C = 159.4(5)°. Leonov, et al.[89] studied the migratory insertion reaction of CO$_2$ with Cp$_3$U(OBu) in benzene.

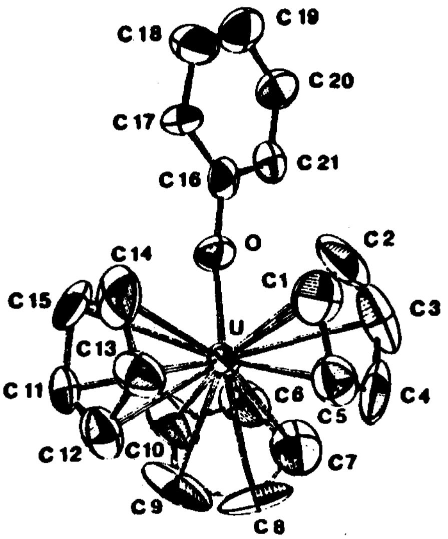


Fig. 50. Cp$_3$U(OPh). (Reprinted with permission from Acta Crystallographica.)

Andersen, et al.[27] investigated the reactivity of $(Cp^tBu)_3U$ with HSR and HOR. Reaction with HSPh led to the dimeric $(Cp^tBu)_4U_2(\mu\text{-}SPh)_2$ which rearranges in solution to give $(Cp^tBu)_3USPh$. When CpMe is utilized the dimer cannot be detected and only the rearrangement products $(CpMe)_3U(OMe)$, $(CpMe)_3U(OCHMe_2)$, $(CpMe)_3U(OPh)$, and $(CpMe)_3USCHMe_2$ were isolated.

Hanusa and Sockwell[30] evaluated published crystal structures of Cp_3An and Cp_2An compounds in an attempt to detect any covalency. The study was not conclusive, being unable to take into consideration steric interactions which may lead to major deviation from expected trends.

(iii) Biscyclopentadienyl compounds. Marks and Lin[90] published a lengthy report on their kinetic, mechanistic, stereochemical, and molecular mechanics studies of olefin insertion reactions into the An-H bond of $Cp^*_2AnH(OR)$. The alkoxides studied included O^tBu, OCH^tBu_2, (1R,2S,5R)-menthoxide, (R)-2-butoxide, [(1S)-endo]-bornoxide, (1R,2S,5R)-neomenthoxide. The olefins investigated included cyclohexene, 1-hexene, ethylene, 4-methoxystyrene, styrene, cis-2-butene, and norbornene.

The reaction of $U(NEt)_4$ with $(CpPPh_2)_2$ gave $(CpPPh_2)_nU(NEt_2)_{4-n}$ (n = 1-4) as reported by Dormond, et al.[91] Reaction of the n = 2 and 4 derivatives with $M(CO)_4(C_7H_8)$ (M = Mo, Cr) gave hetero-binuclear compounds, $((CpPPh_2)_2Mo(CO)_4)U(NEt_2)_2$ and $((CpPPh_2)_2M(CO)_4)U(CpPPh_2)_2$ (M = Mo, Cr).

The cyclopentadienyl-like ligand $C_4Me_4P^-$ was utilized by Baudry, et al.[92] to prepare $(\eta^5\text{-}C_4Me_4P)_2U(BH_4)_2$. The crystal structure of this compound (Figure 51) reveals pentahapto heterocycles with average U-P and U-C distances of 2.905(8) and 2.81(4)Å, respectively. Solution NMR also suggested the presence of the dimeric $[(\eta^5\text{-}C_4Me_4P)_2U(BH_4)]_2$ in which the P or a pentahapto coordinated ligand also participates in a sigma interaction with a second uranium center.

(iv) Monocyclopentadienyl compounds. The bisalkoxides, $CpRU(OR')_2Cl$ (R = H, Me; R' = Et, ^nPr, ^iPr, ^nBu, ^tBu), were prepared by Delavaux-Nicot and Ephritikhine[93] by reaction of $(CpR)_3UCl$ with 2 R'OH. The alkoxides, $(CpR)_{4-n}U(OR')_n$ (n = 1-3), were reported to be intermediates in these reactions.

Domingos, et al.[94] reported the crystal structure of $CpUCl_2[HB(3,5\text{-}Me_2Pz)_3]$ (Figure 52). The average bonding parameters include U-Cp = 2.74(1)Å, U-N = 2.51(2)Å, and U-Cl = 2.60(1)Å.

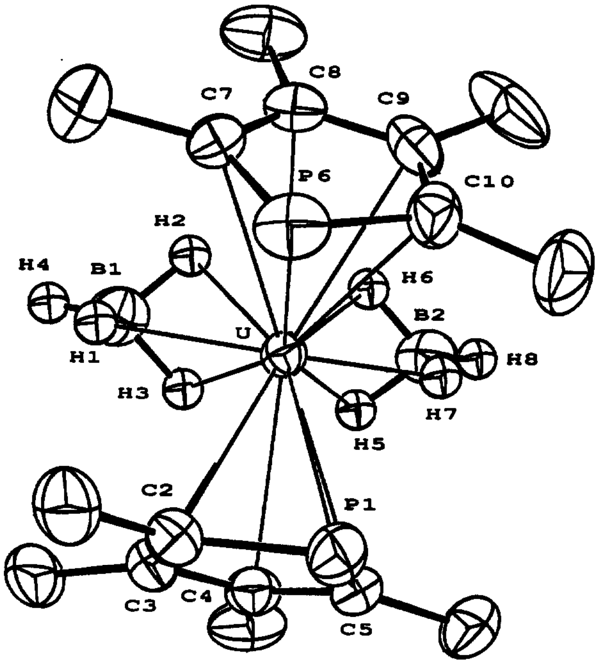


Fig. 51. $(\eta^5\text{-}C_4Me_4P)_2U(BH_4)_2$. (Reprinted with permission from Angewandte Chemie International.)

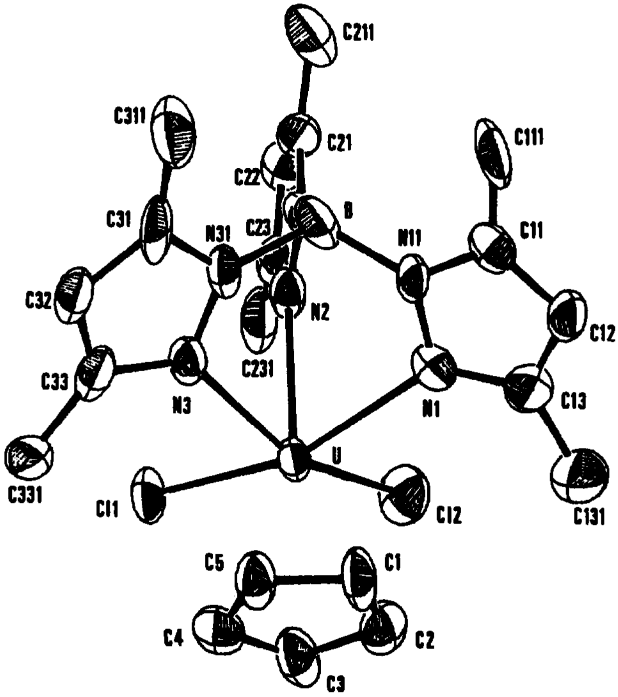


Fig. 52. $CpUCl_2[HB(3,5\text{-}Me_2Pz)_3]$. (Reprinted with permission from Polyhedron.)

(v) Indenyl compounds. Spirlet, *et al.*[95] published the crystal structure of $(IndEt)_3ThCl$ (Figure 53). The three ethylindenyl ligands are trihapto coordinated with Th-C separations ranging from 2.71(1)-2.86(1)Å for the coordinated carbon atoms and 2.89(1)-2.98(1)Å for the remaining carbon atoms in the five membered rings. The Th-Cl distance is 2.673(3)Å.

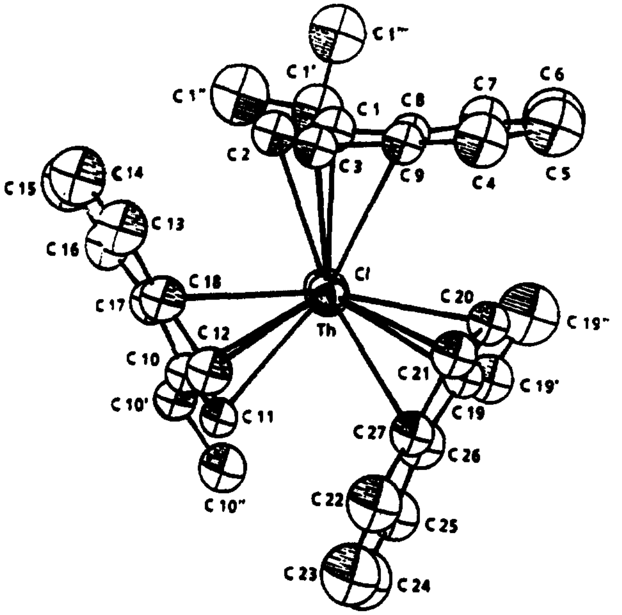


Fig. 53. $(IndEt)_3ThCl$. (Reprinted with permission from Acta Crystallographica.)

Goffart, *et al.*[96] investigated uranium-ligand bond disruption enthalpies in the $Ind_3U/Ind_3UI/Ind_3UMe$ system using iodinolysis batch titration solution calorimetry. The values obtained from toluene solution include U-I = 267(3) kJ mol^{-1} and U-Me = 196(7) kJ mol^{-1}.

(vi) Cyclooctatetraenyl compounds. Streitwieser, *et al.*[97] investigated the uranocene half-sandwich. $(COT)UCl_2$ was prepared by reduction of cyclooctatetraene by UCl_3 or via reaction of UCl_4, cyclooctatetraene, and NaH. The authors measured the activation parameters for coordination of PMe_3 and the reactivity of the half-sandwich with monodentate and bidentate metal-alkyls and metal-alkoxides including MR (M = Li, R = Me, CH_2Ph, Ph, CH_2CMe_3, CH_2SiMe_3; M = MgCl, R = Me, CH_2Ph, CH_2SiMe_3) and MOR (NaO^tBu, KO^tBu, NaOPh). Reaction with Na(acac) (acac = acetylacetonate) led to the isolation of (COT)U(acac)$_2$. The crystal structure of this complex is presented in Figure 54. Reactions of the uranocene half-sandwich with excess pyridine in toluene led to the adduct, (COT)$UCl_2(NC_5H_5)_2$. The crystal structure of this complex is depicted in Figure 55. The unique U-N separations are 2.639(5) and 2.644(6)Å.

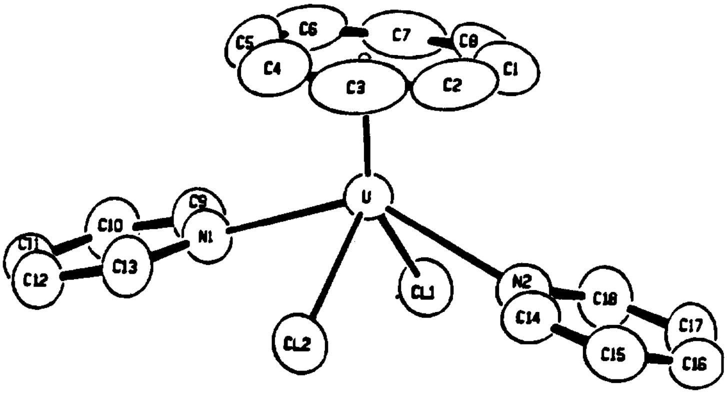


Fig. 54. (COT)U(acac)$_2$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

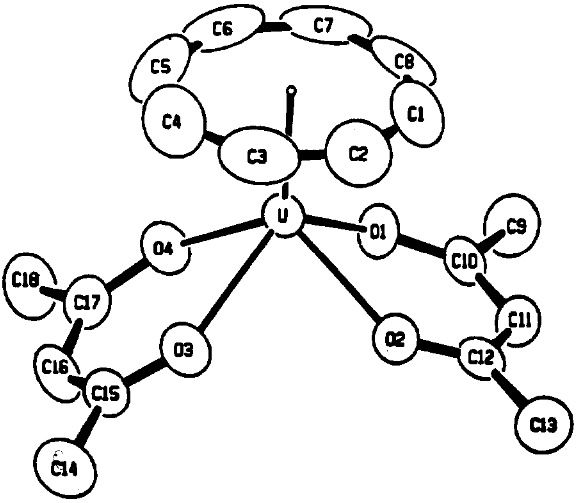


Fig. 55. (COT)$UCl_2(NC_5H_5)_2$. (Reprinted with permission from Organometallics. Copyright 1990 American Chemical Society.)

Streitwieser, et al.[98] studied electron transfer in uranocene, neptunocene, and plutonocene derivatives. The compounds prepared and studied included $K[(COT)_2U]$, $(^tBuCOT)_2An$ (An = Np, Pu), and $K[(^tBuCOT)_2An]$ (An = Np, Pu). Rapid electron exchange on the NMR time scale was noted for An(IV) → An(III).

Baudry, et al.[99] prepared $(COT)U(BH_4)_2$ via reaction of uranocene with $U(BH_4)_4$. The Lewis base adducts $(COT)U(BH_4)_2L$ (L = PPh_3, THF, $OPPh_3$) and the mixed ring compounds $(COT)CpU(BH_4)L$ (L = THF, $OPPh_3$) were prepared. The crystal structure of $(COT)U(BH_4)_2(OPPh_3)$ was determined (Figure 56). The U-O separation is 2.27(1)Å and the average U-C distance is 2.68(1)Å.

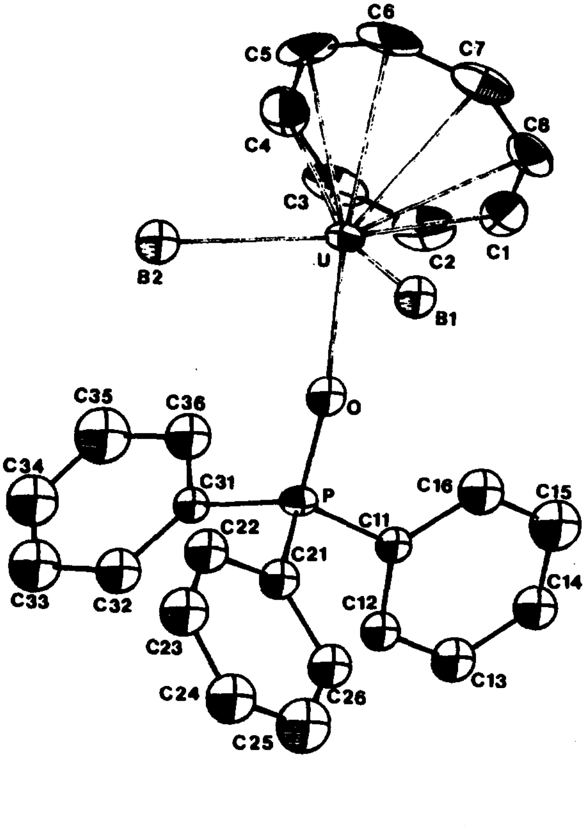


Fig. 56. $(COT)U(BH_4)_2(OPPh_3)$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Bèrthet, et al.[100] published the preparation of $(COT)UI_2(THF)_2$ via the reaction of uranocene with I_2 in THF. This compound was then used as a precursor in the synthesis of (COT)UI$_2$(hexamethylphosphoramide), (COT)U(acac)$_2$, (COT)Cp*UI, and [Li(THF)$_3$][(COT)U(CH$_2$SiMe$_3$)$_3$].

Komarov, *et al.*[101] published a high temperature gas-phase electron diffraction study of uranocene.

(vii) *Cyclohexadienyl compounds*. Baudry, *et al.*[102] investigated cyclohexadienyl uranium compounds. The compound (6-6-dimethylcyclohexadienyl)$_2$U(BH$_4$)$_2$ was prepared by reaction of K(dmch) with U(BH$_4$)$_4$. Reaction of U(BH$_4$)$_4$ and U(BH$_4$)$_2$(dmch)$_2$ gave U(BH$_4$)$_3$(dmch). Anionic compounds could be prepared by reaction of K(dmch) with UCl$_4$ or U(BH$_4$)$_3$(mesitylene) (e.g., [K(18-crown-6)][UX$_2$(dmch)$_2$] (X = Cl, BH$_4$)). The preparations of [K(THF)$_x$][U(BH$_4$)$_2$(dmch)$_2$] and U(BH$_4$)(OPPh$_3$)(dmch)$_2$ were also reported.

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