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Lanthanides and actinides. Annual survey covering the year 1992 ☆

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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 Sc, Y and La have been included because of their similar size and charge to the lanthanides. Abstracts of papers presented at conferences, dissertations and patents have mostly been excluded.

Several general review articles on f-element organometallic compounds appeared in 1992. Ephritikhine [1] published a survey of organoactinide chemistry, focusing on work done since 1985 (184 references). Complexes with cyclopentadienyl and other dienyls (pentadienyl, cyclohexadienyl, indenyl, phospholyl), cyclooctatetraenyl and arene ligands, hydrocarbyls and hydrides and the structures and stability of some organoactinides were the subject of this review. Two annual surveys were published by R.D. Rogers and L.M. Rogers covering the years 1987–1989 (370 references) [2] and 1990 (102 references) [3]. These reviews have been restricted to compounds of the lanthanides and actinides containing M—C bonds.

A few more specialized review articles also appeared in 1992. Fryzuk [4] reported on ligand design in inorganic chemistry. In this article an overview is given of the strategy used to design the tridentate ligand $^{-}N(SiMe_2CH_2PR_2)_2$, which is suitable for coordination to both late and early transition metals. Extension of this chemistry to Group 3 (Y, La) elements and the lanthanides (Ce, Sm, Eu, Er, Yb, Lu) is also discussed (total of 38 references). Evans et al. [5] published a study of the reactivity of hydrazines with organometallic samarium complexes (46 references). This study shows that there is sufficient space in the coordination environment generated by two $(C_5Me_5)_2Sm$ units to derivatize substrates inside the cavity formed by four C_5Me_5 rings. Giardello et al. [6] reviewed organo-f-element thermochemistry. This

☆ No reprints available. For previous annual survey see J. Organomet. Chem., 457 (1993) 41.

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publication shows implications for reactivity and bonding derived from metal–ligand bonding energetics (27 references).

2. Lanthanides

2.1. *Cyclopentadienyl and cyclopentadienyl-like compounds*

2.1.1. *Monocyclopentadienyl compounds*

Schumann et al. [7] prepared $CpLu[CH_2CH(Me)CH_2NMe_2](Cl)(THF)_2$ and $CpLu[(CH_2)_3NMe_2](Cl)(THF)_2$ (Cp ≡ cyclopentadienyl anion $C_5H_5^-$; THF ≡ tetrahydrofuran) by the reaction of $CpLuCl_2(THF)_3$ with $LiCH_2CH(Me)CH_2NMe_2$ or $Li(CH_2)_3NMe_2$:

$$LuCl_3 + NaCp + LiCH_2CH(Me)CH_2NMe_2$$

$$\xrightarrow[-NaCl,\ -LiCl]{THF} Cp\,\overline{Lu[CH_2CH(Me)CH_2}\,\overline{N}Me_2](Cl)(THF)_2$$

$$CpLuCl_2(THF)_3 + Li(CH_2)_3NMe_2 \xrightarrow[-LiCl]{THF} Cp\,\overline{Lu[(CH_2)_3}\,\overline{N}Me_2](Cl)(THF)_2$$

The complexes $CpLu(OSO_2CF_3)_2(THF)_n$ ($n=1, 2$) have been shown to react with two equivalents of $R_2As(CH_2)_3MgCl$ ($R \equiv {}^tBu, Me$) to give $CpLu[(CH_2)_3AsR_2]_2$:

$$CpLu(OSO_2CF_3)_2(THF) + 2ClMg(CH_2)_3AsR_2$$

$$\xrightarrow[-2ClMg(SO_3CF_3)]{THF} Cp\,\overline{Lu[(CH_2)_3}\,\overline{A}sR_2]_2$$

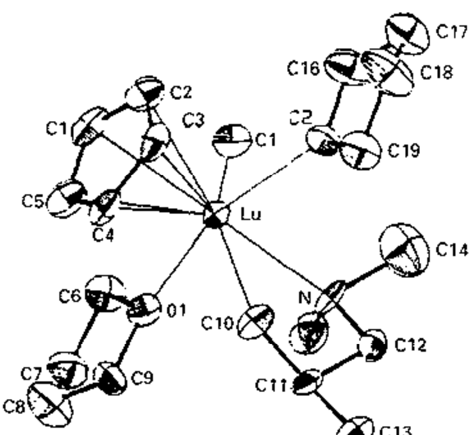
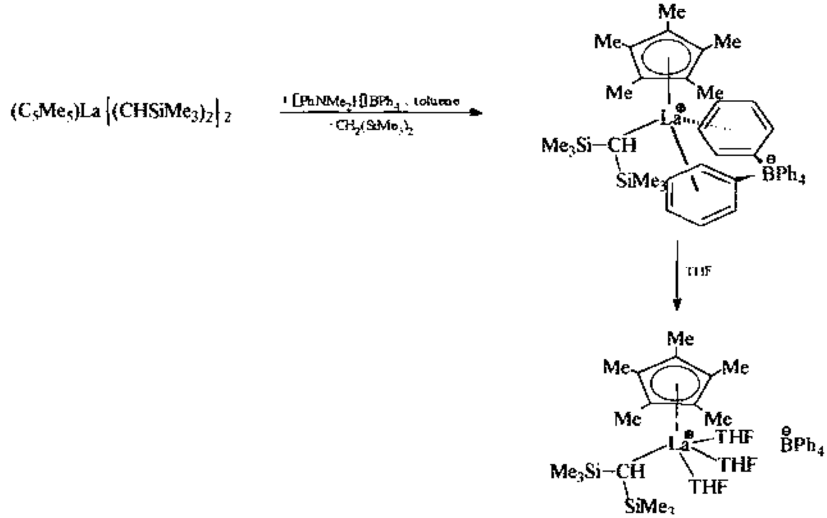


Fig. 1. $CpLu[CH_2CH(Me)CH_2NMe_2](Cl)(THF)_2$. (Reproduced with permission from Journal of Organometallic Chemistry.)

The crystal structure of $CpLu[CH_2CH(Me)CH_2NMe_2](Cl)(THF)_2$ was determined (Fig. 1) and reveals Lu−C(Cp) = 264.3 pm and Lu−O(THF) = 236.5 pm.

Schaverien [8] reported that the reaction of $La(Cp^*)\{CH(SiMe_3)_2\}_2$ ($Cp^* \equiv$ pentamethylcyclopentadienyl anion $C_5Me_5^-$) with $[PhNMe_2H]BPh_4$ affords zwitterionic $La(Cp^*)\{CH(SiMe_3)_2\}BPh_4$. This product reacts irreversibly with THF under displacement of the coordinated tetraphenylborate to afford the first cationic lanthanide alkyl complex $[La(Cp^*)\{CH(SiMe_3)_2\}(THF)_3]BPh_4$:



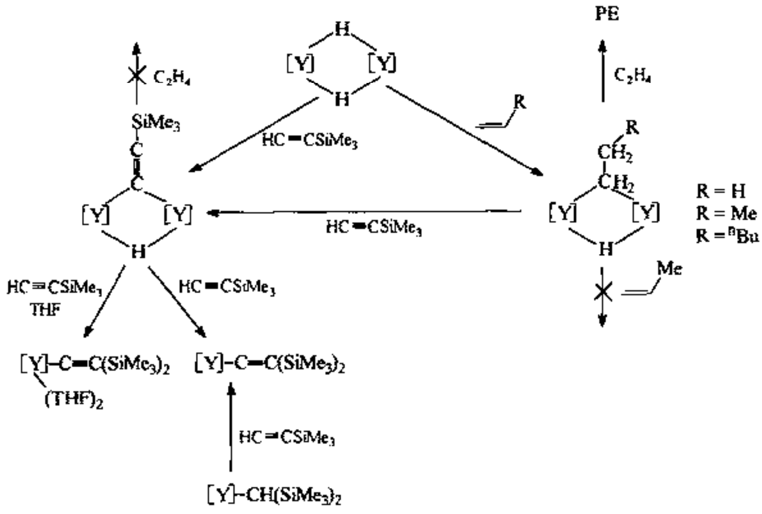
Schaverien [9] also prepared several μ-η-alkyl species $[\{Y(Cp^*)(OAr)\}_2(\mu\text{-}H)(\mu\text{-}CH_2CH_2R)]$ ($R \equiv H$, Me, nBu; $OAr \equiv OC_6H_3{}^tBu_2$), which were formed by the reaction of terminal alkenes $H_2C{=}CHR$ ($R \equiv H$, Me, nBu) with $[\{Y(Cp^*)(OAr)(\mu\text{-}H)\}_2]$. Reaction with $HC{\equiv}CSiMe_3$ produced the alkynyl compound $[\{Y(Cp^*)(OAr)\}_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CSiMe_3)]$ (Scheme 1). The use of these new species as models for the first insertion step in alkene polymerization was also discussed.

Cundari [10] reported ab initio molecular orbital (MO) calculations of transition metal imido complexes of the formula CpLnNH (Ln ≡ Sc, Y, La), which have been experimentally characterized. These Cp complexes are chosen because of high symmetry (C_{5v}), preference of Sc triad metals for the +3 oxidation state and structural similarity to Ir(III) imido complexes.

The compound $CpGdCl_2(THF)_3$ has been prepared by Wu et al. [11] by the reaction of NaCp with $GdCl_3$ in 2:1 molar ratio in THF:

$$3NaCp + 3GdCl_3 \xrightarrow{THF} 3(CpGdCl_2) \xrightarrow{THF} Cp_3Gd\cdot THF + 2GdCl_3$$

A crystal structure determination shows the complex to be monomeric (Fig. 2). The gadolinium has a distorted octahedral geometry coordinated by one Cp ring centroid, three THF oxygen atoms and two chloride anions. The average Gd−O(THF) distance is reported to be 239.7 pm. The Gd−C(Cp) bond lengths range from 267.3 to 269.1 pm and average 268.3 pm.



Scheme 1. $[Y] \equiv Y(C_5Me_5)(OAr)$; PE ≡ polyethylene.

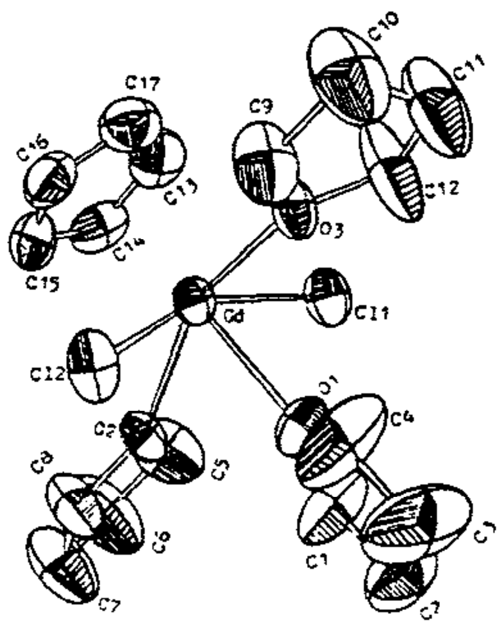
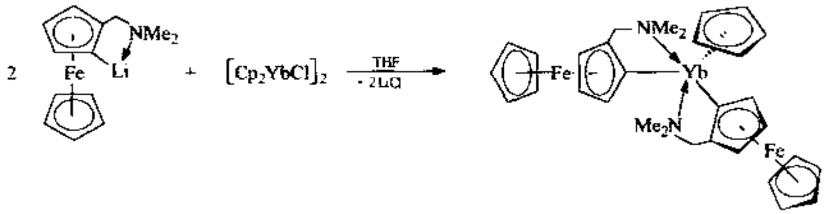


Fig. 2. $CpGdCl_2\cdot(THF)_3$. (Reproduced with permission from Journal of Coordination Chemistry.)

The same gadolinium compound $CpGdCl_2\cdot(THF)_3$ was also prepared and structurally characterized by Ke et al. [12].

Jacob et al. [13] observed the formation of $CpYb(FcN)_2$ in the reaction of

$[Cp_2YbCl]_2$ with two equivalents of Li(FcN) ([2-(dimethylaminomethyl)ferrocenyl]lithium):



The thermally stable compound was characterized by spectroscopic data, magnetic moments and elemental analysis.

Jacob et al. [14] reported the synthesis of the organolanthanide(III) derivatives (Cp)Ln(FcN)Cl (Ln ≡ Dy, Ho) and $(Cp)Dy(FcN)_2 \cdot 2.5THF$ by the treatment of $CpLnCl_2$ with (FcN)Li:

$$C_5H_5LnCl_2 + n(FcN)Li \xrightarrow[20\ ^\circ C]{THF} C_5H_5Ln(FcN)_nCl_{2-n} + nLiCl$$

$$Ln \equiv Dy,\ n = 1,2;\ Ln \equiv Ho,\ n = 1$$

$$C_5H_5DyCl_2 + 2(FcN)Li \xrightarrow[20\ ^\circ C]{THF} C_5H_5Dy(FcN)_2 \cdot 2.5THF + 2LiCl$$

The complexes have been characterized by elemental analysis, IR, ^1H nuclear magnetic resonance (NMR), ^{13}C NMR, UV–visible spectra, mass spectra and their effective magnetic moments.

Yu et al. [15] investigated the synthesis and thermal stability of the pyrrolyl complex $CpLn(pyr)_2(THF)$ (pyr ≡ pyrrolyl ≡ NC_4H_4; Ln ≡ Sm, Dy, Yb, Lu). They found that complexes of the type $Cp_2LnL(THF)$ are thermally more stable than those of the type $CpLnL_2(THF)$ (L ≡ ligand):

$$2(C_5H_5)LnL_2 \rightleftharpoons (C_5H_5)_2LnL + LnL_3$$

The mass spectra of lanthanide organometallics of the type $CpLn(acac)_2$ (Ln ≡ Ce, Nd, Sm, Gd, Dy, Er; acac ≡ acetylacetonato) have been studied by Liang et al. [16] under electron impact conditions and the fragmentation patterns are proposed on the basis of linked scan information of metastable transition in the first field-free region. The disproportionation reaction forming $(Cp)_3Ln$ and $Ln(acac)_3$ may take place when these complexes reach a certain evaporation temperature.

2.1.2. Biscyclopentadienyl compounds

The same authors [16] also described the mass spectra of the biscyclopentadienyl complexes $(Cp)_2Ln(acac)$ (Ln ≡ Ce, Nd, Sm, Gd, Dy, Er).

The formation of stable heterobimetallic compounds of the formula $(Cp)_2Ln(FcN)$ (Ln ≡ Y, Dy, Ho) from the corresponding cyclopentadienyllanthanide(III)chlorides

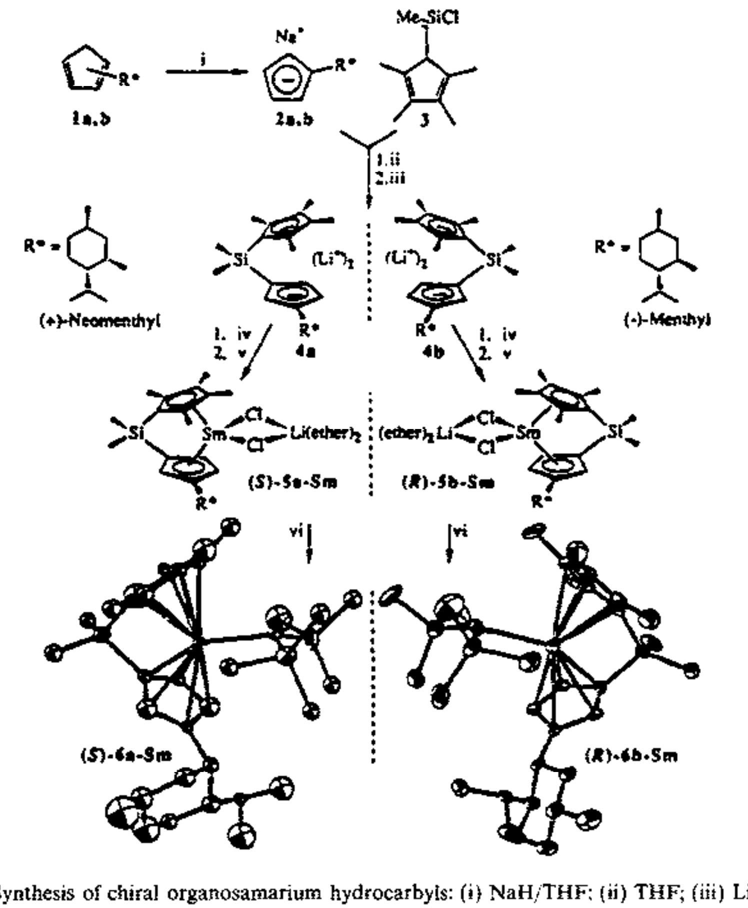
$(Cp)_2LnCl$ and (FcN)Li was described by Jacob et al. [14]:

$$(C_5H_5)_2LnCl + (FcN)Li \xrightarrow[20\,^{\circ}C]{THF} (C_5H_5)_2Ln(FcN) + LiCl$$

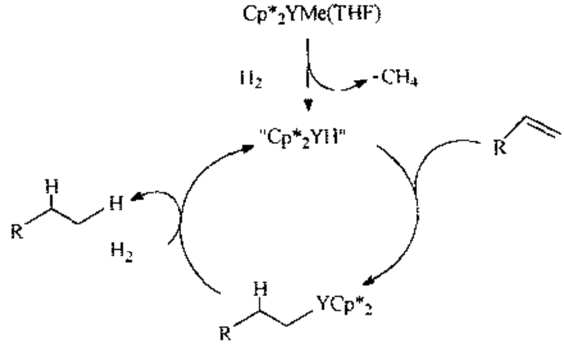
Jusong et al. [17] proposed a new synthetic route to $(Cp)_2Yb(THF)_2$. This compound was obtained by the reaction of $YbCl_3$ with NaCp in the presence of potassium cyclooctadienide in THF. The crystal structure of the complex was determined and discussed.

Conticello et al. [18] reported on a chelating ligand system which was designed to preserve $(Cp^*)_2Ln$ stereoelectronic properties while providing a rigid, chiral template for lateral–transverse substrate enantioface discrimination. The ligand synthesis is shown in Scheme 2. The enantiopure auxiliaries (R*) provide lateral steric discrimination and ensure that the resulting organolanthanides are diastereomeric.

Molander and Hoberg [19] reported that $Cp^*_2YMe(THF)$ is an efficient catalyst



Scheme 2. Synthesis of chiral organosamarium hydrocarbyls: (i) NaH/THF; (ii) THF; (iii) $LiCH_2TMS$/pentane; (iv) $SmCl_3$/THF; (v) diethyl ether; (vi) $LiCH(TMS)_2$/toluene.



Scheme 3.

for the selective reduction of substituted dienes (Scheme 3). The facile process that has been developed provides excellent selectivities and yields of the reduced compounds.

Namy et al. [20] investigated the action of $Sm(Cp)_2$ or SmI_2 on alkyl halides in the hope of gaining a more general understanding of the formation of organosamarium species. $Sm(Cp)_2$ and alkyl halides gave organosamarium compounds stable at −10 °C and reactive towards electrophiles. SmI_2 did not give stable alkylsamarium

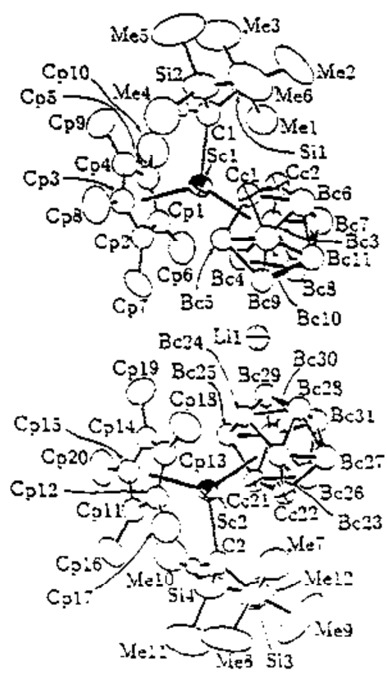


Fig. 3. $[Li(THF)_3]Li[Sc(C_2B_9H_{11})(C_5Me_5)\{CH(SiMe_3)_2\}]_2$. (Reproduced with permission from Acta Crystallographica.)

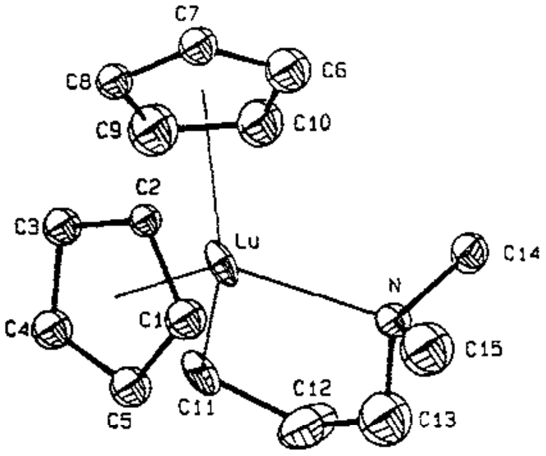
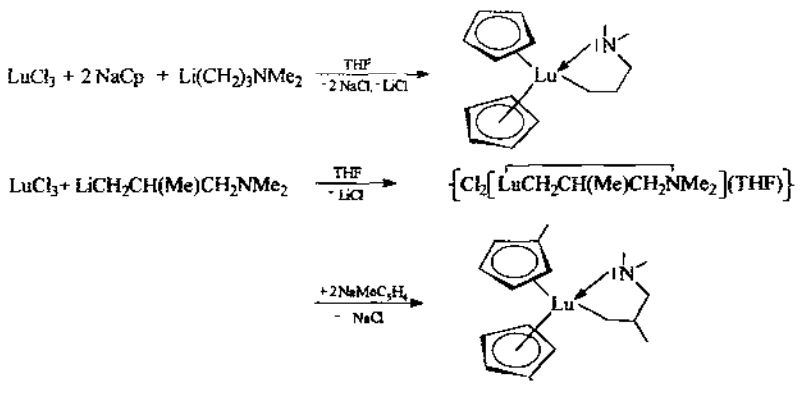


Fig. 4. $(Cp)_2Lu(CH_2)_3NMe_2$. (Reproduced with permission from Journal of Organometallic Chemistry.)

species. These studies established that $Sm(Cp)_2$ is able to replace SmI_2 in Barbier reactions and to reduce benzyl or allyl halides to afford the corresponding samarium organometallics.

The structure of the permethylcyclopentadienyl carbollide scandium complex $[Li(THF)_3]Li[Sc(C_2B_9H_{11})(C_5Me_5)\{CH(SiMe_3)_2\}]_2$ was discussed by Mash et al. [21] (Fig. 3: Sc–centroid(Cp*) = 220.5 and 219.2 pm).

The two compounds $(Cp)_2Lu(CH_2)_3NMe_2$ (Fig. 4: Lu–N = 237.1 pm; Lu–centroid(Cp) = 249.1 and 230.7 pm; Lu–C(alkyl) = 222.1 pm) and $(Cp)_2Y[\eta^2\text{-}O_2C(CH_2)_3NMe_2]$ (Fig. 5: Y–C(Cp) = 264.6, 264.8 pm and 266.0, 266.6 pm) have been prepared and structurally characterized by Schumann et al. [22]. The lutetium alkyl species $(Cp)_2Lu(CH_2)_3NMe_2$ was formed by the reaction between $LuCl_3$, NaCp and $Li(CH_2)_3NMe_2$ in the molar ratio 1:2:1, while an analogous reaction of $LuCl_3$, $NaMeC_5H_4$ and $LiCH_2CH(Me)CH_2NMe_2$ generates the corresponding methylcyclopentadienyl complex $(MeC_5H_4)_2Lu[CH_2CH(Me)CH_2NMe_2]$:



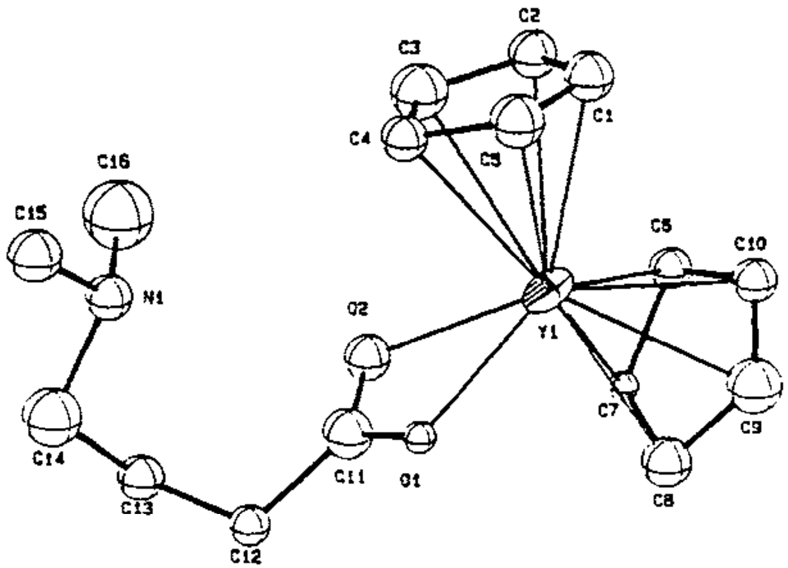
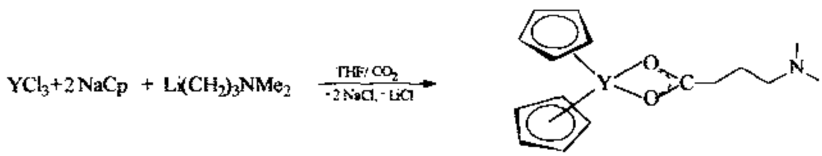
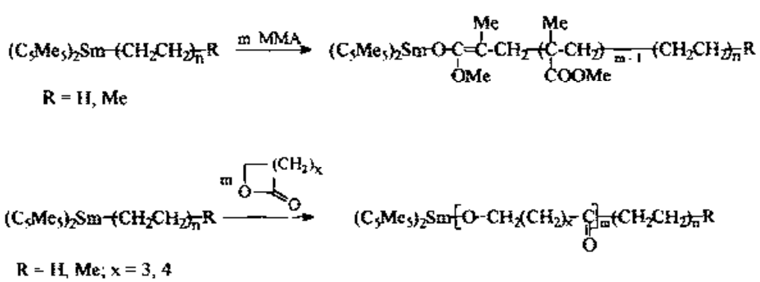


Fig. 5. $(Cp)_2Y[\eta^2\text{-}O_2C(CH_2)_3NMe_2]$. (Reproduced with permission from Journal of Organometallic Chemistry.)

The treatment of YCl_3 with two equivalents of NaCp and one equivalent of $Li(CH_2)_3NMe_2$ in the presence of CO_2 yields the yttrium carboxylate $(Cp)_2Y[\eta^2\text{-}O_2C(CH_2)_3NMe_2]$:



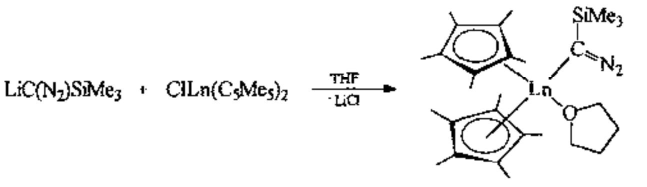
Yasuda et al. [23] described the first example of well-controlled block copolymerization, which was made possible by the unique dual catalytic function of $(Cp^*)_2LnR$ ($Ln \equiv Sm$, Yb, Lu; $R \equiv H$, Me) organolanthanide(III) complexes towards both polar and non-polar olefins (Scheme 4).



Scheme 4. MMA ≡ methyl methacrylate.

Gun'ko et al. [24] reported the formation of $(C_5H_3{}^tBu_2)_2Sm(\mu^2\text{-}D)_2AlD(TMEDA)$ (TMEDA ≡ tetramethylethylenediamine) by the reaction of $(C_5H_3{}^tBu_2)_2Sm(THF)$ with AlD_3 in ether in the presence of TMEDA. They also determined the crystal structure of this new compound (Fig. 6: Sm—centroid(Cp) = 250.9 and 249.8 pm). The metal atoms are bonded by the double bridge SmD_2Al. The coordination polyhedron of Al is a trigonal bipyramid.

Siebald et al. [25] prepared three compounds with metal–carbon σ bonds. The reaction of $LiC(N_2)SiMe_3$ with $(Cp^*)_2LnCl$ (Ln ≡ Y, Lu, Yb) (prepared in situ by adding LiCp* to anhydrous $LnCl_3$ in THF) formed the complexes $[Ln\{C(N_2)SiMe_3\}(Cp^*)_2(THF)]$:



The products are thermally sensitive hygroscopic solids and have been characterized by IR and ¹H NMR spectroscopy.

Zhou and Wu [26] reported the synthesis, thermal stability and crystal structure of $(Cp)_2Yb(OC_{10}H_7)(THF)$ (Fig. 7), which was isolated by the reaction of $(Cp)_3Yb$

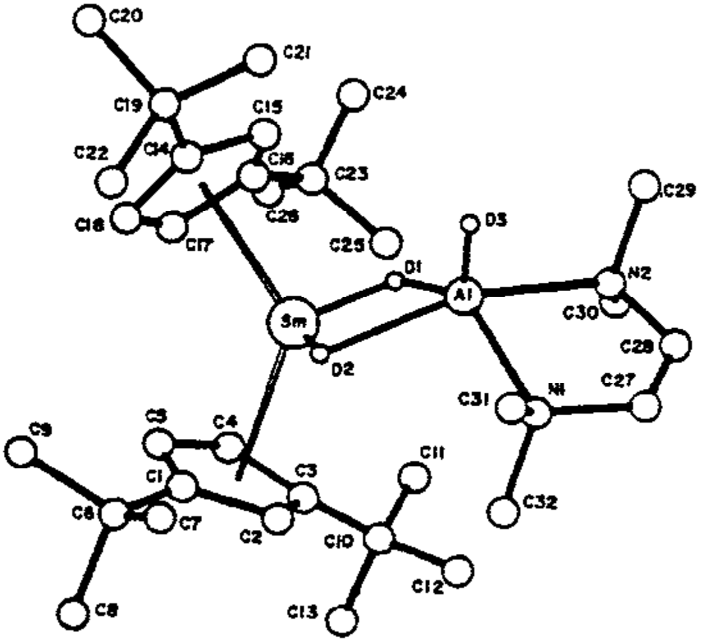


Fig. 6. $(C_5H_3{}^tBu_2)_2Sm(\mu^2\text{-}D)_2AlD(TMEDA)$. (Reproduced with permission from Journal of Organometallic Chemistry.)

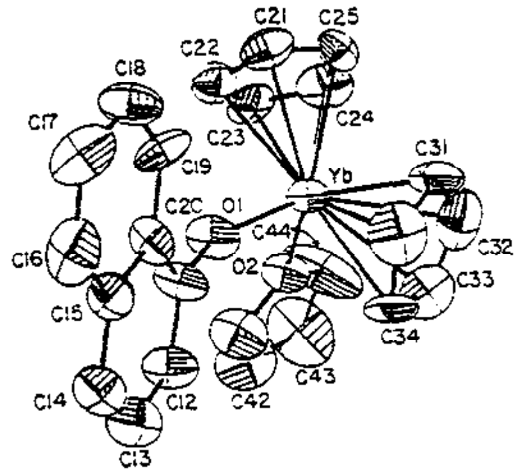


Fig. 7. $(Cp)_2Yb(OC_{10}H_7)(THF)$. (Reproduced with permission from Journal of Organometallic Chemistry.)

with α-naphthol (HNP) in THF. The average Yb—C(Cp) distance is 260.2 pm and the Yb—O(THF) and Yb—O(NP) distances are 230.1 and 206.1 pm respectively. The compound loses the coordinated THF molecule readily by heating under vacuum to give dimeric $[(Cp)_2Yb(NP)]_2$, which finally undergoes disproportionation to give $(Cp)_3Yb$ and $Yb(NP)_3$ on heating above 230 °C.

Heeres et al. [27] studied the reactivity of early lanthanide hydrocarbyls $(Cp^*)_2LnCH(SiMe_3)_2$ (Ln ≡ La, Ce) towards ketones. No reaction was observed with the bulky di-*tert*-butyl ketone. The corresponding lanthanum hydride $[(Cp^*)_2LaH]_2$ is more reactive and afforded the addition product $(Cp^*)_2LaOCH({}^tBu)_2$-$[O{=}C({}^tBu)_2]$. The enolate–ketone adducts $(Cp^*)_2LnOC(Et){=}C(H)Me[O{=}CEt_2]$ (Ln ≡ La, Ce) were formed by the reaction of 3-pentanone with the hydrocarbyls. The formation of lanthanide aldolates $(Cp^*)_2LnOCMe_2CH_2C({=}O)Me$ (Ln ≡ La, Ce) was observed when the carbyls were treated with acetone:

The crystal structure of the cerium compound was also published (Fig. 8: centroid—Ce—centroid = 133.6°; Ce—centroid(Cp*) = 281 and 283 pm). The compound crystallizes in monomeric units with the central cerium atom in a distorted tetrahedral environment.

The bis(cyclopentadienyl) derivates $(Cp)_2Sm(FcN)THF$ and $(Cp)_2Er(FcN)$ were prepared by Jacob et al. [13] by the treatment of $(Cp)_2LnCl(THF)$ with Li(FcN):

$$(C_5H_5)_2LnCl(THF) + Li(FcN) \xrightarrow[20\,^\circ C]{THF} (C_5H_5)_2Ln(FcN)(THF)_n + LiCl$$

$$Ln \equiv Sm,\ n = 1;\ Ln \equiv Er,\ n = 0$$

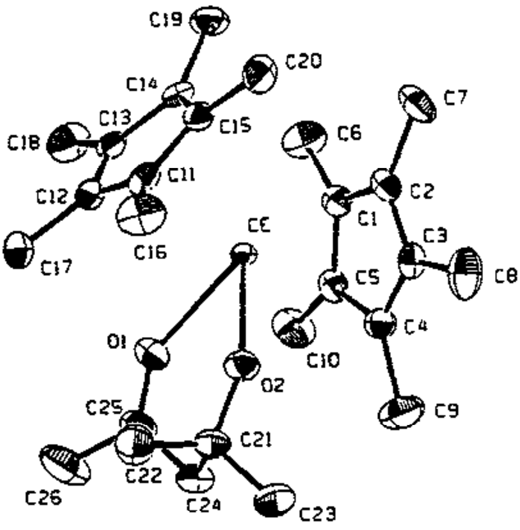
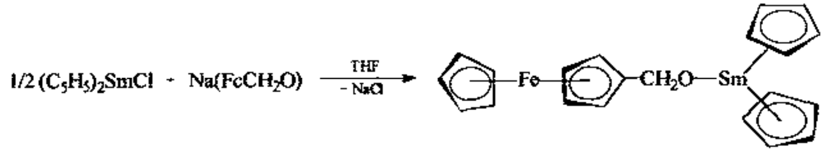


Fig. 8. $(Cp^*)_2CeOCMe_2CH_2C(=O)Me$. (Reproduced with permission from Organometallics.)

The compounds are thermally stable but very sensitive to air and moisture.

The bimetallic compound $(Cp)_2Sm(OCH_2Fc)$ has been synthesized by Gornitzka et al. [28] by the reaction of $Na[FcCH_2O]$ (Fc ≡ ferrocenyl) with $[(Cp)_2SmCl]_2$ in THF. It was proposed that the complex is dimerized via alkoxide bridges:



Deacon et al. [29] studied the reaction of diphenylphosphinocyclopentadiene with $Yb(C_6F_5)_2$ or with ytterbium metal and $Hg(C_6F_5)_2$ in THF to give the phosphinoytterbocene $[Yb(C_5H_4PPh_2)_2(THF)]$:

$$Yb + 2C_5H_5PPh_2 \rightarrow Yb(C_5H_4PPh_2)_2 + 2C_6F_5H$$

$$Yb + Hg(C_6F_5)_2 + 2C_5H_5PPh_2 \rightarrow Yb(C_5H_4PPh_2)_2 + Hg\downarrow + 2C_6F_5H$$

Redox transmetallation between ytterbium metal and $Tl(C_5H_4PPh_2)$ in DME (1,2-dimethoxyethane) gives thallium metal and $[Yb(C_5H_4PPh_2)_2(DME)]$. The ytterbium–transition metal heterobimetallics $[Yb(THF)(C_5H_4PPh_2)_2Z]\cdot n PhMe$ (Z ≡ $Ni(CO)_2$, $Mo(CO)_4$, $PtMe_2$; $n = \frac{2}{3}$ or 1) have been prepared by the reaction of $[Yb(THF)(C_5H_4PPh_2)_2]$ with $Ni(CO)_2(PPh_3)_2$, $Mo(CO)_4(nbd)$ (nbd ≡ norbonadiene) or $PtMe_2(cod)$ (cod ≡ cycloocta-1,5-diene) in toluene. The crystal structure of $[Yb(THF)_2(C_5H_4PPh_2)_2Ni(CO)_2]$ was also reported (Fig. 9). Formal eight-coordination is observed for the ytterbium atom with a pseudotetrahedral array of two THF oxygen atoms and the centroids of two η^5-$C_5H_4PPh_2$ ligands, which have

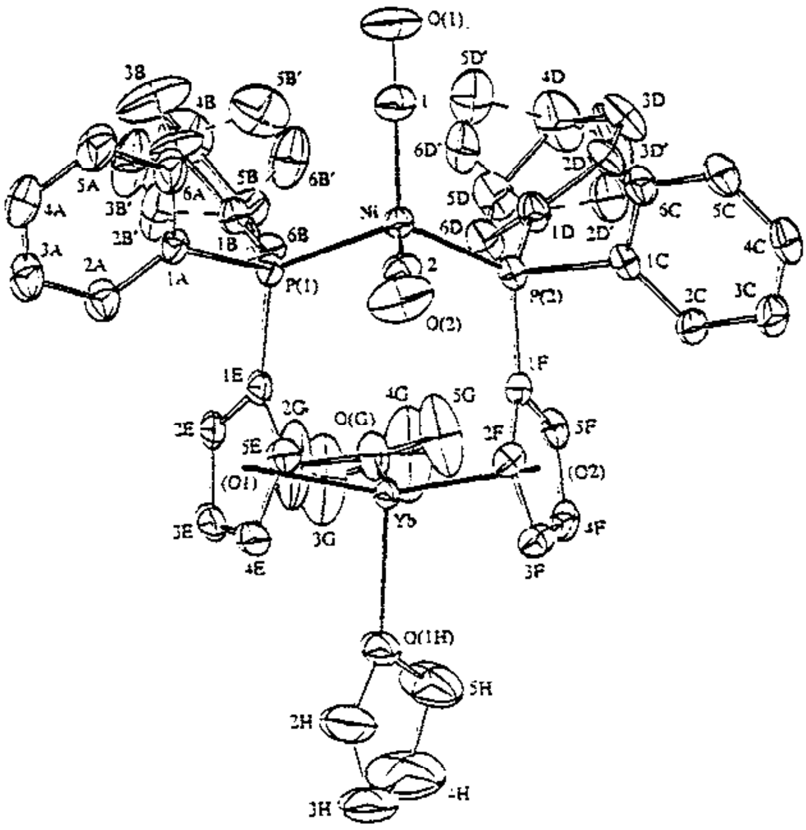


Fig. 9. [$Yb(THF)_2(C_5H_4PPh_2)_2Ni(CO)_2$]. (Reproduced with permission from Australian Journal of Chemistry.)

an eclipsed configuration. The Yb—Ni separation (475.1 pm) rules out any metal-metal interaction. The average Yb—centroid(Cp) distances are 243.8 and 242.9 pm.

Ziegler et al. [30] performed a density functional study on the activation of hydrogen–hydrogen and hydrogen–carbon bonds by $(Cp)_2Sc$–H and $(Cp)_2Sc$–R (R ≡ methyl, ethyl, propyl, vinyl, acetylide). Geometry optimizations reveal an agostic interaction for R ≡ ethyl, whereas methyl and propyl are bound to the metal centre without agostic interactions.

Schumann et al. [31] described the partial hydrolysis of [$O(CH_2CH_2C_5H_4)_2$]-Y(Cp) and [$O(CH_2CH_2C_5H_4)_2$]$Ho(C_5H_4CH_3)$, which results in the formation of the compounds $(MeC_5H_4)_3Y(H_2O)$ and $(MeC_5H_4)_3Ho(H_2O)$. The crystal structure of the holmium complex was also determined (Fig. 10). This holmium derivative was the first water adduct of an organometallic compound of the lanthanides to be characterized crystallographically. The average Ho—C(Cp) distance is 269 pm and the centroid(Cp)—Ho—centroid(Cp) angle is 118.4°.

Bied et al. [32] studied the synthesis and reactivity of benzylic and allylic samarium compounds. These species were prepared by the reaction of benzylic or allylic

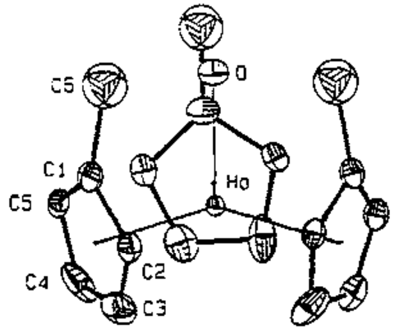


Fig. 10. $(MeC_5H_4)_3Ho(H_2O)$. (Reproduced with permission from Zeitschrift für Anorganische und Allgemeine Chemie.)

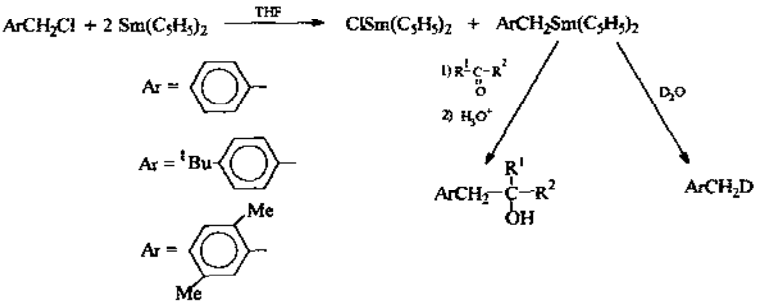
chlorides with $Sm(Cp)_2$ (Scheme 5). The products offer a wide scope of reactivity towards aldehydes, ketones and acid chlorides.

Harrison and Marks [33] reported that organolanthanides are effective homogeneous catalysts for olefin hydroboration and disclosed initial observations on scope, selectivity and mechanism (Scheme 6). $(Cp^*)_2LnR$ ($Ln \equiv La$, Sm; $R \equiv H$, $CH(SiMe_3)_2$), $(Me_2Si(Me_4C_5))_2SmCH(SiMe_3)_2$ and $(Cp^*)_2Sm(THF)$ complexes catalyse the room temperature hydroboration of a variety of dry, degassed olefins with catecholborane at efficient rates.

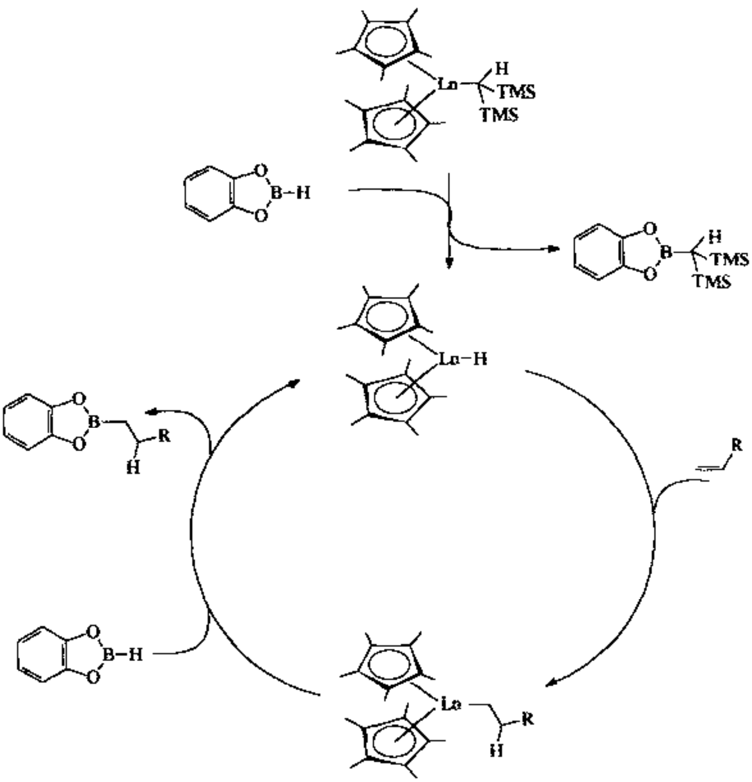
Divalent solvent-free bis(2-methoxyethylcyclopentadienyl) organolanthanide complexes $(MeOCH_2CH_2C_5H_4)_2Sm$ and $(MeOCH_2CH_2C_5H_4)_2Yb$ have been synthesized by Deng et al. [34] by the interaction of $(MeOCH_2CH_2C_5H_4)K$ with LnI_2 ($Ln \equiv Sm$, Yb):

$$LnI_2 + 2(MeOCH_2CH_2C_5H_4)K \xrightarrow{THF} (MeOCH_2CH_2C_5H_4)_2Ln + 2KI$$

The structure of $(MeOCH_2CH_2C_5H_4)_2Yb(THF)$ is presented in Fig. 11 (Yb—centroid(Cp) = 244.0 pm; centroid—Yb—centroid = 128.4°). The two ring centroids of the 2-methoxyethylcyclopentadienyl rings, the two oxygen atoms of



Scheme 5.



Scheme 6. Proposed mechanism of homogeneous organolanthanide-catalysed olefin hydroboration.

ether-substituted groups on the rings and the oxygen atom of the THF form a distorted trigonal bipyramid around the central ytterbium ion.

Green et al. [35] studied the magnitude and sign of the geminal coupling constants $^2J_{(H-D)}$, $^2J_{(H-H)}$ and the isotope shift, together with the temperature dependence of this shift, for [Y(η^5-Cp*)$_2$(CH$_2$D)(THF)]. The isotopic shift for this complex is essentially temperature independent.

Molander and Hoberg [36] presented the first use of organoyttrium catalysts in reductive cyclization reactions of 1,5- and 1,6-dienes. The catalytic cycle investigated is shown in Scheme 7. Cyclization of 1,5-hexadiene was initially explored utilizing [(Cp*)$_2$YH]$_2$ as a catalyst in the presence of H_2. Cyclization of 1,6-dienes is also quite efficient, although the reaction is complicated by reduction of the olefins to form acyclic alkanes.

Drago et al. [37] studied organometallic bond dissociation energies. The organometallic catimers (fragments forming the positive end of the dipole) include e.g. the samarium catimer [η^5-(Cp*)$_2$Sm] — (or some other Mn, U, Mo, Ir, Th, Ru, Pt and Zr catimers). The animers (fragments forming the negative end of the dipole) include organics, halogens and inorganics.

Bis(2-methoxyethylcyclopentadienyl)yttrium and ytterbium tetrahydroborates

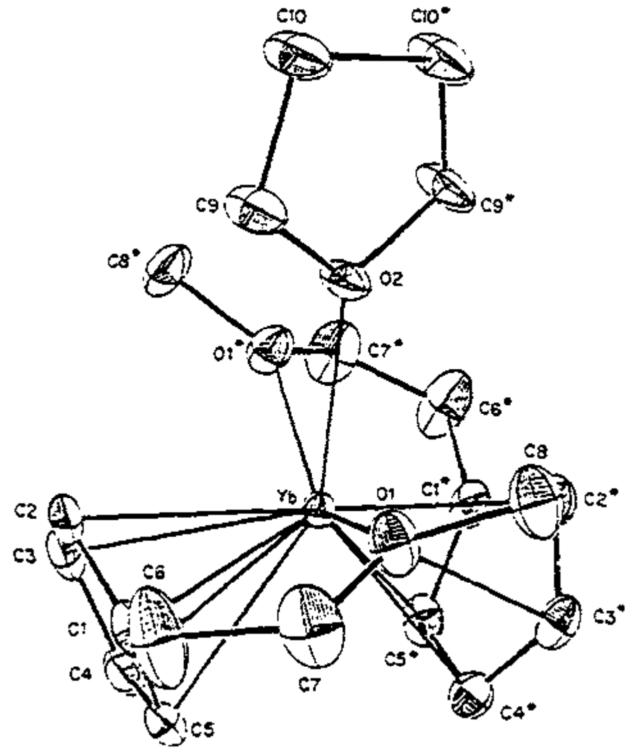
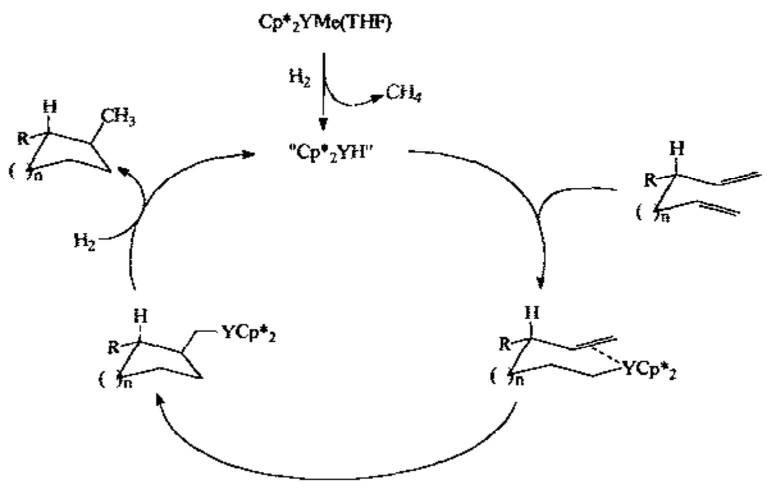


Fig. 11. $(MeOCH_2CH_2C_5H_4)_2Yb(THF)$. (Reproduced with permission from Journal of Organometallic Chemistry.)



Scheme 7.

$(CH_3OCH_2CH_2C_5H_4)_2LnBH_4$(Ln ≡ Y, Yb) have been synthesized by Deng et al. [38] by the reaction of bis(2-methoxyethylcyclopentadienyl)lanthanide chlorides with sodium borohydride in THF at room temperature:

$$LnCl_3 + 2CH_3OCH_2CH_2C_5H_4Na \xrightarrow{THF} (CH_3OCH_2CH_2C_5H_4)_2LnCl + 2NaCl$$

$$(CH_3OCH_2CH_2C_5H_4)_2LnCl + NaBH_4 \xrightarrow{THF} (CH_3OCH_2CH_2C_5H_4)_2LnBH_4 + NaCl$$

Ln ≡ Y, Yb

The crystal structures of both complexes have been determined (Fig. 12: Y—centroid(Cp) = 239.2 and 243.4 pm; Y—B = 277.3 pm; Fig. 13: Yb—B = 280.0 pm; Yb—centroid(Cp) = 235.7 and 239.4 pm). The structures reveal intramolecular coordination bonds between lanthanide metal and ligand oxygen atoms. The tetrahydroborate ligands are coordinated to yttrium and ytterbium in a bidentate fashion.

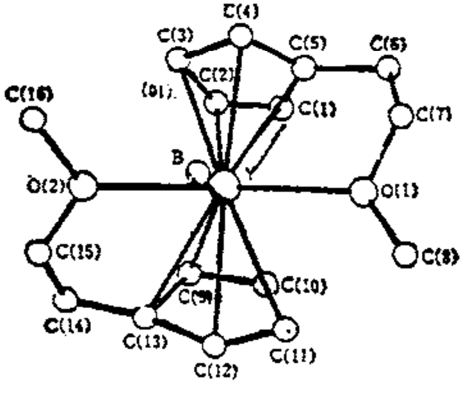


Fig. 12. $(CH_3OCH_2CH_2C_5H_4)_2YBH_4$. (Reproduced with permission from Acta Chimica Sinica.)

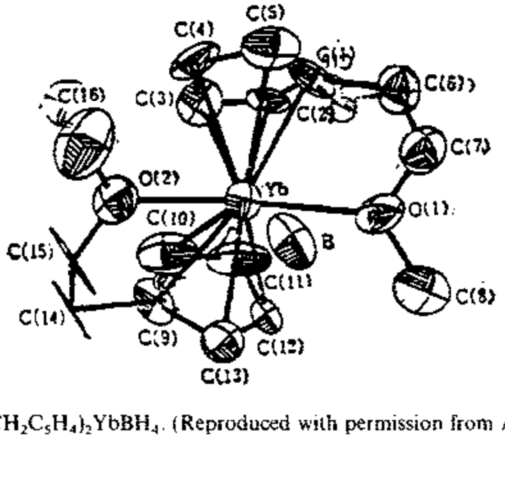


Fig. 13. $(CH_3OCH_2CH_2C_5H_4)_2YbBH_4$. (Reproduced with permission from Acta Chimica Sinica.)

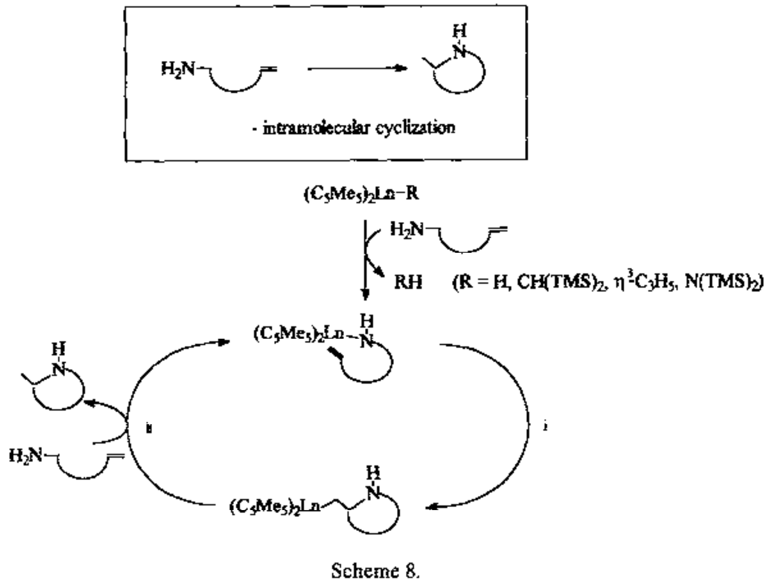
Matsunaga [39] studied electron transfer reactions of bis(pentamethylcyclopentadienyl)ytterbium with organotransition metal complexes. The divalent lanthanide complex $(Cp^*)_2Yb$ reacts with methylcopper to produce a base-free ytterbium−Me complex of the formula $(Cp^*)_2YbMe$. This product forms an asymmetric, methyl-bridged dimer in the solid state. The trivalent titanium species $(Cp^*)_2TiX$ (X ≡ Cl, Br, Me, BH_4) form bimetallic coordination complexes with $(Cp^*)_2Yb$. The magnetic behaviour of the products indicated that electron transfer did not occur. The solid state structures of the chloride and bromide complexes show unusual bond angles for the halide bridges between ytterbium and titanium. The bimetallic Me complex contains a linear Me bridge between ytterbium and titanium.

Gagné et al. [40] studied the kinetics, mechanism and diastereoselectivity of the cyclization of N-unprotected amino olefins. They reported the efficient, regiospecific $(Cp^*)_2LnR$ (R ≡ H, $CH(SiMe_3)_2$, η^3-C_3H_5, $N(SiMe_3)_2$; Ln ≡ La, Nd, Sm, Y, Lu)-catalysed hydroamination–cyclization of the amino olefins $H_2NCHR^1R^2CH{=}CH_2$ to yield the corresponding heterocycles $HNCH(R^1)R^2CHCH_3$ (R^1, R^2 ≡ H, $(CH_2)_2$; H, CMe_2CH_2; H, $(CH_2)_3$; CH_3, $(CH_2)_2$; H, $CH(Me)CH_2$; o-C_6H_4, CH_2) (Scheme 8). The crystal structure of $(Cp^*)_2LaNHCH_3(H_2NCH_3)$ was also discussed (Fig. 14).

Yu et al. [15] investigated the synthesis and thermal stability of pyrrolyl complexes of the general formula $(Cp)_nLn(pyr)_{(3-n)}(THF)$ (pyr ≡ pyrrolyl ≡ NC_4H_4; Ln ≡ Sm, Dy, Yb, Lu; $n = 0, 1, 2$). They are classified into three series: $Ln(pyr)_3(THF)$, $CpLn(pyr)_2(THF)$ and $(Cp)_2Ln(pyr)(THF)$. $(Cp)_2Ln(pyr)(THF)$ tends to disproportionate into $(Cp)_3Ln$ and $Ln(pyr)_3$ at high temperatures:

$$3(C_5H_5)_2LnL \rightleftharpoons 2(C_5H_5)_3Ln + LnL_3$$

L ≡ ligand



Scheme 8.

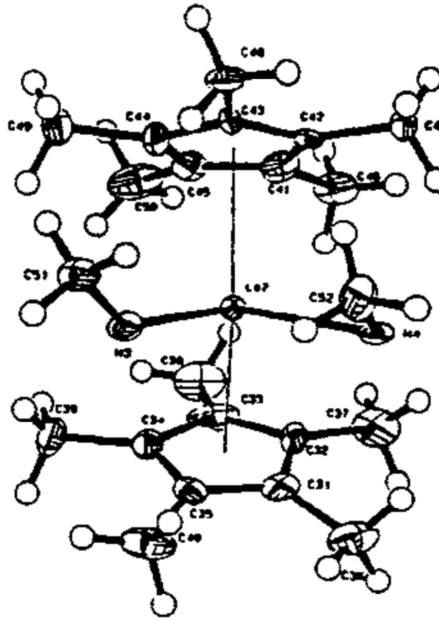


Fig. 14. $(Cp^*)_2LaNHCH_3(H_2NCH_3)$. (Reproduced with permission from Journal of the American Chemical Society.)

SCF-Xα-SW calculations have been carried out on $(Cp)_2Yb(C_2H_2)$ and $(Cp)_2Yb(CO)_2$ by Min [41]. Both non-relativistic and relativistic schemes have been tried. CO interacts with Yb more strongly than C_2H_2 does; the coordinating effect of a σ ligand is stronger than that of a π ligand. The results of these calculations are consistent with the experimental results that the divalent compounds are unstable and easily oxidized.

The first example of high molecular weight poly(methyl methacrylate) with unusually narrow polydispersity was reported by Yasuda et al. [42] using the unique catalytic function of organolanthanide(III) complexes. They also described the reaction of $[(Cp^*)_2SmH]_2$ with MMA (MMA ≡ methyl methacrylate) to yield the organolanthanide(III) intermediate $(Cp^*)_2Sm(MMA)_2H$. The crystal structure of this complex is presented in Fig. 15.

Folga et al. [43] reported a theoretical study on the hydrogen exchange reaction between $(Cp)_2Lu{-}H$ or $(Cp^*)_2Lu{-}H$ and H_2. This study was based on approximate density functional theory.

Deacon et al. [44] studied the synthesis and crystal structure of $[Yb(Cp)_2(OPPh_3)(OPPh_2C_5H_4)]$. This complex was prepared by the reaction of $[Yb(Cp)_2(DME)]$ (DME ≡ 1,2-dimethoxyethane) with thallium(I)diphenylphosphorylcyclopentadienide and triphenylphosphine in THF:

$$Yb(C_5H_5)_2 + Ph_3PO + Tl(C_5H_4Ph_2PO)$$
$$\xrightarrow{THF} Tl\downarrow + [Yb(C_5H_5)_2(OPPh_3)(OPPh_2C_5H_4)]\cdot(THF)$$

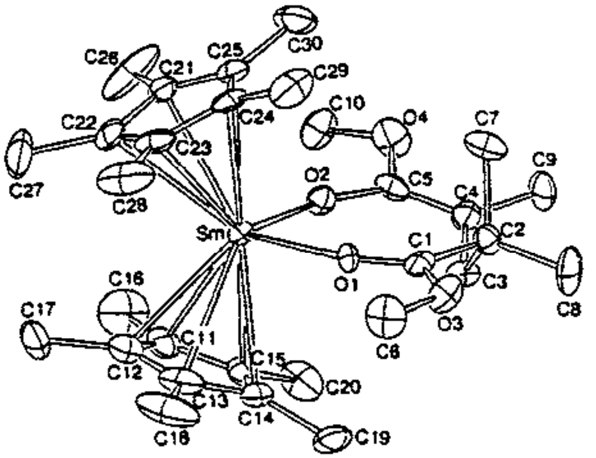
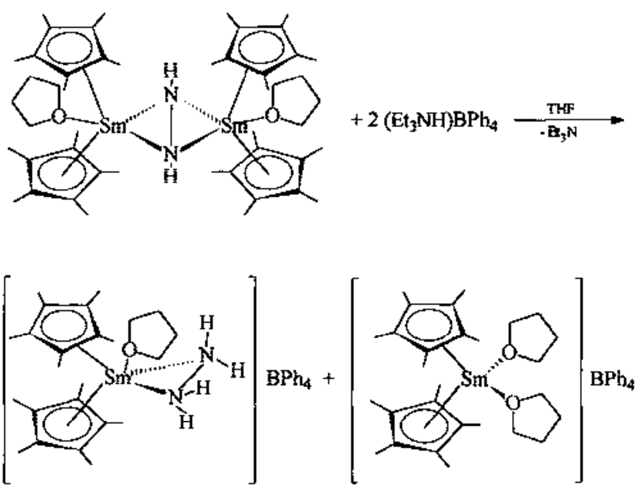


Fig. 15. $(Cp^*)_2Sm(MMA)_2H$. (Reproduced with permission from Journal of the American Chemical Society.)

The crystal structure of the compound (Fig. 16: Yb—centroid(Cp) = 233.4 and 230.6 pm; centroid—Yb—centroid = 127.7°) shows it to be monomeric with eight-coordinated ytterbium and a pseudotetrahedral arrangement of the centroids of two η^5-bonded cyclopentadienyl rings and the oxygen atoms of Ph_3PO and $(OPPh_2C_5H_4)^-$, rather than 10-coordinated with η^5-$(C_5H_4PPh_2O)^-$.

Evans et al. [45] reported the synthesis and crystal structure of $[\{(Cp^*)_2Sm\}(NH_2NH_2)(THF)]BPh_4$, which was prepared by protonation of $[\{(Cp^*)_2Sm(THF)\}_2(\mu\text{-}\eta^2:\eta^2\text{-HNNH})]$ with two equivalents of $(Et_3NH)BPh_4$ in THF (Fig. 17: average Sm—C(Cp*) = 273.2 pm; Sm—N = 249.2 and 252.3 pm; N—N = 147.1 pm; centroid—Sm—centroid = 138.9°):



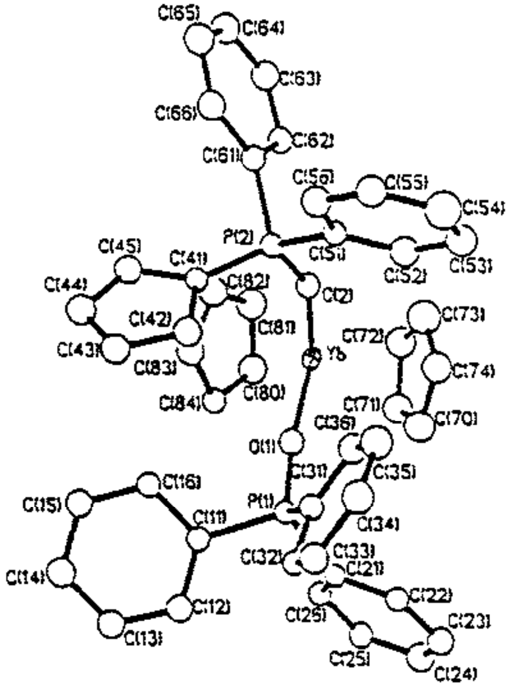


Fig. 16. [$Yb(Cp)_2(OPPh_3)(OPPh_2C_5H_4)$]. (Reproduced with permission from Australian Journal of Chemistry.)

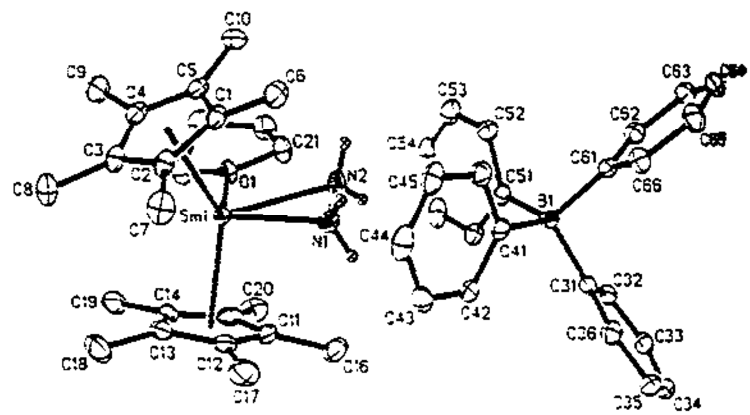


Fig. 17. [{$(Cp^*)_2Sm$}(NH_2NH_2)THF)]BPh_4. (Reproduced with permission from Angewandte Chemie.)

This molecule is considered a model complex for the biological fixation of molecular nitrogen.

Jahns et al. [46] published an INDO (this model is a semiempirical valence electron method) study of two para-dimetallated σ-phenylene complexes

$[\{(Cp^*)_2M\}_2C_6H_4]$ ($M \equiv Sc$, Lu). The lutetium complex has a small $M-C_{\alpha}^{aryl}-C_{\beta}^{aryl}$ angle of 88°. This unusual geometry is attributed to an agostic interaction between the metal atom and the $(C-H)_{\beta}$ group of the σ-bonded aryl ring. The corresponding angle of the analogous scandium compound is reported to be 118°. The article described a detailed analysis of the bonding situation in these two organolanthanide complexes.

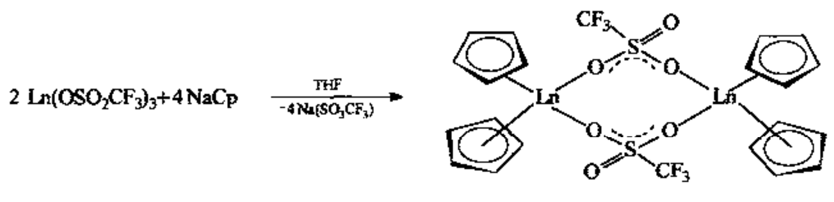
Makhaev and Borisov [47] prepared bis(cyclopentadienyl)tetrahydroborato complexes of scandium from the reaction of scandium tetrahydroborate with sodium cyclopentadienides:

$$Sc(BH_4)_3(THF)_2 + 2C_5H_5Na \xrightarrow{THF} (C_5H_5)_2ScBH_4 + 2NaBH_4$$

$$Sc(BH_4)_3(THF)_2 + 2MeC_5H_4Na \xrightarrow{THF} (MeC_5H_4)_2ScBH_4 + 2NaBH_4$$

2.1.3. Bridged cyclopentadienyl compounds

Schumann et al. [22] reported that the solvent-free rare earth triflates $[Cp_2Ln(OSO_2CF_3)]_2$($Ln \equiv Sc$ and Lu) are dimeric:



Wang et al. [48] studied the reaction of Cp_3Ln ($Ln \equiv Pr$, Nd, Sm, Gd, Dy, Ho, Er, Y, Tm, Yb) with cyclohexanoneoxime in THF to yield $[(Cp)_2Ln(ONC_6H_{10})]_2$:

$$2(C_5H_5)_3Ln + 2C_6H_{10}NOH \xrightarrow{THF} [(C_6H_{10}NO)Ln(C_5H_5)_2]_2 + 2C_5H_6$$

The complexes are considered to be oxygen-bridged dimers. Disproportionation on heating was observed for $Ln \equiv Pr$, Nd, Sm. The compounds were characterized by mass spectral data and IR spectroscopy.

Bochkarev et al. [49] described the synthesis and crystal structure (Fig. 18: $Yb-Cp-Yb = 180.0°$) of the polymeric two-dimensional multidecker complex $[(\eta^5\text{-}Cp)V(\mu\text{-}\eta^6:\eta^2\text{-}C_{10}H_8)Yb(THF)(\eta^5\text{-}Cp)]_n$, which was formed by the reaction of $(Cp)_2V$ with an excess of $(C_{10}H_8)Yb(THF)_2$ in THF:

$$(C_{10}H_8)Yb(THF)_2 + (C_5H_5)_2V \xrightarrow{THF} [(\eta^5\text{-}C_5H_5)V(\mu\text{-}\eta^6:\eta^2\text{-}C_{10}H_8)Yb(THF)(\eta^5\text{-}C_5H_5)]_n$$

The product was also obtained by the treatment of $YbI_2(THF)_2$ with an equimolar

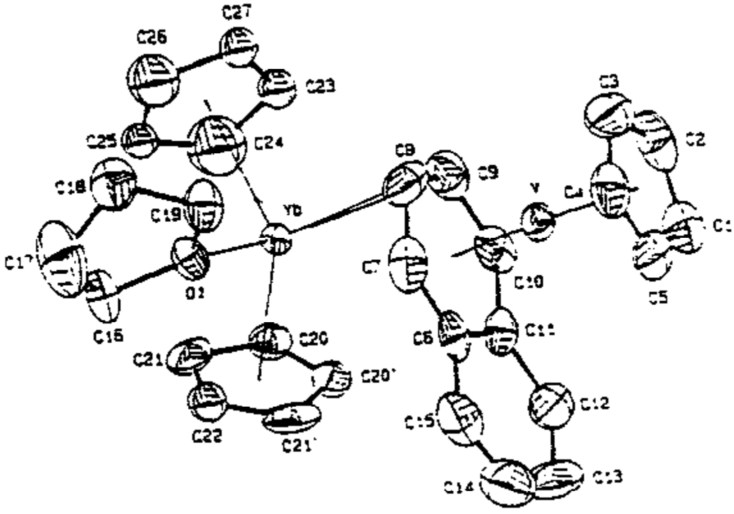


Fig. 18. $[(\eta^5\text{-Cp})V(\mu\text{-}\eta^6:\eta^2\text{-}C_{10}H_8)Yb(THF)(\eta^5\text{-Cp})]_n$. (Reproduced with permission from Inorganica Chimica Acta.)

mixture of KCp and $K[(Cp)V(C_{10}H_8)]$ in THF. The molecular structure consists of infinite zigzag chains (Fig. 19) formed by $(\eta^5\text{-Cp})Yb$ moieties and with one $(\eta^5\text{-Cp})V(\eta^6\text{-}C_{10}H_8)$ unit coordinated η^2 via the naphthalene to each Yb atom.

Deng et al. [50] reported the formation and crystal structure of

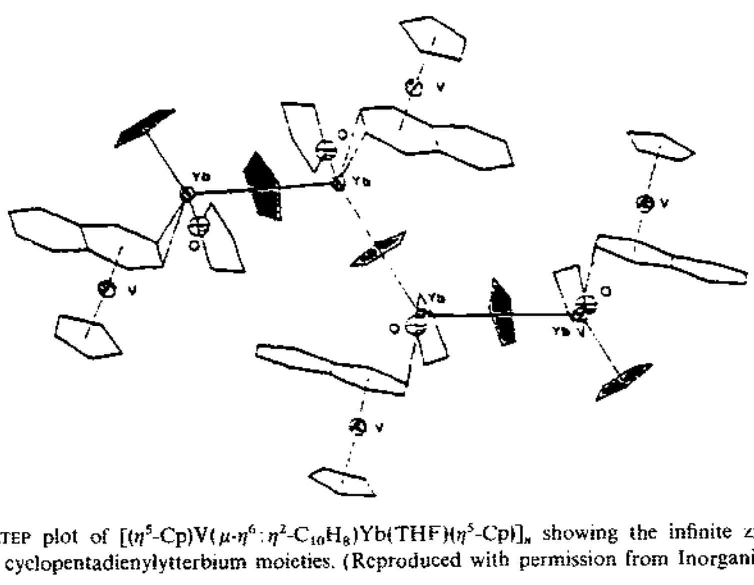
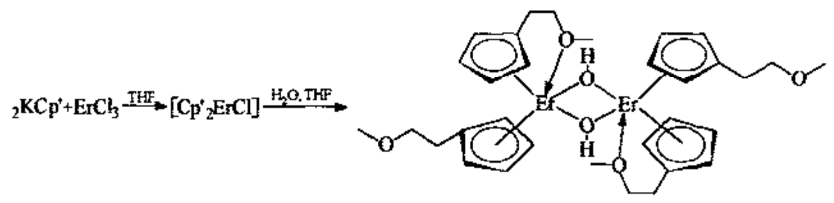


Fig. 19. ORTEP plot of $[(\eta^5\text{-Cp})V(\mu\text{-}\eta^6:\eta^2\text{-}C_{10}H_8)Yb(THF)(\eta^5\text{-Cp})]_n$ showing the infinite zigzag chain formed by cyclopentadienylytterbium moieties. (Reproduced with permission from Inorganica Chimica Acta.)

$[(CH_3OCH_2CH_2C_5H_4)_2Er(\mu\text{-}OH)]_2$. This compound was obtained by the partial hydrolysis of $(CH_3OCH_2CH_2C_5H_4)_2ErCl$:



The molecular structure (Fig. 20) shows the hydroxyl groups bridging with distances Er—O = 225.8 and 221.7 pm and the methoxyethyl group coordinating with distances Er—O = 254.2 pm. The Er—centroid(Cp) distances are 239.8 and 216.8 pm and the centroid—Er—centroid bond angles are 71.6° and 73.2°.

The dimeric complexes $[(^tBuCp)_2LnCl]_2$ (Ln ≡ Pr, Gd, Er) were prepared by Song et al. [51] by the reaction of lanthanide trichlorides with two equivalents of sodium

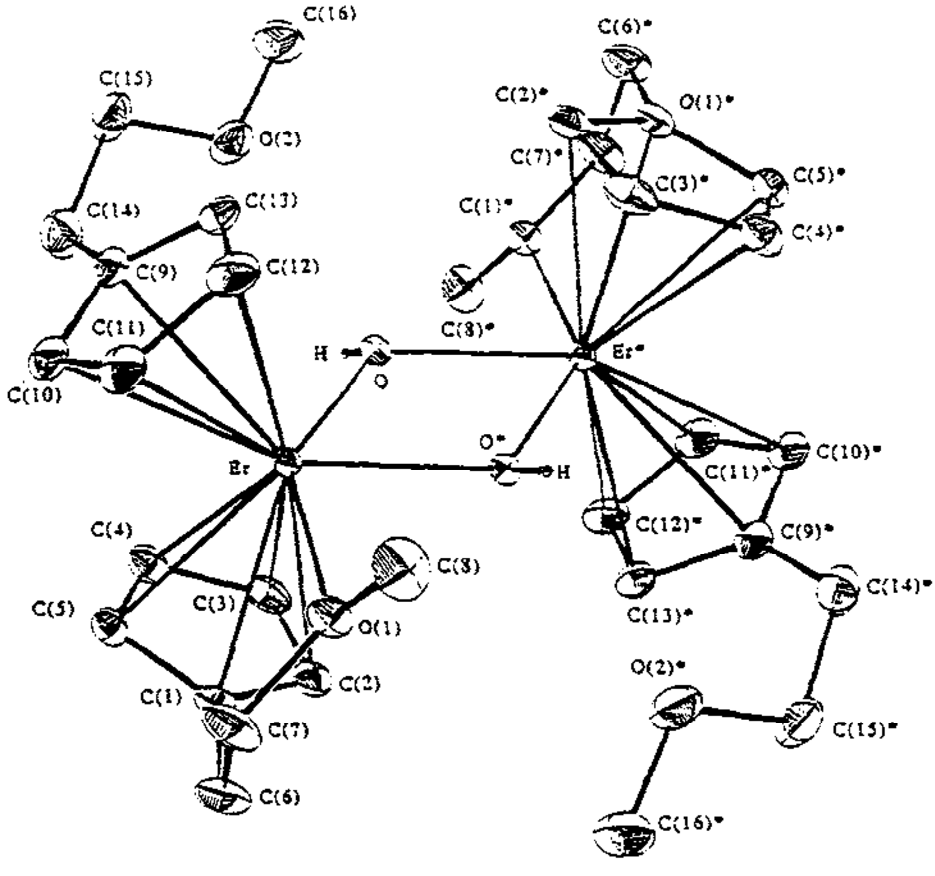


Fig. 20. $[(CH_3OCH_2CH_2C_5H_4)_2Er(\mu\text{-}OH)]_2$. (Reproduced with permission from Polyhedron.)

t-butylcyclopentadienide in THF.

$$LnCl_3 + 2Na(^tBuCp) \xrightarrow{THF} (^tBuCp)_2LnCl(THF)_x + 2NaCl$$

$$Ln \equiv Pr, Nd, n = 2; Ln = Yb, n = 1$$

These complexes are thermally stable and soluble in ethers and aromatic solvents. The praseodymium and gadolinium complexes were also structurally characterized (Fig. 21). The crystal structures show that the two complexes are isostructural. The two $(^tBuCp)_2Ln$ units are linked by symmetrical chloride bridges and the coordination number for both complexes is eight. The Pr···centroid(Cp) and Gd—centroid(Cp) distances are 249.0 and 241.7 pm respectively and the centroid—Pr—centroid and centroid—Gd—centroid angles are 130.7° and 130.3° respectively.

Marsh et al. [52] determined the crystal structure of the silicon-bridged bis(substituted Cp)yttrium complex $[Li(THF)_2][Y(C_{26}H_{48}Si_3)Cl_2]$ (Fig. 22). There are two virtually identical molecules in the asymmetric unit. In each molecule the Y atom is tetrahedrally coordinated to a substituted Si-bridged bis(cyclopentadienyl)ligand and two Cl ions. The Li atom is separated by 235 pm from each Cl ion and two molecules of THF are connected to the Li, thus completing its tetrahedral coordination sphere.

Hajela et al. [53] determined the crystal structure of a permethylcyclopentadienyl-μ-tetramethylcyclopentadienylmethylene scandium dimer (Fig. 23). Two bis(pentamethylcyclopentadienyl)scandium molecules are joined across a centre of symmetry. One of the Cp* methyl groups has lost an H atom. The Sc—centroid (Cp*) distances are 218.1 and 221.2 pm.

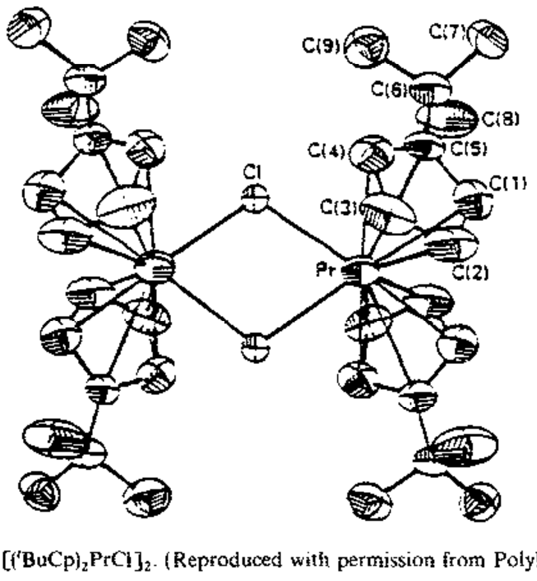


Fig. 21. $[(^tBuCp)_2PrCl]_2$. (Reproduced with permission from Polyhedron.)

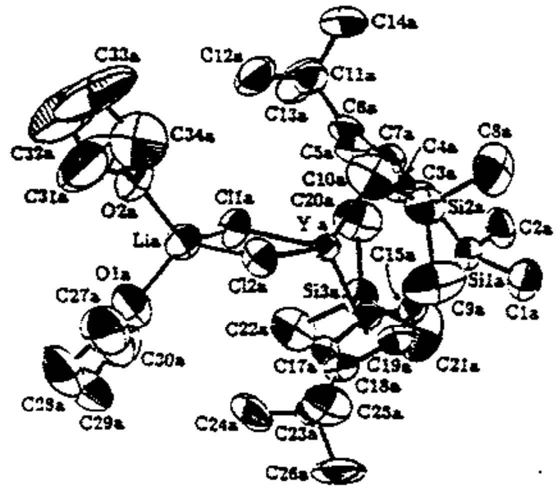


Fig. 22. $[Li(THF)_2][Y(C_{26}H_{48}Si_3)Cl_2]$. (Reproduced with permission from Acta Crystallographica.)

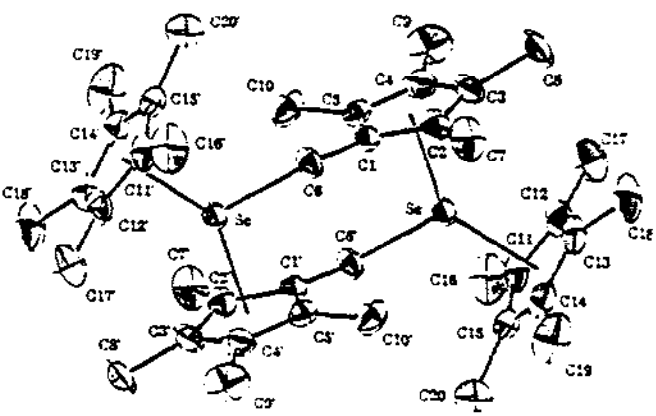


Fig. 23. $[Sc_2(C_5Me_5)_2(C_{10}H_{14})_2]$. (Reproduced with permission from Acta Crystallographica.)

Schaefer et al. [54] reported the synthesis and crystal structure of a silicon-bridged scandium complex of the formula $\{(\eta^5\text{-}C_5Me_4)SiMe_2[\eta^5\text{-}C_5H_3CH_2CH_2P\text{-}(CMe_3)_2]\}ScCH(SiMe_3)_2$ (Fig. 24: Sc—centroid(Cp) = 220.3 pm; Sc—centroid (Cp*) = 220.0 pm).

Jin et al. [55] prepared the dimeric erbium complex $\{[(C_5H_9C_5H_4)Er(THF)]_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2Na(THF)_2\}\cdot THF$ ($C_5H_9C_5H_4$ ≡ cyclopentylcyclopentadienyl) by the reaction of $ErCl_3$ with one equivalent of $C_5H_9C_5H_4Na$:

$$2ErCl_3 + 2C_5H_9C_5H_4Na \xrightarrow{THF} \{[(C_5H_9C_5H_4)Er(THF)]_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2Na(THF)_2\} + NaCl$$

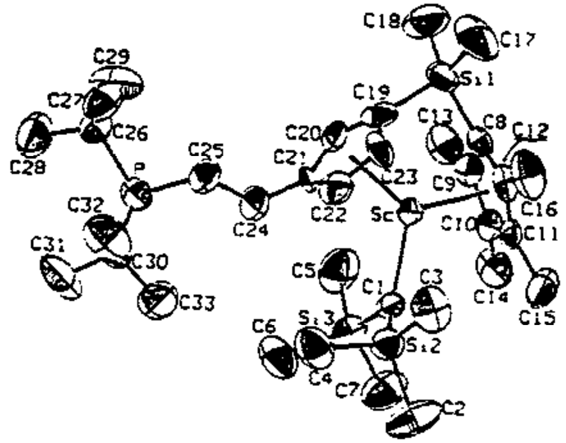


Fig. 24. $\{(\eta^5\text{-}C_5Me_4)SiMe_2[\eta^5\text{-}C_5H_3CH_2CH_2P(CMe_3)_2]\}ScCH(SiMe_3)_2$. (Reproduced with permission from Acta Crystallographica.)

The compound crystallizes from hexane/THF and the crystal structure shows (Fig. 25: Er—centroid = 234.4 pm) that each erbium atom is surrounded by one $C_5H_9C_5H_4$ ligand, two μ_3-Cl, two μ_2-Cl and one THF in a distorted octahedral arrangement.

The crystal structures of $[Ln(^tBuCp)_2(\mu\text{-}OH)]_2$ (Ln ≡ Nd, Dy) were discussed by Herrmann et al. [56] (Fig. 26: Nd—centroid = 246.7 and 250.9 pm; centroid—

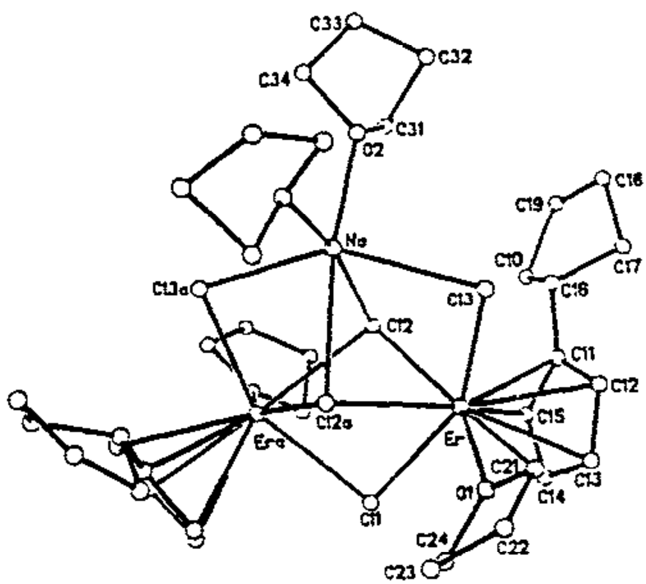


Fig. 25. $\{[(C_5H_9C_5H_4)Er(THF)]_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2Na(THF)_2\}\cdot THF$. (Reproduced with permission from Polyhedron.)

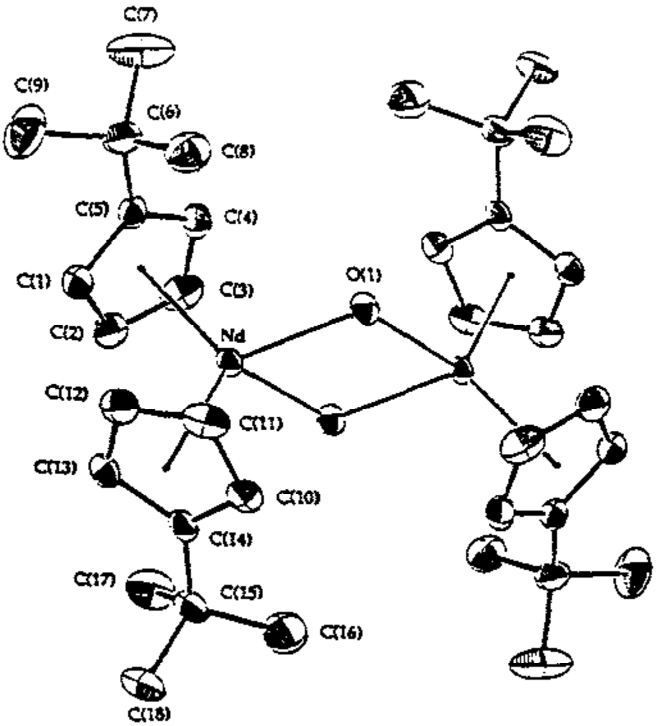


Fig. 26. [Nd(^{t}BuCp)$_2$(μ-OH)]$_2$. (Reproduced with permission from Chemische Berichte.)

Nd−centroid = 124.5°; for the dysprosium complex: Dy−centroid = 237.8 and 241.2 pm; centroid−Dy−centroid = 125.5°). These complexes were formed by the partial hydrolysis of Ln(^{t}BuCp)$_3$.

Wang et al. [57] reported the reaction of (Cp*)$_2$Sm with excess hydrazine to give the yellow crystalline tetranuclear organolanthanide hydrazido complex [Cp*Sm]$_4$(NHNH)$_2$(NHNH$_2$)$_4$(NH$_3$)$_2$ in high yields:

$$4(C_5Me_5)_2Sm + 6N_2H_4$$
$$\rightarrow [(C_5Me_5)Sm]_4(NHNH_2)_4(NHNH)_2 + 4C_5Me_5H + 2H_2$$

The product was crystallographically characterized (Fig. 27: Sm−Cp* = 250.3 and 262.0 pm), showing the molecule to consist of a distorted tetrahedral arrangement of samarium atoms with bridging hydrazido anions on each edge of the tetrahedron.

Stehr and Fischer [58] prepared and structurally characterized [(Cp)$_2$Yb(μ-O$_3$SCF$_3$)]$_2$ (Fig. 28). The reaction of Yb(O$_3$SCF$_3$)$_3$ with NaCp in toluene produced the compound:

$$2Yb(O_3SCF_3)_3 + 4NaC_5H_5 \xrightarrow{\text{toluene}} [(\eta^5\text{-}C_5H_5)_2Yb(\mu\text{-}O_3SCF_3)]_2 + 4NaO_3SCF_3$$

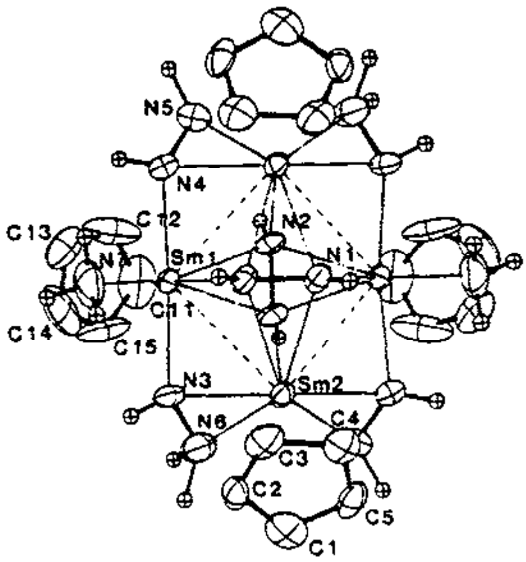


Fig. 27. $[Cp^{*}Sm]_4(NHNH)_2(NHNH_2)_4(NH_3)_2$. (Reproduced with permission from Organometallics.)

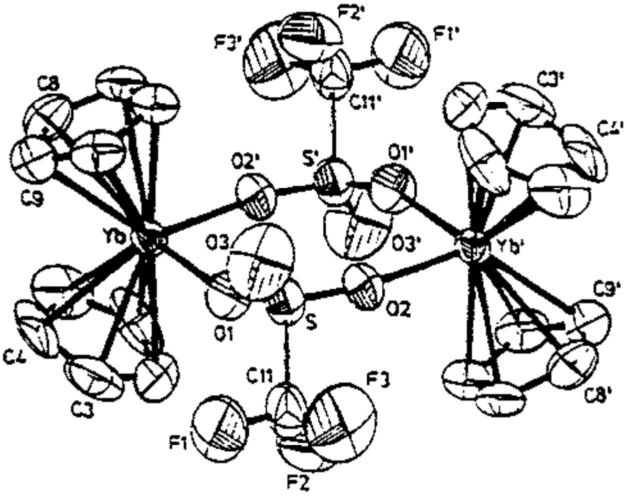


Fig. 28. $[(Cp)_2Yb(\mu\text{-}O_3SCF_3)]_2$. (Reproduced with permission from Journal of Organometallic Chemistry.)

This complex contained bridging triflate ligands with Yb—centroid(Cp) distances of 227.7 and 227.9 pm.

Evans et al. [59] showed that $(Cp^{*})_2Sm$ reacts with $Sb(^{n}Bu)_3$ in toluene to form $[(Cp^{*})_2Sm]_3(\mu\text{-}\eta^2:\eta^2:\eta^1\text{-}Sb_3)(THF)$. The crystal structure of this compound is depicted in Fig. 29. The $(Sb_3)^{3-}$ ion has indistinguishable Sb—Sb distances of 268.9

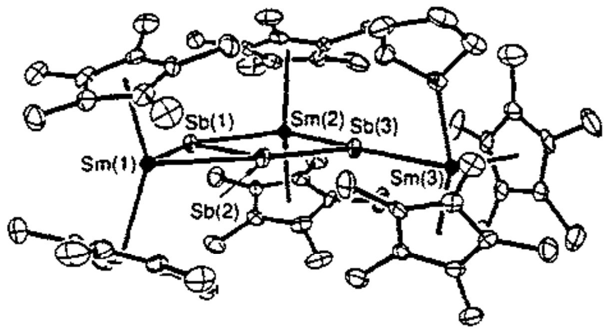


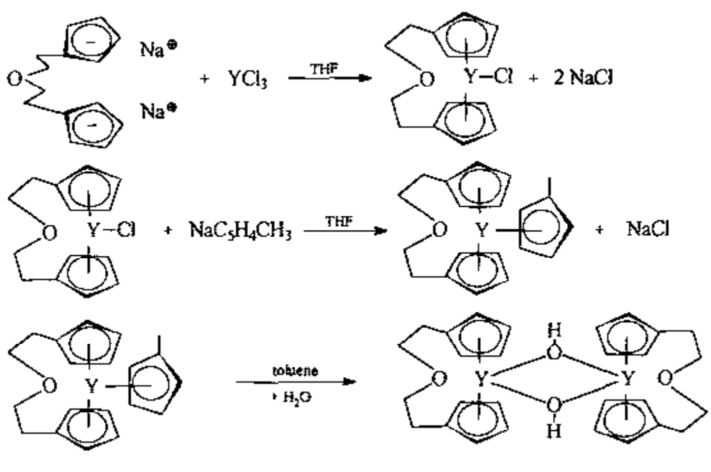
Fig. 29. $[(Cp^*)_2Sm]_3(\mu\text{-}\eta^2:\eta^2:\eta^1\text{-}Sb_3)(THF)$. (Reproduced with permission from Journal of the Chemical Society, Chemical Communications.)

and 268.6 pm. Five of the six Sm–Sb distances fall in the narrow range of 316.2–320.5 pm.

Schumann et al. [31] reported the partial hydrolysis of $[O(CH_2CH_2C_5H_4)_2]Y(C_5H_4CH_3)$, which results in the formation of the complex $[\{O(CH_2CH_2C_5H_4)_2\}Y(\mu\text{-}OH)]_2$ (Scheme 9).

The crystal structure of the complex was determined (Fig. 30) and shows a dinuclear complex with two bridging hydroxyl groups. The average yttrium–cyclopentadienyl carbon distance is reported to be 269.2 pm.

Evans et al. [45] reported the synthesis and crystal structure of $[\{(Cp^*)_2Sm(THF)\}_2(\mu\text{-}\eta^2:\eta^2\text{-}HNNH)]$, which was formed by the treatment of $[\{(Cp^*)_2Sm\}_2(\mu\text{-}\eta^2:\eta^2\text{-}HNNH)]$ with THF (Fig. 31). The average Sm–centroid(Cp) distance is reported to be 282.4 pm and the average centroid–Sm–centroid angle is 125.8°.



Scheme 9.

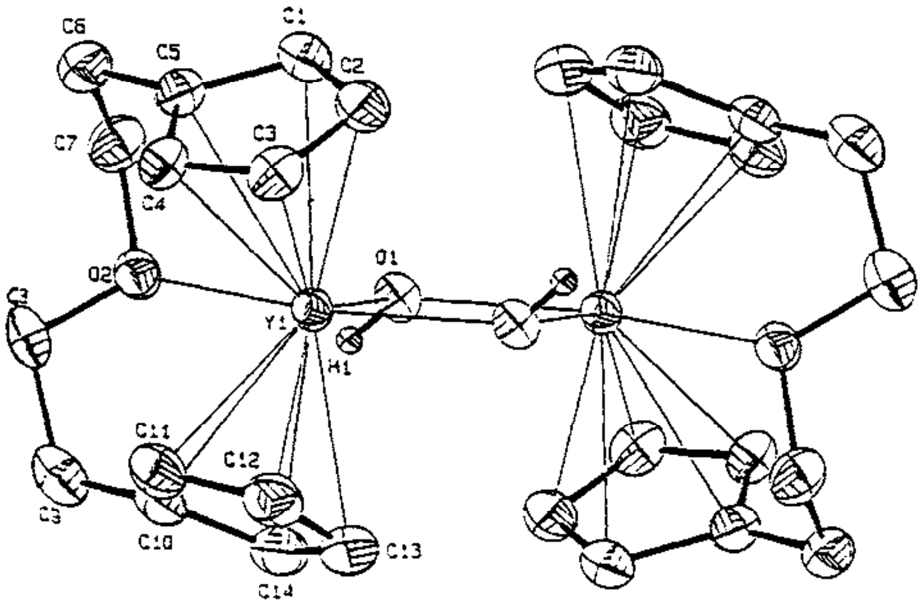


Fig. 30. $[O(CH_2CH_2C_5H_4)_2Y(\mu\text{-}OH)]_2$. (Reproduced with permission from Zeitschrift für Anorganische und Allgemeine Chemie.)

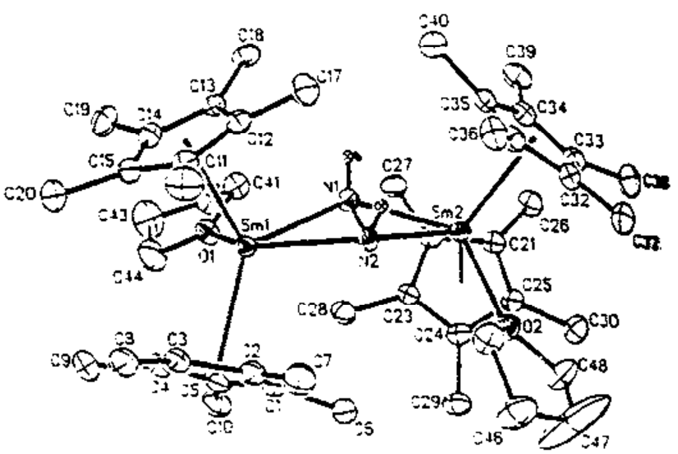


Fig. 31. $[\{(Cp^*)_2Sm(THF)\}_2(\mu\text{-}\eta^2:\eta^2\text{-}HNNH)]$. (Reproduced with permission from Angewandte Chemie.)

Gun'ko et al. [60] reported the reaction of lanthanidocene aluminohydrides $(Cp''_2LnAlH_4 \cdot L)_2$ ($Cp'' \equiv C_5H_3{}^tBu_2$; $Ln \equiv Ce$, Sm; $L \equiv THF$, NEt_3) with an excess of triethylamine-alane to form unsolvated hydrides $[(Cp'')_2Ln(\mu\text{-}H)]_2$:

$$Cp''_2LnCl + 2NaAlH_4 \xrightarrow[THF]{NEt_3} (Cp''_2LnAlH_4 \cdot NEt_3)_2 \rightarrow 2AlH_3 \cdot NEt_3 + (Cp''_2LnH)_2$$

The samarium complex was also obtained by the redox reaction of $(Cp'')_2Sm \cdot THF$ with $AlH_3 \cdot NEt_3$:

$$Cp''_2Sm \cdot THF + AlH_3 \cdot NEt_3 \xrightarrow{Et_2O} \tfrac{1}{2}(Cp''_2SmH)_2 + Al + NEt_3 + H_2$$

The crystal structures of the two lanthanidocene hydrides and of $[(Cp'')_2Sm(\mu\text{-}BH_4)]_2$ were determined: $[(Cp'')_2Ce(\mu\text{-}H)]_2$ (Fig. 32: Ce—centroid(Cp″) = 255 and 252 pm; centroid—Ce—centroid = 133.5°), $[(Cp'')_2Sm(\mu\text{-}H)]_2$ (Sm—centroid(Cp″) = 247 and 245 pm; centroid—Sm—centroid = 121.5°) and $[(Cp'')_2Sm(\mu\text{-}BH_4)]_2$ (Fig. 33: Sm—centroid(Cp″) = 246 pm; centroid—Sm—centroid = 115.3°).

Hitchock et al. [61] prepared lanthanocene(II) complexes of the formula $[\{Ln(\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3)_2\}_\infty]$ (Ln ≡ Yb, Eu) by the desolvation via sublimation of $[Yb(\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3)_2(OEt_2)]$ and $[Eu(\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3)_2(THF)]$ (Scheme 10).

The two complexes were structurally characterized (Fig. 34: centroid—Yb—centroid = 138.0°; Yb—centroid(Cp) = 238.2 and 236.6 pm; Fig. 35: Eu—centroid (Cp) = 257.6 and 261.0 pm; centroid—Eu—centroid = 122°). Each complex has unique intermolecular agostic-like interactions. The ytterbium derivative adopts a bent metallocene conformation. The europium compound exhibits an unprecedented conformation with a cyclopentadienyl ring bridging $\eta^5:\eta^3$ between two non-equivalent europium atoms.

Three binuclear organolanthanide complexes of the formula $[(Cp)_2Ln(\mu\text{-}OCH_2CH_2CH_3)]_2$ (Ln ≡ Dy, Ho, Yb) have been synthesized by Wu et al. [62] by

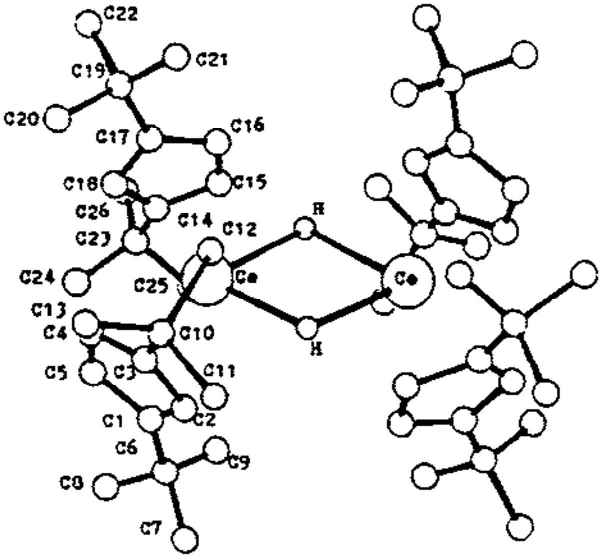


Fig. 32. $[(C_5H_3{}^tBu_2)_2Ce(\mu\text{-}H)]_2$. (Reproduced with permission from Journal of Organometallic Chemistry.)

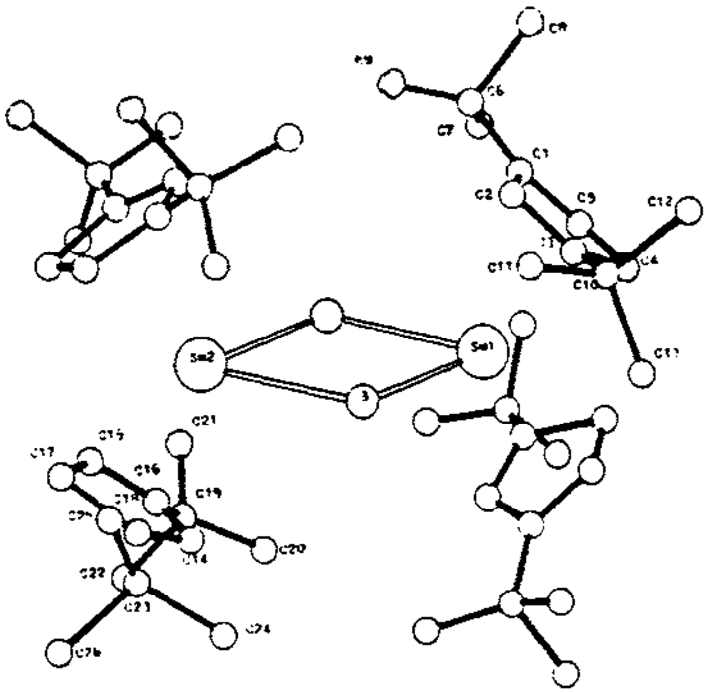
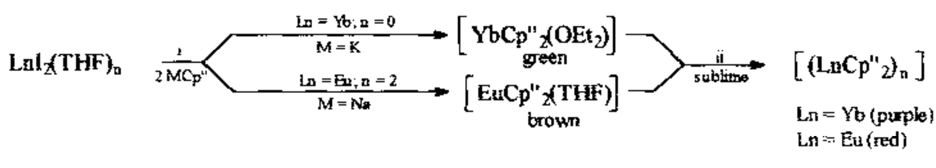


Fig. 33. $[(C_5H_3{}^tBu_2)_2Sm(\mu\text{-}BH_4)]_2$. (Reproduced with permission from Journal of Organometallic Chemistry.)



Scheme 10.

the reaction of $(Cp)_3Ln$ with equimolar amounts of *n*-propanol in THF:

$$2(C_5H_5)_3Ln + 2HOCH_2CH_2CH_3$$

$$\xrightarrow{THF} 2C_5H_6 + [(C_5H_5)_2Ln(\mu\text{-}OCH_2CH_2CH_3)]_2$$

The crystal structure of the ytterbium compound was also determined (Fig. 36). The Yb_2O_2 unit is planar and the ytterbium atom is coordinated by two Cp ring centroids and two oxygen atoms of two *n*-propoxide ligands to form a distorted tetrahedral geometry. The average Yb—C(Cp) bond distance is reported to be 258.9 pm and the average Yb—O distance is 219.9 pm.

Jizhu et al. [63] determined the crystal structure of $(C_5H_9C_5H_4)_3Er_4(\mu_2\text{-}Cl)_6(\mu_3\text{-}Cl)(\mu_4\text{-}O)(THF)_3$. The complex is composed of four Er atoms bridged

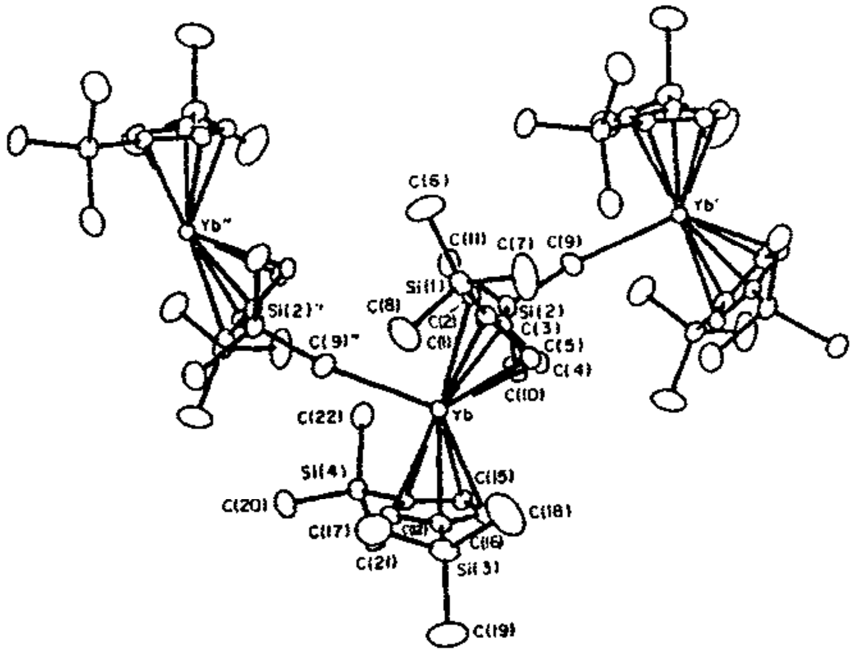


Fig. 34. [{Yb(η-$C_5H_3(SiMe_3)_2$-1,3)$_2$}$_\infty$]. (Reproduced with permission from Journal of Organometallic Chemistry.)

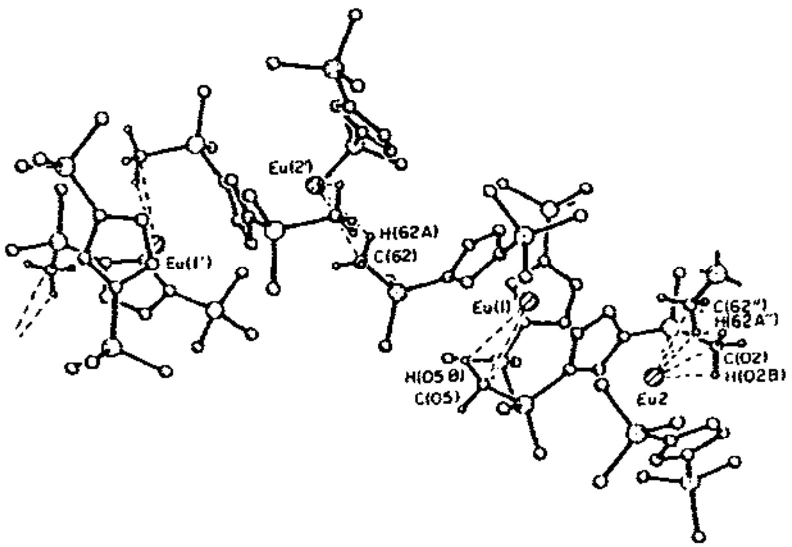


Fig. 35. [{Eu(η-$C_5H_3(SiMe_3)_2$-1,3)$_2$}$_\infty$]. (Reproduced with permission from Journal of Organometallic Chemistry.)

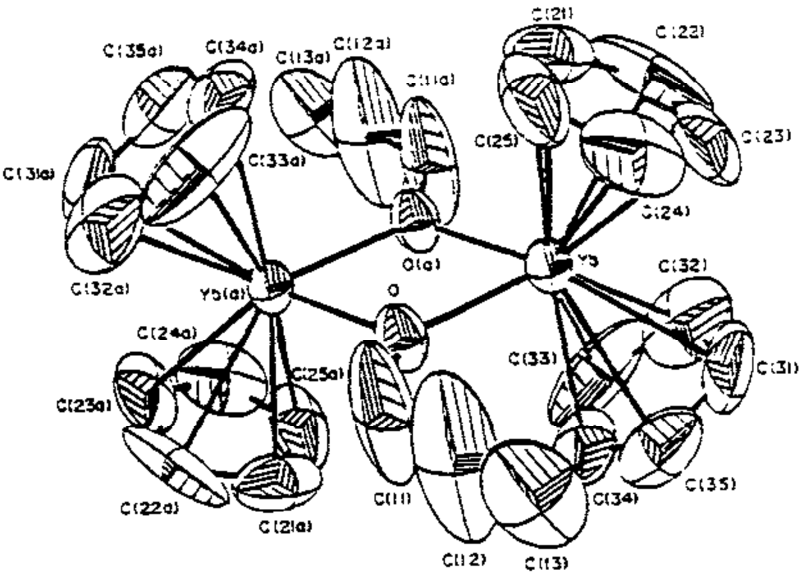


Fig. 36. $[(Cp)_2Yb(\mu\text{-}OCH_2CH_2CH_3)]_2$. (Reproduced with permission from Polyhedron.)

by seven Cl atoms and one O atom, with three of the Er atoms each bonded to a cyclopentylcyclopentadienyl group and the other Er atom bonded to three THF ligands. The Er atoms constitute a distorted tetrahedron.

Jizhu et al. [64] prepared complexes of the formula $(C_5H_9C_5H_4)_2LnCl(THF)_n$ ($Ln \equiv Nd$, Sm, $n=1$; $Ln \equiv Er$, Yb, $n=0$) by the treatment of $LnCl_3$ with sodium cyclopentylcyclopentadienyl in THF:

$$LnCl_3 + 2Na(C_5H_9C_5H_4) \xrightarrow{THF} (C_5H_9C_5H_4)_2LnCl(THF)_n + 2NaCl$$

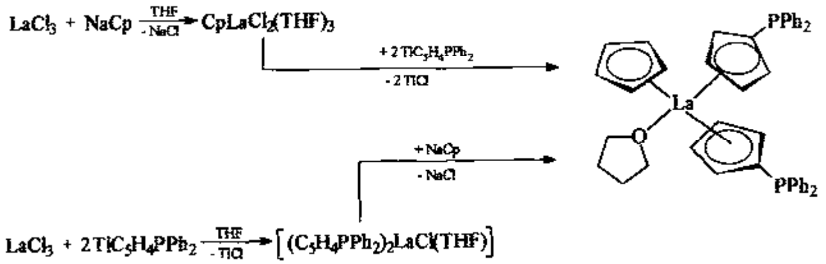
The crystal structures of $[(C_5H_9C_5H_4)_2SmCl(THF)]_2$ and $[(C_5H_9C_5H_4)_2ErCl_2]_2$ were determined. The central metal atom in the samarium complex is coordinated to two cyclopentylcyclopentadienyl rings, two bridging chlorine atoms and one THF, forming a distorted trigonal bipyramid. The central metal atom in the erbium complex is coordinated to two cyclopentylcyclopentadienyl rings and two bridging chlorine atoms, forming a pseudotetrahedron.

Chaode et al. [65] reported the synthesis and crystal structure of a tetramethylethylene-bridged dicyclopentadienylsamarium(III) complex of the formula $[(CH_3)_4C_2(C_5H_4)_2]Sm(Cp)(THF)$. The samarium atom is bonded to three cyclopentadienyl rings and an oxygen atom of the THF ligand. The three centroids of the cyclopentadienyl rings and the O form a tetrahedral configuration around the samarium atom. The average Sm–C(Cp) bond distances for the three cyclopentadienyl groups are 272.3, 276.3 and 278.3 pm. The Sm–O bond is 253.1 pm.

The crystal structure of the dimeric complex $[(Cp)_2ErCl(THF)]_2$ was discussed by Jizhu et al. [66]. The oxygen atom of the THF ligand is bonded to Er^{3+} and the bond length of Er—O is 249.1 pm. The average bond length of Er—C(Cp) is 264.9 pm. The Er···Er distance is 442 pm and the Cl—Er—Cl bond angle is 72.2°.

2.1.4. Triscyclopentadienyl compounds

Schumann et al. [67] reported the synthesis and crystal structure (Fig. 37: La—centroid(Cp) = 256.1, 259,1 and 265.1 pm; centroid—La—centroid = 115°, 118° and 119°) of the monomeric derivative $CpLa(C_5H_4PPh_2)_2(THF)$, which is formed by the reaction of $LaCl_3$ with $TlC_5H_4PPh_2$ and NaCp in 1 : 2 : 1 molar ratio:



Adam et al. [68] found that the adduct $(Cp)_3Sm(NCCH_3)$ crystallizes not only in the already reported orthorhombic form but also as a triclinic modification (Fig. 38: Sm—centroid(Cp) = 276.3 pm).

$(MeOCH_2CH_2C_5H_4)_3Ln$ (Ln ≡ La, Pr) complexes have been synthesized by Qian et al. [69] by the reaction of $LnCl_3$ with $MeOCH_2CH_2C_5H_4Na$ in THF:

$$LnCl_3 + 3MeOCH_2CH_2C_5H_4Na \xrightarrow{THF} (MeOCH_2CH_2C_5H_4)_3Ln + 3NaCl$$

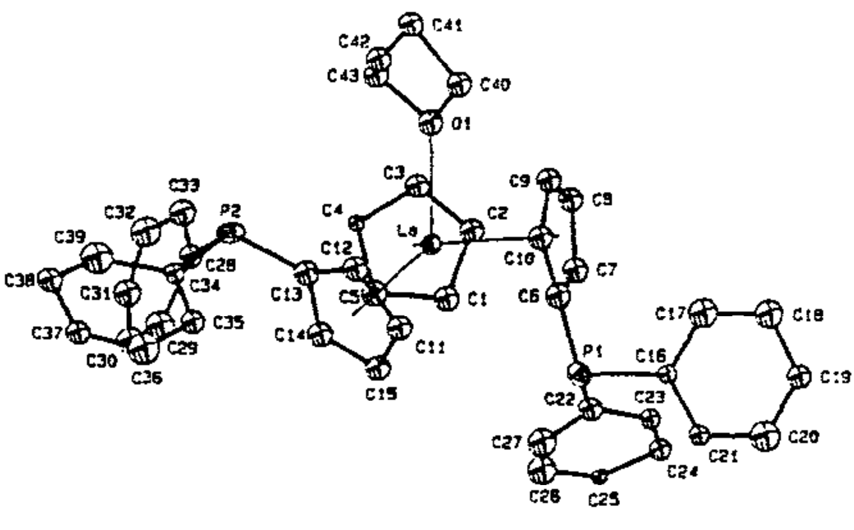


Fig. 37. $CpLa(C_5H_4PPh_2)_2(THF)$. (Reproduced with permission from Journal of Organometallic Chemistry.)

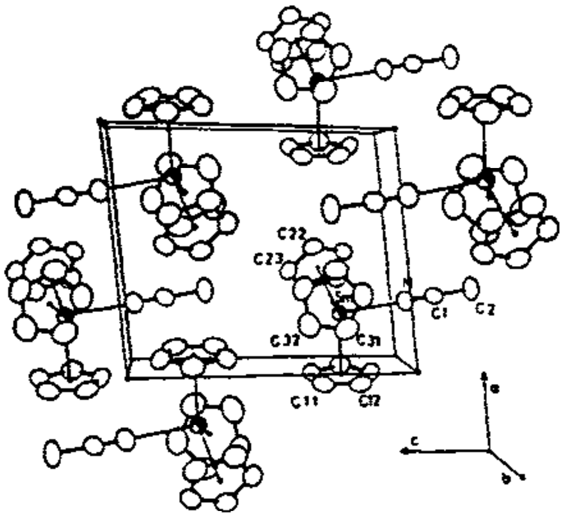


Fig. 38. $(Cp)_3Sm(NCCH_3)$. (Reproduced with permission from Journal of Organometallic Chemistry.)

The crystal structure of $(MeOCH_2CH_2C_5H_4)_3Pr$ (Fig. 39) shows the complex to be monomeric. The coordination number of the central Pr atom is 11. The Pr—centroid(Cp) bond distances are reported to be 254.2, 254.8 and 256.9 pm and the centroid—Pr—centroid angles are 119.0°, 121.7° and 119.3°.

Gao et al. [70] reported the synthesis and crystal structure of $[Li(DME)_3]^+$-$[(\eta^5\text{-}Cp)_3NdC_6H_5]^-$, which was prepared by the reaction of $NdCl_3 \cdot 2LiCl$, two equivalents of NaCp and one equivalent of phenyllithium in THF at −78 °C (DME ≡ dimethoxyethane). The complex consists of the separated ion pairs $[Li(DME)_3]^+$ and $[(\eta^5\text{-}Cp)_3NdC_6H_5]^-$. The neodymium atom is connected to three η^5-bonded cyclopentadienyl rings and one σ-bonded phenyl in a distorted tetrahedral arrangement with Nd—C(σ) = 259.3, 261.3 and 260.1 pm and Nd—C(Cp) = 282.9, 282.0 and 282.9 pm (Fig. 40).

Maier et al. [71] determined the electric dipole moments of $Pr[N(SiMe_3)_2]_3(THF)$ and $(Cp)_3Pr(NCC_2H_5)$ with quasi-C_{3v} molecular symmetry and of $Sc[N(SiMe_3)_2]_3$ and $(Cp)_3La(NCC_2H_5)$ with D_{3h} molecular symmetry in benzene solutions. The compounds with D_{3h} symmetry do not exhibit a dipole moment, while the compounds with C_{3v} symmetry show a dipole moment higher than 4 D.

Maier and Kanellakopulos [72] measured the dielectric constants and dipole moments of 1 : 1 adducts of the triscyclopentadienyl compounds of the trivalent lanthanides La to Lu (with the exception of the Pm complex) with coordinated THF, $(Cp)_3Ln(THF)$. The crystal structure of $(Cp)_3Dy(THF)$ was also determined (Fig. 41: Dy—centroid(Cp) = 247.2, 246.7 and 244.7 pm; centroid—Dy—centroid = 113.9°, 119.6° and 118.9°).

Borisov et al. [73] studied the triple-point temperatures of the triscyclopentadienyl complexes of lanthanum, cerium, praseodymium, neodymium, samarium and

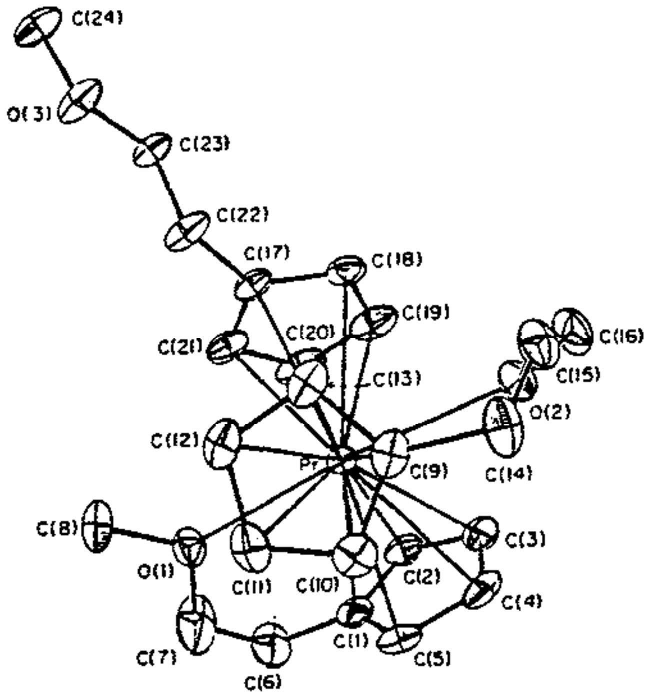


Fig. 39. $(MeOCH_2CH_2C_5H_4)_3Pr$. (Reproduced with permission from Journal of Organometallic Chemistry.)

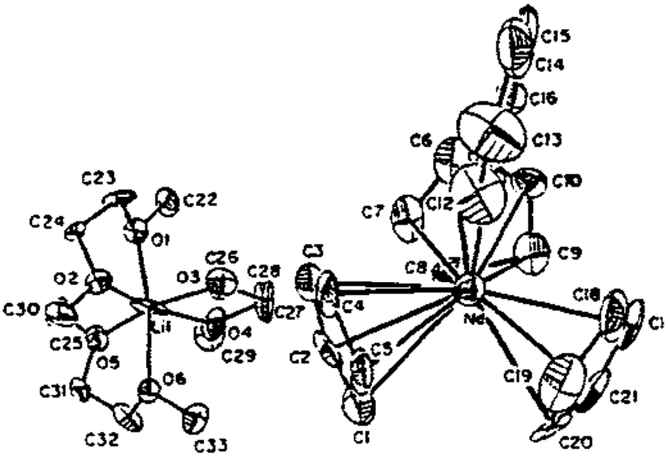


Fig. 40. $[Li(DME)_3][(\eta^5\text{-}Cp)_3NdC_6H_5]$. (Reproduced with permission from Journal of Organometallic Chemistry.)

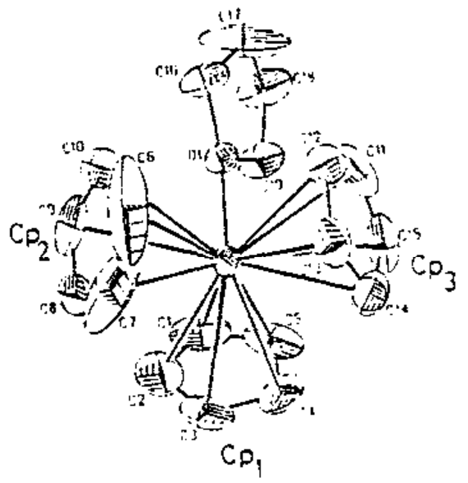
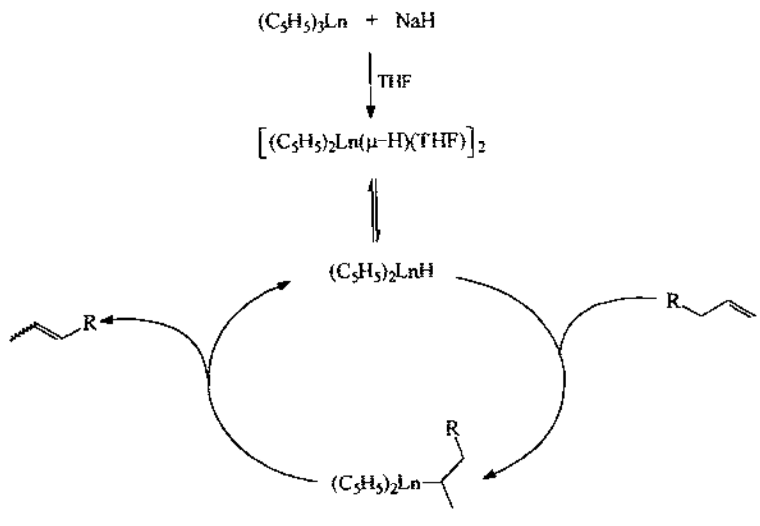


Fig. 41. $(Cp)_3Dy(THF)$. (Reproduced with permission from Journal of Organometallic Chemistry.)

gadolinium. The vapour pressures of these complexes have been measured by the static method in the temperature range 240–390 °C. The heats of sublimation were calculated from the temperature variation of the vapour pressure.

Qian et al. [74] studied the isomerization of several 1-alkenes catalysed by organolanthanide complex/sodium hydride ($(Cp)_3Ln/NaH$; Ln ≡ Y, Er, Lu) systems in THF at 45 °C (Scheme 11). These reactions afford *cis*- and *trans*-2-alkenes in very good yields. The effects of solvents and π ligand of the complexes on this isomerization were also determined.

Schulz and Amberger [75] inspected single crystals of various ester adducts



Scheme 11. Catalytic cycle.

derived from $(Cp)_3Ln$ ($Ln \equiv La$, Pr, Sm, Tb, Er, Tm) in a polarizing microscope. The crystal structure of the butylacetate (BA) adduct derived from $(Cp)_3La$ was determined (Fig. 42: La—centroid(Cp) = 258.9, 259.5 and 258.7 pm; centroid—La—centroid = 117.2°, 118.4° and 116.5°). The complex crystallizes in the molecular space group $P2_1/n$ with four molecules in the unit cell. Selected regions of the α, σ and π absorption spectra of $(Cp)_3La(BA)$: Pr were interpreted.

The crystallization properties of 150 adducts derived from $(Cp)_3Ln$ and $(Cp')_3Ln$ ($Cp' \equiv C_5H_5R$; R ≡ methyl, ethyl, *t*-butyl, benzyl, phenyl, trimethylsilyl) have been examined by Schulz et al. [76]. The crystal structures of $(Cp)_3Pr(BA)$ (BA ≡ *n*-butylacetate) and $(Cp)_3Tb(NCCH_3)$ were determined. The Pr—centroid(Cp) distances are 255.3, 255.6 and 255.0 pm; the Tb—centroid(Cp) distances are reported to be 244.2, 246.7 and 245.6 pm (Figs. 43 and 44).

The absorption spectrum of a $Cp_3Nd(NCCH_3)_2$ single crystal has been measured by the same authors [77] using liquid nitrogen as coolant. From these data a truncated crystal field splitting pattern could be derived.

Apostolidis et al. [78] reported the results of absorption, emission and magnetochemical measurements on mono- and bisacetonitrile adducts derived from $(Cp)_3Pr$. On the basis of these measurements, the truncated crystal field splitting pattern of $(Cp)_3Pr(NCCH_3)$, the structure of which was determined by Schulz et al. [76], could be derived. The absorption and luminescence spectra of $(Cp)_3Pr(NCCH_3)_2$ lead to two different splitting patterns.

Song et al. [79] described the synthesis of the byproduct $[(^tBuCp)_3NdBrLi(THF)_3]$, which was formed by the treatment of $(^tBuCp)_2NdCl$ with one equivalent of phenyllithium in THF (the phenyllithium solution used in this study contained LiBr, so that one bromine atom coordinates to the Nd atom). In this experiment the authors attempted to obtain the complex $(^tBuCp)_2NdC_6H_5 \cdot 2THF$:

$$(^tBuCp)_2NdCl \cdot 2THF + LiC_6H_5 \xrightarrow[-LiCl]{Et_2O} (^tBuCp)_2NdC_6H_5 \cdot 2THF$$

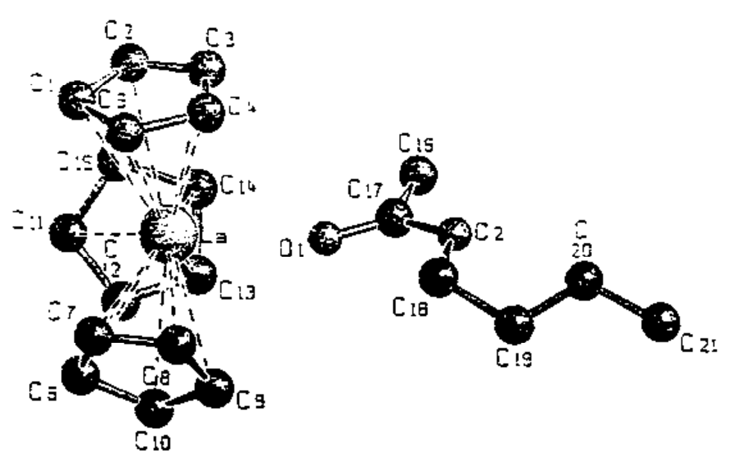


Fig. 42. $(Cp)_3La(BA)$. (Reproduced with permission from Journal of Organometallic Chemistry.)

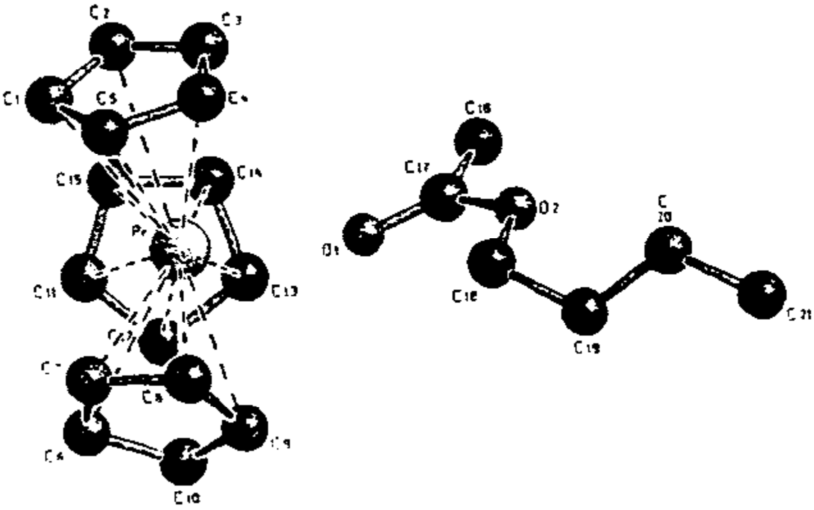


Fig. 43. $(Cp)_3Pr(BA)$. (Reproduced with permission from Journal of Organometallic Chemistry.)

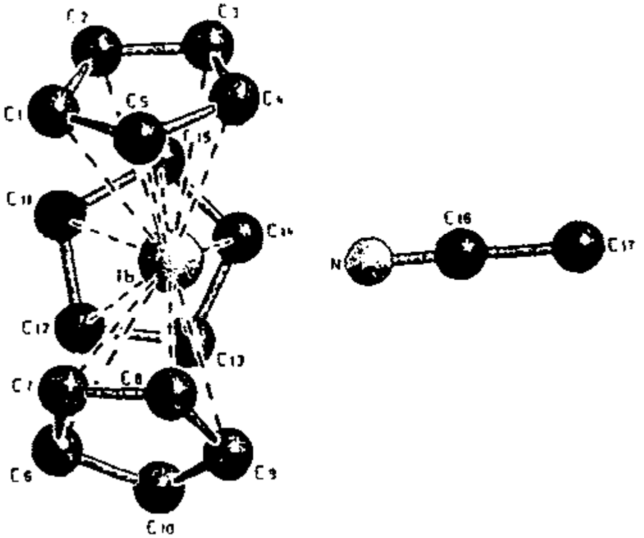


Fig. 44. $(Cp)_3Tb(NCCH_3)$. (Reproduced with permission from Journal of Organometallic Chemistry.)

The crystal structure shows that the neodymium atom is bonded to three *tert*-butyl-cyclopentadienyl groups and one bromine atom, forming a distorted pseudo-tetrahedron (Fig. 45: Nd−Br = 297.8 pm; Nd−centroid(Cp) = 255.7, 256.5 and 258.2 pm; centroid−Nd−centroid = 117.0° and 116.0°).

The formation of some sublimable homoleptic tris(*tert*-butylcyclopentadienyl) complexes of the formula $Ln(^tBuCp)_3$ (Ln ≡ Nd, Dy, Tm) was reported by Herrmann et al. [56]:

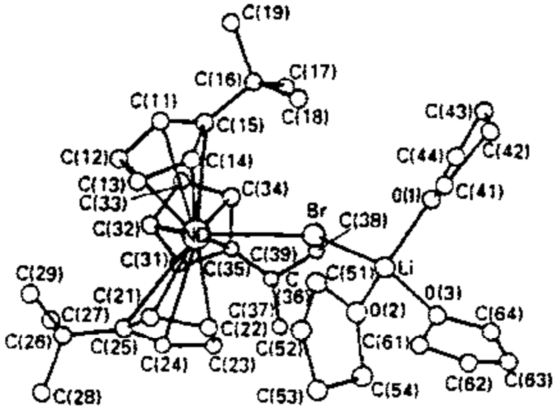
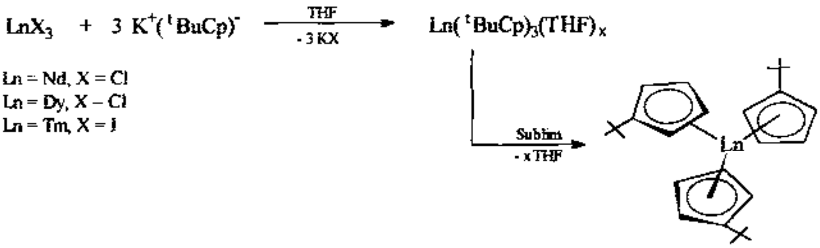


Fig. 45. [(^{t}BuCp)$_3$NdBrLi(THF)$_3$]. (Reproduced with permission from Polyhedron.)



These compounds were obtained by the reaction of $LnCl_3$ with the potassium salt K(^{t}BuCp) in THF. Their thermal behaviour makes them potential precursors for metalorganic chemical vapour deposition (MOCVD) techniques.

2.1.5. Compounds with cyclooctatetraenyl and cyclopentadienyl ligands

Visseaux et al. [80] reported the synthesis of dimethylphosphinotetramethylcyclopentadiene, $HC_5Me_4PMe_2$, and its potassium salt $KC_5Me_4PMe_2$. Reactions of $KC_5Me_4PMe_2$ with $[(COT)Sm(\mu\text{-}Cl)(THF)_2]_2$ ($COT \equiv \eta^8\text{-}C_8H_8^{2-}$) gave compounds such as $(COT)Sm(C_5R_4PR'_2)(THF)_n$ ($R \equiv H$, Me; $R' \equiv Me$, Ph; $n = 0, 2$):

$$\tfrac{1}{2}[(COT)SmCl(THF)_2]_2 \xrightarrow[MC_5R_4PR'_2]{THF} (COT)Sm(C_5R_4PR'_2)(THF)_n$$

$M \equiv Li$; $R \equiv H$; $R' \equiv C_6H_5$; $n = 2$; blue

$M \equiv K$; $R \equiv CH_3$; $R' \equiv C_6H_5$; $n = 0$; red-brown

$M \equiv K$; $R \equiv R' \equiv CH_3$; $n = 0$; dark green crystals, deep red solution

All these metallophosphines reacted with $CpRh(CO)_2$ to form phosphido-bridged bimetallic samarium(III)rhodium(I) complexes $(COT)Sm(\mu\text{-}C_5R_4PR'_2)Rh(Cp)$–(CO) ($R \equiv H$, Me; $R' \equiv Me$, Ph):

$$(COT)Sm(C_5R_4PR'_2)(THF) \xrightarrow{(C_5H_5)Rh(CO)_2} (COT)Sm(\mu\text{-}C_5R_4PR'_2)Rh(C_5H_5)(CO)$$

$R \equiv H$; $R' \equiv C_6H_5$

$R \equiv CH_3$; $R' \equiv C_6H_5$

$R \equiv R' \equiv CH_3$

The crystal structure of $(COT)Sm(C_5H_4PPh_2)(THF)_2$ was determined and discussed (Fig. 46: Sm—centroid(Cp) = 252.7 pm; Sm—centroid(COT) = 198.4 pm; centroid(Cp)–Sm—centroid(COT) = 137.1°). The complex exhibits a very distorted pseudotetrahedral geometry.

Ke et al. [81] described the synthesis of $(\eta^5\text{-Cp})Ln(\eta^8\text{-COT})(THF)_2$ (Ln ≡ Pr, Nd, Gd) by the reaction of $LnCl_3$ with NaCp and K_2COT in THF:

$$LnCl_3 + NaC_5H_5 + K_2C_8H_8 \xrightarrow{THF} (\eta^5\text{-}C_5H_5)Ln(\eta^8\text{-}C_8H_8)(THF)_2 + 2KCl + NaCl$$

The crystal structure of $(\eta^5\text{-Cp})Pr(\eta^8\text{-COT})(THF)_2$ was determined. The centroids of the Cp ring and the COT ring and the two oxygen atoms from the two THF ligands form a distorted tetrahedron.

2.1.6. Compounds with cyclooctatetraenyl and other ligands

$(COT)Ln(C_9H_7)(THF)_2$ (Ln ≡ Pr, Nd) complexes were prepared by Ke et al. [82] by the reaction of $LnCl_3$ with $K(C_9H_7)$ (C_9H_7 ≡ indenyl) in the presence of K_2COT

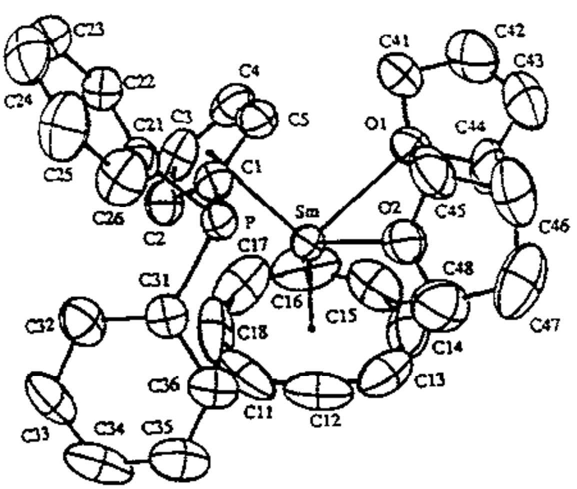


Fig. 46. $(COT)Sm(C_5H_4PPh_2)(THF)_2$. (Reproduced with permission from Journal of Organometallic Chemistry.)

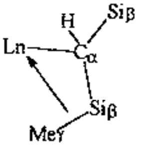
in THF:

$$LnCl_3 + K_2C_8H_8 + K(C_9H_7) \xrightarrow{THF} (C_8H_8)Ln(C_9H_7)(THF)_2 + 3KCl$$

The crystal structure of the praseodymium compound showed that a five-membered ring centroid of C_9H_7, the COT centroid and the two oxygen atoms from the two THF ligands form a distorted tetrahedral geometry around the metal.

2.1.7. Compounds with trimethylsilylalkyl ligands

Schaverien and Nesbitt [83] prepared series of related complexes [La(Cp*){CH(SiMe$_3$)$_2$}$_2$], [Ln(Cp*)$_2${CH(SiMe$_3$)$_2$}] (Ln ≡ La, Lu), [Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K] and the homoleptic tris-alkyls [Ln{CH(SiMe$_3$)$_2$}$_3$] Ln ≡ Lu, La) to investigate the factors influencing the fluxionality of their CH(SiMe$_3$)$_2$ groups. The determinations of these complexes have shown that the CH(SiMe$_3$)$_2$ groups remain rather mobile in the solid state. It is suggested that in electrophilic complexes containing a CH(SiMe$_3$)$_2$ ligand the metal may be stabilized by a β-Si—Me—M interaction:



2.2. Compounds without supporting cyclopentadienyl ligands

2.2.1. Indenyl compounds

Fuxing et al. [84] reported the synthesis of indenylgadolinium dichloride tristetrahydofuranate, ($C_9H_7GdCl_2 \cdot 3THF$)THF, by the reaction of $GdCl_3$ with KC_9H_7 in THF:

$$GdCl_3 + KC_9H_7 \xrightarrow{THF} (C_9H_7GdCl_2 \cdot 3THF)THF + KCl$$

A crystal structure determination showed the Gd in the centre of the octahedron and a coordination number of eight (Fig. 47). The Gd—centroid (five membered ring) distance is 247 pm.

Jusong et al. [85] described the synthesis of triindenyllanthanide complexes (η^5-C_9H_7)$_3$Ln(THF) (Ln ≡ Nd, Gd, Er) by the reaction of $LnCl_3$ with indenylpotassium and cyclooctadienylpotassium in THF. The crystal structures of (η^5-C_9H_7)$_3$Ln(THF) (Ln ≡ Nd, Gd) were discussed.

2.2.2. Alkoxides

The monomeric chelate [La{CH(SiMe$_3$)$_2$}{1,1′-(2-OC$_6$H$_2$^{t}Bu$_2$-3,5)$_2$}] was prepared by the reaction of [La{CH(SiMe$_3$)$_2$}$_3$] with one equivalent of 3,3′,5,5′-tetra-

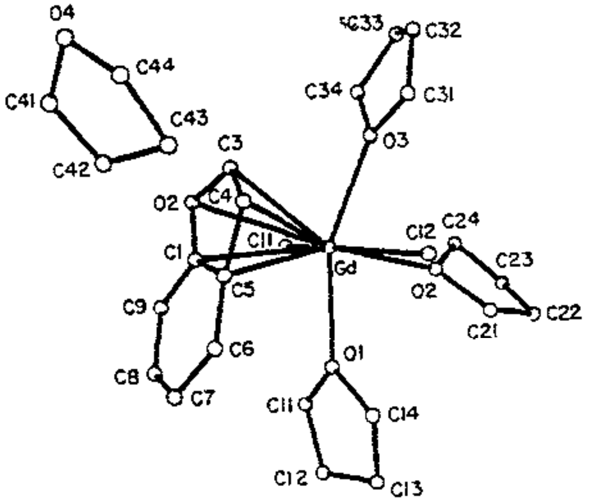
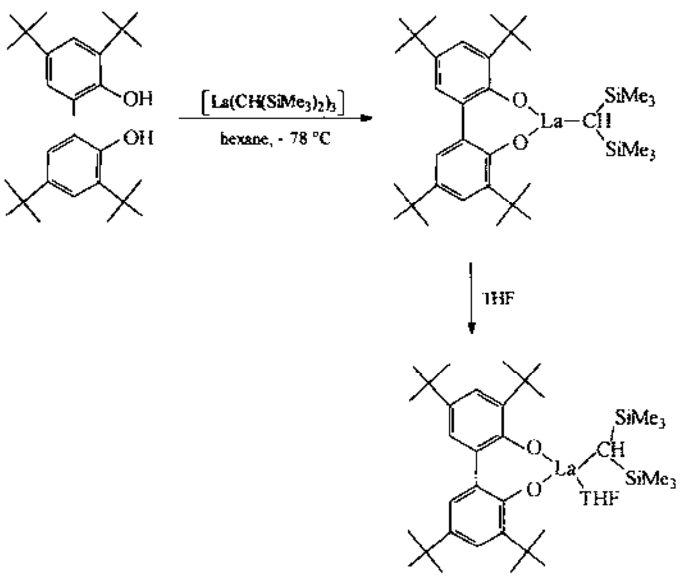


Fig. 47. ($C_9H_7GdCl_2 \cdot 3THF$)THF. (Reproduced with permission from Journal of Organometallic Chemistry.)

tert-butylbiphenyl-2,2′-diol by Schaverien et al. [86] (Scheme 12). The mono- and tris-THF adducts have been synthesized and the tris-THF adduct was characterized by a crystal structure determination (Fig. 48). The lanthanum atom is ligated by a σ-bonded alkyl group with a bond length La−C(alkyl) = 267.6 pm. The La−O(bis-phenoxide) distances are 227.1 and 221.7 pm. The reaction of [La{CH(SiMe$_3$)$_2$}{1,1′-



Scheme 12.

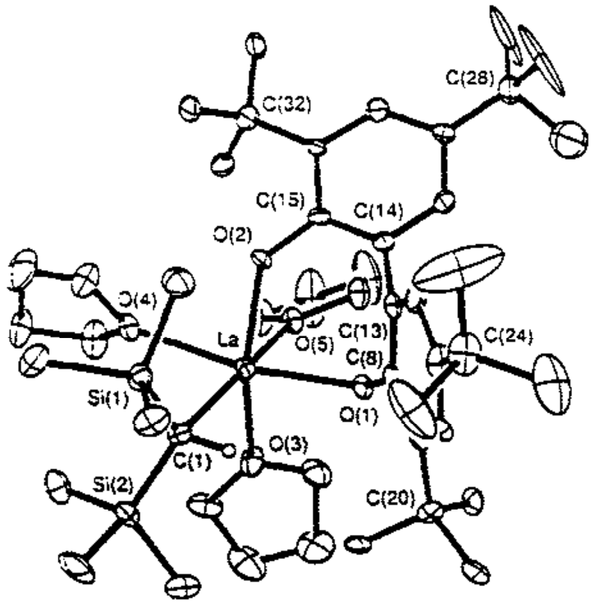


Fig. 48. [La{CH(SiMe$_3$)$_2$}{1,1'-(2-OC$_6$H$_2$^{t}Bu$_2$-3,5)$_2$}(THF)$_3$]. (Reproduced with permission from Journal of the Chemical Society, Chemical Communications.)

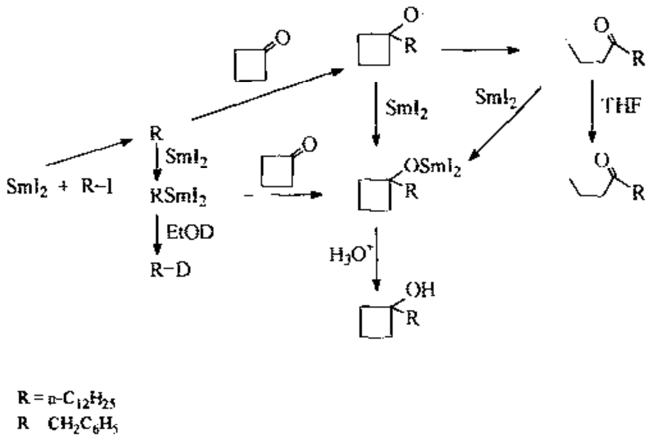
(2-OC$_6$H$_2$^{t}Bu$_2$-3,5)$_2$}] with 3,3'-bis(triphenylsilyl)-1,1'-binaphthyl-2,2'-diol affords [La{CH(SiMe$_3$)$_2$}{1,1'-(2-OC$_{10}$H$_5$SiPh$_3$-3)$_2$}(OEt$_2$)], which was also described in Ref. [86].

2.2.3. *Alkyl and arene compounds*

Namy et al. [20] performed some Barbier reactions in the presence of samarium(II) iodide in THF. It is concluded that under standard conditions (in the absence or presence of hexamethylphosphoramide) an unstable and reactive organosamarium species is formed, which is immediately trapped by the carbonyl compound. The mechanism of the reaction of *n*-dodecyl iodide or benzyl bromide with cyclobutanone is shown in Scheme 13. The authors found evidence that organosamarium species are present under the Barbier reaction conditions and are probably involved in the product formation for intermolecular reactions, which should be useful for synthetic applications.

King and Marks [87] published thermochemical information on some formally zero-valent lanthanide bis(arene) sandwich complexes of the formula Ln(η^6-1,3,5-^{t}Bu$_3$C$_6$H$_3$)$_2$ (Ln ≡ Y, Gd, Dy, Ho, Er). These investigations indicate that the metal–arene bonds are very strong.

Reetz et al. [88] published their experiences with ligand effects in selective carbonyl addition reactions of cerium reagents. These cerium complexes RCe(O^{i}Pr)$_3$MgX (R ≡ methyl, phenyl; X ≡ Cl) react selectively with aldehydes in the presence of ketone functionality. The compounds were prepared by the reaction of cerium triisoprop-



Scheme 13.

oxide with RMgCl or RLi:

$$RMgCl + Ce(O^iPr)_3 \rightarrow RCe(O^iPr)_3MgCl$$

$$RLi + Ce(O^iPr)_3 \rightarrow RCe(O^iPr)_3Li$$

(R ≡ methyl, *n*-butyl, phenyl)

The Ce–Mg complexes are highly aldehyde selective in simple competition reactions involving 1:1 mixtures of benzaldehyde and acetophenone.

Bauschlicher et al. [89] compared the coupled cluster (CCSD(T)) and internally contracted averaged coupled pair functional (ICACPF) levels of theory for the calculation of the MCH_2^+ binding energies for M ≡ Sc to Cu. The conclusion is that the CCSD(T) method yields binding energies that are in excellent agreement with the ICACPF results.

2.2.4. Ferrocenyl compounds

Jacob et al. [13] reported the reactions of anhydrous lanthanide trichlorides $LnCl_3$ (Ln ≡ La, Ce, Pr, Nd, Yb) with [2-(dimethylaminomethyl)ferrocenyl]lithium (Li(FcN)) to give complexes of the type $(FcN)_2LaCl$, $(FcN)_3Ln \cdot LiCl \cdot THF$ (Ln ≡ Ce, Pr, Nd) and $(FcN)_3Yb$:

$$LaCl_3 + 3Li(FcN) \xrightarrow[20\,^\circ C]{THF} (FcN)_2LaCl + Li(FcN) + 2LiCl$$

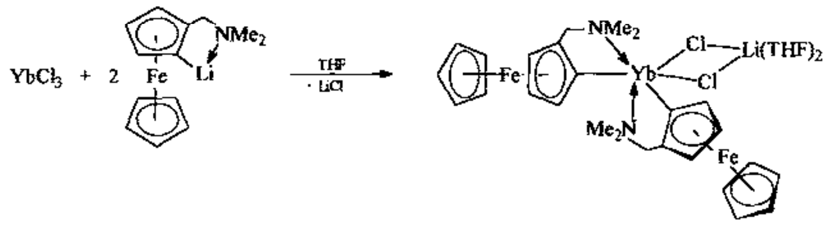
$$LnCl_3 + 3Li(FcN) \xrightarrow[20\,^\circ C]{THF} (FcN)_3Ln \cdot LiCl \cdot THF + 2LiCl$$

Ln ≡ Ce, Pr, Nd

$$YbCl_3 + 3Li(FcN) \xrightarrow[20\,^\circ C]{THF} (FcN)_3Yb + 3LiCl$$

The compounds possess high thermal stability, which can be explained by the chelating properties of the FcN ligand.

Dark red crystalline $[(FcN)_2Yb(\mu\text{-}Cl)_2Li(THF)_2]$ has been prepared by Gornitzka et al. [90] by the treatment of anhydrous $YbCl_3$ with (FcN)Li in 1:2 molar ratio:



This complex represents the first example of a diorganolanthanide(III) halide containing σ-bonded organic ligands. The molecular structure of the complex has been determined and discussed (Fig. 49): Yb—C = 265.1 and 237.2 pm; Cl—Yb—Cl = 80.9°).

3. Actinides

3.1. Cyclopentadienyl and cyclopentadienyl-like compounds

3.1.1. Monocyclopentadienyl compounds

Eisen and Marks [91] reported kinetic and mechanistic studies of arene hydrogenation by the supported organoactinide complex $(Cp)Th(CH_2C_6H_5)_3$/DA

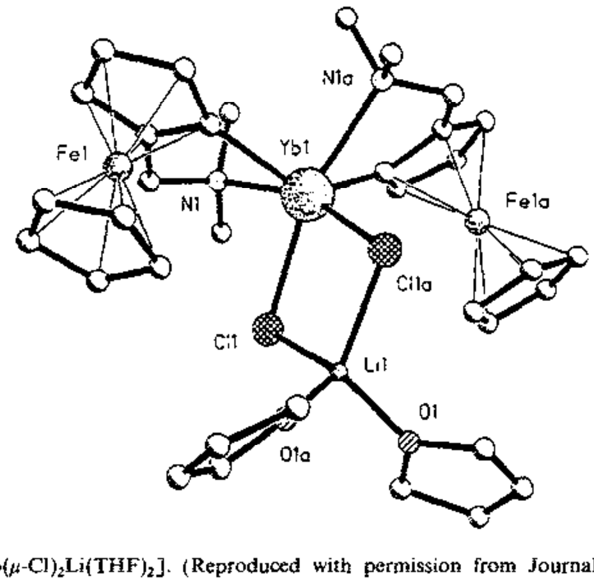


Fig. 49. $[(FcN)_2Yb(\mu\text{-}Cl)_2Li(THF)_2]$. (Reproduced with permission from Journal of Organometallic Chemistry.)

(DA ≡ dehydroxylated γ-alumina). This derivative is a highly active catalyst for ethylene polymerization and propylene hydrogenation, but it is not active for propylene polymerization.

3.1.2. Biscyclopentadienyl compounds

Arney et al. [92] reported the synthesis and structure (Fig. 50: centroid(Cp*)—U—centroid(Cp*) = 141.9°) of the first bis(organoimido) complex of uranium(VI), $(Cp^*)_2U(NC_6H_5)_2$. The reaction of $(Cp^*)_2U(CH_3)Cl$ with one equivalent of $LiNHC_6H_5$ in diethyl ether in the presence of one equivalent of TMEDA results in the formation of brown-orange $[Li(TMEDA)](Cp^*)_2U(NC_6H_5)Cl$:

$$(C_5Me_5)_2U(CH_3)Cl + LiNHC_6H_5 + TMEDA$$

$$\xrightarrow[-CH_4]{(C_2H_5)_2O} [Li(TMEDA)](C_5Me_5)_2U(NC_6H_5)Cl$$

The addition of one equivalent of phenyl azide to the lithium compound in diethyl ether results in the formation of $(Cp^*)_2U(NC_6H_5)_2$:

$$[Li(TMEDA)](C_5Me_5)_2U(NC_6H_5)Cl + N_3C_6H_5 \xrightarrow[N_2]{(C_2H_5)_2O} (C_5Me_5)_2U(NC_6H_5)_2$$

Another preparation of the uranium(VI) complex was also achieved by the reaction of 1-lithio-1,2-diphenylhydrazine with $(Cp^*)_2U(CH_3)Cl$ in diethyl ether:

$$(C_5Me_5)_2U(CH_3)Cl + LiN(C_6H_5)NH(C_6H_5) \xrightarrow[-CH_4]{(C_2H_5)_2O} (C_5Me_5)_2U(NC_6H_5)_2$$

The crystal structures of the two isostructural complexes $[(Cp^*)_2UCl_2]$ (Fig. 51: U—centroid(Cp*) = 247.3 pm; centroid—U—centroid = 132.1°) and $[(Cp^*)_2ThCl_2]$ (Th—centroid = 253.4 pm; centroid—Th—centroid = 128.4°) were determined and discussed by Spirlet et al. [93]. The coordination geometry about the actinide atom is that of a distorted tetrahedron formed by the two Cl atoms and the centroids of

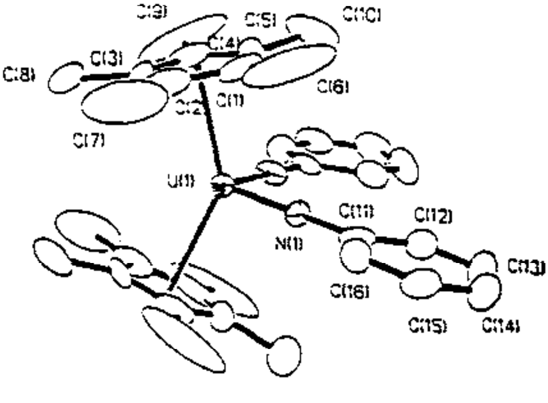


Fig. 50. $(Cp^*)_2U(NC_6H_5)_2$. (Reproduced with permission from Journal of the American Chemical Society.)

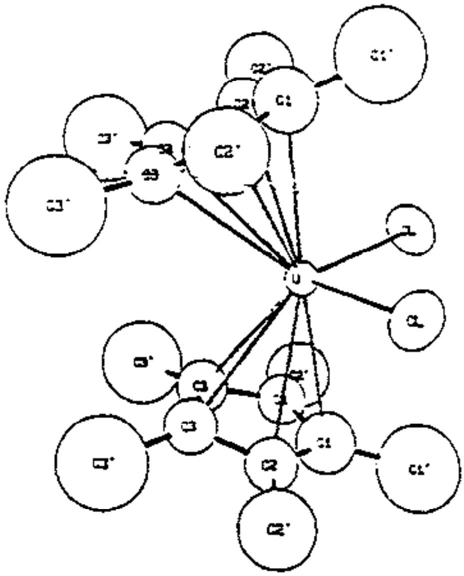


Fig. 51. [$(Cp^*)_2UCl_2$]. (Reproduced with permission from Acta Crystallographica.)

the two cyclopentadienyl rings. The molecular geometry of both complexes appears to be heavily influenced by intramolecular non-bonded interactions. The complexes were prepared by the reaction of uranium (or thorium) tetrachloride and potassium pentamethylcyclopentadienylide:

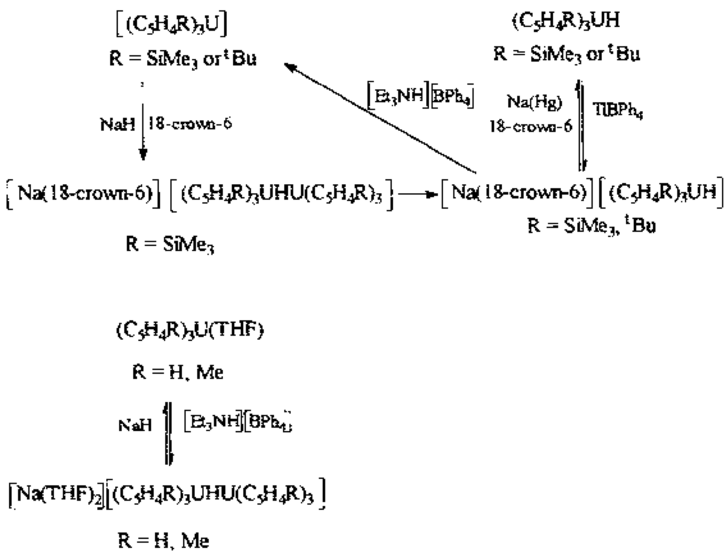
$$UCl_4 + 2KC_5Me_5 \xrightarrow[-2KCl]{\text{pentane}} (C_5Me_5)_2UCl_2$$

3.1.3. *Triscyclopentadienyl compounds*

Maier and Kanellakopulos [72] measured the dielectric constants and dipole moments of the complexes $(Cp)_3An(THF)$ (An ≡ Th, U, Np, Pu). From the partial electric moment for the metal–oxygen bond, the distribution of the 5f electrons with respect to the total electric dipole moment of the molecule was calculated.

Berthet et al. [94] reported that the addition of H^- to [$(C_5H_4R)_3U$] (R ≡ H, Me, $SiMe_3$, ^tBu) or sodium amalgam reduction of the U(IV) hydrides [$(C_5H_4R)_3UH$] (R ≡ $SiMe_3$, ^tBu) afforded the hydrido-bridged anions [$(C_5H_4R)_3UHU(C_5H_4R)_3$]$^-$ (R ≡ H, Me) or the monomeric anions [$(C_5H_4R)_3UH$]$^-$ (R ≡ $SiMe_3$, ^tBu) (Scheme 14). The crystal structure of [Na(18-crown-6)$(THF)_2$][$(C_5H_4SiMe_3)_3UHU(C_5H_4$-$SiMe_3)_3$] was also discussed (Fig. 52: centroid(Cp)−U = 257.1, 255.8 and 257.0 pm). This compound was obtained from an equimolar mixture of [Na(18-crown-6)][$(C_5H_4SiMe_3)_3UH$] and [$(C_5H_4SiMe_3)_3U$].

Villiers et al. [95] reported the transformation of the triscyclopentadienyluranium acyl complexes [$U(\eta^5\text{-}Cp)_3(\eta^2\text{-}COR)$] leading to the corresponding alkylbenzene



Scheme 14.

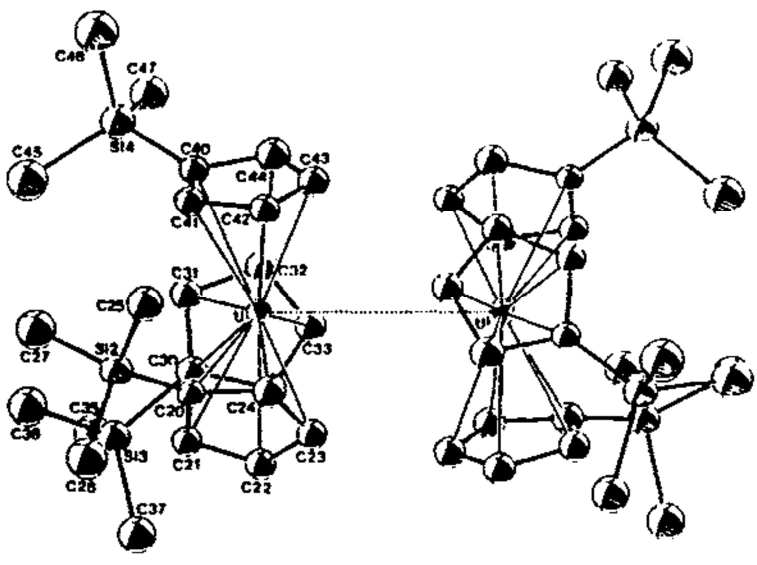
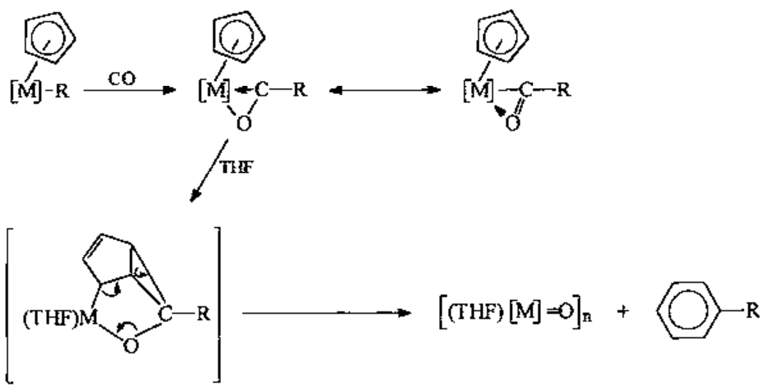


Fig. 52. $[Na(18\text{-crown-6})(THF)_2][(C_5H_4SiMe_3)_3UHU(C_5H_4SiMe_3)_3]$. (Reproduced with permission from Journal of Organometallic Chemistry.)

molecules C_6H_5R (Scheme 15) ($R \equiv Me$, ^nBu, ^iPr, ^tBu). These derivatives have been formed by deoxygenation of the acyl group and ring enlargement of a cyclopentadienyl ligand. The authors reported that in the Fischer–Tropsch reaction, CO insertion into metal–alkyl species is generally considered as a chain termination step, leading



Scheme 15. [M] ≡ $U(Cp)_2$; R ≡ Me, ^nBu, ^iPr, ^tBu.

to oxygenated products, even if carbene or alkyl complexes could be obtained by treating acyl derivatives with metal hydride species.

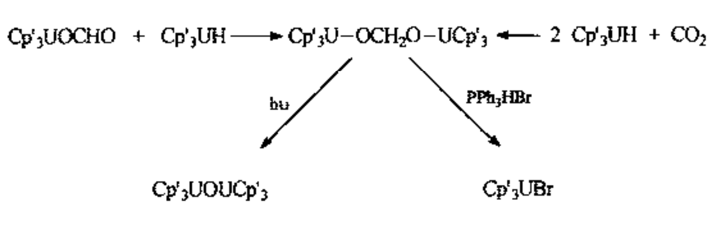
Berthet and Ephritikhine [96] described the reaction of the uranium(IV) hydride $(C_5H_4SiMe_3)_3UH$ with carbon dioxide to give $(C_5H_4SiMe_3)_3UOCHO$, which reacted further with $(C_5H_4SiMe_3)_3UH$ to form the dioxymethylene complex $(C_5H_4SiMe_3)_3UOCH_2OU(C_5H_4SiMe_3)_3$. This complex is thermally stable and its photolysis by UV light gave $((C_5H_4SiMe_3)_3U)_2(\mu\text{-}O)$ (Scheme 16). The reaction of the dioxymethylene complex with $[PPh_3H]Br$ quantitatively produced $(C_5H_4SiMe_3)_3UBr$.

Zwick et al. [97] reported an alternative synthesis of $(\eta^5\text{-}Cp)_3Pu(THF)$ by the reaction of plutonium triiodide with three equivalents of LiCp in THF:

$$PuI_3(THF)_4 + 3Li(C_5H_5) \xrightarrow{THF} (C_5H_5)_3Pu(THF) + 3LiI$$

3.1.4. *Tetrakiscyclopentadienyl compounds*

Gramoteeva et al. [98] studied reactions of $(Cp)_4U$ with the aryl halides PhBr, $PhCH_2Cl$ and Ph_3CCl. The direction of the reaction was determined by the structure



Scheme 16.

of the aryl halide. PhBr gave $(Cp)_3UPh$ and $(Cp)_3UBr$, whereas $PhCH_2Cl$ gave $(Cp)_3UCH_2Cl$ and $CpU(CH_2Ph)_3$, while Ph_3CCl gave only $(Cp)_3UCl$.

3.2. *Compounds without supporting cyclopentadienyl ligands*

3.2.1. *Alkyl and arene compounds*

Zwick et al. [97] prepared homoleptic alkyl complexes of the formula $An[CH(SiMe_3)_2]_3$ (An ≡ Np, Pu) by the reaction of three equivalents of $LiCH(SiMe_3)_2$ with $An[O\text{-}2,6\text{-}(t\text{-}C_4H_9)_2C_6H_3]_3$ in hexane:

$$An[O\text{-}2,6\text{-}(t\text{-}C_4H_9)_2C_6H_3]_3 + 3LiCH(SiMe_3)_2$$
$$\rightarrow An[CH(SiMe_3)_2]_3 + 3LiO\text{-}2,6\text{-}(t\text{-}C_4H_9)_2C_6H_3$$

Both complexes are extremely air sensitive and thermally unstable, decomposing as solids within 1–2 days to intractable materials.

Eisen and Marks [91] reported a kinetic and mechanistic study of facile arene hydrogenation with the supported organoactinide complex $Th(1,3,5\text{-}CH_2C_6H_3Me_2)_4/DA$ (DA ≡ dehydroxylated γ-alumina). They found that the activity for benzene hydrogenation follows the order $(Cp)Th(benzyl)_3/DA < Th(1,3,5\text{-}CH_2C_6H_3Me_2)_4/DA < Th(\eta^3\text{-allyl})_4/DA$.

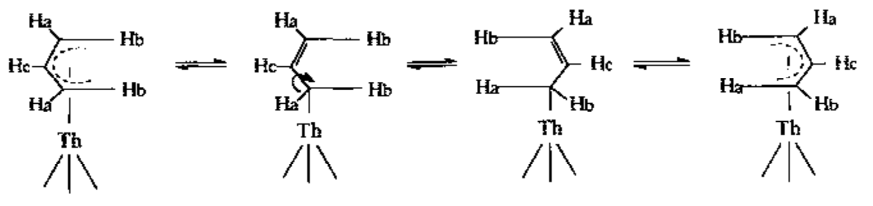
3.2.2. *Allyl compounds*

Eisen and Marks [91] prepared tetraallylthorium by the low temperature reaction of $ThCl_4(THF)_3$ with an excess of allylmagnesium bromide in diethyl ether:

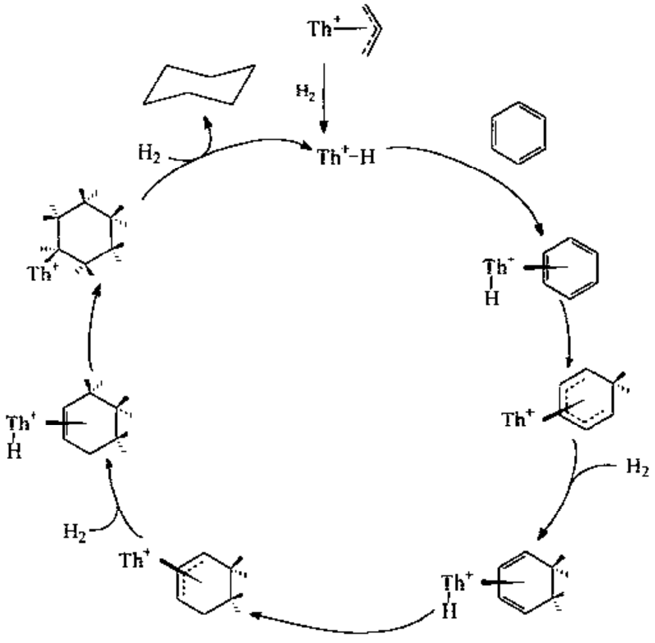
$$ThCl_4(THF)_3 + 4(C_3H_5)MgBr \xrightarrow[-78\,^\circ C]{Et_2O} Th(\eta^3\text{-}C_3H_5)_4(Et_2O)_2 + 4MgClBr$$

$$Th(\eta^3\text{-}C_3H_5)_4(Et_2O)_2 \xrightarrow[-20\,^\circ C]{\text{toluene, pentane}} Th(\eta^3\text{-}C_3H_5)_4 + 2Et_2O$$

The product is stereochemically non-rigid in solution, with the exchange of syn and anti η^3-allyl protons observable by variable-temperature dynamic ^1H NMR spectroscopy (Scheme 17). Marks and Eisen also reported kinetic and mechanistic studies of arene hydrogenation by supported tetraallylthorium (Scheme 18), $Th(\eta^3\text{-allyl})_4/DA$, which presents an interesting contrast to both conventional homogeneous and heterogeneous arene hydrogenation catalysts.



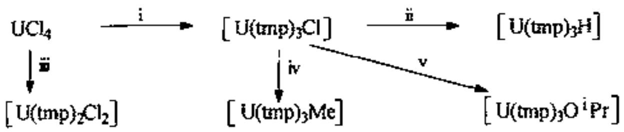
Scheme 17.



Scheme 18. Possible scenario for Th(η^3-allyl)$_4$/DA-catalysed arene hydrogenation.

3.2.3. Heteroatom five-membered ring anions

Gradoz et al. [99] reported the synthesis, crystal structure and some derivatives of chlorotris(tetramethylphospholyl)uranium. They used the tetramethylphospholyl group (η-$C_4Me_4P \equiv$ tmp) which is a steric mimic of the Cp* ligand, while rendering the metal centre more electrophilic. The uranium complex [U(tmp)$_3$Cl] was obtained by the treatment of UCl_4 with three equivalents of tmpK in toluene. The complex [U(tmp)$_2$Cl$_2$] was prepared by the reaction of UCl_4 with only one equivalent of the phospholyl anion. [U(tmp)$_3$Cl] was a precursor for a series of [U(tmp)$_3$X] derivatives (Scheme 19). The crystal structure of chlorotris(tetramethylphospholyl)uranium revealed that the three phospholyl ligands are pentahapto bonded to the uranium (Fig. 53: U–Cl = 267.1 pm; U–P = 292.7 pm; U–centroid(ring) = 261.1 pm; centroid–U–centroid = 119.1°).



Scheme 19. Reagents and conditions: (i) tmpK, 16 h; (ii) KBEt$_3$H, 2 h; (iii) tmpK (one equivalent), 1 h; (iv) MeLi, 2 h; (v) ^{i}PrONa, 2 h. All reactions in toluene.

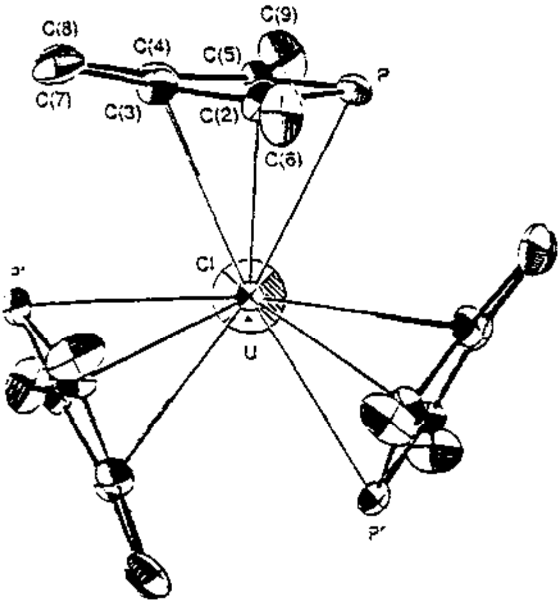


Fig. 53. [U(η-C_4Me_4P)$_3$Cl]. (Reproduced with permission from Journal of the Chemical Society, Chemical Communications.)

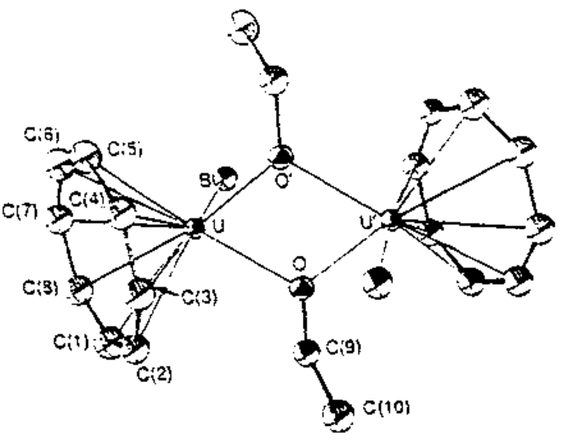


Fig. 54. [{U(COT)(BH_4)(μ-OEt)}$_2$]. (Reproduced with permission from Journal of the Chemical Society, Dalton Transactions.)

3.2.4. *Cyclooctatetraenyl complexes*

The alkoxide derivatives [U(COT)(BH_4)(OR)] and [U(COT)$(OR)_2$] (COT ≡ η^8-$C_8H_8^{2-}$; R ≡ Et, ^{i}Pr, ^{t}Bu) were prepared by Arliquie et al. [100] by the treatment of [U(COT)$(BH_4)_2$] with ROH. The complexes of the formula [U(COT)(BH_4)(OR)] are monomeric in THF, whereas the other compounds [U(COT)$(OR)_2$] are dimeric in this solvent and monomeric in pyridine. The crystal structures of

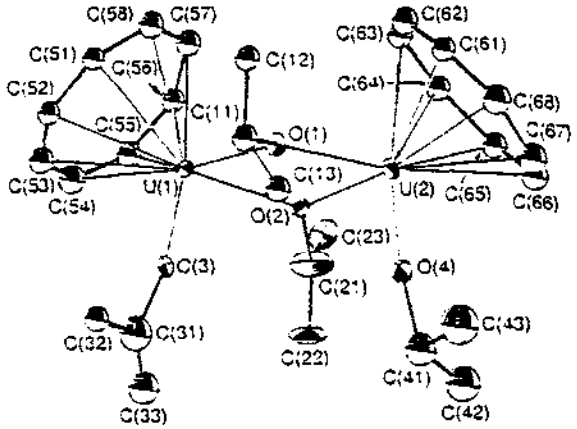


Fig. 55. [{U(COT)(O^{i}Pr)(μ-O^{i}Pr)}$_2$]. (Reproduced with permission from Journal of the Chemical Society, Dalton Transactions.)

[{U(COT)(BH_4)(μ-OEt)}$_2$] and [{U(COT)(O^{i}Pr)(μ-O^{i}Pr)}$_2$] have been determined (Fig. 54: U−centroid(COT) = 194.1 pm; U−B = 259.5 pm; U−U = 378.9 pm; Fig. 55: U−centroid(COT) = 199.2 and 198.3 pm; U−U = 378.1 pm). Both complexes are dimeric in the solid state and the two monomeric units are bridged by two alkoxide groups.

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