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Lanthanides and actinides. Annual survey covering the year 1991 *

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1. 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 because of their similar size and charge to the lanthanides. Abstracts of papers presented at conferences, dissertations, and patents have been excluded.

Several general review articles on f-element organometallic compounds appeared in 1991. The annual survey in this series covering the years 1984–1986 (314 references) was published [1]. Jones [2] published the annual progress report on scandium, yttrium, the lanthanides and actinides (224 references), and f-elements were included in Winter's [3] review of complexes containing metal–carbon σ-bonds of the groups scandium to manganese (407 total references).

A few more specialized review articles also appeared in 1991. Poli [4] reviewed monocyclopentadienyl halide complexes of the d- and f-block elements (697 references). The electronic structure of cyclopentadienyl actinide complexes (145 references) [5] and actinide containing molecules in general (239 references) [6] were the subject of two reviews by Bursten and co-workers. Organometallic derivatives of actinide polypyrazolylborates were reviewed by Domingos *et al.* [7] (18 references), while Khattar *et al.* [8] looked at the potential of lanthanide metallacarboranes as high energy fuel additives. Deacon [9] included some discussion of lanthanide organometallic compounds in his review of rare earth elements (13 references). Utimoto *et al.* [10] reviewed highly selective synthesis reactions utilizing organolanthanoid reagents (15 references).

2. Lanthanides

2.1. *Cyclopentadienyl and cyclopentadienyl-like compounds*

2.1.1. *Monocyclopentadienyl compounds*

Schaverien *et al.* [11] prepared $Cp^*Y[CH(SiMe_3)_2](OC_6H_3{}^tBu_2)$ (Cp^* = pentamethylcyclopentadienyl anion, $C_5Me_5^-$) by reaction of $Cp^*Y(OC_6H_3{}^tBu_2)_2$ with $Li[CH(SiMe_3)_2]$. Hydrogenation of the product gave $[Cp^*Y(OC_6H_3{}^tBu_2)(\mu\text{-}H)]_2$. A crystal structure determination of the starting alkoxide (Fig. 1) and ^{89}Y NMR of the new compounds were also reported. The Y–O distances are 2.096(4) and 2.059(3) Å, the Y–Centroid(Cp^*) separation is 2.363(3) Å.

Ke *et al.* [12] prepared the mixed ligand complexes $Cp(COT)Ln(THF)_n$ (Cp = cyclopentadienyl anion, $C_5H_5^-$; COT = cyclooctatetraene dianion $C_8H_8^{2-}$;

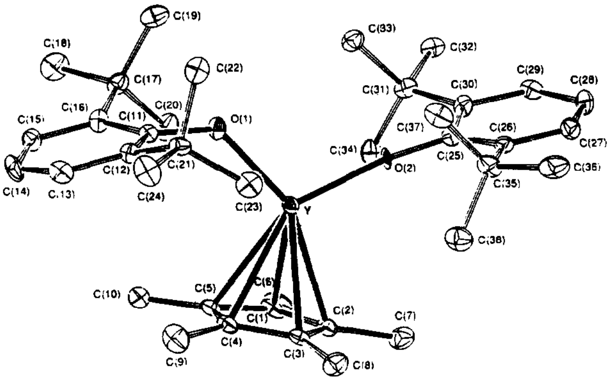

Fig. 1. $Cp^*Y(OC_6H_3{}^tBu_2)_2$. (Reprinted with permission from *Journal of the Chemical Society, Chemical Communications*.)

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* No reprints available. For previous Annual survey see *J. Organomet. Chem.*, *442* (1992) 225.

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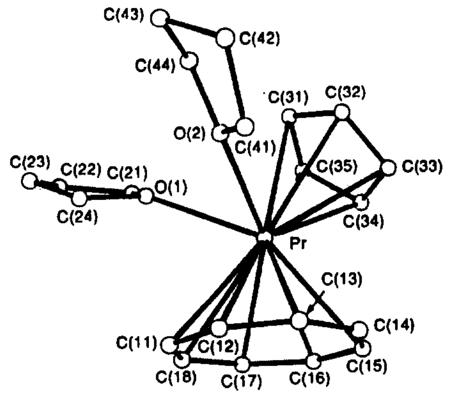

Fig. 2. Cp(COT)Pr(THF)$_2$. (Reprinted with permission from *Journal of the Chemical Society, Chemical Communications*.)

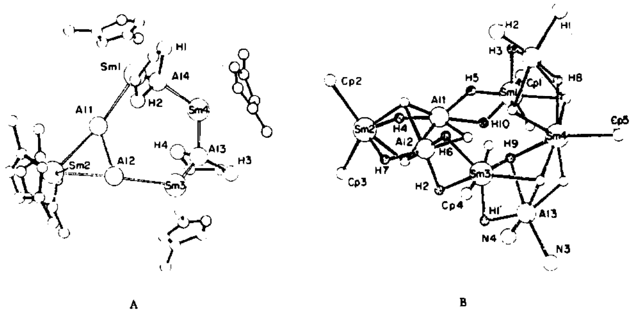

Fig. 3. The metal core (A) and hydride bonding system (B) in $(Cp^tBu_2)Sm[(\mu_2\text{-}H)_2(\mu_3\text{-}H)_2Al(Me_2NC_2H_4NMe_2)]_2[(Cp^tBu_2)SmH]_2[(\mu_2\text{-}H)_3Al(\mu_2\text{-}H)Al(\mu_2\text{-}H)_3][(\mu_3\text{-}H)_2Sm(Cp^tBu_2)_2]$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

THF = tetrahydrofuran; Ln = Pr, Nd, $n = 2$; Ln = Gd, $n = 1$) by reaction of LnCl$_3$ with NaCp and K$_2$(COT). The crystal structure of Ln = Pr was determined (Fig. 2) and reveals Pr–C(Cp) = 2.805(5) Å and Pr–C(COT) = 2.736(8) Å. Edelmann *et al.* [13] prepared a similar compound, Cp*(COT)Sm(THF), by reaction of cyclooctatetraene with Cp$_2^*$Sm(THF)$_2$.

Belsky *et al.* [14] reported that the reaction of SmI$_3$ with Na(Cp^{t}Bu) (Cp^{t}Bu = tert-butylcyclopentadienyl anion, C$_5$H$_4^t$Bu$^-$) in THF gave the monosubstituted (Cp^{t}Bu)SmI$_2$(THF)$_3$ and the disubstituted (Cp^{t}Bu)$_2$-SmI(THF). Reaction of the latter with CH$_3$CN in pentane afforded (Cp^{t}Bu)SmI · 2CH$_3$CN. Both of the monocyclopentadienyl complexes were crystallographically investigated.

Li *et al.* [15] reacted Cp$_3$Nd(THF) with NdCl$_3$ · 2LiCl · *n*THF in THF at room temperature and crystallized (from DME) [Li(DME)$_2$THF]$_2$[Cp$_4$Nd$_4$(μ_4-O)(μ_2-Cl)$_8$]. The crystal structure of the new compound was determined and revealed discreet ion pairs.

The mixed ligand complexes CpLnCl[OCOC$_6$H$_4$(*o*-X)] (Ln = Sm, Yb; X = H, F, Br, I, and OMe) were synthesized by Yu *et al.* [16]. Infrared spectroscopy, mass spectrometry, and XPS were used to determine that the complexes are dimers bridged by carboxylate groups. Some weak coordination of the X group is proposed.

Wu and Ye [17] reacted Cp$_3$Ln with *o*-nitrophenol or α-nitroso-β-naphthol to make CpLn(*o*-nitrophenolate)$_2$ and CpLn(α-nitroso-β-naphtholate)$_2$ (Ln = Nd, Yb). Infrared spectroscopy and mass spectrometry indicate the compounds have bidentate chelating ligands.

Cloke *et al.* [18] prepared the divalent lanthanide stannyl derivative, Yb[Sn(CH$_2{}^t$Bu)$_3$]$_2$(THF)$_2$, and determined its crystal structure. Reaction of this compound with Cp*H produced Cp*$_2$Yb(THF)$_2$ and Cp*Yb[Sn(CH$_2{}^t$Bu)$_3$](THF)$_2$.

Belsky *et al.* [19] determined the crystal structure of $(Cp^tBu_2)Sm[(\mu_2\text{-}H)_2(\mu_3\text{-}H)_2Al(Me_2NC_2H_4NMe_2)]_2[(Cp^tBu_2)SmH]_2[(\mu_2\text{-}H)_3Al(\mu_2\text{-}H)Al(\mu_2\text{-}H)_3][(\mu_3\text{-}H)_2Sm(Cp^tBu_2)_2]$ (Fig. 3). The reaction of (Cp^{t}Bu$_2$)$_2$Sm with AlH$_3$ in ether or (Cp^{t}Bu$_2$)$_2$Sm(THF) with AlH$_3$ in THF in the presence of an excess of TMEDA (tetramethylethylenediamine) or pentane produced the complex as a di-TMEDA solvate.

2.1.2. Triscyclopentadienyl compounds

Evans *et al.* [20] published the synthesis and crystal structure of the first trispentamethylcyclopentadienyl metal complex, Cp*$_3$Sm (Fig. 4). The compound was isolated as a byproduct in the preparation of Cp*(COT)Sm by reaction of Cp*$_2$Sm with cyclooctatetraene. The Sm–C bond distances average 2.82(5) Å.

Xie *et al.* [21] prepared and structurally characterized [(CpMe)$_3$La]$_4$ (Fig. 5; CpMe = methylcyclopentadienyl anion, C$_5$H$_4$Me$^-$). Reaction of LaCl$_3$ with an excess of Na(CpMe) in THF produced the compound,

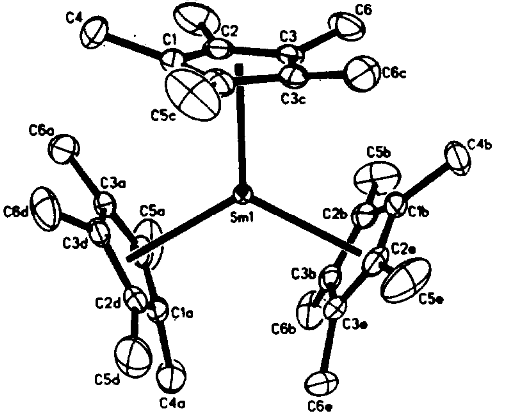

Fig. 4. Cp*$_3$Sm. (Reprinted with permission from *Journal of the American Chemical Society*. Copyright 1991 American Chemical Society.)

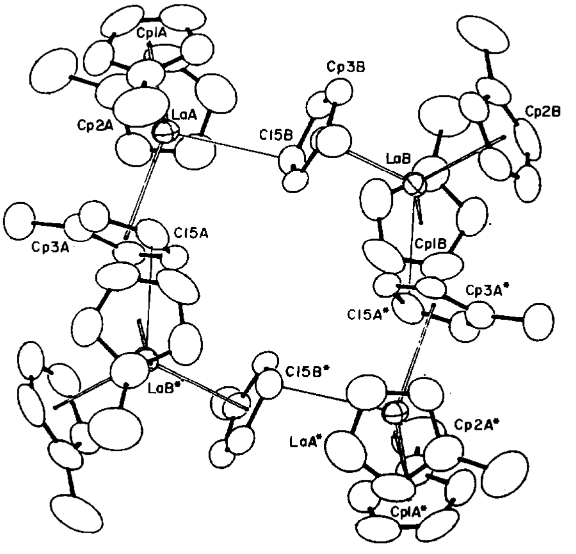

Fig. 5. $[(CpMe)_3La]_4$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

crystals of which were grown by sublimation. The compound crystallizes as an $\eta^1:\eta^5$ tetramer.

Belsky *et al.* [22] reported that crystallization of Cp_3Sm from diethylether resulted in a new crystalline modification. This form crystallized as contact dimers.

The yttrium analog, Cp_3Y, was structurally determined by Adam *et al.* [23] (Fig. 6). The Cp_3Y units are close packed to form loosely aligned zigzag chains. The average Y–C separation is 2.706 Å.

The crystal structure of the furan adduct, $Cp_3Nd(OC_4H_6)$, was determined by Shi *et al.* [24]. The average Nd–C distance is 2.766 Å.

Amberger and co-workers studied the absorption spectra of $(C_5D_5)_3Nd(OC_4D_8)$ [25] and the n-butylacetate adduct of Cp_3Pr [26]. The results were interpreted in terms of crystal field calculations and the observed ESR and NMR spectra.

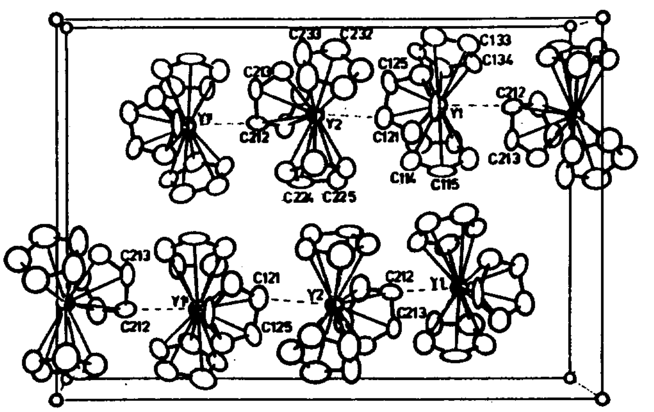

Fig. 6. Cp_3Y. (Reprinted with permission from *Acta Crystallographica*.)

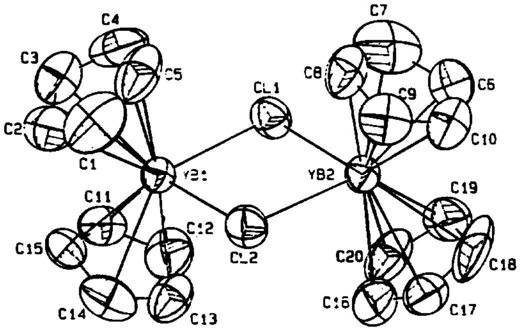

Fig. 7. $[Cp_2YbCl]_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

Strittmatter and Bursten [27] compared the bonding in Cp_3An (An = U, Np, Pu, Am, Cm, Bk, and Cf) with that in lanthanide compounds. The results are summarized in the actinide section.

Qian *et al.* [28] studied the reductive dehalogenation of aryl and vinyl halides with Cp_3Ln/NaH (Ln = La, Sm, Gd, Y, and Lu) to produce the corresponding aromatic and alkane products. The reactions with alkyl halides were reported to produce alkylated products which in turn gave alkyl cyclopentadienes *via* hydrolysis.

2.1.3. *Biscyclopentadienyl compounds*

Fischer *et al.* [29] determined the crystal structure of a new modification of $[Cp_2YbCl]_2$ grown from solution (Fig. 7). The crystallographic parameters are different from those observed when crystals are grown by sublimation. However, the two determinations give essentially the same bonding parameters.

Belsky *et al.* [14] reported the formation of $(Cp^tBu)_2SmI(THF)$ from the reaction of SmI_3 with $Na(Cp^tBu)$. Similar reactions with $LnCl_3$ in THF were studied by Shen and co-workers [30]. The compounds $(Cp^tBu)_2LnCl(THF)_n$ (Ln = Pr, Nd, $n = 2$; Ln = Gd, Yb, $n = 1$) were prepared. The crystal structures of $(Cp^tBu)_2PrCl(THF)_2$ (Fig. 8) and $(Cp^tBu)_2YbCl(THF)$ (Fig. 9) were also reported. The average Pr–C and Yb–C distances are 2.81(2) and 2.63(1) Å, respectively. The synthesis and structure of the Yb compound were also reported by the same authors in a separate publication [31].

The crystal structures of the unsolvated dimers, $[(Cp^tBu)_2LnCl]_2$ (Ln = Sm, Lu) and the unsubstituted cyclopentadienyl compound, $[Cp_2LuCl]_2$ were published by Belsky and co-workers [32], who also reported the reactions of the Cp^tBu_2Sm and –Lu derivatives with $LiAlH_4$ in THF or TMEDA and the crystal struc-

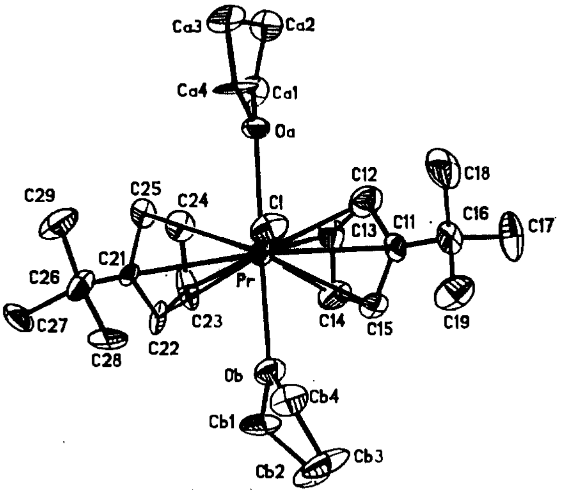

Fig. 8. $(Cp^tBu)_2PrCl(THF)_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

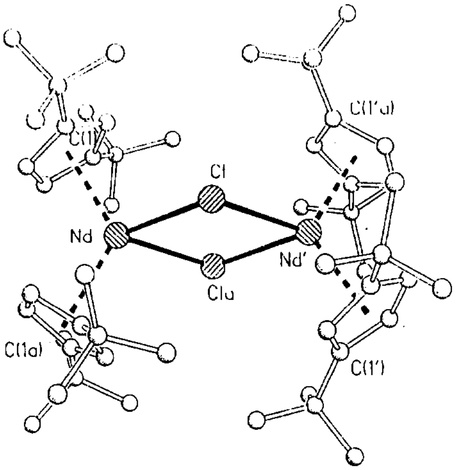

Fig. 10. $[(Cp^tBu_2)_2NdCl]_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

tures of $(Cp^tBu_2)_2SmCl_2Li(TMEDA)$ and $(Cp^tBu_2)_2LuCl_2Li(THF)_2$ [33].

The (Cp^tBu_2Nd) derivative was prepared by Fischer *et al.* [34] by reaction of $NdCl_3$ with $K(Cp^tBu_2)$ in THF. The structure of $[(Cp^tBu_2)_2NdCl]_2$ is presented in Fig. 10. The average Nd–C separation is reported to be 2.761 Å. The use of 2,4,6-trisubstituted benzamidinate anions as steric equivalents of bulky Cp ligands was also discussed.

Teuben *et al.* [35] reported the protolysis of $Cp^*_2CeCH(SiMe_3)_2$ by $[NHEt_3][BPh_4]$ to yield $[Cp^*_2CeL_2][BPh_4]$ [L = THF, THT (tetrahydrothiophene)]. The crystal structure of the THT derivative (Fig. 11) exhibited Ce–S distances of 3.058(1) and 3.072(1) Å and an average Ce–C separation of 2.74(3) Å.

Compounds containing Sm–chalcogenide bonds (S, Se, Te) were prepared by Edelmann *et al.* [36] *via* the reaction of $Cp^*_2Sm(THF)_2$ with disulfides, diselenides, and ditellurides. The crystal structures of three compounds with Sm–chalcogenide bonds were determined: $Cp^*_2Sm(S_2CNMe_2)$ (Fig. 12: Sm–S = 2.808(2) Å, Sm–C = 2.711(7) Å), $Cp^*_2Sm(TeC_6H_2Me_3)(THF)$ (Fig. 13: Sm–Te = 3.088(2) Å, Sm–C = 2.73(1) Å), and $Cp^*_2Sm[SeC_6H_2(CF_3)_3](THF)$ (Fig. 14: Sm–Se = 2.919(1) Å, Sm–C = 2.734(4) Å).

Edelmann *et al.* [13] reported the reaction of $Cp^*_2Sm(THF)_2$ with 1,4-diazadienes to give 1 : 1 adducts, one of which was crystallographically characterized: $Cp^*_2Sm(^tBuN{=}CHCH{=}N^tBu)$ (Fig. 15: Sm–N = 2.480(5), 2.489(5) Å, Sm–C = 2.773(7) Å). Reaction with 2-pyridinealdazine produced the binuclear complex $[Cp^*_2Sm]_2(\mu\text{-}C_{12}H_{10}N_4)$.

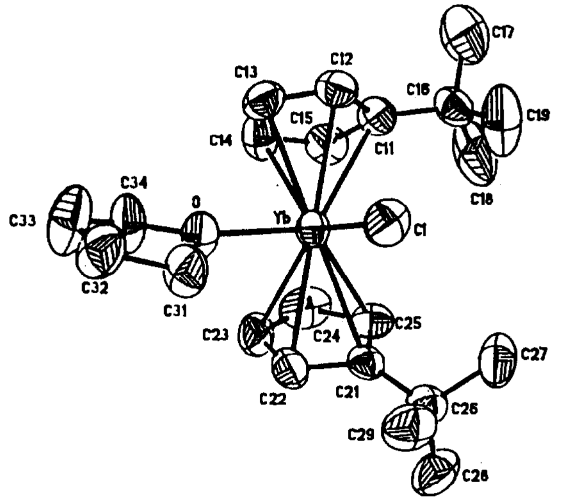

Fig. 9. $(Cp^tBu)_2YbCl(THF)$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

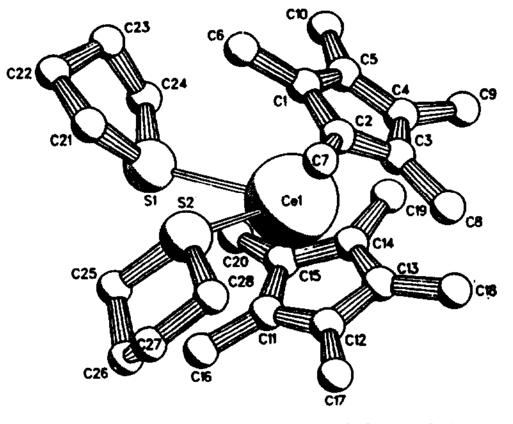

Fig. 11. The cation in $[Cp^*_2Ce(THT)_2][BPh_4]$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

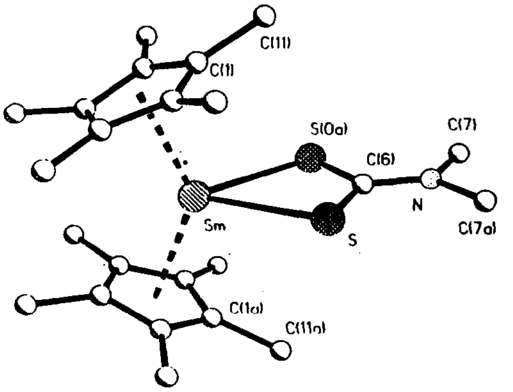

Fig. 12. $Cp^*_2Sm(S_2CNMe_2)$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

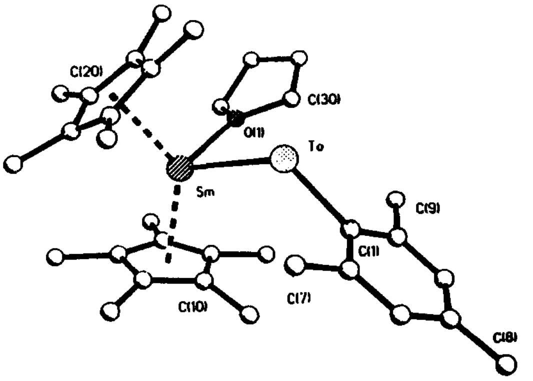

Fig. 13. $Cp^*_2Sm(TeC_6H_2Me_3)(THF)$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

Chen *et al.* [37] reported the crystal structure (Fig. 16) of $Cp_2Yb(DME)$ (DME = dimethoxyethane). The Yb–C distances average 2.658 Å.

Wu and Ye [17] prepared Cp_2LnL (Ln = Nd, Yb; L = *o*-nitrophenolate, α-nitroso-β-naphtholate) by reactions of the alcohol with Cp_3Ln. The ligands are bidentate chelates.

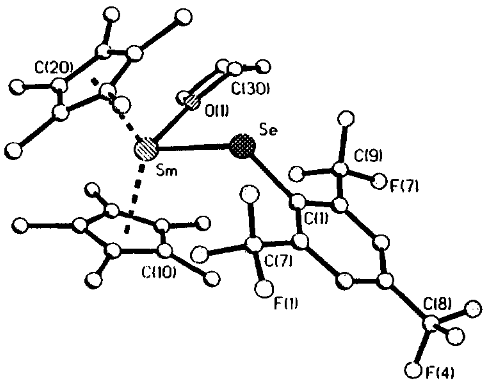

Fig. 14. $Cp^*_2Sm[SeC_6H_2(CF_3)_3](THF)$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

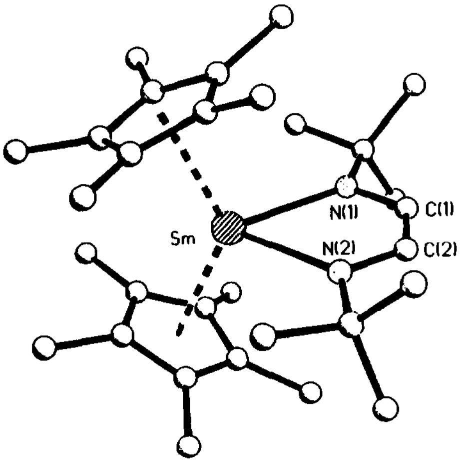

Fig. 15. $Cp^*_2Sm(^tBuN{=}CHCH{=}N^tBu)$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

Fischer *et al.* [38] crystallographically characterized the μ_2-oxide, $[(CpMe)_2Yb(THF)]_2O$ (Fig. 17). The compound exhibits a linear Yb–O–Yb bridge at 2.015(1) Å and Yb–C separations of 2.667 Å.

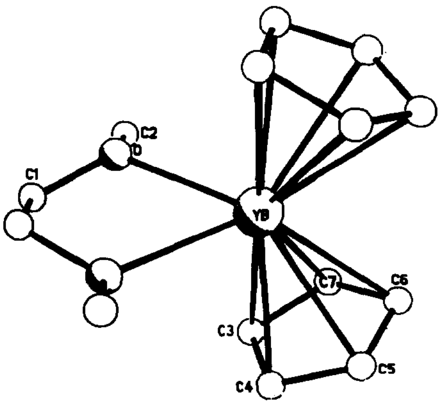

Fig. 16. $Cp_2Yb(DME)$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

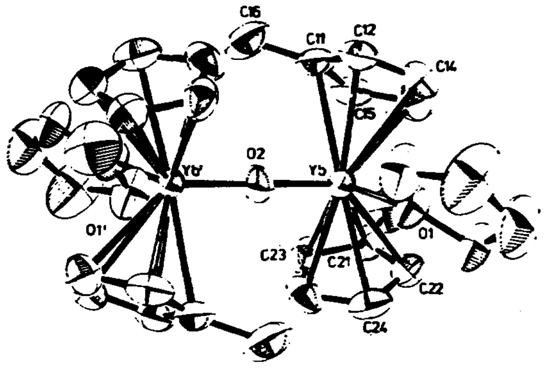

Fig. 17. $[(CpMe)_2Yb(THF)]_2O$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

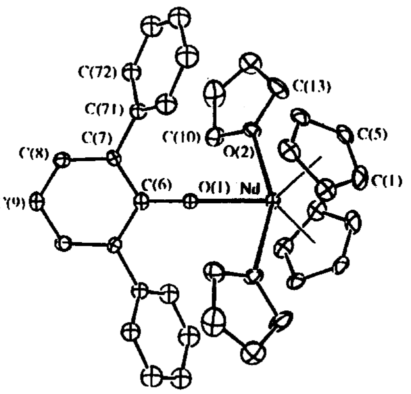

Fig. 18. $Cp_2Nd(OC_6H_3Ph_2)(THF)_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

Deacon *et al.* [39] prepared the alkoxide, $Cp_2Nd(OC_6H_3Ph_2)(THF)_2$, by reaction of the phenol with Cp_3Nd in THF. The crystal structure (Fig. 18) exhibits a Nd–O(alkoxide) separation of 2.239(8) Å and an average Nd–C separation of 2.80 Å.

Hitchcock *et al.* [40] prepared the hydroxides, $[Cp''_2Sm(OH)]_2$ (Cp'' = 1,3-bistrimethylsilylcyclopentadienyl anion, $C_5H_3(SiMe_3)_2^-$) and $[Cp'_2Yb(OH)]_2$ (Cp' = trimethylsilylcyclopentadienyl anion, $C_5H_4SiMe_3^-$) by reaction of $Cp''_2Sm(THF)$ or $Cp'_2Yb(OEt_2)$ with water in an ether solution. The crystal structures of the Sm-hydroxide (Fig. 19) and Yb-hydroxide (Fig. 20) reveal Sm–O = 2.40(2) Å, Sm–C = 2.72(3) Å and Yb–O = 2.29(2) Å, Yb–C = 2.61(4) Å.

Heeres and Teuben [41] studied the compounds $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Y, La, Ce) as catalyst precursors for the oligomerization of terminal alkynes. The results suggest that lanthanide acetylides $[Cp^*_2LnC{\equiv}CR]_n$ are the active species. The compounds $[Cp^*_2CeC{\equiv}CR]_n$ (R = ^tBu, Me) were prepared on a preparative scale. The regioselectivity and extent of oligomerization were controlled by the lanthanide used.

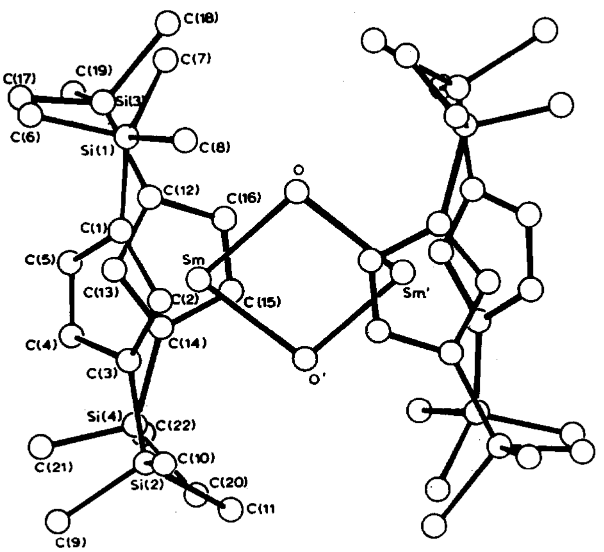

Fig. 19. $[Cp''_2Sm(OH)]_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

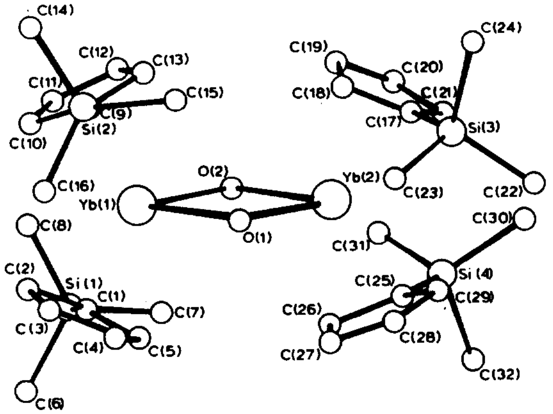

Fig. 20. $[Cp'_2Yb(OH)]_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

Teuben *et al.* [42] studied ring hydrogen C–H activation in the same series of compounds. Thermolysis in cyclohexane led to hydrogen abstraction from a Cp* ligand and elimination of $CH_2(SiMe_3)_2$. The crystal structures of the end product $[Cp^*_3(\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Ce_2]_2$ (Fig. 21) and of $Cp^*_2CeCH_2Ph$ (Fig. 22) were also published.

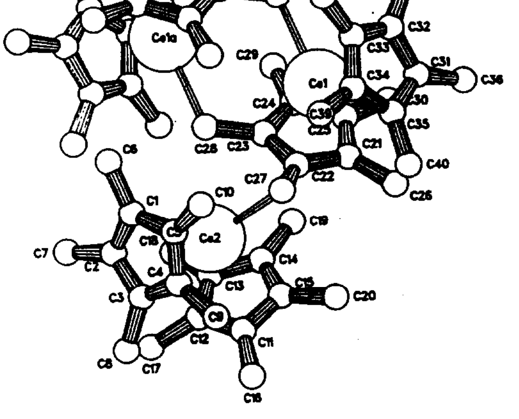

Fig. 21. $[Cp^*_3(\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Ce_2]_2$: Ce–C($\eta^5$) = 2.80(3) Å, Ce–C($\eta^1$) = 2.64(4) Å. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

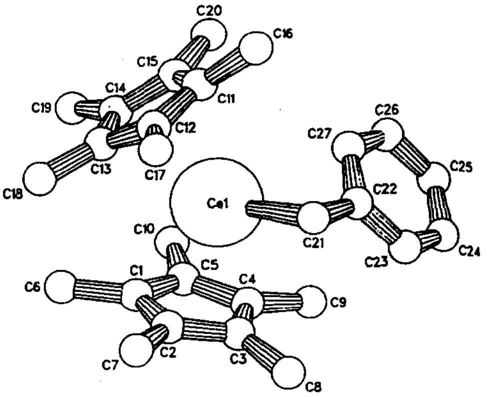

Fig. 22. $Cp^*_2CeCH_2Ph$: Ce–C(η^5) = 2.78(3) Å, Ce–C(σ) = 2.596(5) Å. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

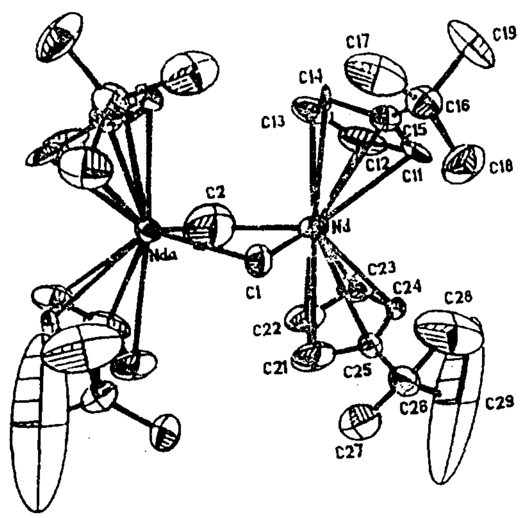

Fig. 23. $[(\mathrm{Cp^tBu})_2NdMe]_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

The methyl complexes, $[(\mathrm{Cp^tBu})_2LnMe]_2$ (Ln = Nd, Gd) were prepared by Shen *et al.* [43] by reaction of $[(\mathrm{Cp^tBu})_2LnCl]_2$ with LiMe in ether/THF. The crystal structure of Ln = Nd (Fig. 23) revealed asymmetric methyl bridges with Nd–C(σ) = 2.70(2) and 2.53(2) Å, and Nd–C(η^5) = 2.78(6) Å.

Thiele *et al.* [44] prepared and structurally characterized a butadiene–lanthanide compound, $[Cp^*_2La(THF)(\mu\text{-}\eta^1,\eta^3\text{-}C_4H_6)LaCp^*_2]$ (Fig. 24) by reaction of $Cp^*_2LaCl_2K(DME)_2$ with $Mg(C_6H_4)(THF)_2$. The important bond distances include La–C(η^1) = 2.633(4) Å and La–C(η^3) = 2.73(3) Å.

Evans *et al.* [45] investigated the reactivity of $[Cp^*_2SmH]_2$ in ether and arene solvents. Decomposition by internal metalation to form $Cp^*_2Sm(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)SmCp^*$ (Fig. 25) and H_2 was reported in alkanes or benzene. In toluene, additional

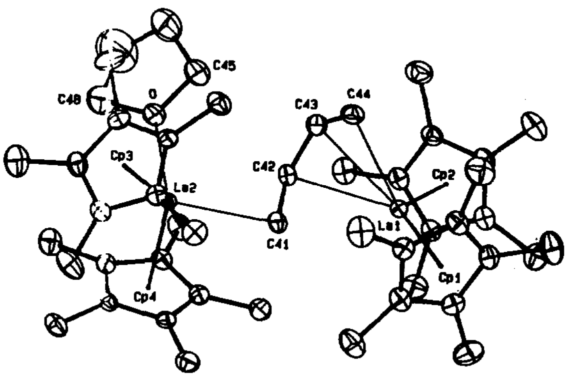

Fig. 24. $[Cp^*_2La(THF)(\mu\text{-}\eta^1,\eta^3\text{-}C_4H_6)LaCp^*_2]$. (Reprinted with permission from *Angewandte Chemie, International Edition English*.)

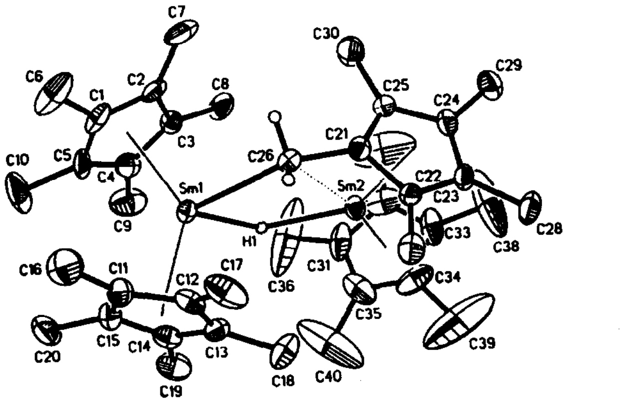

Fig. 25. $Cp^*_2Sm(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)SmCp^*$: Sm–C($\eta^1$) = 2.628(7) Å, Sm–C($\eta^5$) = 2.73(3) Å. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

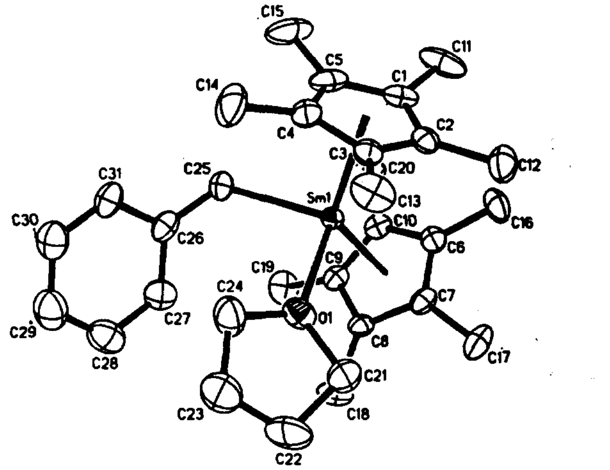

Fig. 26. $Cp^*_2Sm(CH_2Ph)(THF)$: Sm–C(σ) = 2.528(8) Å, Sm–C(η^5) = 2.76(2) Å. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

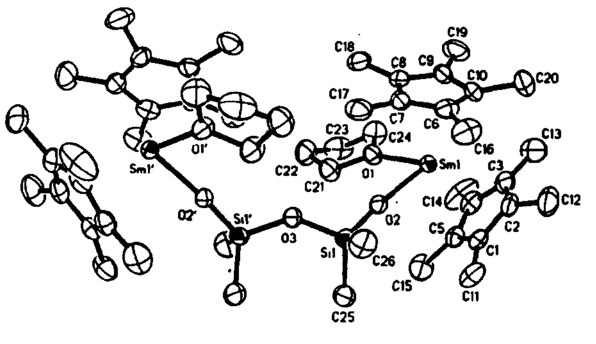

Fig. 27. $[Cp^*_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$: Sm–O(siloxide) = 2.157(5) Å, Sm–C(η^5) = 2.75(3) Å. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

metalation of the solvent produced $Cp^*_2Sm(CH_2Ph)$ which was isolated as its THF solvate (Fig. 26). The hydride dissolved in THF can react with high-vacuum grease or hexamethylcyclotrisiloxane to yield $[Cp^*_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$ (Fig. 27).

Bulychev *et al.* [46] reacted $CeCl_3$ with $Na(Cp^tBu_2)$ to prepare $[(Cp^tBu_2)_2CeCl]_2$ (Fig. 28) which was further reacted with $LiBH_4$ to produce $[(Cp^tBu_2)_2Ce(\mu:\eta^4\text{-}(\eta^3\text{-}H)_2B(\mu_2\text{-}H)_2)]_2$ (Fig. 29). The two compounds are isostructural.

Bulychev and co-workers [47] reported that the aluminohydride complexes $[(Cp^tBu_2)_2LnAlH_4(L)]_2$ are unstable and decompose by desolvation, dissociation of solvated AlH_4, and destruction of the metallocene to produce $[(Cp^tBu_2)LuH]_4[AlH_4OEt_2]_2[AlH_4]_2$. The crystal structure of this complex is depicted in Fig. 30. The Lu–C bond lengths average 2.58(4) Å.

The same authors also published the crystal structures of several additional hydride compounds. These include $[Cp_2Yb(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)AlH_2NEt_3]_2 \cdot C_6H_6$ [48] (Fig. 31: Yb–C = 2.60 Å), $[Cp_2Lu(\mu_2\text{-}H)]_2[(\mu_2\text{-}H)_2AlHNEt_3]_2 \cdot C_6H_6$ [48] (Fig. 32: Lu–C = 2.59 Å), $[Cp_2Lu]_3(\mu_2\text{-}H)_2(\mu_3\text{-}H)$ [48] (Fig. 33: Lu–C = 2.55 Å), $[Cp_2Sm(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)_2AlHNEt_3]_2$ [49] (Fig. 34: Sm–C = 2.72(3) Å), and $[(Cp^tBu)_2Sm]_2(\mu_2\text{-}H)\mu\text{-}[(\mu_3\text{-}H)_2Al(\mu_2\text{-}H)_2TMEDA]$ [49] (Fig. 35: Sm–C = 2.77(4) Å).

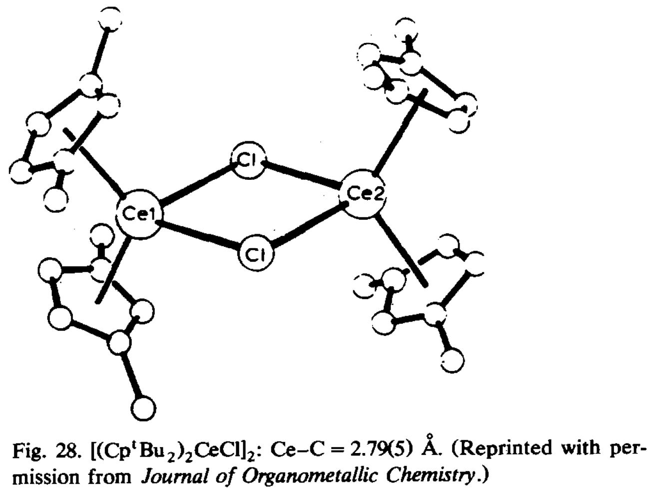

Fig. 28. $[(Cp^tBu_2)_2CeCl]_2$: Ce–C = 2.79(5) Å. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

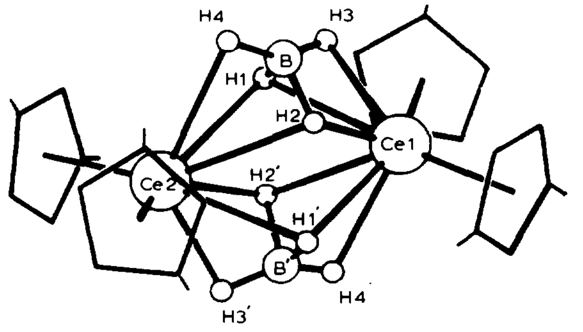

Fig. 29. $[(Cp^tBu_2)_2Ce(\mu{:}\eta^4\text{-}(\eta^3\text{-}H)_2B(\mu_2\text{-}H)_2)]_2$: Ce–C = 2.81(5) Å. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

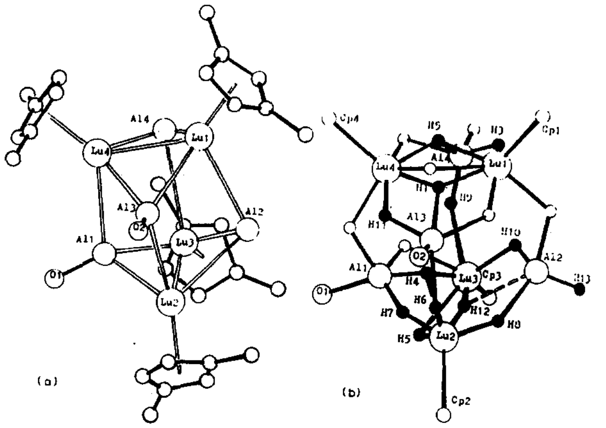

Fig. 30. $[(Cp^tBu_2)LuH]_4[AlH_4OEt_2]_2[AlH_4]_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

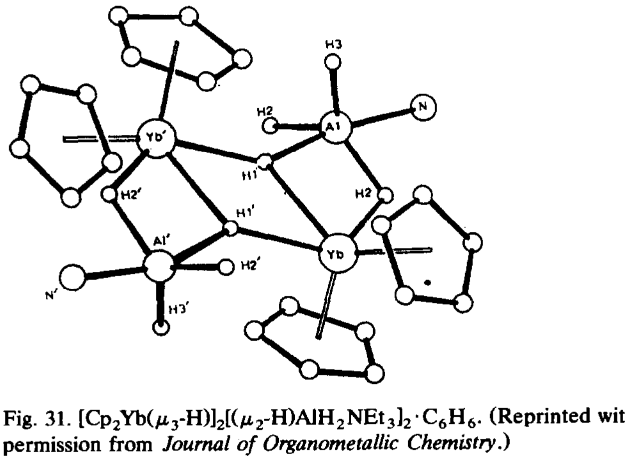

Fig. 31. $[Cp_2Yb(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)AlH_2NEt_3]_2 \cdot C_6H_6$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

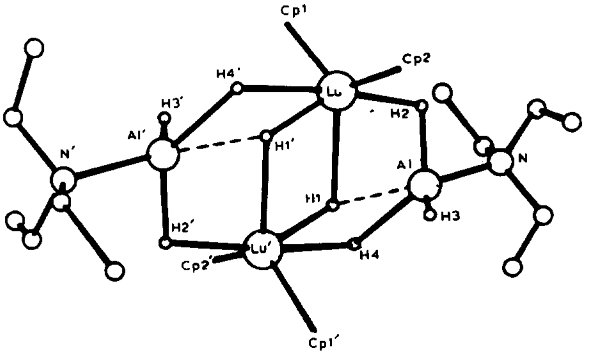

Fig. 32. $[Cp_2Lu(\mu_2\text{-}H)]_2[(\mu_2\text{-}H)_2AlHNEt_3]_2 \cdot C_6H_6$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

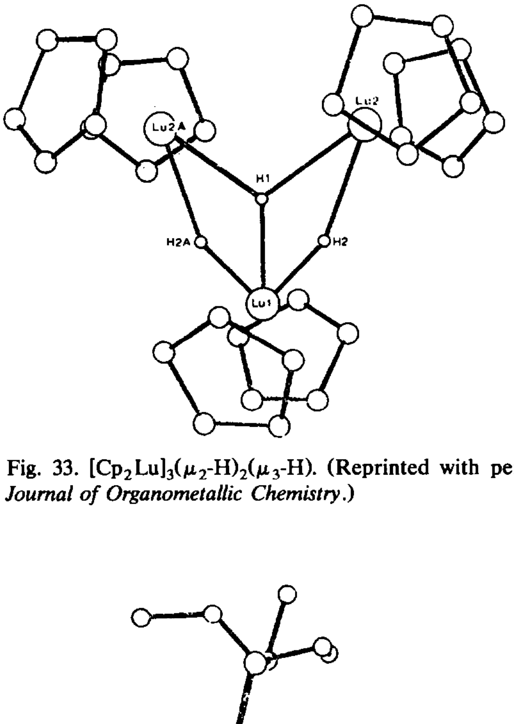

Fig. 33. $[Cp_2Lu]_3(\mu_2\text{-}H)_2(\mu_3\text{-}H)$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

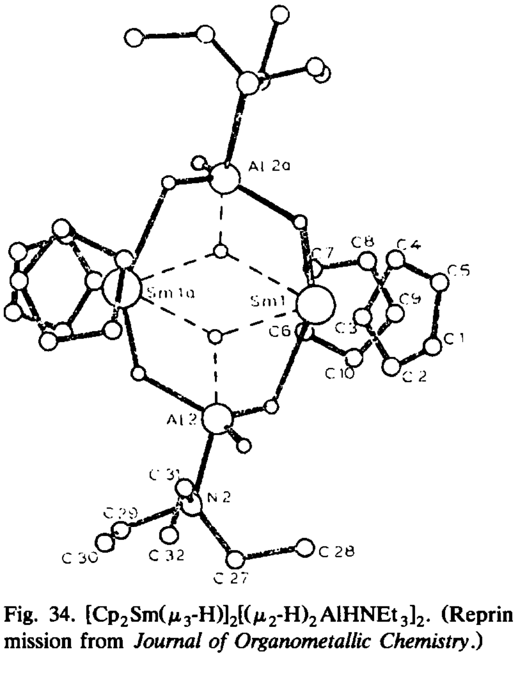

Fig. 34. $[Cp_2Sm(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)_2AlHNEt_3]_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

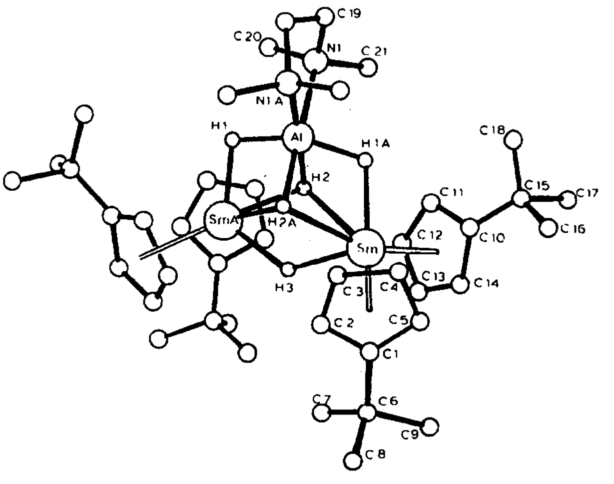

Fig. 35. $[(Cp^tBu)_2Sm]_2(\mu_2\text{-}H)\mu\text{-}[(\mu_3\text{-}H)_2Al(\mu_2\text{-}H)_2TMEDA]$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

The crystal structure of a lanthanide-iron compound, $[Cp^*{}_4Dy_2(\mu\text{-}OCO)Fe_2(CO)(\mu\text{-}CO)_2Cp_2]_2 \cdot$ toluene, was reported by Wu *et al.* [50]. A second similar compound was structurally characterized by Edelmann *et al.* [51]. The reaction of $Cp^*{}_2Sm(THF)_2$ with $[Cp^*Fe(CO)_2]_2$ produced $[Cp^*{}_2Sm(\mu\text{-}OC)_2Fe\text{-}Cp^*]_2$ (Fig. 36). The average Sm–C distance is 2.694(9) Å.

Evans *et al.* [52] utilized $Cp^*{}_2Sm$ to prepare Bi–Bi bonds by reaction with $BiPh_3$ in benzene, toluene, or cyclohexane. The crystal structure of $[Cp^*{}_2Sm]_2(\mu\text{-}\eta^2,\eta^2\text{-}Bi_2)$ (Fig. 37) revealed a planar Sm_2Bi_2 core. The Sm–Bi and Sm–C separations average 3.29(2) and 2.72(2) Å, respectively.

Marks *et al.* [53] studied the catalytic dehydrogenative oligomerization of $PhSiH_3$ by $Cp^*{}_2LnR$ (Ln = La, Nd, Sm, Y, Lu; R = H, $CH(SiMe_3)_2$), $Cp^*{}_2Sm$, and $Cp^*{}_2Sm(THF)_2$). A four center heterolytic bond-scission/bond-formation mechanism was proposed.

Qian *et al.* [54] studied the acylative cleavage of the Y–C(η^5) bond and THF ring in the reactions of $[Cp_2YCl]_2$ with aromatic and aliphatic acid chlorides in THF. Tanaka *et al.* [55] investigated the catalytic hydrosilylation of alkenes with di- or trihydrosilanes by $[Cp^*{}_2NdH]_2$ and $Cp^*{}_2NdCH(SiMe_3)_2$.

2.1.4. *Bridged-cyclopentadienyl compounds*

Schumann *et al.* [56] utilized a bridged cyclopentadienyl ligand containing an oxygen donor in the bridge to stabilize organolanthanide complexes *via* intramolecular coordination of the oxygen to the metal. The 1,1'-(3-oxapentamethylene)cyclopentadienyl anion ($[O(CH_2CH_2Cp)_2]^{2-}$) was utilized in the reaction of $[O(CH_2CH_2Cp)_2]LnCl$ (Ln = Y, Lu) with $NaN_2C_3HMe_2$ to prepare $[O(CH_2CH_2Cp)_2]Ln(N_2C_3HMe_2)$. Partial hydrolysis led to the structurally characterized

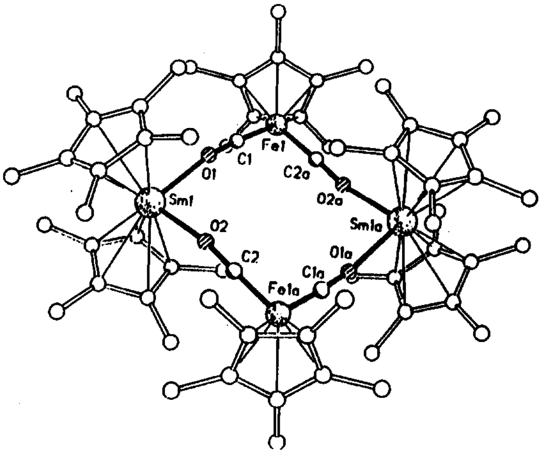

Fig. 36. $[Cp^*_2Sm(\mu\text{-}OC)_2FeCp^*]_2$. (Reprinted with permission from *Chemiche Berichte*.)

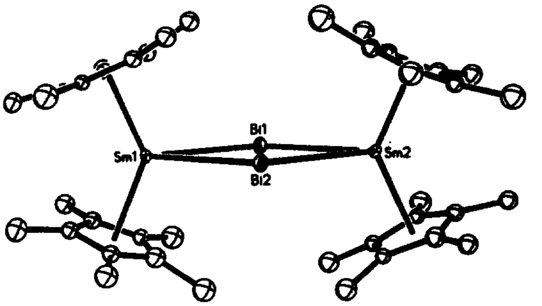

Fig. 37. $[Cp^*_2Sm]_2(\mu\text{-}\eta^2,\eta^2\text{-}Bi_2)$. (Reprinted with permission from *Journal of the American Chemical Society*. Copyright 1991, American Chemical Society.)

compounds $\{[O(CH_2CH_2Cp)_2]Ln\}_2(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$ [Ln = Y (Fig. 38), Lu]. The two compounds are isostructural and exhibit intramolecular coordination of the oxygen in the cyclopentadienyl bridge. The Ln–C(η^5) distances average 2.674(5) Å (Y) and 2.623 Å (Lu).

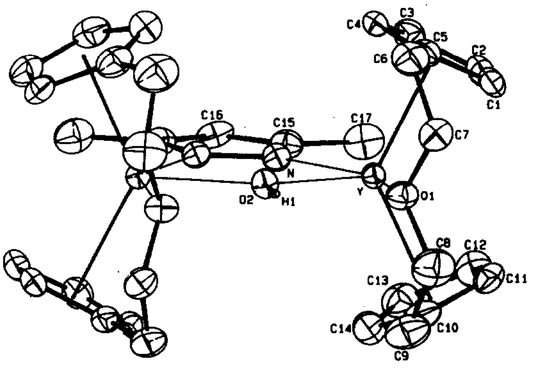

Fig. 38. $\{[O(CH_2CH_2Cp)_2]Y\}_2(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

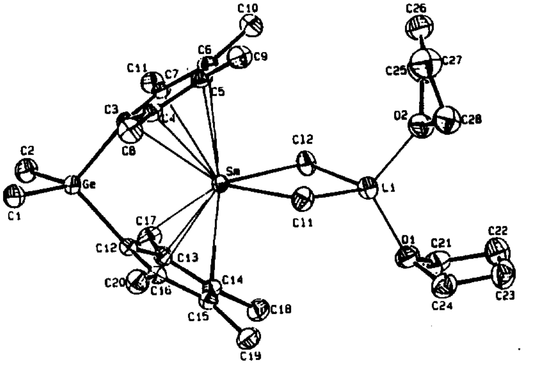

Fig. 39. $(Me_2GeCp^*_2)SmCl_2Li(THF)_2$. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

Schumann *et al.* [57] also utilized dimethylgermanium to bridge cyclopentadienyl anions. The dimethylgermyl ligand was prepared by metathesis of Me_2GeCl_2 with LiC_5Me_4H followed by deprotonation with LiMe. A similar reaction with Me_2SnCl_2 led to $SnMe_4$. Reaction of $LnCl_3$ (Ln = Nd, Sm, Ho, Lu) with the dilithium salt of the ligand, $Li_2(Me_2GeCp^*_2)$, led to $(Me_2GeCp^*)_2LnCl_2Li(THF)_2$. Further reaction of Ln = Nd and Ho with $LiCH(SiMe_3)_2$ produced $(Me_2GeCp^*)_2LnCH(SiMe_3)_2$. The crystal structures of several of the new compounds were reported including $(Me_2GeCp^*_2)LnCl_2Li(THF)_2$ [Ln = Sm {Fig. 39: Sm–C = 2.70(5) Å}, Lu {Lu–C = 2.61(5) Å}] and $(Me_2GeCp^*_2)HoCH(SiMe_3)_2$ [Fig. 40: Ho–C = 2.65(6) Å]. Marks *et al.* [53] utilized the silyl derivative, $(Me_2SiCp^*_2)NdCH(SiMe_3)_2$, to study catalyzed dehydrogenative coupling of silanes.

Fischer *et al.* [29] prepared $[(Me_2SiCp_2)YbBr]_2$ (Fig. 41) by reaction of the disodium salt of the ligand with $YbBr_3$. Unlike the germyl derivative above, the silyl compound contains bridging $Me_2SiCp_2{}^{2-}$ anions. The average Yb–C separation is 2.58(2) Å.

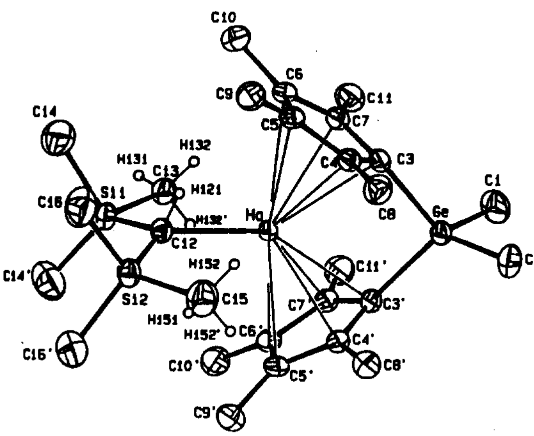

Fig. 40. $(Me_2GeCp^*_2)HoCH(SiMe_3)_2$. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

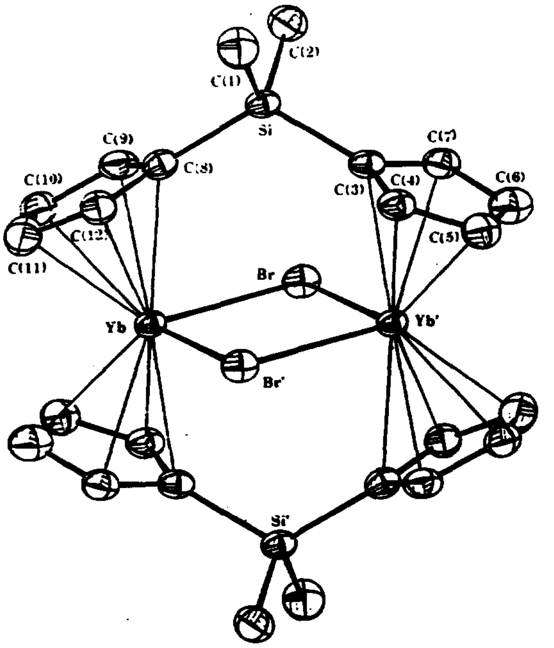

Fig. 41. $[(Me_2SiCp_2)YbBr]_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

The ethylene bridged biscyclopentadienyl compounds, $(Me_4C_2Cp_2)LnCl_2Mg_2Cl_3(THF)_n$ (chelating) and $(Me_4C_2Cp_2)Ln_2Cl_4Mg_2Cl_4(THF)_n$ (bridging), were prepared by Yan and Chen [58] *via* reaction of $LnCl_3$ in THF with the $MgCl^+$ salt of the ligand. A crystal structure of $(Me_4C_2Cp_2)YbCl_2Mg_2Cl_3(THF)_6$ was included in this report.

Recknagel and Edelmann [59] synthesized the same ligand *in situ* in reactions of 6,6-dimethylfulvene with activated Sm or Yb powder in THF. The lanthanide(II) compounds $(Me_4C_2Cp_2)Ln$ (Ln = Sm, Yb) were synthesized.

Ye *et al.* [60] prepared several lanthanide hydrides utilizing a trimethylene-bridged-biscyclopentadienyl dianion. Reactions of the disodium salt of the ligand with $LnCl_3$ (Ln = Y, Dy, Er, Lu) in THF produced the monochloride derivatives. Further reaction with Li^tBu gave the corresponding alkyl compounds which were reacted with H_2 to prepare $[((CH_2)_3Cp_2)LnH(THF)]_2$ (Ln = Y, Dy, Er, Lu). Qian *et al.* [61] prepared similar hydrides, $\{[O(CH_2CH_2Cp)_2]LnH\}_2$ (Ln = Gd, Er, Yb, Lu, Y). The intramolecular coordination of the oxygen from the ligand allowed the isolation of the solvent free complexes.

2.1.5. Indenyl compounds

Wenqi *et al.* [12,62] synthesized the mixed ligand compound (Ind)(COT)Ln (Ind = indenyl anion, $C_9H_7^-$; Ln = Pr, Nd) by reaction of $LnCl_3$ with K(Ind) and $K_2(COT)$. The crystal structure of $(Ind)(COT)Pr(THF)$ [12] is depicted in Fig. 42. The average Pr–C distances are 2.87 Å (Ind) and 2.72 Å (COT).

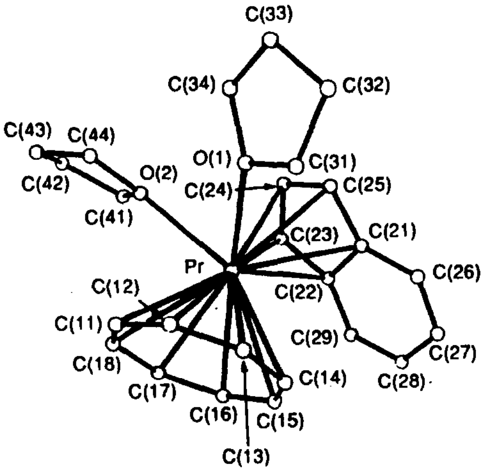

Fig. 42. $(Ind)(COT)Pr(THF)_2$. (Reprinted with permission from *Journal of the Chemical Society, Chemical Communications*.)

The same authors [63] also prepared $(Ind)_3Ln(THF)$ (Ln = Nd, Gd, Er) in the same reaction but with stoichiometry $LnCl_3/2K(Ind)/K_2(COT)$. The crystal structures of the Nd (Fig. 43) and Gd derivatives were determined. The average Ln–C separations are 2.812 Å (Nd) and 2.795 Å (Gd).

2.1.6. Heteroatom five-membered ring anions

Nief and Mathey [64] prepared diphosphametallocene complexes of divalent Yb and Sm. The compounds, $(\eta^5\text{-}C_4Me_4P)_2Ln(THF)_2$ (Ln = Yb, Sm), were prepared by reaction of $K(C_4Me_4P)$ with SmI_2 or YbI_2 in THF, and by reaction of the metallic powders with $(C_4Me_4P)_2$.

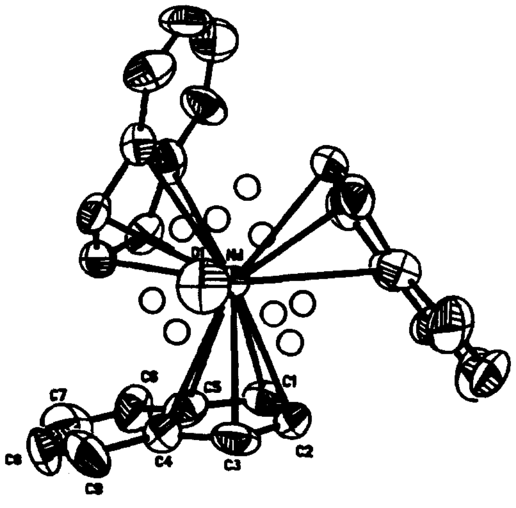

Fig. 43. $(Ind)_3Nd(THF)$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

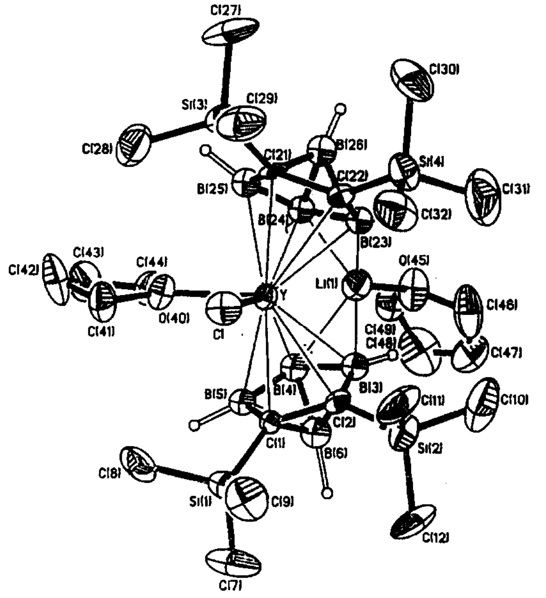

Fig. 44. The anion in $[Li(THF)_4]\{[\eta^5\text{-}(SiMe_3)_2C_2B_4H_4]_2YCl(THF)\text{-}Li(THF)\}$. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

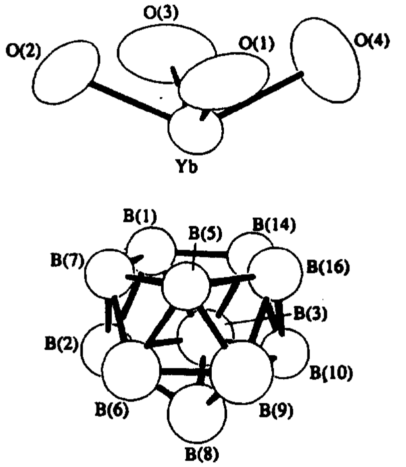

Fig. 45. *closo*-1,1,1,1-$(DMF)_4$-1,2,3-$YbC_2B_9H_{11}$. The two carbon atoms in the upper ring are disordered with the three boron positions over all five positions. Only the oxygen atoms of the DMF ligands are represented. (Reprinted with permission from *Inorganic Chemistry*. Copyright 1991, American Chemical Society.)

Hosmane *et al.* [65] prepared the first yttracarborane sandwich compound, $[Li(THF)_4]\{[\eta^5\text{-}(SiMe_3)_2C_2\text{-}B_4H_4]_2YCl(THF)Li(THF)\}$, by reaction of the dilithium salt of the anion with YCl_3 in benzene. The crystal structure of the anion is depicted in Fig. 44. Average values of $Y\text{–}C(\eta^5) = 2.73(2)$ Å and $Y\text{–}B(\eta^5) = 2.73(3)$ Å were reported.

Hawthorne and co-workers explored lanthanide compounds of [*nido*-7,8-$C_2B_9H_{11}{}^{2-}$] [66] and [*nido*-7,9-$C_2B_{10}H_{12}{}^{2-}$] [67] by reaction of disodium salts of these ligands with iodide salts of divalent Sm, Yb, and Eu in THF. The crystal structures of *closo*-1,1,1,1-$(DMF)_4$-1,2,3-$YbC_2B_9H_{11}$ (DMF = *N*,*N*-dimethylformamide, Fig. 45) and $[PPN][3,3\text{-}(THF)_2$-*commo*-3,3′-$Sm(3,1,2\text{-}SmC_2B_9H_{11})_2]$ [PPN = bis(triphenylphosphoranylidene)ammonium cation, Fig. 46] were determined. Other compounds prepared and spectroscopically characterized included *closo*-1,1,1,1-$(THF)_4$-1,2,3-$LnC_2B_9H_{11}$ (Ln = Sm, Yb) and $[PPN][3,3\text{-}(THF)_2$-*commo*-3,3′-$Yb(3,1,2\text{-}YbC_2B_9H_{11})_2]$. In addition, the Eu sandwich compound $[NEt_4]_2[1,1\text{-}(THF)_2$-*commo*-1,1′-$Eu(1,2,4\text{-}EuC_2B_{10}H_{12})_2]$ was prepared and structurally characterized (Fig. 47).

2.1.7. *Pentadienyl compounds*

Ernst *et al.* [68] prepared a bridged bispentadienyl dianion by double deprotonation of two methyl groups in 2,4,7,9-tetramethyl-1,3,7,9-decatetraene. The dipotassium salt of the ligand was used to form $Yb[4,4'\text{-}(CH_2)_2(2\text{-}C_6H_8)_2](THF)_2$ from YbI_2 in THF. The crystal structure reveals a chelating rather than bridging ligand (Fig. 48). Longer Yb–C distances (2.80 Å average) than observed in non-bridged pentadienyl compounds of Yb^{2+} suggest a weaker interaction.

Chen *et al.* [69] published the preparation and structure of $(COT)Sm(2,4\text{-}C_7H_{11})(THF)$ (Fig. 49). The precursor, $(COT)SmCl(THF)_2$, was prepared first by reaction of $SmCl_3$ with $K_2(COT)$. Further reaction with $K(2,4\text{-}C_7H_{11})$ led to the mixed ligand compound. The $Sm\text{–}C(\eta^8)$ distances average 2.66 Å while the Sm–C(pentadienyl) separations range from 2.71(1) to 2.89(1) Å.

Schumann and Dietrich [70] prepared the trispentadienyl compound, $Lu(\eta^5\text{-}2,4\text{-}C_7H_{11})_2(\eta^3\text{-}2,4\text{-}C_7H_{11})$ (Fig. 50) by reaction of $LuCl_3$ with KC_7H_{11} in THF.

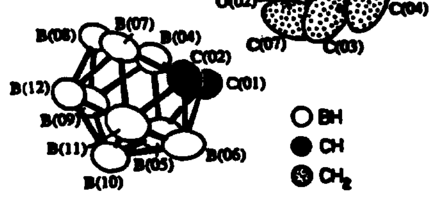

Fig. 46. The anion in $[PPN][3,3\text{-}(THF)_2$-*commo*-3,3′-$Sm(3,1,2\text{-}SmC_2B_9H_{11})_2]$. (Reprinted with permission from *Inorganic Chemistry*. Copyright 1991, American Chemical Society.)

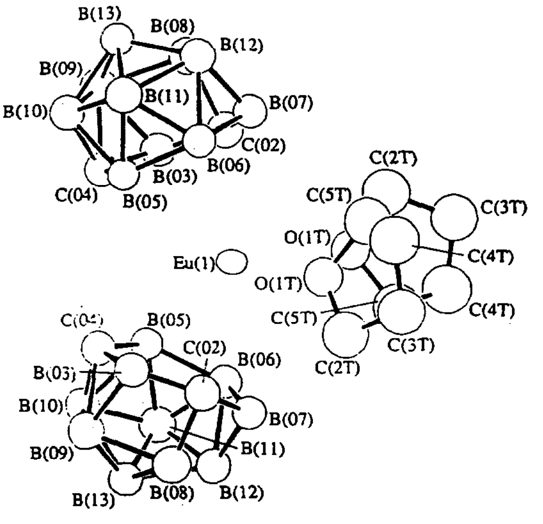

Fig. 47. The anion in $[NEt_4]_2[1,1\text{-}(THF)_2\text{-}commo\text{-}1,1'\text{-}Eu(1,2,4\text{-}EuC_2B_{10}H_{12})_2]$. (Reprinted with permission from *Inorganic Chemistry*. Copyright 1991, American Chemical Society.)

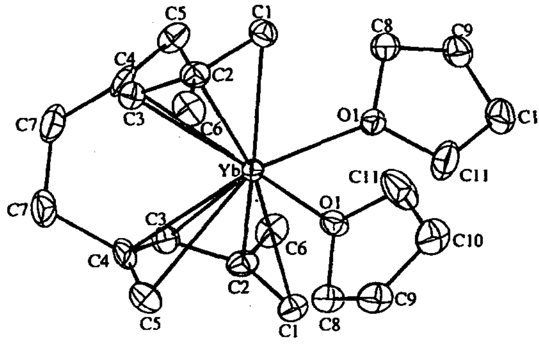

Fig. 48. $Yb[4,4'\text{-}(CH_2)_2(2\text{-}C_6H_8)_2](THF)_2$. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

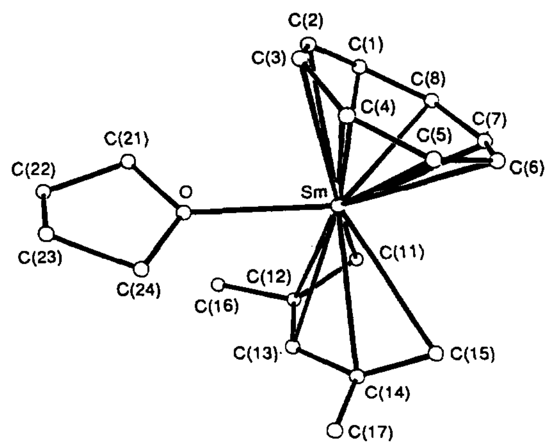

Fig. 49. $(COT)Sm(2,4\text{-}C_7H_{11})(THF)$. (Reprinted with permission from *Journal of the Chemical Society, Chemical Communications*.)

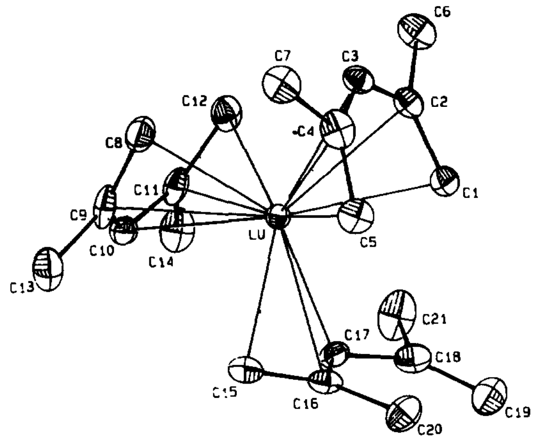

Fig. 50. $Lu(\eta^5\text{-}2,4\text{-}C_7H_{11})_2(\eta^3\text{-}2,4\text{-}C_7H_{11})$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

The Lu–C(η^5) distances average 2.64 Å while the Lu–C(η^3) separations average 2.59(1) Å.

Qiu and Liu [71] reported the same reaction with $TbCl_3$ to yield the hemi-THF solvate $Tb(2,4\text{-}C_7H_{11})_3 \cdot 1/2(THF)$. A crystal structure determination was reported to show three η^5-ligands. Cai *et al.* [72] used similar reactions to prepare $Ln(2,4\text{-}C_7H_{11})Cl_2(THF)_3$ (Ln = Nd, Sm, Gd), $Ln(2,4\text{-}C_7H_{11})_2Cl(THF)$ (Ln = Nd, Sm), and $Ln(2,4\text{-}C_7H_{11})_3$ (Ln = La, Sm, Gd).

2.2. *Compounds without supporting cyclopentadienyl ligands*

2.2.1. *Cyclooctatetraene compounds*

Several mixed ligand-COT/Cp, COT/Ind, and COT/pentadienyl-compounds were described in sections above. These are $Cp(COT)Ln(THF)_2$ [12] [Ln = Pr (Fig. 2), Nd], Cp(COT)Gd(THF) [12], (Ind)(COT)Ln (Ln = Pr, Nd) [12,62], $(Ind)(COT)Pr(THF)_2$ [62] (Fig. 42), and $(COT)Sm(2,4\text{-}C_7H_{11})(THF)$ [69] (Fig. 49).

Streitwieser *et al.* [73] determined the crystal structures of $(MeCOT)_2Ce$ (Fig. 51) and [K(diglyme)]-$[(COT)_2Yb]$ (Fig. 52). The average bonding parameters include Ce–C(η^8) = 2.692(6) Å, Centroid–Ce–Centroid = 176.03°, Yb–C(η^8) = 2.598(4), 2.610(8) Å, and Centroid–Yb–Centroid = 179.88°. A comparison of other structurally determined COT compounds was also presented.

Chen *et al.* [74] prepared a tetranuclear COT complex $(COT)Er(\mu\text{-}COT)K(\mu\text{-}COT)Er(\mu\text{-}COT)K(THF)_4$ and determined its structure (Fig. 53). The Er–C bond lengths range from 2.57(1) to 2.66(2) Å.

2.2.2. *Arene compounds*

Ren and Amberger [75] performed molecular mechanics calculations on $(\eta^6\text{-}C_6H_6)_2Gd$ and (η^6-

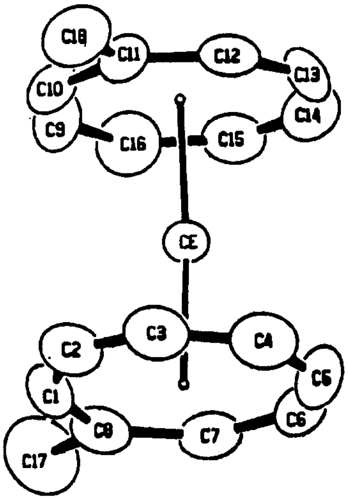

Fig. 51. (MeCOT)$_2$Ce. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

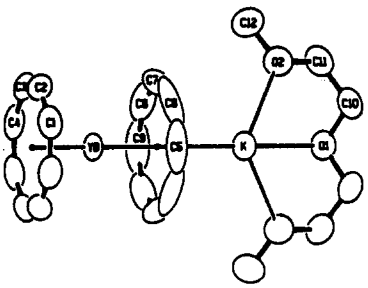

Fig. 52. [K(diglyme)][(COT)$_2$Yb]. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

^{t}Bu$_3$C$_6$H$_3$)$_2$Ln (Ln = Gd, Yb, Y). Steric effects were shown to be a major cause of compound instability.

Fan and co-workers [76,77] prepared (η^6-C$_6$H$_6$)Sm(AlCl$_4$)$_3$ and (η^6-Me$_2$C$_6$H$_4$)Sm(AlCl$_4$)$_3$ by reaction of activated aluminum powder with SmCl$_3$ in the corresponding arene. Crystal structures were reported for both compounds.

2.2.3. Allyl compounds

Wu *et al.* [78] reacted LnCl$_3$ with allyl Grignard reagents and TMEDA in THF to prepare Ln(η^3-C$_3$H$_5$)$_2$Cl$_5$Mg$_2$(TMEDA)$_2$ (Ln = La, Ce, Pr, Nd, Sm). Three crystal structures were reported: Ce(η^3-C$_3$H$_5$)$_2$(μ_2-Cl)$_2$(μ_3-Cl)$_2$Mg(TMEDA)(μ_2-Cl)Mg(TMEDA) (Fig. 54) and Ln(η^3-C$_3$H$_5$)$_2$(μ_2-Br)$_2$(μ_3-Br)$_2$Mg(OEt$_2$)$_2$(μ_2-Br)M g(OEt$_2$)$_2$ [Ln = Ce (Fig. 55), Nd]. The range in Ln–C bond lengths was Ce–C = 2.69(1)–2.79(2) Å (TMEDA adduct), Ce–C = 2.65(2)–2.67(2) Å (OEt$_2$ adduct), and Nd–C = 2.61(2)–2.69(2) Å.

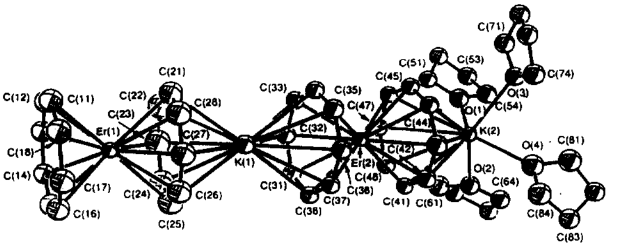

Fig. 53. (COT)Er(μ-COT)K(μ-COT)Er(μ-COT)K(THF)$_4$. (Reprinted with permission from *Journal of the Chemical Society, Chemical Communications*.)

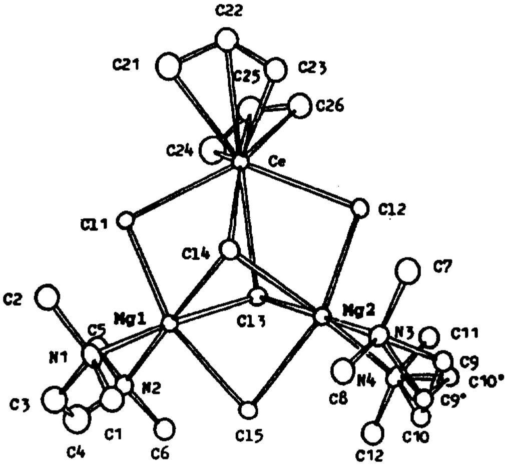

Fig. 54. Ce(η^3-C$_3$H$_5$)$_2$(μ_2-Cl)$_2$(μ_3-Cl)$_2$Mg(TMEDA)(μ_2-Cl)Mg(TMEDA). (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

Li *et al.* [79] prepared LiLn(C$_3$H$_3$)$_4$(dioxane)$_n$ (Ln = La, n = 3; Ln = Ce, Pr, Nd, Sm, Gd, n = 2; Ln = Y, n = 2.5) by reaction of LnCl$_3$ with Li(C$_3$H$_3$) (1:4) in THF/dioxane. The structure of the Ce compound was determined.

Kagan *et al.* [80] studied the preparation and reactivity of samarium allyl compounds. Reaction of these

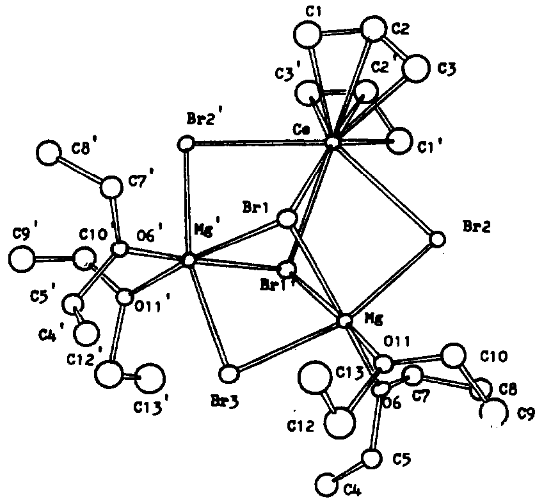

Fig. 55. Ce(η^3-C$_3$H$_5$)$_2$(μ_2-Br)$_2$(μ_3-Br)$_2$Mg-(OEt$_2$)$_2$(μ_2-Br)Mg(OEt$_2$)$_2$. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

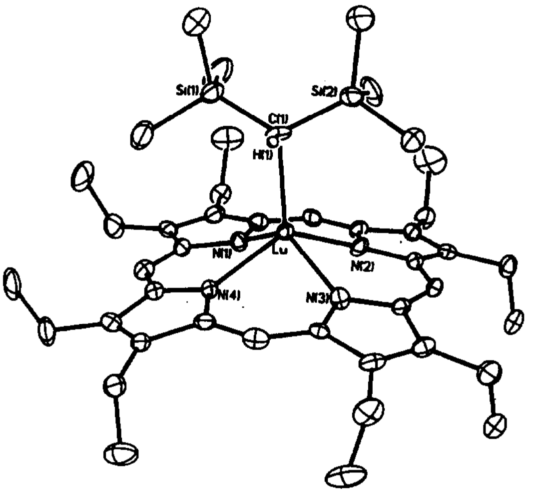

Fig. 56. (OEP)Lu(CH(SiMe$_3$)$_2$). (Reprinted with permission from *Inorganic Chemistry*. Copyright 1991, American Chemical Society.)

compounds with acid chloride produced β,γ-unsaturated ketones.

2.2.4. Fullerenes

Huang and Freiser [81] prepared externally bound LaC$_{60}^+$ ions. Smalley *et al.* [82] produced fullerene with one La atom trapped inside.

2.2.5. Alkane, alkene, alkyne, and σ-bonded arene compounds

Schaverien [83] prepared (OEP)Y(μ-Me)$_2$AlMe$_2$ (OEP = octaethylporphyrin) from (OEP)YOC$_6$H$_3{}^t$Bu$_2$ and (OEP)Y(μ-Me)$_2$Li(OEt$_2$). The compound is selectively oxidized by O$_2$ to give (OEP)Y(μ-OMe)$_2$AlMe$_2$. In a second paper with Orpen [84], this chemistry was further explored. Reaction of Ln(CH(SiMe$_3$)$_2$)$_3$ with OEPH$_2$ gave (OEP)-Ln(CH(SiMe$_3$)$_2$) (Ln = Lu, Y). The crystal structure of the Lu compound is depicted in Fig. 56. Protonolysis with HCC^{t}Bu yielded [(OEP)-LnCC^{t}Bu]$_n$ (Ln = Lu, Y).

Schaverien and Van Mechelen [85] reported the reactions of Lu(CH(SiMe$_3$)$_2$)$_3$ with KCl in OEt$_2$ and of LuCl$_3$ with K(CH(SiMe$_3$)$_2$) in ether, both of which yielded Lu(CH(SiMe$_3$)$_2$)$_3$(μ-Cl)K(OEt$_2$). After removal of the ether under vacuum and dissolution in toluene the crystallographically characterized compound Lu(CH(SiMe$_3$)$_2$)$_3$(μ-Cl)K(η^6-C$_7$H$_8$)$_2$ (Fig. 57) could be isolated. The Lu–C bond lengths average 2.34(1) Å.

Schumann *et al.* [86] utilized [Li(TMEDA)]$_3$[SmMe$_6$] to prepare [Li$_5$Sm(O^{t}Bu)$_8$] by reaction with ^{t}BuOH in OEt$_2$. Fryzuk *et al.* [87] prepared LnR[N(SiMe$_2$CH$_2$-PMe$_2$)$_2$]$_2$ (Ln = Y, R = Ph, CH$_2$Ph; Ln = Lu, R = Ph) by replacement of the chloride in LnCl[N(SiMe$_2$CH$_2$-PR$_2$)$_2$]$_2$. Cyclometalation in these compounds results from thermal instability and the crystal structure of one such product was determined, Y[N(SiMe$_2$CHPMe$_2$)-(SiMe$_2$CH$_2$PMe$_2$)][N(SiMe$_2$CH$_2$PMe$_2$)$_2$] (Fig. 58). The Y–C bond length is 2.65(1) Å.

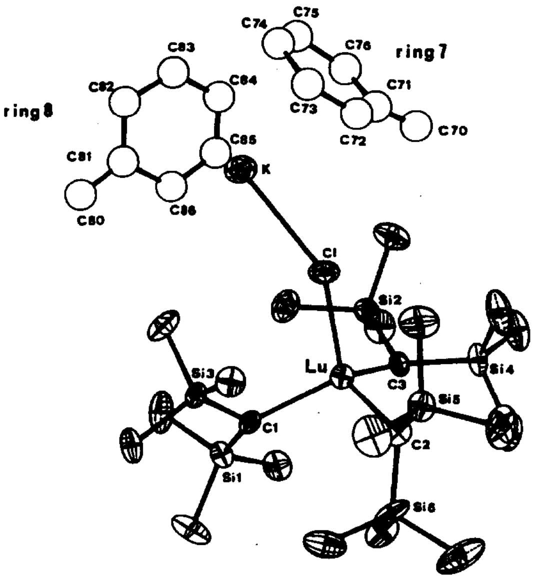

Fig. 57. Lu(CH(SiMe$_3$)$_2$)$_3$(μ-Cl)K(η^6-C$_7$H$_8$)$_2$. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

Blomberg *et al.* [88] conducted an *ab initio* study of the reaction of second row transition metal atoms (including Y) with methane. Freiser *et al.* [89] studied

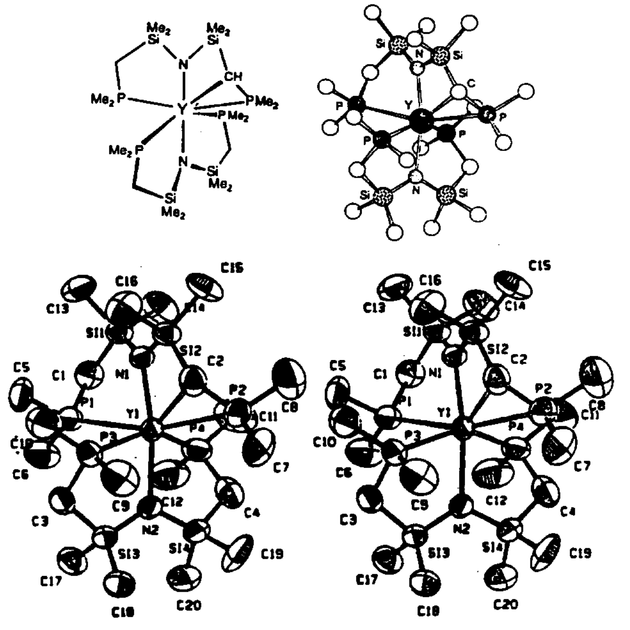

Fig. 58. Y[N(SiMe$_2$CHPMe$_2$)(SiMe$_2$CH$_2$PMe$_2$)][N(SiMe$_2$CH$_2$-PMe$_2$)$_2$]. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

ligand displacement reactions in the gas phase for Y^{2+} alkanes and alkenes. Alkanes were found to displace alkenes. Bauschlicher and Langhoff [90] studied the interaction of Y with +1 and +2 ions of C_2H_2, C_2H_4, and C_3H_6 with electronic structure calculations. Freiser *et al.* [91] investigated the gas phase chemistry of YMe^+.

Shustov *et al.* [92] studied the reactions of $Ln(C{\equiv}CPh)_3$ (Ln = Pr, Sm, Tb) with EtOAc and MeO_2CCHMe_2. These reactions led to the formation of $Ln[R(R'O)C(C{\equiv}CPh)O]_3$ (R = Me, R' = Et; R = Me_2CH, R' = Me).

Emel'yanova *et al.* [93] reported that the reduction of LnI_3 (Ln = Y, La, Ce, Pr, Nd) with lithium naphthalenide in THF led to $Ln_x(C_{10}H_8)(THF)_y$. The Yb compound was utilized to prepare $Ph_3SnYb(THF)_2(\mu\text{-}Ph)_3Yb(THF)_3$ [94], Cp_2Yb [95], and $[Yb_4(\mu\text{-}\eta^2,\eta^2\text{-}Ph_2N_2)_4(\mu_3\text{-}PhN)_2(THF)_4]$ [96].

Lin *et al.* [97] reported the crystal structure of $GdPhCl_2(THF)_4$. The Gd–C bond length is 2.44(2) Å.

3. Actinides

3.1. Cyclopentadienyl and cyclopentadienyl-like compounds

3.1.1. Monocyclopentadienyl compounds

Baudry *et al.* [98] prepared $CpCo[P(O)(OEt_2)]_3\text{-}CpUCl_2$ and determined its crystal structure (Fig. 59). The compound was prepared by first reacting UCl_4 with $NaCpCo[P(O)(OEt_2)]_3$ to prepare $CpCo[P(O)\text{-}(OEt_2)]_3UCl_3$ followed by reaction of the trichloride with TlCp.

Baudin *et al.* [99] reported the preparation of $CpUCl(^tBu_3CO)$ in a paper discussing the chemistry of $^tBu_3CO$ related to the isosteric Cp ligand. Alkyl and allyl compounds with this supporting ligand are discussed in the last section of this review.

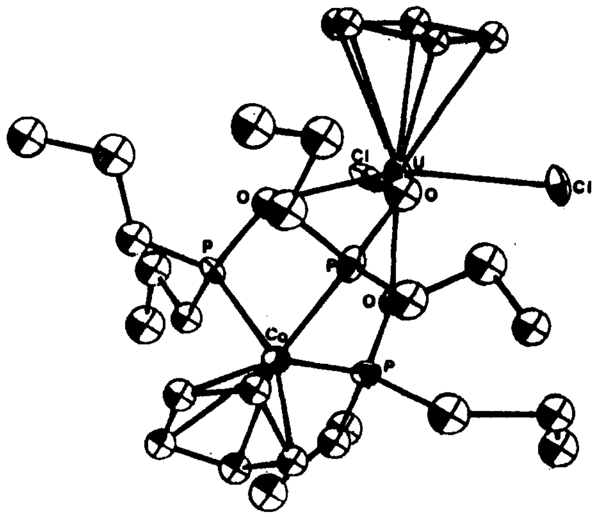

Fig. 59. $CpCo[P(O)(OEt_2)]_3CpUCl_2$. (Reprinted with permission from *Inorganic Chemistry*. Copyright 1991, American Chemical Society.)

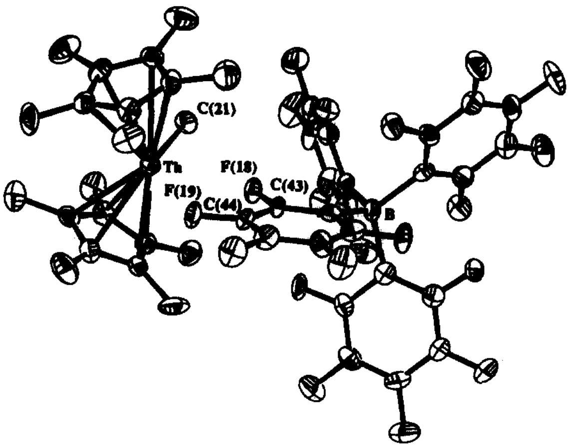

Fig. 60. $[Cp^*_2ThMe][B(C_6F_5)_4]$. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

3.1.2. Biscyclopentadienyl compounds

Marks *et al.* [100] prepared $[Cp^*_2ThMe][B(C_6F_5)_4]$ by reaction of $Cp^*_2ThMe_2$ with $[NH^nBu_3][B(C_6F_5)_4]$. The crystal structure (Fig. 60) revealed weak coordination of the anion: Th–C(Cp*) = 2.754(3) Å, Th–Me = 2.399(8) Å, Th–F(18) = 2.757(4) Å, Th–F(19) = 2.675(5) Å.

Two compounds with P_6 and P_3 ligands were prepared by Scherer *et al.* [101]. Reaction of $(Cp^tBu_2)_2\text{-}Th(\eta^4\text{-}C_4H_6)$ with P_4 in toluene led to $(Cp^tBu_2)_2\text{-}Th(\mu\text{-}\eta^3,\eta^3\text{-}P_6)Th(Cp^tBu_2)_2$ (Fig. 61). Reaction with P_4 in the presence of $MgCl_2$ gave instead $(Cp^tBu_2)_2\text{-}Th(\mu\text{-}\eta^3\text{-}P_3)ThCl(Cp^tBu_2)_2$ (Fig. 62).

3.1.3. Bridged cyclopentadienyl compounds

Fischer *et al.* [102] prepared the disodium salt of a 2,6-pyridyl bridged biscyclopentadienyl dianion, $Na_2\text{-}[2,6\text{-}C_5H_3N(CH_2Cp)_2]$. The reagent was reacted with

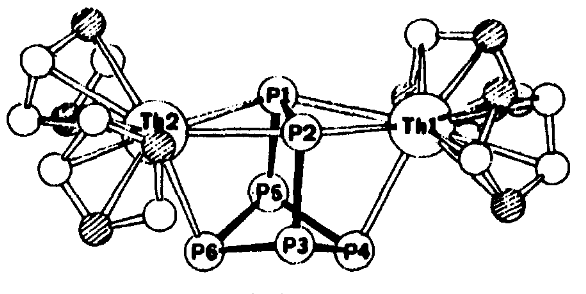

Fig. 61. $(Cp^tBu_2)_2Th(\mu\text{-}\eta^3,\eta^3\text{-}P_6)Th(Cp^tBu_2)_2$. The shaded atoms represent the location of the ^tBu groups. Th–P = 2.84–2.92 Å. (Reprinted with permission from *Angewandte Chemie, International Edition English*.)

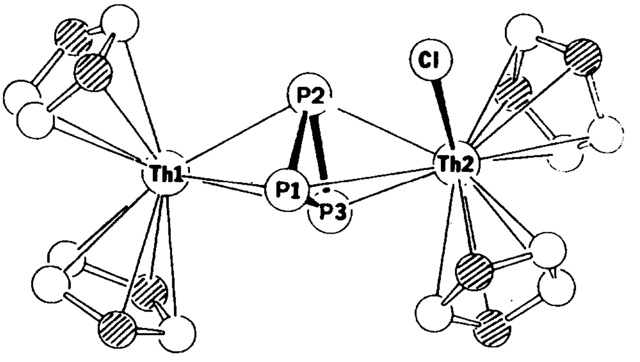

Fig. 62. $(Cp^tBu_2)_2Th(\mu\text{-}\eta^3\text{-}P_3)Th(Cp^tBu_2)_2$. Th–P = 2.81–2.99 Å. (Reprinted with permission from *Angewandte Chemie, International Edition English*.)

UCl_4 in THF to make $[2,6\text{-}C_5H_3N(CH_2Cp)_2]UCl_2$. The crystal structure of this compound (Fig. 63) revealed the anion to be chelating with a strong U–N interaction (2.62(1) Å). The average U–C distance is 2.70(1) Å, while the U–Cl separations are asymmetric at 2.615(3) Å and 2.636(3) Å. Low temperature NMR and mass spectroscopic data were also presented.

3.1.4. Triscyclopentadienyl compounds

Strittmatter and Bursten [27] presented Xα-SW molecular orbital calculations for Cp_3An (An = U, Np, Pu, Am, Cm, Bk, Cf). The 5f orbital participation in An–Cp bonding increases from left to right in the actinide series with a corresponding decrease in 6d orbital participation. The actinide compounds are compared to the corresponding Cp_3Ln compounds.

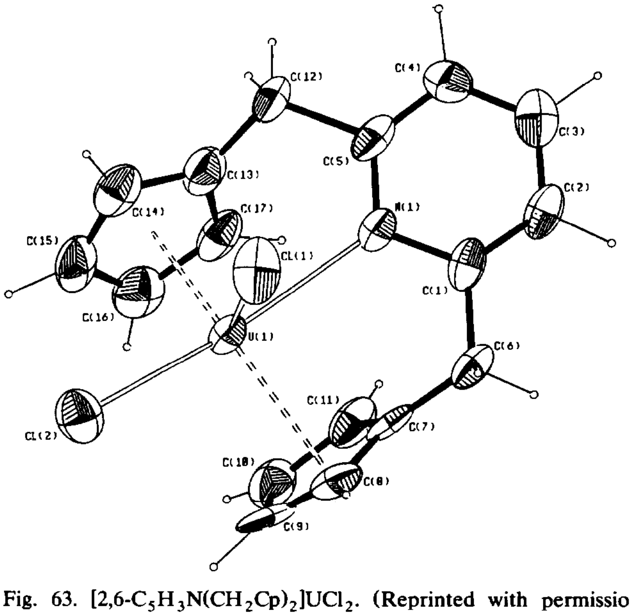

Fig. 63. $[2,6\text{-}C_5H_3N(CH_2Cp)_2]UCl_2$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

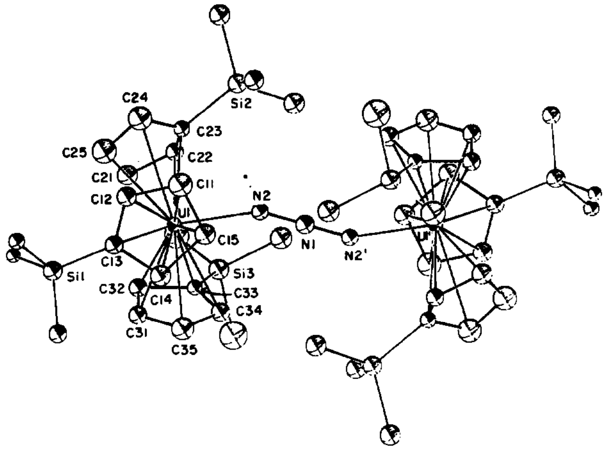

Fig. 64. The anion in $[Na(18\text{-}crown\text{-}6)]\{[Cp'_3U]_2(N_3)\}$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

Ephritikhine *et al.* [103] prepared the first stable organouranium(IV) hydride, Cp'_3UH. Reversible sodium amalgam reduction of this compound led to the first anionic uranium(III) monohydride, $[Na(18\text{-}crown\text{-}6)][Cp'_3UH]$. Reactions of these compounds to form $[Cp'_3U][BPh_4]$, Cp'_3U, and $[Na(18\text{-}crown\text{-}6)][Cp'_3UCl]$ were also described.

Villiers and Ephritikhine published two accounts of the reactivity of Cp_3UR^- (R = Me, Pr, Me_2CH, Bu, allyl, CH_2Ph) [104] and Cp_3UR (R = Me, Pr, Bu, CH_2Ph) [105]. The anions react with organic halides (R′X) to yield Cp_3UR and Cp_3UR'. The neutral compounds react with LiR to yield $Cp_3UMe_2^-$ and $Cp_2UR_3^-$. Homolytic U–C bond cleavage leads to Cp_3UR^-.

Berthet *et al.* [106] prepared the azide compounds, $Cp'_3U(N_3)$, $[Na(18\text{-}crown\text{-}6)][Cp'_3U(N_3)]$, $\{[Cp'_3U]_2(N_3)\}[BPh_4]$, $[Na(18\text{-}crown\text{-}6)]\{[Cp'_3U]_2(N_3)\}$, and $[Cp'_3U]_2(N_3)$. The crystal structure of $[Na(18\text{-}crown\text{-}6)]\{[Cp'_3U]_2(N_3)\}$ is depicted in Fig. 64. Bonding parameters for the anion include U–N = 2.40(2) Å.

Ephritikhine *et al.* [107] prepared the oxo-bridged $[Cp'_3U]_2O$ by reaction of Cp'_3U with CO_2 or N_2O. The crystal structure (Fig. 65) exhibits a linear U–O–U bridge (U–O = 2.1053(2) Å) and an average U–C separation of 2.80 Å.

Hauchard *et al.* [108] conducted an electrochemical study of Na/Hg reduction of Cp_3UCl in $[NBu_4][PF_6]$/THF. Oxidation gave a U^{5+} compound, Cp_3UCl^+, which disproportionated. Reduction led to $[NBu_4][Cp_3UCl]$.

Spirlet *et al.* [109] determined the crystal structure of Cp_3UI (Fig. 66). The average U–C separation is 2.73(4) Å and U–I = 3.059(2) Å.

Marks *et al.* [110] published data on uranium–metal bond disruption enthalpies for $Cp_3U\text{–}MPh_3$ (M = Si,

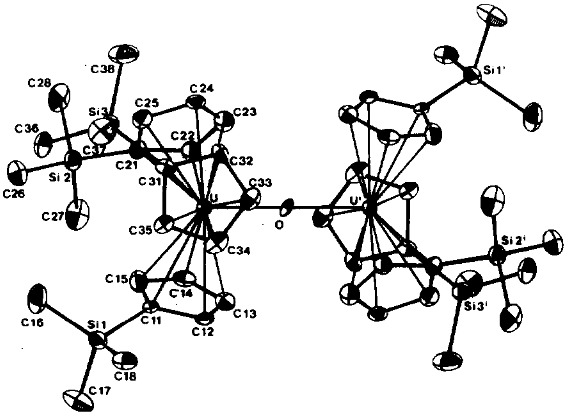

Fig. 65. $[Cp'_3U]_2O$. (Reprinted with permission from *Journal of Organometallic Chemistry*.)

Ge, Sn) and $Cp_3U{-}M(CO)_2Cp$ (M = Fe, Ru). The data indicate weak heterobimetallic bonding.

3.1.5. Tetrakiscyclopentadienyl compounds

Kanellakopulos *et al.* [111] measured the dipole moments of Cp_4An (An = Th, U, Np) in benzene. The dipole moments were not zero despite the approximately tetrahedral solid state environment.

3.1.6. Indenyl compounds

Jemine *et al.* [112] measured the bond disruption enthalpy in $(Ind)_3U(THF)$. The value for $(Ind)_3U{-}THF$ in toluene is 71(5) kJ mol^{-1}.

3.2. Compounds without supporting cyclopentadienyl ligands

3.2.1. Cyclooctatetraene compounds

Arliguie *et al.* [113] prepared alkyl and alkoxide compounds of $(COT){-}U^{2+}$. Reaction of $2Li(CH_2SiMe_3)$ with $(COT)UI_2(HMPA)_2$ led to formation of $(COT)U(CH_2SiMe_3)_2(HMPA)$. Reaction of $(COT)U(BH_4)_2$ with ROH (R = Et, $CHMe_2$, CMe_3) gave the alkoxides, $(COT)U(BH_4)(OR)$ and $(COT)U(OR)_2$. Addition of BH_4^- to $(COT)U(BH_4)_2$ and $(COT)U(BH_4)(OEt)$ led to $(COT)U(BH_4)_3^-$ and $(COT)U(BH_4)_2(OEt)^-$.

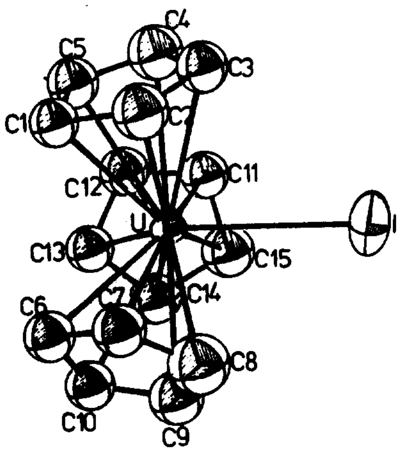

Fig. 66. Cp_3UI. (Reprinted with permission from *Acta Crystallographica*.)

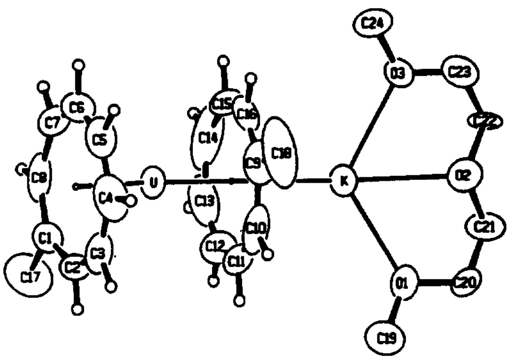

Fig. 67. $[K(diglyme)][(MeCOT)_2U]$. (Reprinted with permission from *Organometallics*. Copyright 1991, American Chemical Society.)

The crystal structure of $[K(diglyme)][(MeCOT)_2U]$ was described by Streitwieser *et al.* [73]. The compound (Fig. 67) exhibits average U–C distances of 2.707(7) and 2.732(8) Å. The longer distances correspond to the $MeCOT^{2-}$ dianion bridging U^{3+} and K^+.

3.2.2. Alkyl and allyl compounds

Baudin *et al.* [99] prepared alkyl and allyl compounds utilizing $^tBu_3CO$ as a supporting ligand isosteric with Cp. The new compounds included $U(^tBu_3CO)_2R_2$ (R = C_3H_5, CH_2Ph). Leonov and Solov'eva [114] studied insertion reactions of CO and CO_2 into the U–C bonds in $U(CH_2Ph)_4MgCl_2$. The compounds prepared included $[U(CH_2Ph)_3(COCH_2Ph)MgCl_2]_2$ from reactions with CO, and $[U(CH_2Ph)(O_2CCH_2Ph)MgCl_2]_2$, $[U(CO_2CH_2Ph)_4MgCl_2]_2$, and $U_2(CO_2CH_2Ph)_4MgCl_2$ from reactions with CO_2.

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