

Lanthanides and actinides. Annual survey of their organometallic chemistry covering the year 1994

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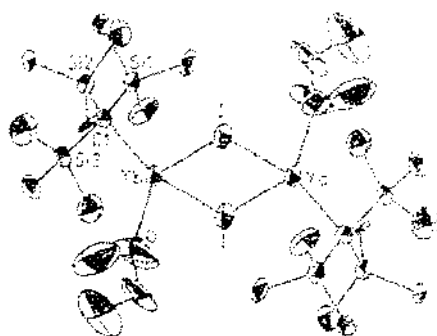
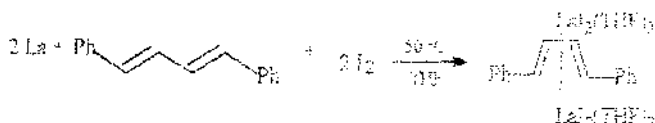


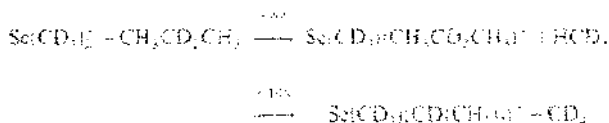
Fig. 1. Molecular structure of $[\text{La}_2(\text{THF})_3(\mu_2\text{-}\eta^2\text{-1,3,5-hexatriene})]_2$.

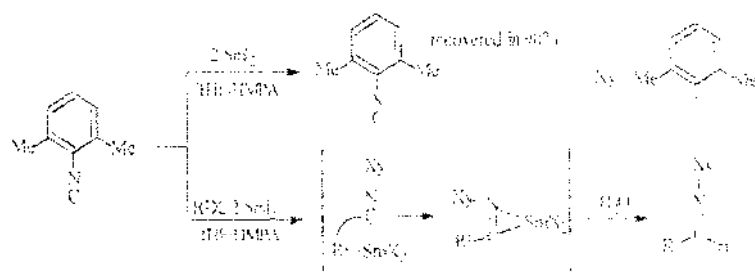
Masima et al. [2] reported the synthesis and structure of the diene-bridged dilaithanum complex, $[\text{La}_2(\text{THF})_3(\mu_2\text{-}\eta^2\text{-1,3,5-hexatriene})]_2$. The complex was obtained from metallic lanthanum, 1,4-diphenylbuta-1,3-diene and iodine in THF.



The complex crystallizes as a centrosymmetric molecule (Fig. 1); each La atom exhibits a pseudooctahedral six-coordination through one η^2 -interaction with the bridging diene unit. Three THF molecules are in *mer*-arrangement and two *trans* ligands are *trans* to each other. The La-I distances are 3.176(1) and 3.175(1) Å, the average La-C is 2.895 Å.

Perry and Condon [3] determined the Sc^+ alkyl bond strengths. The authors calculated dissociation energies for Sc^+ alkyl bonds and predicted thermochemistry for the σ -bond metathesis reaction: $\text{Sc}^+\text{R} + \text{R}'\text{H} \rightarrow \text{Sc}^+\text{R}' + \text{RH}$. The results for $\text{R} = \text{CH}_3$, C_2H_5 , $i\text{-C}_4\text{H}_9$, and $n\text{-C}_4\text{H}_9$ suggest that the $\text{Sc}^+\text{-R}$ bond strengths decrease in the order methyl > primary > secondary > tertiary, correlating with the electron affinities of the radicals. The results for $\text{R} = \text{C}_2\text{H}_5$ and $n\text{-C}_4\text{H}_9$ suggest that the $\text{Sc}^+\text{-R}$ bond strength increases with the size of the ligand. The chemistry in gas-phase σ -bond metathesis reactions of $\text{Sc}(\text{CH}_3)_3^+$ with alkanes (C_2H_6 , C_3H_8 , and $n\text{-C}_4\text{H}_{10}$) can be readily explained by the trends in the pertinent Sc^+ alkyl bond strengths:





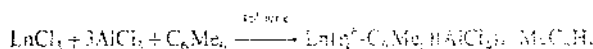
Scheme 2

were generated by treatment of organic halides and 2,6-xylyl isocyanide with SnI_2 (Scheme 2).

When a carbonyl compound was added to the reaction mixture, α -hydroxy imine was formed (Scheme 3).

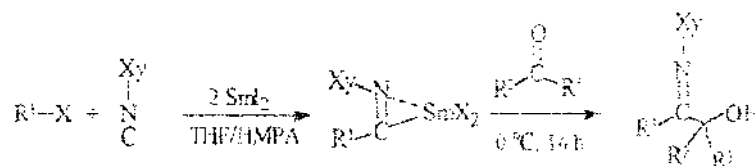
Unsymmetrical α -diketones were obtained by autooxidation of the resulting α -hydroxy imines. 4-*tert*-Butyldimethylsiloxy-2,6-xylyl isocyanide was used in the SnI_2 -mediated three-component coupling reaction for the stereoselective synthesis of 2-amino alcohols via reduction and subsequent oxidative α -de-arylation. Double insertion of 2,6-xylyl isocyanide into an organic halide mediated by SnI_2 provided a synthetic method for hydroxy diketones and vicinal trichlorones.

Liang et al. [7] described the arene complexes $\text{Ln}(\eta^6\text{-C}_6\text{Me}_6)_2\text{AlCl}_2$, which were synthesized by the reaction of LnCl_3 with AlCl_3 and C_6Me_6 in the molar ratio of 1:3:1.2.



$\text{Ln} = \text{Nd, Sm, Gd, Yb}$

In the molecular structure of $\text{Yb}(\eta^6\text{-C}_6\text{Me}_6)_2\text{AlCl}_2 \cdot \text{Me}_6\text{C}_6\text{H}_5$ (Fig. 4) the coordination polyhedron of the Yb atom is a distorted pentagonal bipyramid. Five chlorine atoms are located in an equatorial plane; the sixth chlorine atom Cl(2) occupies one apical position and C_6Me_6 occupies the other one. The mean distances of $\text{Yb} \cdots \text{Cl}^{\text{eq}}$



Scheme 3

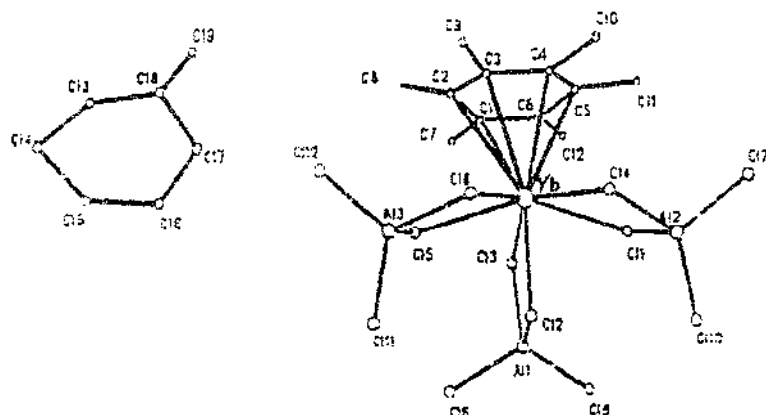
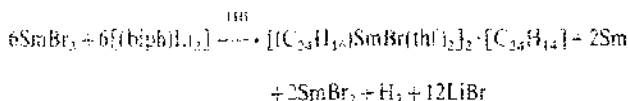


Fig. 4. Molecular structure of $\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)\text{AlCl}_2(\eta^5\text{-MeC}_5\text{H}_5)$.

(Cl in the plane) and $\text{Yb}-\text{Cl}^2$ (Cl in the apical position) are 2.795(7) Å and 2.734(10) Å respectively.

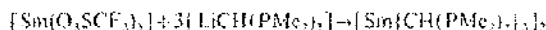
Boje and Magull [8] reported the reaction between SmBr_3 and $[(\text{biph})\text{Li}]_2$ in THF, which led to the complex $[(\text{C}_{24}\text{H}_{16})\text{SmBr}(\text{thf})_2]_2 \cdot [\text{C}_{24}\text{H}_{14}]$.



As result of this reaction, two biphenyl units are coupled to afford $[(\text{C}_{24}\text{H}_{16})\text{SmBr}(\text{thf})_2]_2 \cdot [\text{C}_{24}\text{H}_{14}]$ with the hydrocarbon $\text{C}_{24}\text{H}_{14}$ intercalated. In the dimeric structure of $[(\text{C}_{24}\text{H}_{16})\text{SmBr}(\text{thf})_2]_2 \cdot [\text{C}_{24}\text{H}_{14}]$ (Fig. 5) the Sm ions are bridged by two Br^- . The Sm-Br distances are 2.986(2) and 2.992(2) Å. Each Sm ion is octahedrally coordinated.

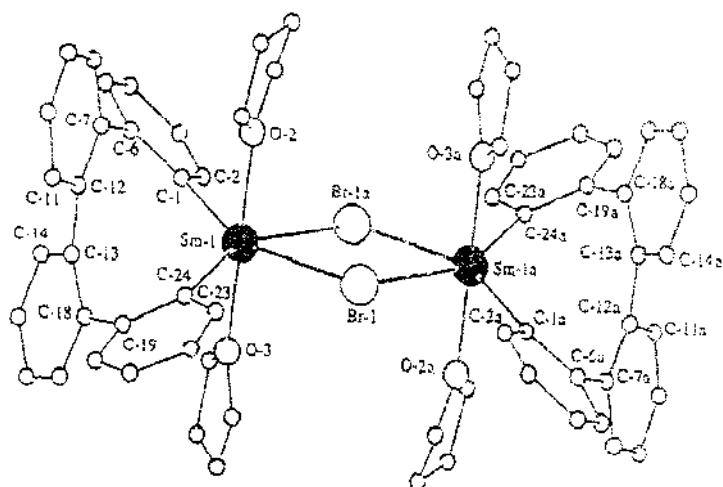
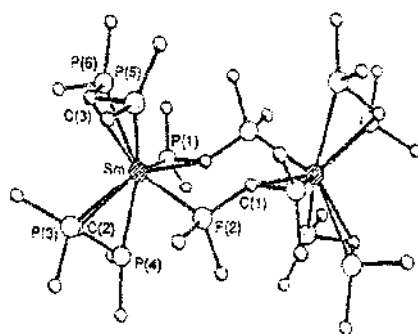
2.1.2. Complexes with phosphine ligands

Karsch et al. [9] described the dimeric complex $[\text{Sm}\{\text{CH}(\text{PMe}_2)_2\}_2]_2$, obtained from $[\text{Sm}(\text{O}_3\text{SCF}_3)_3]$ and $[\text{LiCH}(\text{PMe}_2)_2]$.

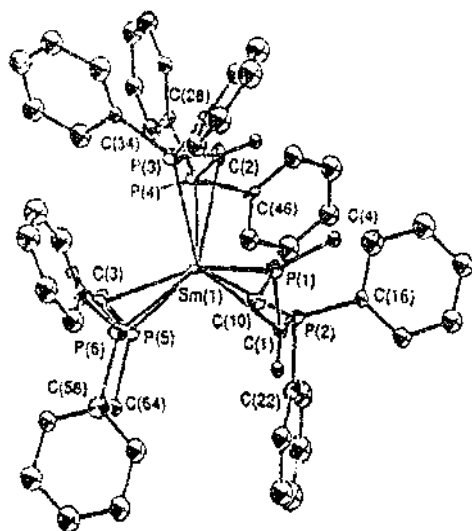


An X-ray structure determination revealed a centrosymmetric dimer in a chair conformation, formed by two bridging diphosphinomethanide ligands via the P(2) and C(1) atoms (Fig. 6). Together with P(1), C(1) is also a member of a three-membered ring (SmCP) as a substructural unit. Both samarium atoms are additionally ligated by two diphosphinomethanide ligand in a π -type coordination. Thus the complex contains four π -type and two bridging σ -type coordinated ligands.

Gambarotta and coworkers [10] prepared and characterized the complexes

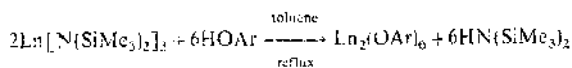
Fig. 5. Molecular structure of $[\text{C}_{12}\text{H}_{16}]_2\text{SmBr}_2$ ($[\text{C}_{14}\text{H}_{18}]$).Fig. 6. Molecular structure of $[\text{Sm}(\text{CH}_3)_2\text{PM}_2\text{Ph}_3]_2$.

$[\text{Cr}(\text{Ph}_2\text{PC}(\text{H})\text{PPh}_2)_2][\mu\text{-Cl}][\mu\text{-Cl}(\text{H})\text{PPh}_2][\text{Cr}(\text{Ph}_2\text{PC}(\text{H})\text{PPh}_2)]$ and $\text{Sm}[\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{PPh}_2]_2$. The samarium complex was obtained by the reaction of $[\text{LiCH}(\text{PPh}_2)_2]$ with $\text{SmCl}_3(\text{THF})_3$ in THF. $\text{Sm}[\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{PPh}_2]_2$ is monomeric with the Sm atom nine-coordinated by three identical diphosphenomethanide ligands (Fig. 7). The Sm–C and Sm–P distances range from 2.720(9) to 2.787(9) Å and from 2.818(3) to 2.903 Å respectively.

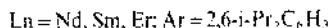
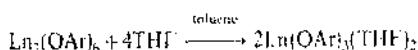
Fig. 7. Molecular structure of $\text{Sm}[\eta^1\text{-Ph}_2\text{PC(=O)H(PPH}_2\text{)}]_2$.

2.1.3. Alkoxides and aryloxides

Barnhart et al. [11] reported the synthesis, properties, and X-ray structures of several lanthanide arene-bridged aryloxide dimers. The reaction of 2,6-diisopropylphenol with the monomeric amides $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ ($\text{Ln} = \text{Nd, Sm, Er}$) in toluene under reflux gave the tris(aryloxide) complexes $\text{Ln}_2(\text{O-2,6-i-Pr}_2\text{C}_6\text{H}_3)_6$.

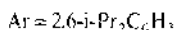
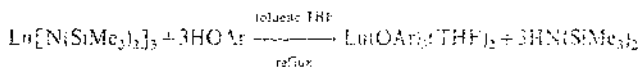


The addition of a Lewis base such as THF to a benzene solution of $\text{Ln}_2(\text{OAr})_6$ led to the cleavage of the dimeric unit and formation of monomeric THF bis-adducts $\text{Ln}(\text{O-2,6-i-Pr}_2\text{C}_6\text{H}_3)_3(\text{THF})_2$.

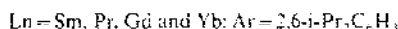
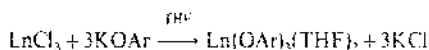


The bis(THF) adduct of lutetium $\text{Lu}(\text{O-2,6-i-Pr}_2\text{C}_6\text{H}_3)_3(\text{THF})_2$ was prepared by the interaction of $\text{Lu}[\text{N}(\text{SiMe}_3)_2]_3$ with three equivalents of 2,6-diisopropylphenol

in refluxing toluene in the presence of THF.



The reaction of anhydrous LnCl_3 ($\text{Ln} = \text{Sm}, \text{Pr}, \text{Gd}$ and Yb) with $\text{KO-2,6-i-Pr}_2\text{C}_6\text{H}_3$ in THF also gave the bis(THF) adducts $\text{Ln}(\text{O-2,6-i-Pr}_2\text{C}_6\text{H}_3)_3(\text{THF})_2$:



Six lanthanide complexes containing 2,6-diisopropylphenoxide ligation have been examined by single-crystal X-ray diffraction techniques: $\text{Ln}_2(\text{OAr})_6$ ($\text{Ln} = \text{Nd}, \text{Sm}$) and $\text{Ln}(\text{OAr})_3(\text{THF})_2$ ($\text{Ln} = \text{Er}, \text{Lu}, \text{Pr}, \text{Gd}$) ($\text{Ar} = 2,6\text{-i-Pr}_2\text{C}_6\text{H}_3$). The molecules of $\text{Ln}_2(\text{OAr})_6$ contain centrosymmetric, dimeric $\text{Ln}_2(\text{O-2,6-i-Pr}_2\text{C}_6\text{H}_3)_6$ units bridged by intermolecular $\eta^6\text{-}\pi\text{-arene}$ interactions of a unique aryloxy ligand (Fig. 8). The coordination geometry of each lanthanide atom approximates a three-legged piano stool. Each metal is bound to three terminal aryloxy oxygen atoms, and six carbon atoms of one of the aromatic rings of an aryloxy ligand are bound to the symmetry-related metal atom in the dimeric unit.

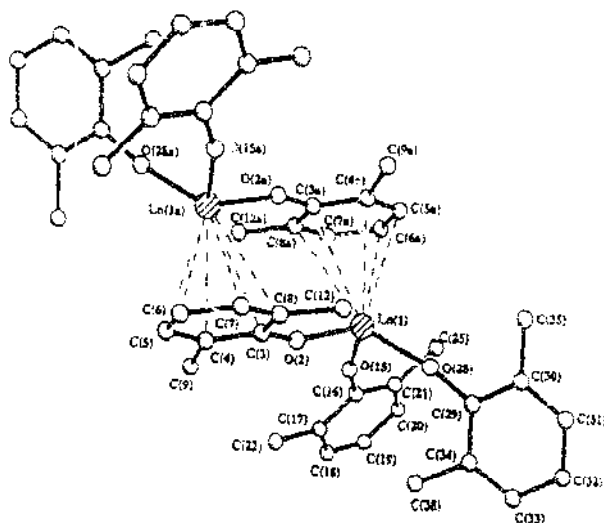
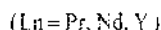
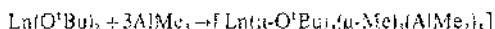


Fig. 8. Molecular structure of $\text{Ln}_2(\text{OAr})_6$ ($\text{Ln} = \text{Nd}, \text{Sm}$)

Previously known 4f-element- π -arene complexes display the three basic structural types exemplified by $[(\eta\text{-arene})\text{Ln}(\text{AlCl}_2)_3]_2$ (I), $\text{Yb}(\text{O}-2,6\text{-Ph}_2\text{C}_6\text{H}_3)_3$ (II) and $(\eta\text{-arene})_2\text{Gd}$ (III) (Fig. 9). The π -arene-dimers $\text{Ln}_2(\text{OAr})_6$ ($\text{Ln} = \text{Nd}, \text{Sm}$) represent a new structural type for 4f-element- π -arene complexes (IV).

The four bisadducts $\text{Ln}(\text{O}-2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)_2(\text{THF})_2$ ($\text{Ln} = \text{Er}, \text{Lu}, \text{Pr}, \text{Gd}$) are isostructural. The molecular structure consists of a lanthanide metal centre coordinated in a distorted trigonal bipyramidal fashion by three equatorial aryloxide and two axial THF ligands (Fig. 10).

Biagini et al. [12] described a series of new mixed-bridged alkyl-alkoxy lanthanide complexes. The complexes $[\text{Ln}(\mu\text{-O}^t\text{Bu})_3(\mu\text{-Me})_3(\text{AlMe}_2)_3]$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Y}$) were obtained from the reaction of AlMe_3 with $\text{Ln}(\text{O}^t\text{Bu})_3$ in toluene.



The complex $[\text{Nd}(\mu\text{-O}^t\text{Bu})_3(\mu\text{-Me})_3(\text{AlMe}_2)_3]$ was characterized by single-crystal X-ray diffraction. In the structure (Fig. 11) the Nd atom is bonded to three crystallographically equivalent moieties $(\mu\text{-O}^t\text{Bu})$, $(\mu\text{-Me})$, (AlMe_2) giving rise to a highly

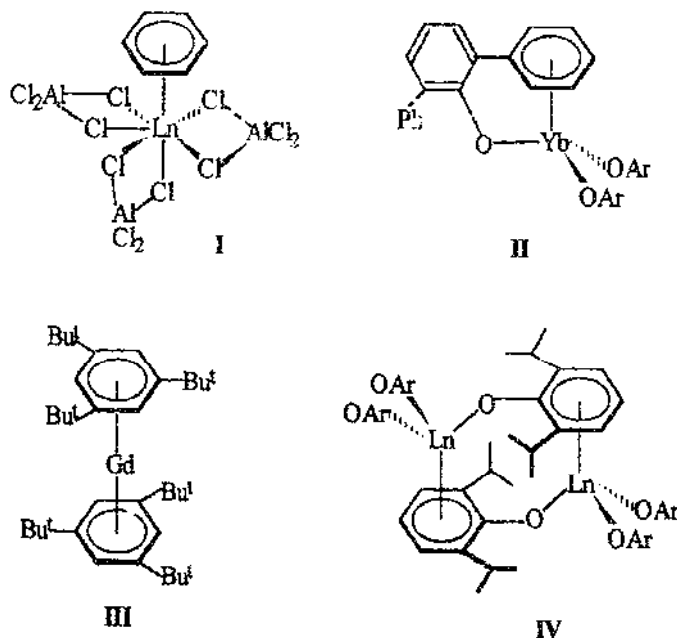


Fig. 9. Basic structural types of 4f-element- π -arene complexes.

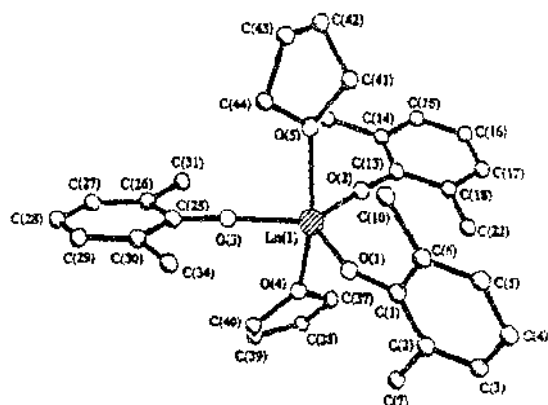


Fig. 10. Molecular structure of $\text{Ln}(\text{O}-2,6\text{-di-Pr}_2\text{C}_6\text{H}_3)_2 \cdot \text{THF}_{1/2}$ ($\text{Ln} = \text{Er}$, Lu, Pr, Gd).

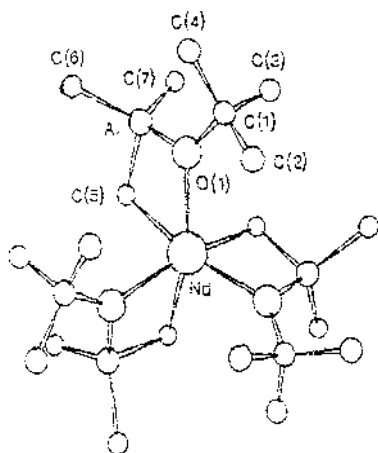
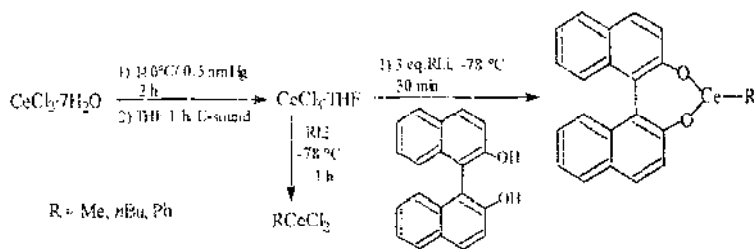


Fig. 11. Molecular structure of $[\text{Nd}(\mu\text{-O'Bu})(\mu\text{-Me})(\text{AlMe}_2)_2]$.

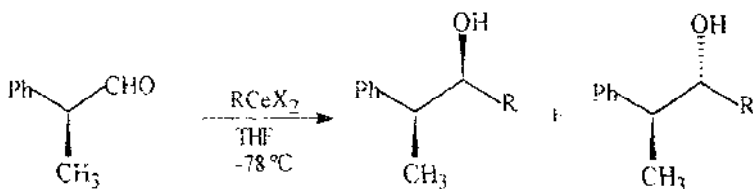
distorted octahedral coordination. The distances $\text{Nd}-\text{O}(1)$ and $\text{Nd}-\text{C}(5)$ are 2.303(7) Å and 2.764(11) Å respectively.

Greeves et al. [13] investigated the diastereoselective addition of organocerium reagents to aldehydes and cyclic ketones. The organocerium reagents were prepared according to Scheme 4.

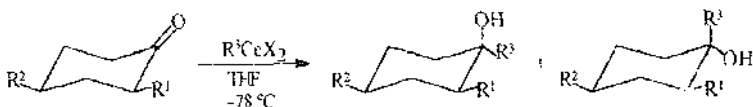
The reagents were used in the reaction with the Cram's original aldehyde (Scheme 5) and with various cyclohexanones (Scheme 6).



Scheme 4.



Scheme 5.



Scheme 6.

The diastereoselectivity of these chiral dialkoxo- and diaryloxyorgano cerium reagents in the reactions was compared with that of conventional organocerium reagents.

2.1.4. Fullerenes

Capp et al. [14] reported an improved high-pressure toluene extraction of the lanthanum-containing fullerenes $\text{La}@\text{C}_n$ for even n from 74 to 90. $\text{La}@\text{C}_n$ was coaxed from the prewashed soot with a high-pressure, high-temperature extraction technique which could be called a 'bomb' extraction. Analysis of the toluene extract of the lanthanum bomb soot was accomplished by laser desorption Fourier transform ion cyclotron resonance mass spectrometry (LD/FT/ICR/MS). The positive ion mass spectrum was dominated by $\text{La}@\text{C}_{82}^+$ but also showed other $\text{La}@\text{C}_n^+$, including $n=74, 76, 78, 80, 84, 86, 88$ and 90. Analysis of peak intensities suggested that, by mass, the material was 20% $\text{La}@\text{C}_n$ and 11% $\text{La}@\text{C}_{82}$. The average size of an empty fullerene in the sample was 100.9 carbon atoms.

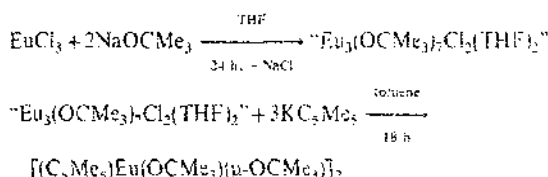
2.2. Cyclopentadienyl complexes

2.2.1. Mono(cyclopentadienyl) complexes

Zhou et al. [15] reported the synthesis and structure of $\text{CpYCl}_2(\text{THF})_3$ ($\text{Cp} = \text{C}_5\text{H}_5$). The complex was obtained by reaction of YCl_3 with one equivalent of sodium cyclopentadienyl in THF. The complex $\text{CpYCl}_2(\text{THF})_3$ is monomeric with the central metal Y coordinated by one Cp, three oxygen atoms from three THF molecules, and two chlorine atoms to form a distorted octahedral geometry. The average Y–C(Cp) bond is 2.65(3) Å. The Y–Cl bond lengths are 2.630(8) Å and 2.625(7) Å respectively. The complex is isostructural with known organolanthanide derivatives of Nd, Gd, Ho, Er and Yb.

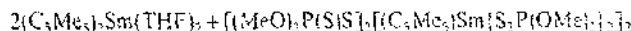
Depaoli et al. [16] reported the crystal structure of $\text{CpEuCl}_2(\text{THF})_3$ (Fig. 12). The structure has a nonaxial symmetry about the Eu(III) ion in agreement with the observed asymmetry parameter of 0.46.

Evans et al. [17] published the synthesis and characterization of the pentamethylcyclopentadienyl complex of trivalent europium $\{(\text{C}_5\text{Me}_5)_2\text{Eu}(\text{OCMe}_3)_2(\mu\text{-OCMe}_3)_2\}_2$.



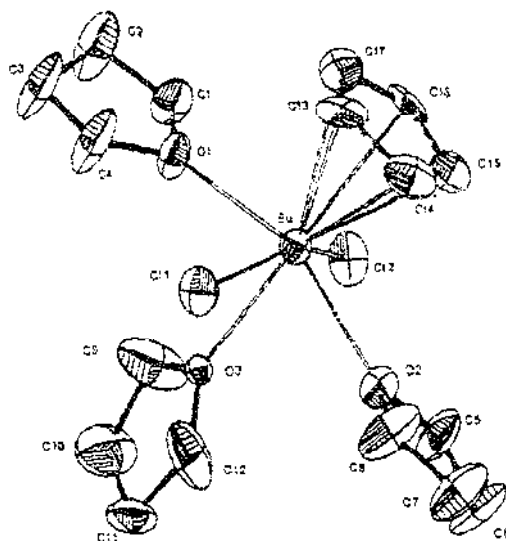
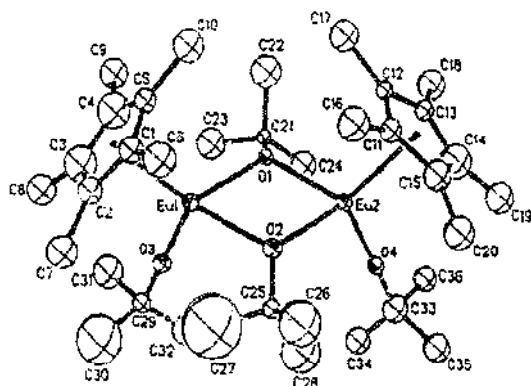
The complex is dimeric (Fig. 13). The plane formed by two europium atoms and the two oxygen atoms of the bridging ligands is perpendicular to the plane formed by the two C_5Me_5 ring centroids and the oxygen atoms from the terminal OCMe_3 groups.

Edelmann and coworkers [18] reported the synthesis and structure of the $\{(\text{C}_5\text{Me}_5)_2\text{Sm}\{\text{S}_2\text{P}(\text{OMe})_2\}_2\}_2$. The complex was obtained by the reaction of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ with the $\{(\text{MeO})_2\text{P}(\text{SiS})_2\}_2$.

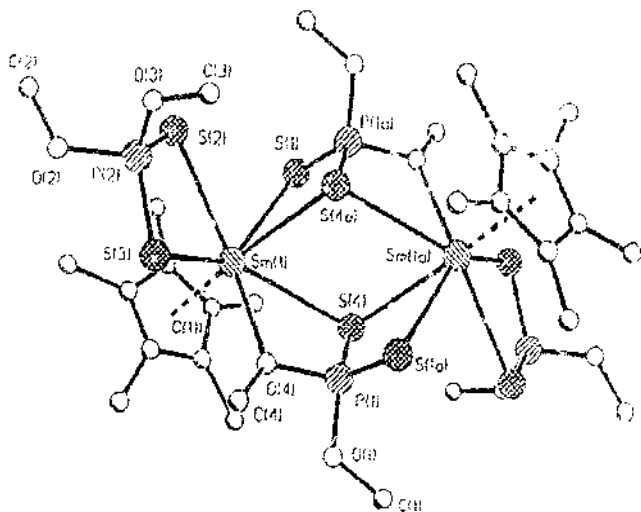
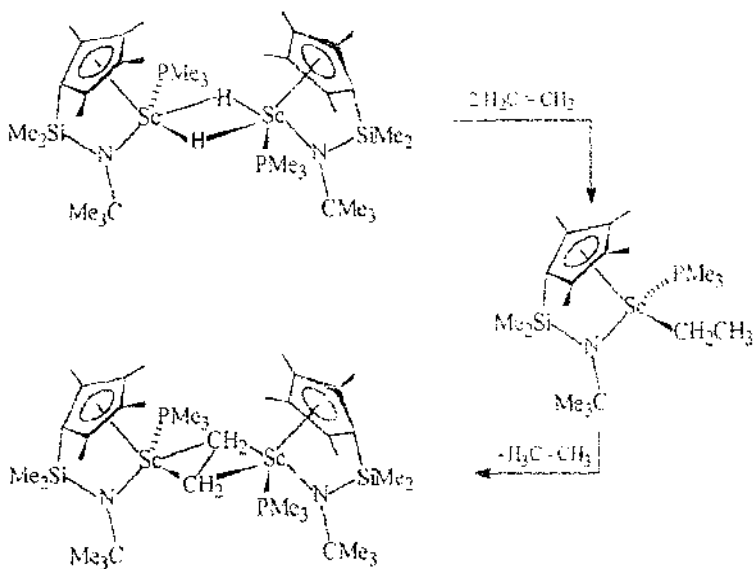


The structure of the complex is dimeric with triply bridging *O,O'*-dimethyldithiophosphate ligands in which one of the methoxy groups is involved in the coordination to samarium (Fig. 14). The samarium atom has a formal coordination number of nine. The Sm–S bond distances range from 290.9(2) to 304.7(2) Å.

Bercaw and coworkers [19] investigated the model Ziegler–Natta α -olefin polymerization catalysts derived from $\{(\eta^5\text{-C}_5\text{Me}_5)\text{SiMe}_2(\eta^1\text{-NCMe}_3)(\text{PMe}_3)\text{Sc}(\mu_2\text{-H})\}_2$ and $\{(\eta^5\text{-C}_5\text{Me}_5)\text{SiMe}_2(\eta^1\text{-NCMe}_3)\text{Sc}(\mu_2\text{-CH}_2\text{CH}_2\text{CH}_3)\}_2$. The scandium hydride complex $\{(\text{Cp}^*\text{SiNR})(\text{PMe}_3)\text{Sc}(\mu_2\text{-H})\}_2$ ($(\text{Cp}^*\text{SiNR}) = (\eta^5\text{-C}_5\text{Me}_5)\text{SiMe}_2(\eta^1\text{-NCMe}_3)$) was obtained by hydrogenation of $(\text{Cp}^*\text{SiNR})\text{ScCH}(\text{SiMe}_3)_2$ in the presence of PMe_3 . The reaction (Scheme 7) of the complex with two equivalents of ethylene leads to the ethylene-bridged scandium

Fig. 12. Molecular structure of $\text{CpEuCl}_3(\text{THF})_3$.Fig. 13. Molecular structure of $[(\text{C}_4\text{Me}_5)\text{Eu}(\text{OCMe}_2)_2(\mu\text{-O-CMe}_2)]_2$.

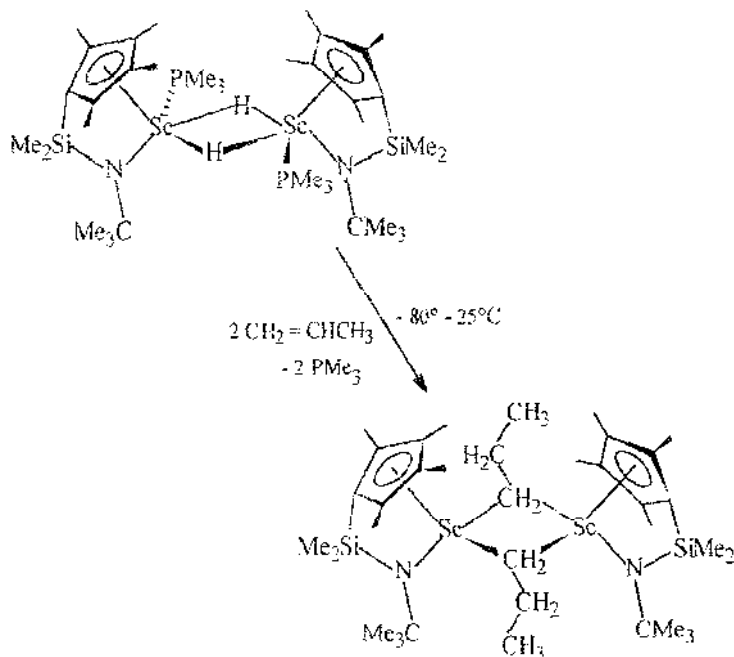
dimer $(\mu, \eta^2, \eta^2\text{-C}_2\text{H}_4)[(\text{Cp}^*\text{SiNR})(\text{PMe}_3)\text{Sc}]_2$. In the structure of $(\mu, \eta^2, \eta^2\text{-C}_2\text{H}_4)[(\text{Cp}^*\text{SiNR})(\text{PMe}_3)\text{Sc}]_2$ (Fig. 15) the $\text{Sc}_2(\mu, \eta^2, \eta^2\text{-C}_2\text{H}_4)$ core is the most unusual feature. The C-C bond length of the ethylene bridge (1.433(12) Å) is

Fig. 14. Molecular structure of $[Cp_2(Me_3Si)_2Pt_2P(OMe)_2]_2$.

Scheme 7.

intermediate between that of a single and double C-C bond, comparable with the bond lengths observed in transition metal olefin complexes.

Reaction of $[(Cp^*SiNR)(PMe_3)Sc(\mu_2-H)]_2$ with one equivalent of propylene per scandium gave the PMe_3 -free scandium propyl derivative $(\mu-CH_2CH_2CH_3)_2[(Cp^*SiNR)Sc]_2$ (Scheme 8).



Scheme 8.

According to the X-ray structure analysis, the complex $(\mu-CH_2CH_2CH_3)_2[(Cp^*SiNR)Sc]_2$ is a dimer with a three-centre, two-electron propyl-bridged core, $[Sc_2(\mu-CH_2CH_2CH_3)]$. The Sc-C-Sc bridge angle of $89.4(2)^\circ$ is considerably more acute than the corresponding Sc-H-Sc angle (114.1°) in the $[(Cp^*SiNR)(PMe_3)Sc(\mu_2-H)]_2$. Bulkier alkyl ligands such as 2-methylpentyl and isobutyl do not form stable μ -alkyl bridges, as they readily and more competitively retain PMe_3 in their coordination sphere. Reaction of $[(Cp^*SiNR)(PMe_3)Sc(\mu_2-H)]_2$ with styrene led to a double-insertion product (Scheme 9) arising from sequential 1,2- and 2,1-styrene insertion.

The dimeric PMe_3 -free alkyl complexes such as $(\mu-CH_2CH_2CH_3)_2[(Cp^*SiNR)Sc]_2$ are considerably more active catalyst precursors for α -olefin polymerization than the $[(Cp^*SiNR)(PMe_3)Sc(\mu_2-H)]_2$.

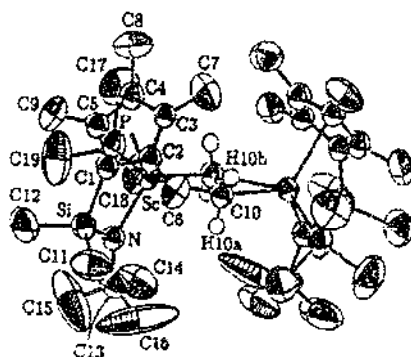
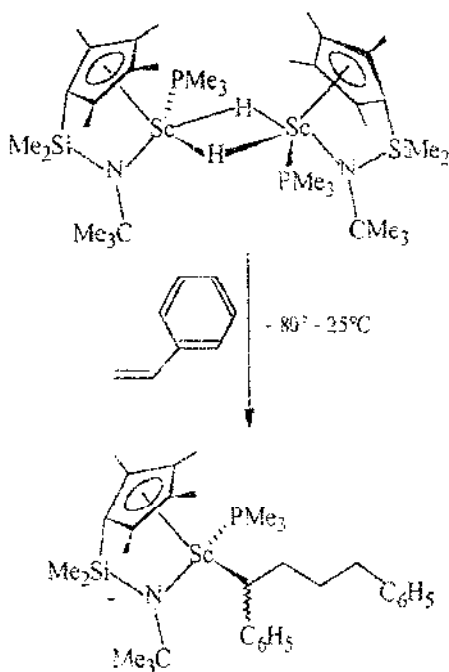
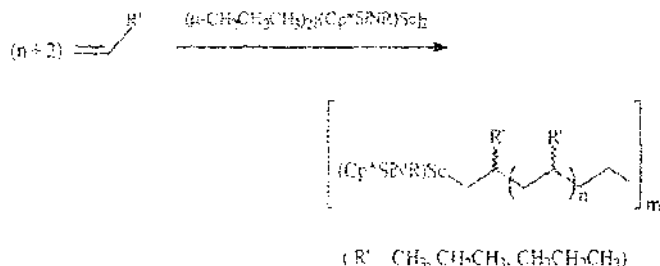


Fig. 15. Molecular structure of $(\eta, \eta^3, \eta^2\text{-C}_7\text{H}_9)(\text{Cp}^*\text{SiNRHPhMe}_3\text{SC})_2$.

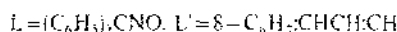
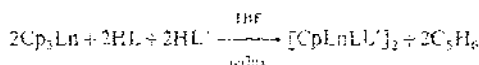


Scheme 9



The kinetic analysis of 1-pentene polymerization catalysed by the above mentioned complexes has been discussed.

Shen et al. [20] reported the synthesis of new organolanthanide complexes $[\text{Cp}_3\text{LnLL}']_2$ (Cp = C₅H₅; Ln = Gd, Tb, Dy, Ho, Er, Tm, Yb; HL = benzophenoneoxime; HL' = 8-quinolinol) from Cp₃Ln in THF.

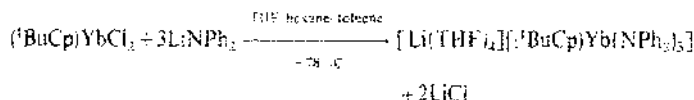


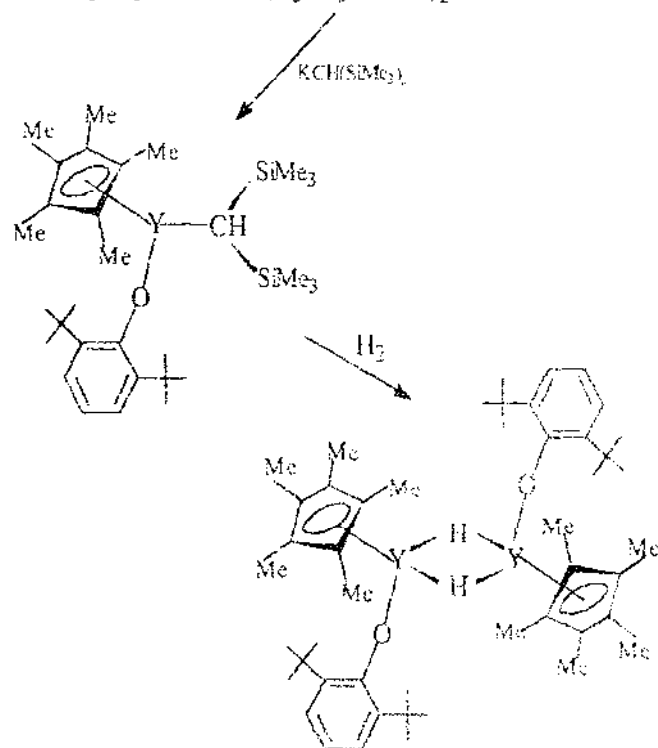
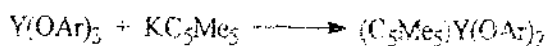
The complexes have been characterized by elemental analyses, IR and MS spectroscopy. According to the data the complexes were considered to be oxo-bridged dimers.

Schaverien [21,22] published the synthesis, reactivity of, and olefin polymerization by the μ -hydride- μ -alkyl compounds $[\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})\text{Bu}_3]_2(\mu\text{-H})(\mu\text{-alkyl})$. The hydrogenation of $\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})\text{CH}(\text{SiMe}_3)_2$ in hexane under 10 bar of H₂ yielded $[\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})(\mu\text{-H})]_2$ (Scheme 10). The latter reacted with terminal olefins $\text{H}_2\text{C}=\text{CHR}$ (R = H, Me, Et, *n*-Bu) to form the μ -*n*-alkyl complexes *trans*- $[\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})]_2(\mu\text{-H})(\mu\text{-CH}_2\text{CH}_2\text{R})$ (Scheme 11). The μ -compounds polymerize α -olefins and dienes. The reaction of $[\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})(\mu\text{-H})]_2$ with the terminal acetylene $\text{HC}\equiv\text{CSiMe}_3$ led to the acetylide derivative $[\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})]_2(\mu\text{-H})(\mu\text{-C}\equiv\text{CSiMe}_3)$. Further treatment with excess of $\text{HC}\equiv\text{CSiMe}_3$ in the presence of THF gave the monomeric acetylide $\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})\text{C}\equiv\text{CSiMe}_3(\text{THF})_2$ (Scheme 12).

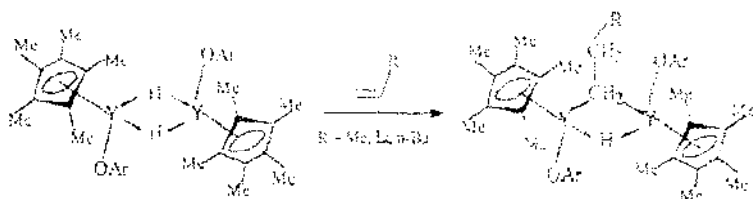
The methyl derivatives $[\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})(\mu\text{-Me})]_2$ and $[\text{Y}(\text{C}_5\text{Me}_5)(\mu\text{-Me})_2]_2$ were prepared by the reactions of $\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})_2$ with MeLi (one equivalent and 1.6 equivalents respectively). Cleavage of the derivatives $[\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})(\mu\text{-Me})]_2$ by THF led to $\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})(\text{Me})(\text{THF})_2$.

The synthesis and crystal structure of $[\text{Li}(\text{THF})_4][(\text{t-BuCp})\text{Yb}(\text{NPh}_2)_3]$ were described by Mao et al. [23]. The complex was synthesized from the *t*-butylcyclopentadienyl ytterbium dichloride and three equivalents of LiNPh₂.



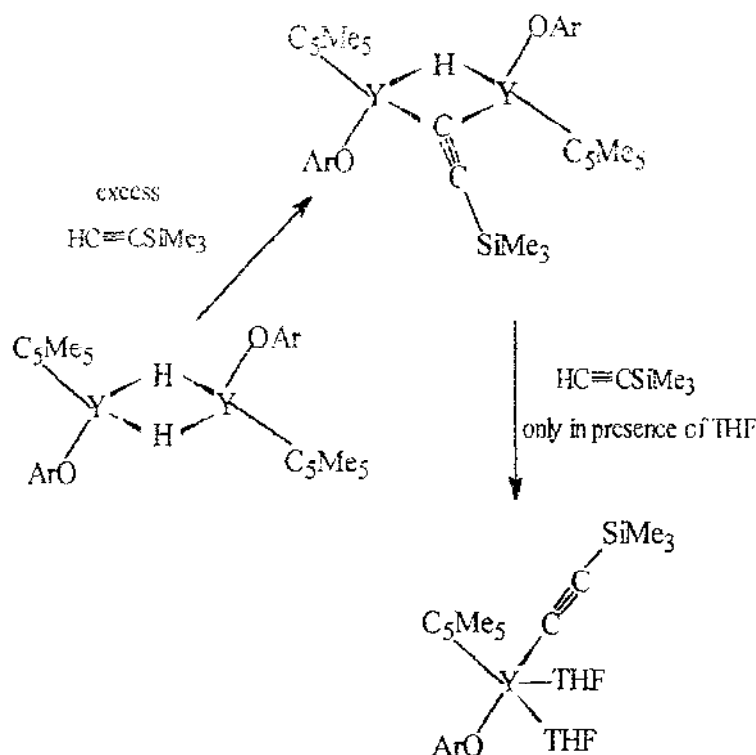


Scheme III



Scheme IV

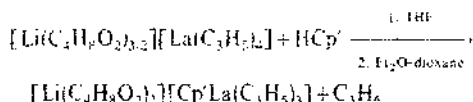
The complex consists of isolated ion pairs $[Li^+THF]_2^{+}$ and $[(^tBu-Cp)Yb(NPh)_3]^{-}$ (Fig. 16). In the anion, the central Yb atom is surrounded by one tBuCp and three diphenylamino groups to form a distorted tetrahedron. The



Scheme 12.

average Yb-N distance is 2.264(9) Å. In the cation the lithium is coordinated by four oxygen atoms from four THF molecules, forming a tetrahedral structure with average Li-O distances of 1.935(31) Å.

Taube and Windisch [24] reported the preparation of the monocyclopentadienyl tris(allyl)lanthanate(III) complexes $[\text{Li}(\text{C}_4\text{H}_8\text{O}_2)][\eta^5\text{-Cp}^*\text{La}(\eta^3\text{-C}_3\text{H}_5)_3]$ ($\text{Cp}^* = \text{C}_5\text{H}_5$, C_5Me_5 , C_9H_7 , C_{13}H_9) by partial protolysis of the $[\text{Li}(\text{C}_4\text{H}_8\text{O}_2)_{1.2}][\text{La}(\eta^3\text{-C}_3\text{H}_5)_3]$ with one equivalent of the corresponding HCp^*



2.2.2. Biscyclopentadienyl complexes

Shen and Xie [25] prepared seven new organolanthanide complexes $(\text{Cp}_2\text{Ln}_2\text{L}_2\text{L}_2)$ ($\text{Ln} = \text{Gd}$, Tb, Dy, Ho, Er, Tm, Yb; $\text{Cp} = \text{C}_5\text{H}_5$) from Cp_2Ln and

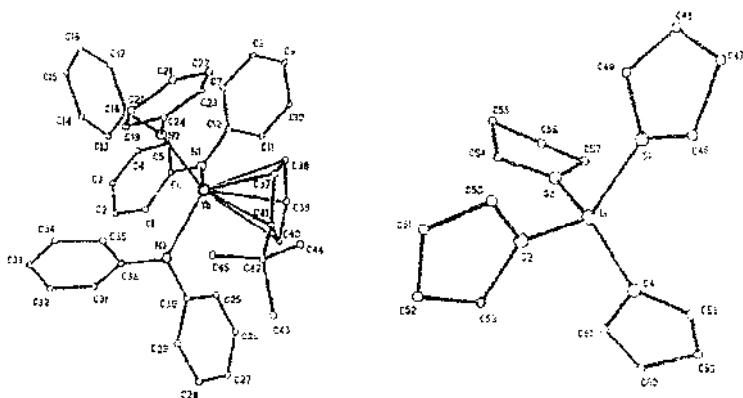
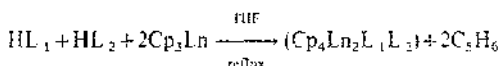


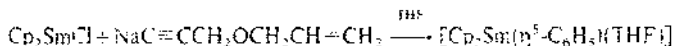
Fig. 16. Molecular structure of $[\text{LiOTf}]_2[(t\text{BuCp})\text{Yb}(\text{NPh})_2]$.

benzophenoneoxime (HL_1) or cyclohexanoneoxime (HL_2) in THF. The compounds were characterized by elemental analyses, IR and MS spectra. According to the data these complexes were found to be dimers with oxo-bridged bonds.



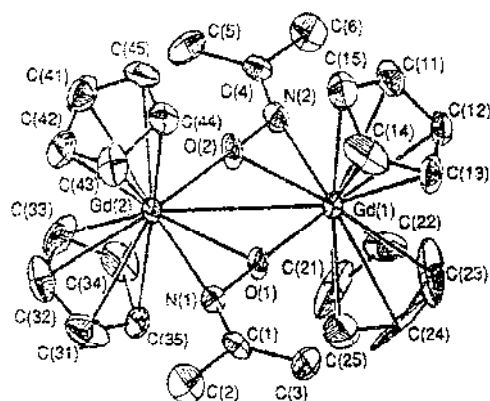
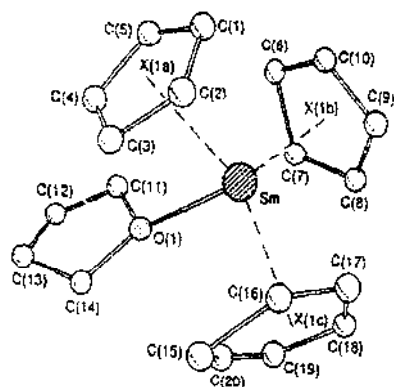
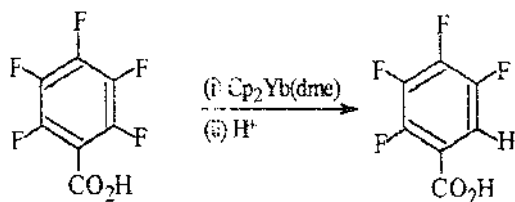
Wu et al. [26] published the synthesis and X-ray crystal structure of bis[acetoneoximatobis(cyclopentadienyl)gadolinium] $[\text{Cp}_2\text{Gd}(\mu\text{-}\eta^2\text{-ONCMe}_2)]_2$. The complex was obtained by the reaction of Cp_2Gd with acetone oxime (HONCMe_2) in THF. According to the X-ray structure the molecule is asymmetric with the O-N fragment of the oximate-group acting as both a bridging and side-on donating ligand (Fig. 17). The Gd atom has a distorted trigonal-bipyramidal geometry with oxygen and nitrogen atoms in an axial position. The Gd_2N_2 unit forms a near-parallelogram which contains the rhombic quadrilateral unit Gd_2O_2 . The average Gd-C(Cp) distance is 2.68(2) Å, the Gd-O bond distances range from 2.25(1) to 2.38(1) Å.

Wang et al. [27] reported the synthesis of $[\text{Cp}_2\text{Sm}(\eta^5\text{-C}_6\text{H}_5)(\text{THF})]$ by the reaction of Cp_2SmCl with sodium allyloxypropylylide in THF.

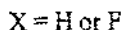
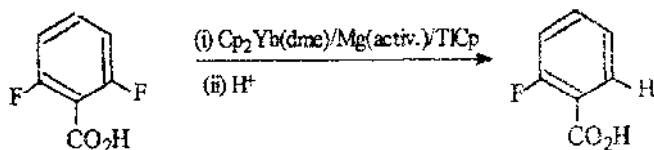


According to the X-ray structure the Sm atom in the complex $[\text{Cp}_2\text{Sm}(\eta^5\text{-C}_6\text{H}_5)(\text{THF})]$ has a tetrahedral arrangement (Fig. 18). The ligand $\eta^5\text{-C}_6\text{H}_5$ is the anionic form of cyclohexen-4-yne. The Sm-X(1c) distance is 2.590 Å (X(1c) represents the plane formed by C(16), C(17), C(18), C(19) and C(20)).

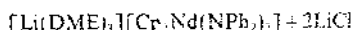
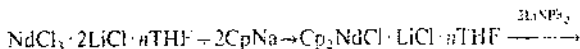
Deacon et al. [28] investigated the regiospecific replacement of fluorine by hydrogen in an aromatic ring induced by $\text{Yb}(\text{Cp}_2\text{dme})$. The reaction of pentafluorobenzoic acid with $\text{Cp}_2\text{Yb}(\text{dme})$ gave, after hydrolysis, the 2,3,4,5-tetrafluorobenzoic acid.

Fig. 17. Molecular structure of $[\text{Cp}_2\text{Gd}(\mu\text{-}\eta^2\text{-ONCMe}_3)_2]$.Fig. 18. Molecular structure of $[\text{Cp}_2\text{Sm}(\eta^5\text{-C}_5\text{H}_5)(\text{THF})]$.

The effects of coreductants Zn, Yb, Mg and activated (by I_2) magnesium were investigated. With activated magnesium as coreductant, near quantitative yields were obtained. The defluorination of *o*-fluorobenzoic and 2,6-difluorobenzoic acid by reaction with $YbCp_2(dme)$, activated magnesium and thallous cyclopentadienide have also been achieved.



Guan et al. [29] described the synthesis and crystal structure of a bis(cyclopentadienyl)amido complex of neodymium, $[Li(DME)_3][Cp_2Nd(NPh_2)_2]$. The complex was obtained by the reaction of $NdCl_3 \cdot 2LiCl \cdot nTHF$, $CpNa$ and $LiNPh_2$ in THF followed by recrystallization from DME.



According to the X-ray structure the complex consists of the anion $[Cp_2Nd(NPh_2)_2]^-$ and the cation $[Li(DME)_3]^+$ (Fig. 19). In the anion the Nd atom has a distorted tetrahedral arrangement. The average Nd-Cp distances are 2.783(8), 2.767(9) Å and the Nd-N distance is 2.428(7) Å.

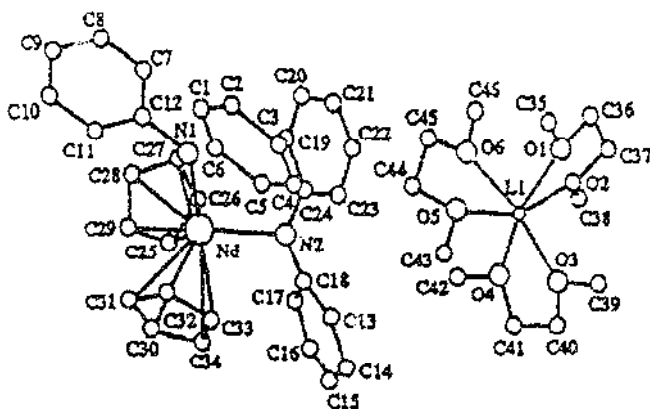
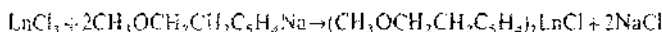


Fig. 19. Molecular structure of $[Li(DME)_3][Cp_2Nd(NPh_2)_2]$.

Qian et al. [30] published the synthesis and X-ray crystal structure of bis[(2-methoxyethyl)cyclopentadienyl] rare earth metal chlorides. The series of bis[(2-methoxyethyl)cyclopentadienyl] lanthanide chlorides $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_5)_2\text{LnCl}$ ($\text{Ln} = \text{La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb, Lu, Y}$) were obtained by the reaction of the corresponding LnCl_3 with two equivalents of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{Na}$.



All these complexes have been characterized by elemental analyses, MS, IR and NMR spectra. The complexes $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_5)_2\text{LnCl}$ ($\text{Ln} = \text{La, Dy, Yb}$) have also been studied by X-ray diffraction analyses. The structure of $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_5)_2\text{LaCl}$ is dimeric with two chloride bridges (Fig. 20). Besides two cyclopentadienyl ligands and two chlorine atoms, each lanthanum atom is coordinated by two oxygen atoms from the $\text{CH}_3\text{OCH}_2\text{CH}_2$ -groups. The formal coordination number of La is ten and the metal atom has a distorted octahedral arrangement. In contrast, the structures of the Dy and Yb analogues are monomeric. The coordination of the Ln atoms by two Cp-rings, one chlorine atom and two oxygen atoms form distorted trigonal bipyramids. Thus the structures of the complexes depend on the radius of the lanthanide ions.

Qian et al. [31] also reported the syntheses and X-ray crystal structures of bis[(2-methoxyethyl)cyclopentadienyl] rare earth iodides $(\text{MeO}-$

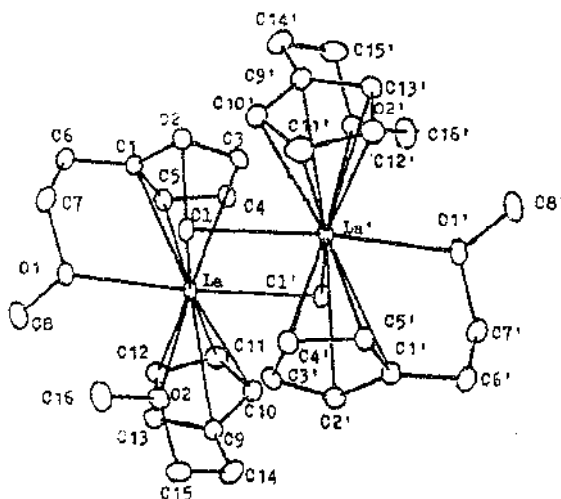
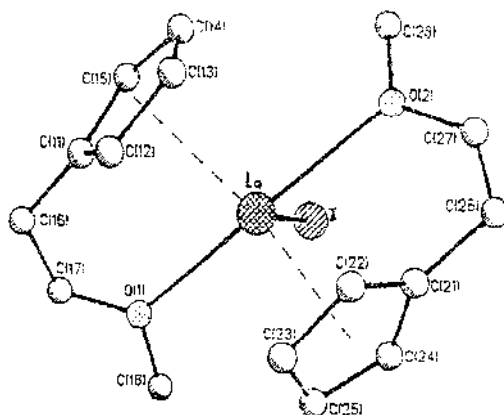
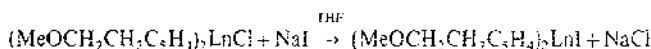


Fig. 20. Molecular structure of $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_5)_2\text{LaCl}$.

Fig. 21. Molecular structure of $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LaI}$.

$\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnI}$ ($\text{Ln} = \text{La}$ or Y). The complexes were obtained according to equation

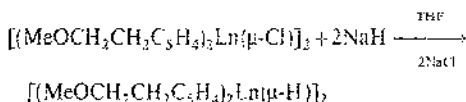


$\text{Ln} = \text{La}, \text{Y}$

The lanthanum and yttrium complexes are isostructural. In the molecules (Fig. 21) the Ln atom is coordinated by two cyclopentadienyl ligands, one iodine atom and two oxygen atoms. The structure has a trigonal bipyramidal coordination geometry. The most striking feature of these compounds is the formation of the intramolecular coordination bond from the oxygen atom of the ligand to the central rare earth metal.

Zhang et al. [32] prepared the complexes $(\text{C}_4\text{H}_7\text{OCH}_2\text{C}_5\text{H}_4)_2\text{LnCl}$ ($\text{Ln} = \text{Nd}, \text{Gd}, \text{Dy}, \text{Yb}$) from the appropriate lanthanide trichlorides and sodium tetrahydrofurfurylcyclopentadiene in THF. The dysprosium derivative $(\text{C}_4\text{H}_7\text{OCH}_2\text{C}_5\text{H}_4)_2\text{DyCl}$ was characterized by X-ray crystallography. The structure has C_2 symmetry about the Dy–Cl axis. The central Dy atom is coordinated by two Cp, two oxygens of tetrahydrofurfuryl and one chlorine to form a distorted trigonal bipyramid. The two oxygen atoms are at both apices, and chlorine, dysprosium and the two Cp-centroids form the equatorial plane.

Deng et al. [33] published the synthesis, spectroscopic and X-ray crystallographic characterization of new early organolanthanide, organoyttrium hydride and organo-holmium hydroxide complexes. Bis(2-methoxyethylcyclopentadienyl) hydride complexes of the type $\{(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Ln}(\mu\text{-H})\}_2$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Ho}, \text{Y}$) were obtained by reaction of the corresponding halide precursors $\{(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Ln}(\mu\text{-Cl})\}_2$ with excess NaH in THF.



According to an X-ray structure determination and IR data the complex $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-H})]_2$ is dimerized via hydrogen-bridges (Fig. 22). In the unit cell there are two dimers which are not identical, but in both dimers each Y atom is coordinated by two cyclopentadienyl ligands, one oxygen from one ether substituent-group and two hydrogen atoms. Thus each Y atom has a distorted trigonal bipyramidal coordination geometry (if the cyclopentadienyl rings are regarded as occupying a single polyhedral vertex). The average lengths of Y-C(Cp) bonds for the two dimers are 2.676, 2.674 Å and 2.674, 2.683 Å.

The product of hydrolysis $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Ho}(\mu\text{-OH})]_2$ of the holmium hydride was also obtained and structurally characterized. The complex forms a dimer with two hydroxyl-bridges. The Ho atom has a distorted trigonal-bipyramidal arrangement with the three oxygen atoms nearly lying in the equatorial plane. The

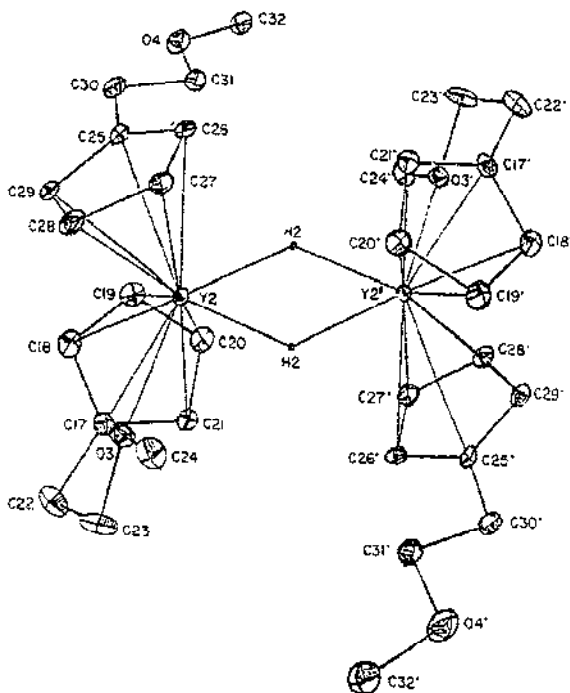
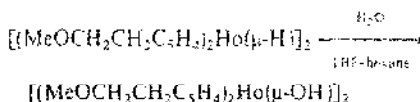
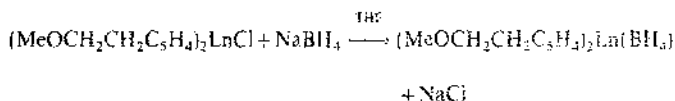


Fig. 22. Molecular structure of $[(\text{tMeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-H})]_2$.

average Ho-C(Cp) bonds lengths are 2.694 and 2.711 Å.



Deng et al. [34] also described the synthesis of five new bis[(2-methoxyethyl)cyclopentadienyl]lanthanide tetrahydroborates (Ln = La, Pr, Nd, Sm or Gd) from the corresponding $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_3\text{LnCl}$ and NaBH_4 .



Ln = La, Pr, Nd, Sm or Gd

The complexes have been characterized by elemental analyses, MS, ^1H NMR and IR spectra. The praseodymium and neodymium tetrahydroborate complexes have also been structurally characterized. Both complexes are monomeric (Fig. 23) with the metal ions coordinated by two Cp-rings, two $\text{MeOCH}_2\text{CH}_2$ - and one BH_4 -groups. Since the hydride ligands cannot be located, the coordination environment about the central metal was difficult to describe. The Pr-B and Nd-B distances are 2.757 Å and 2.664 Å respectively.

The same cyclopentadienyl ligand was used by Deng et al. [35] in the synthesis of organolanthanide complexes $[\text{Ln}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe})_2(\text{THF})][\text{Co}(\text{CO})_4]$ (Ln = Sm or Yb, thf = tetrahydrofuran). The complexes were obtained by the reaction of $[\text{Ln}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe})_2]$ with $\text{K}[\text{Co}(\text{CO})_4]$ in THF, or by the one-electron

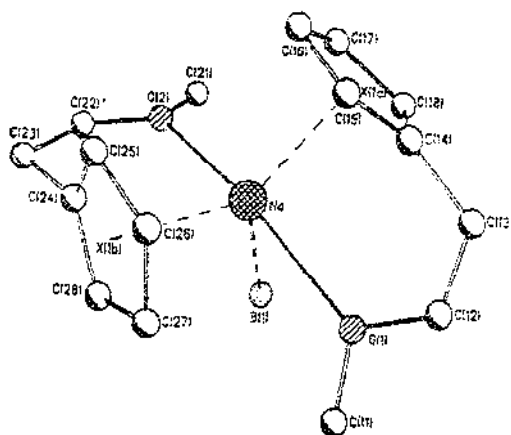


Fig. 23. Molecular structure of $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Nd}(\text{BH}_4)$.

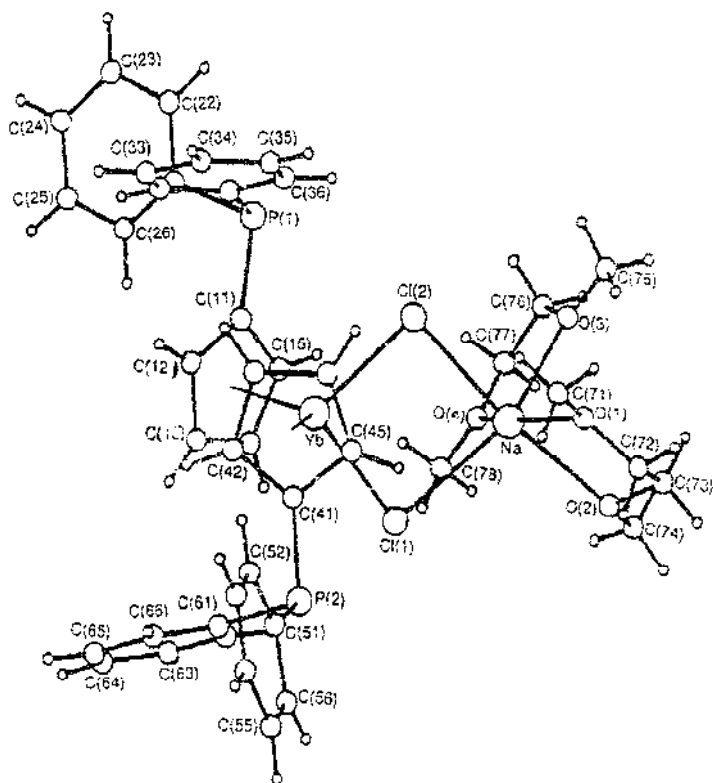
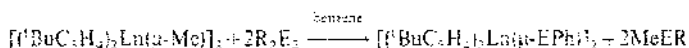


Fig. 25. Molecular structure of $[\eta\text{-C}_5\text{H}_5]_2\text{Pr}\eta^3\text{-C}_5\text{H}_4\text{H}_2 \cdot 8(p\text{-Cl})_2\text{Na}(\text{C}_2\text{H}_5\text{O})_2]$.

The crystal structures of $[\text{Yb}\{\eta\text{-C}_5\text{H}_5(\text{CMe}_2\text{CH}_2\text{C}_3\text{H}_4\text{N-2})\}_2]$ (Fig. 26) and $[\text{Yb}\{\eta\text{-C}_5\text{H}_5(\text{SiMe}_3)(\text{CMe}_2\text{C}_3\text{H}_4\text{N-2})\}_2]$ involve a distorted tetrahedral arrangement of the ligands around the metal with the coordination of both the pyridyl groups to the ytterbium.

Beletskaya et al. [38] investigated the reaction of alkyl derivatives of yttrium and lutetium with organic disulphides and diselenides. The series of dimeric bis(1-butylcyclopentadienyl)lanthanide organosulphides or organoselenides $[(^t\text{BuC}_5\text{H}_4)_2\text{Ln}(\mu\text{-EPh})_2]$ ($\text{Ln} = \text{Y}$, $\text{E} = \text{S}$, $\text{R} = \text{Ph}$, ^nBu , ^iBu or CH_3Ph ; $\text{Ln} = \text{Y}$, $\text{E} = \text{Se}$, $\text{R} = \text{Ph}$; $\text{Ln} = \text{Lu}$, $\text{E} = \text{S}$, $\text{R} = \text{Ph}$ or CH_3Ph ; $\text{Ln} = \text{Lu}$, $\text{E} = \text{Se}$, $\text{R} = \text{Ph}$) were obtained from the appropriate $[(^t\text{BuC}_5\text{H}_4)_2\text{Ln}(\mu\text{-Me})_2]$ and the corresponding organic disulphides RSSR or diphenylselenide PhSeSePh in benzene.



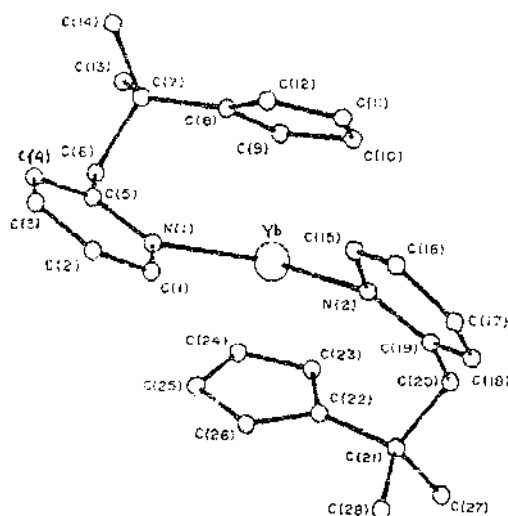


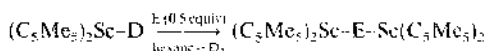
Fig. 26. Molecular structure of $[\text{Yb}(\eta\text{-C}_6\text{H}_4(\text{CMe}_3)\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2)]$.

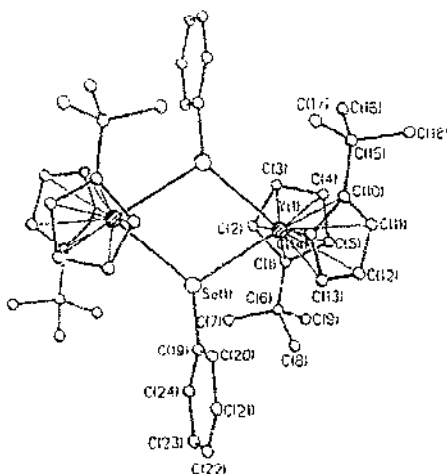
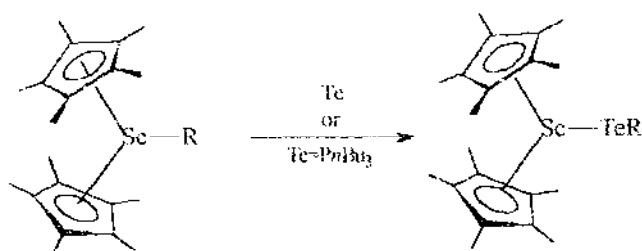
The structure of $[(\text{i-BuC}_5\text{H}_4)_2\text{Y}(\mu\text{-SePh})_2] \cdot \text{C}_6\text{H}_6$, consists of dimeric molecules with two bridging SePh groups (Fig. 27). The Y_2Se_2 unit is planar, with the Y–Se distances 2.915(1) and 2.912(1) Å. The coordination of the Y atoms is that of a distorted tetrahedron Cp_2YSe_2 . Each bridging Se atom is on top of a trigonal pyramid with the two Y atoms and the *ipso*-carbon atom of the phenyl group forming the base.

Piers et al. [39] published the synthesis and study of the permethylscandocene chalcogenolates and chalcogenides. Use of either elemental tellurium or $\text{Te}=\text{P}^n\text{Bu}_3$ allowed for incorporation of one tellurium atom to form the permethylscandocene tellurolate (Scheme 13). The insertion of elemental selenium into the Sc–C bond of $(\text{C}_5\text{Me}_5)_2\text{ScCH}_2\text{SiMe}_3$ gave the analogous selenolate $(\text{C}_5\text{Me}_5)_2\text{Sc}-\text{SeCH}_2\text{SiMe}_3$.

The tellurolates are monomeric, as inferred from the X-ray structure of $(\text{C}_5\text{Me}_5)_2\text{ScTeCH}_2\text{C}_6\text{H}_5$ (Fig. 28). The tellurolate ligand occupies the central position of the metallocene wedge. The ligand features an sp^2 -hybridized tellurium atom ($\text{Sc}-\text{Te}-\text{C}1 = 121.61(21)^\circ$), the Sc–Te bond distance is 2.8337(14) Å.

The reaction of tellurium or selenium with the deuteride $(\text{C}_5\text{Me}_5)_2\text{ScD}$ led to chalcogenide dimers $[(\text{C}_5\text{Me}_5)_2\text{Sc}]_2(\mu\text{-E})$ (E = Te, Se).



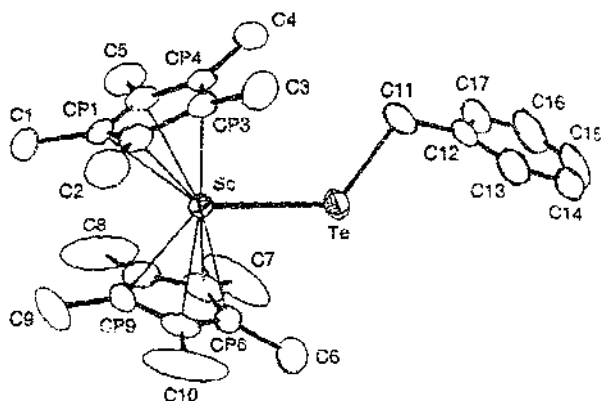
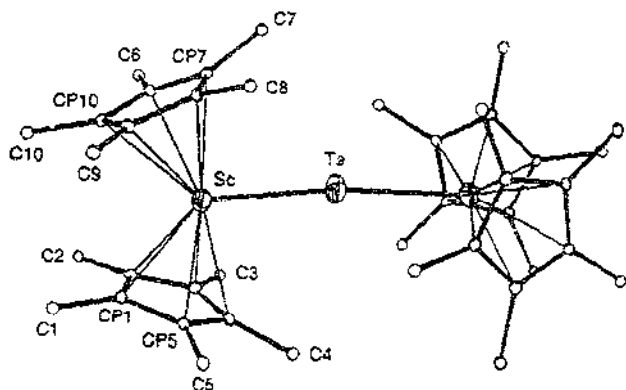
Fig. 27. Molecular structure of $[(^{18}\text{CrC}_3\text{H}_4)_2(\mu\text{-SePh})] \cdot \text{C}_6\text{H}_6$.

$\text{R} = -\text{CH}_2\text{SiMe}_3, -\text{CH}_2\text{C}_6\text{H}_5, \text{eryth. } \Delta\text{-CH}(\text{D})\text{CH}(\text{D})\text{-iC}_4\text{H}_9,$

$-\text{CH}_2\text{CH}(\text{D})(\text{CH}_2)_2\text{CH}=\text{CMe}_2, -\text{C}_6\text{H}_5, -\text{CH}_2(\text{c-C}_5\text{H}_9)$

Scheme 13.

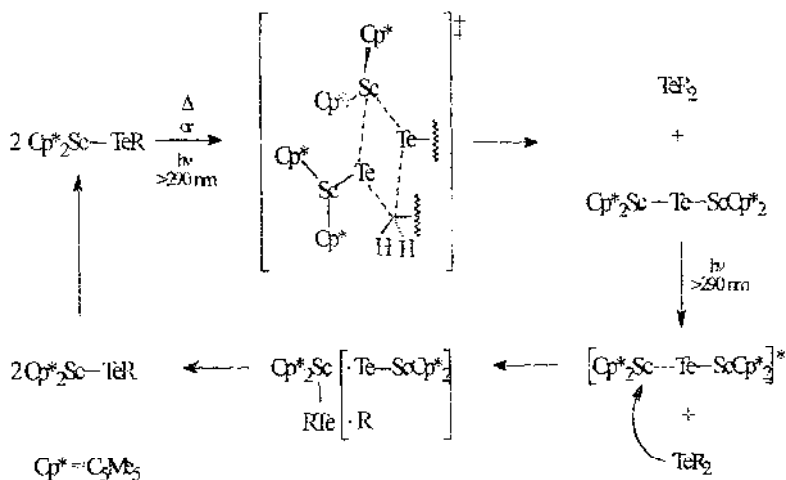
The telluride dimer $\{(\text{C}_5\text{Me}_5)_2\text{Sc}\}_2(\mu\text{-Te})$ was also obtained by the thermal or photochemical extrusion of TeR_2 from the tellurelates $(\text{C}_5\text{Me}_5)_2\text{ScTeR}$. According to X-ray structures the complexes $\{(\text{C}_5\text{Me}_5)_2\text{Sc}\}_2(\mu\text{-E})$ are μ -chalcogenide dimers with a slightly distorted D_{2d} symmetry (Fig. 29). The Sc-E bond distances are 2.5425(16) Å for $\text{E}=\text{Se}$ and 2.7528(12) Å for $\text{E}=\text{Te}$; the Sc-E-Sc bridges are nearly linear.

Fig. 28. Molecular structure of $(C_5Me_5)_2ScTeCH_3C_6H_5$.Fig. 29. Molecular structure of $[C_5Me_5]_2[Sc]_2(\mu-Te)$.

Thermal and photochemical interconversion of the permethylscandocene tellurolates have been studied with a variety of mechanistic experiments (Scheme 14). Experiments utilizing tellurolates indicated that both the thermal and photochemical eliminations of TeR_2 proceeded from a transition state without involving $Te-C$ bond cleavage, leading to $R^\cdot$ intermediates.

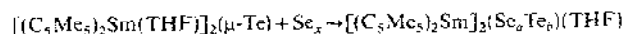
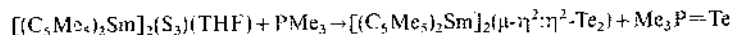
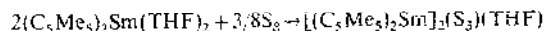
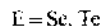
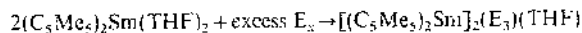
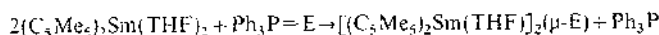
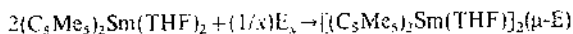
Using the 1,2- $[^2H_2]$ -ncohexyl stereochemical probes, Piers [40] has also demonstrated that the extrusion of TeR_2 from permethylscandocene tellurolates proceeds via a concerted transition state (Scheme 15).

Evans et al. [41] described the syntheses and study of the series of organosamar-

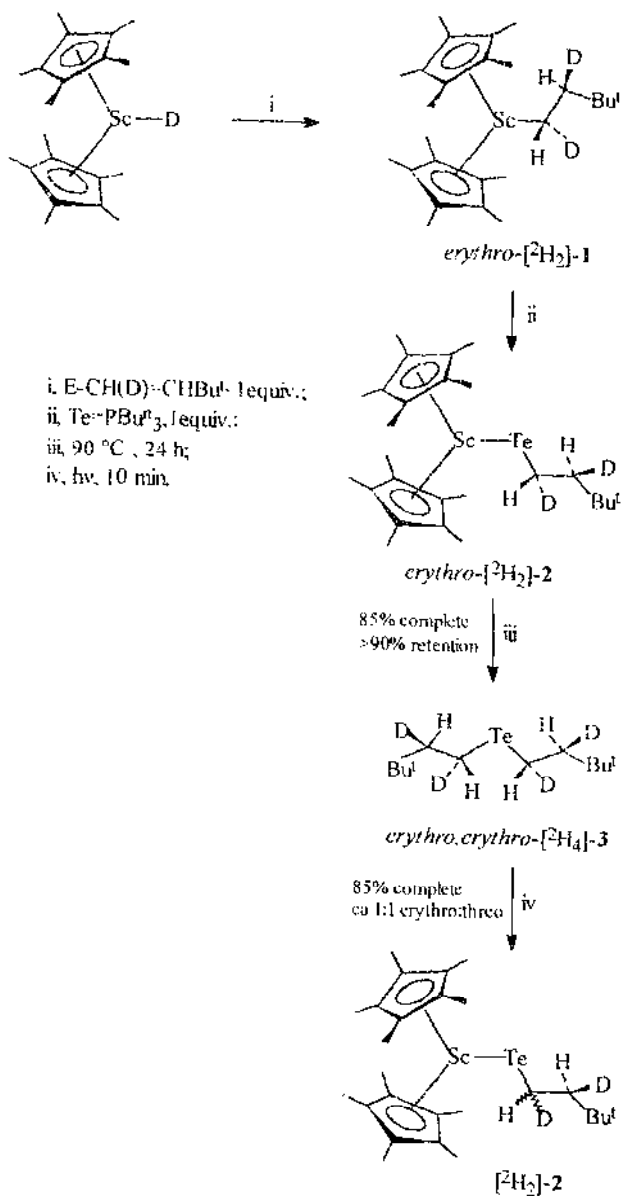


Scheme 14.

ium complexes with Group 16 element anions: [(C₅Me₅)₂Sm(THF)]₂(μ-E), [(C₅Me₅)₂Sm]E₃(THF) (E = S, Se, Te), [(C₅Me₅)₂Sm]₂(μ-η²:η²-Te₂) and mixed chalcogenide complexes [(C₅Me₅)₂Sm]₂(E_aE_b)(THF) (a + b = 3).

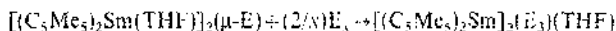


+ other products

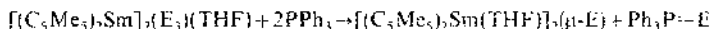


Scheme 15.

Complexes $[(C_5Me_5)_2Sm]_2(E_3)(THF)$ can also be interconverted with $[(C_5Me_5)_2Sm(THF)]_2(\mu-E)$.



$E = Se, Te$



$E = S, Se$

The complexes $[(C_5Me_5)_2Sm(THF)]_2(\mu-E)$ ($E = S, Se, Te$) are isostructural (Fig. 30) and have a formally eight-coordinate local environment around each Sm atom. The Sm-E distances follow a progression consistent with the differences in the radii of the chalcogens (Sm-Te = 2.998(2) Å, Sm-Se = 2.782(1) Å and Sm-S = 2.663(1) Å).

Complex $[(C_5Me_5)_2Sm]_2(Se_3)(THF)$ (Fig. 31) contains two distinct types of Sm atom. Sm(1) is formally nine-coordinate and Sm(2) is formally eight-coordinate. The Sm-Se distances in the molecule (3.007(1), 3.198(1) and 2.917(1) Å) are much longer than the corresponding distances in $[(C_5Me_5)_2Sm(THF)]_2(\mu-Se)$.

In the structure of $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^1-Te_2)$ (Fig. 32), the two bent metallocene units are oriented such that the four pentamethylcyclopentadienyl ring centroids describe a square plane rather than a tetrahedron. The Sm-Te distances are 3.213(1) and 3.204(1) Å. The Te-Te distance of 2.773(1) Å is in the single bond range.

Scholz et al. [42] reported the reactions of $[(C_5Me_5)_2La(\mu-Cl)_2K(dme)]$ with sodium 2,3-dimethylquinoxaline (Scheme 16) or with sodium phenazine. The reactions led to dimeric complexes which were structurally characterized. The structure

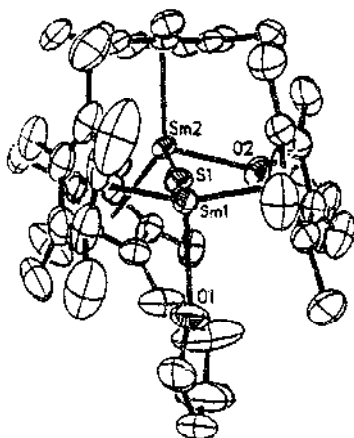
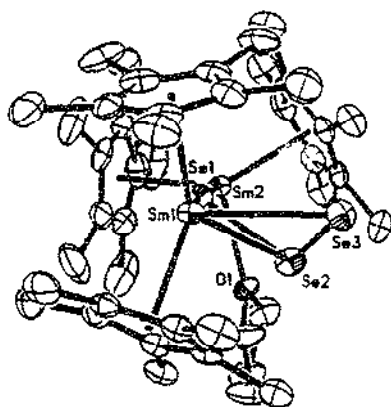
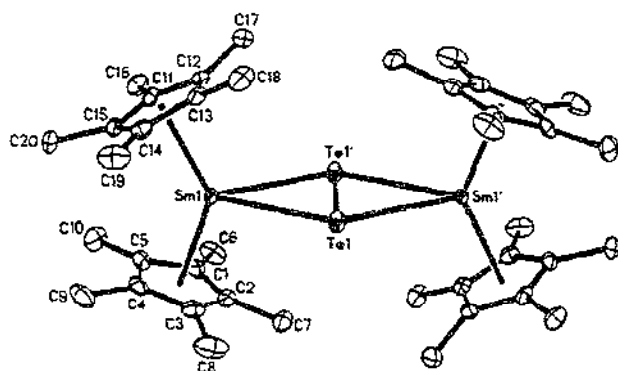
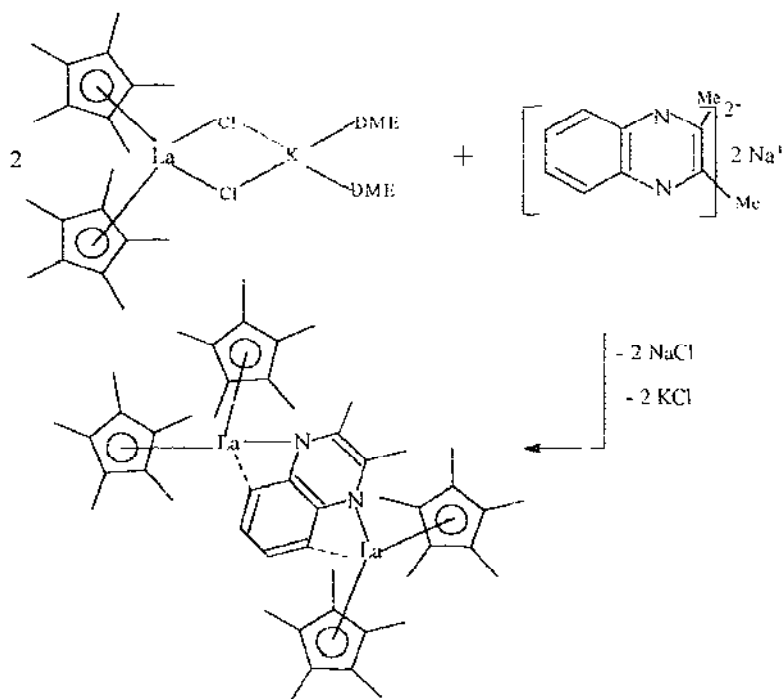


Fig. 30. Molecular structure of $[(C_5Me_5)_2Sm(THF)]_2(\mu-S)$.

Fig. 31. Molecular structure of $[(C_5Me_5)_2Sm]_2(Se_2)(THF)$.Fig. 32. Molecular structure of $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-Te_2)$.

with 2,3-dimethylquinoxaline contains two Cp^*La fragments, which are bound by the quinoxaline dianion. The La-N distances are 2.409(4) and 2.444(4) Å. The La-C(dimethylquinoxaline) distances of 2.903(5) and 2.891(5) Å are essentially longer than La-C(Cp^*) (from 2.789 to 2.806 Å) or La-C distances in the ion $[La(\eta^3-C_3H_5)_4]^-$ (La-C_{av} 2.811 Å). The phenazine complex (Fig. 33) has a similar dimeric structure with the La-N(1) and La-C(22) distances being 2.452(2) Å and 2.931(2) Å respectively.

Evans et al. [43] investigated the reactivity of decamethylsamarocene with polycyclic aromatic hydrocarbons. A series of new bimetallic complexes of samarium

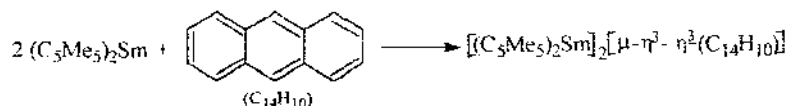


Scheme 16

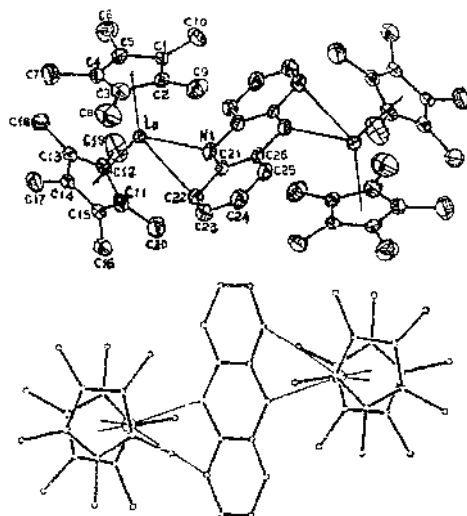
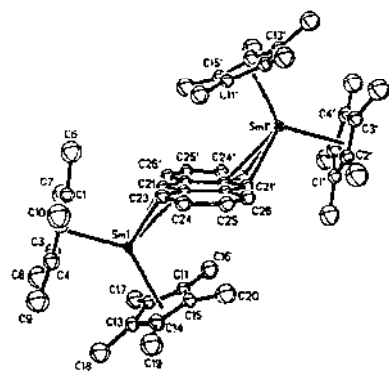
was obtained by the reactions of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}$ with various aromatic hydrocarbons and related nitrogen heterocycles. The reaction with anthracene (Scheme 17) gave the $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2[\mu\text{-}\eta^3\text{-}\eta^3\text{-(C}_{14}\text{H}_{10})]$.

According to X-ray data (Fig. 34) the planar $\text{C}_{14}\text{H}_{10}$ unit in the complex is coordinated on each side by the $(\text{C}_5\text{Me}_5)_2\text{Sm}$ groups with the shortest Sm-C (polycyclic ligand) distances of 2.595(4) Å, 2.840(4) Å and 2.791(4) Å for C(9), C(9a), and C(1) carbon atoms (anthracene numbering) respectively.

The analogous reaction (Scheme 18) with pyrene led to the complex $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2[\mu\text{-}\eta^3\text{-}\eta^3\text{-(C}_{16}\text{H}_{10})]$, which was also structurally characterized. In the

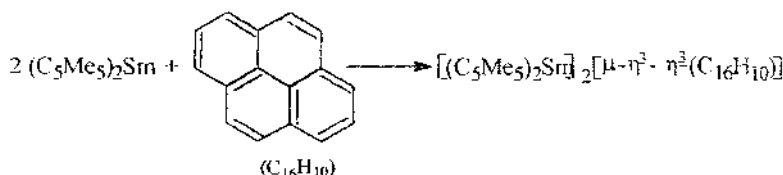


Scheme 17.

Fig. 33. Molecular structure of $[i(C_5Me_5)_3La]_3C_{12}H_8N_3$.Fig. 34. Molecular structure of $[i(C_5Me_5)_2Sm]_2[\mu-\eta^3-\eta^3-(C_{14}H_{10})]$

complex, two $(C_5Me_5)_2Sm$ units also coordinated to opposite sides of the planar polycyclic system, but they are on the same end of the tetracyclic unit. The Sm-C(polycyclic ligand) distances range from 2.660 to 2.806(4) Å.

$(C_5Me_5)_2Sm$ was also found to react in a similar manner with 2,3-benzanthracene, 9-methylanthracene, acenaphthylene and phenazine to give $[(C_5Me_5)_2Sm]_2[\mu-\eta^3-\eta^3-$



Scheme 18.

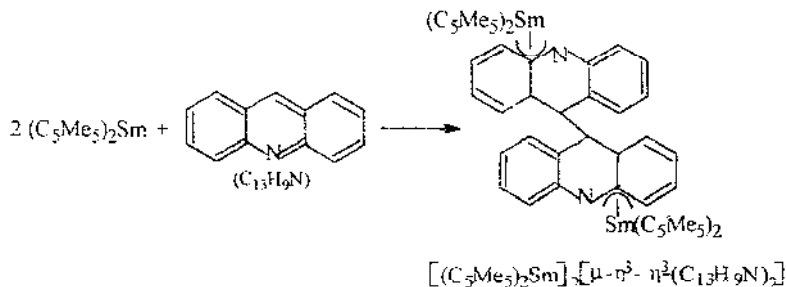
(C₁₈H₁₂), [(C₅Me₅)₂Sm]₂(C₁₅H₁₂), [(C₅Me₅)₂Sm]₂(C₁₂H₈), and [(C₅Me₅)₂Sm]₂[μ-η³-η³-(C₁₂H₈N₂)] respectively. The complexes [(C₅Me₅)₂Sm]₂[μ-η³-η³-(C₁₈H₁₂)] and [(C₅Me₅)₂Sm]₂[μ-η³-η³-(C₁₂H₈N₂)] were also structurally characterized.

The reaction of (C₅Me₅)₃Sm with azulene produced (C₅Me₅)₃Sm and another product which was not fully established. A similar reaction with acridine (C₁₃H₉N) led to the complex [(C₅Me₅)₂Sm]₂[μ-η³-η³-(C₁₃H₉N)₂] (Scheme 19) which, according to X-ray diffraction, contains nonplanar C₁₃H₉N units. The Sm-N distance is 2.380(5) Å. The polycyclic ligand in the complex [(C₅Me₅)₂Sm]₂[μ-η³-η³-(C₁₃H₉N)₂] exhibits a larger deviation from planarity (±0.26 Å) than any of the previously described complexes.

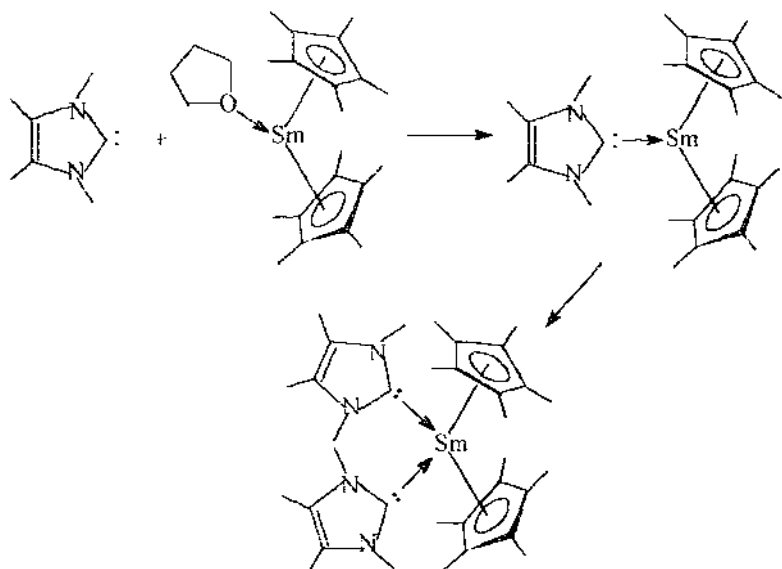
Arduengo et. al. [44] described the synthesis and structures of new lanthanide carbene complexes. 1,3,4,5-Tetramethylimidazol-2-ylidene reacted with bis(pentamethylcyclopentadienyl)samarium according to Scheme 20 giving the samarium(II) carbene complexes.

Schumann et al. [45] reported the synthesis of new carbene complexes of divalent samarium and ytterbium. The (imidazol-2-ylidene)lanthanide (Sm, Yb) complexes were obtained from 1,3,4,5-tetramethyl-imidazol-2-ylidene or 1,4-diisopropyl-2,3-dimethylimidazol-2-ylidene and the corresponding bis(cyclopentadienyl) complexes of Sm(II) and Yb(II) (Scheme 21).

The molecular structure of the ytterbium carbene complex (C₅H₅Bu₂)₂Yb·CN(Me)CMe-CMeN(Me) was studied by X-ray diffraction (Fig. 35). In the



Scheme 19.

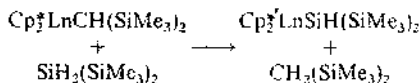


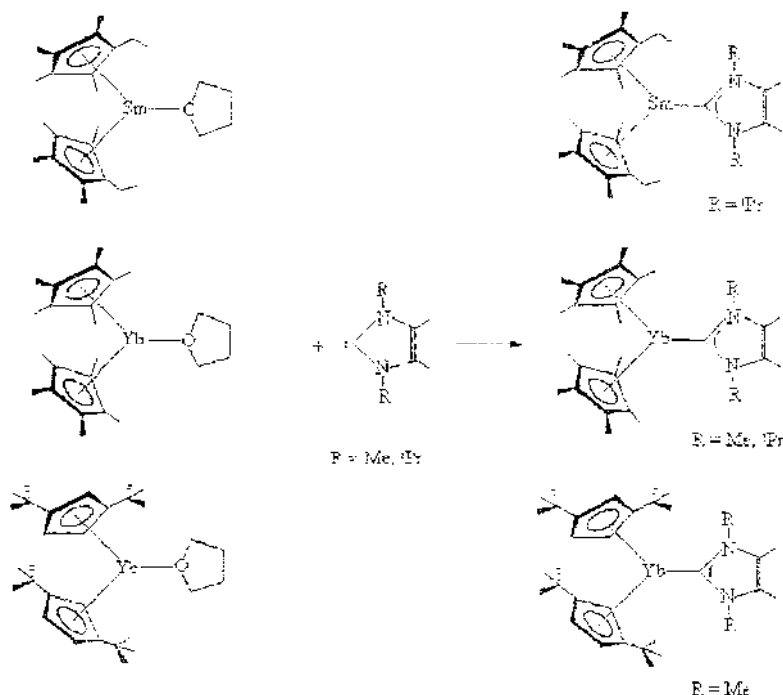
Scheme 20.

structure the seven-coordinated Yb atom has a pseudo-trigonal ligand-arrangement. The Yb-C27 distance is 2.558(3) Å.

Tilley and coworkers [46] prepared lanthanide-tungsten heterobimetallic complexes via σ -bond metathesis. Reaction of $[W(C_5H_5)_2H_2]$ with $[Ln(C_5Me_5)_2H_2]$ ($Ln=Y, Sm$) in toluene at room temperature (Scheme 22) led to the metallated cyclopentadienyl derivative $[(C_5Me_5)_2Ln(\mu-\eta^1, \eta^5-C_5H_4)(\mu-H)_2W(C_5H_5)]$. The molecular structure of the samarium complex consists of two metallocene fragments linked by a Sm-C(C_5H_4) bond (Fig. 36). The Sm-W distance (3.402(1) Å) is greater than the sum of the atomic radii for Sm and W, suggesting the absence of a direct Sm-W bond. The overall conformation of the molecule implied the presence of bridging hydride ligands.

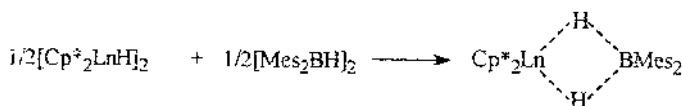
Radu and Tilley [47] also reported about σ -bond metathesis reactions involving lanthanide-silicon and lanthanide-hydrogen bonds. The lanthanide silyl complexes $Cp^*_2LnSiH(SiMe_3)_2$ ($Ln=Sm, Nd, Y$; $Cp^*=\eta^5-C_5Me_5$) were obtained by reaction of the appropriate $Cp^*_2LnCH(SiMe_3)_2$ with $SiH_2(SiMe_3)_2$.

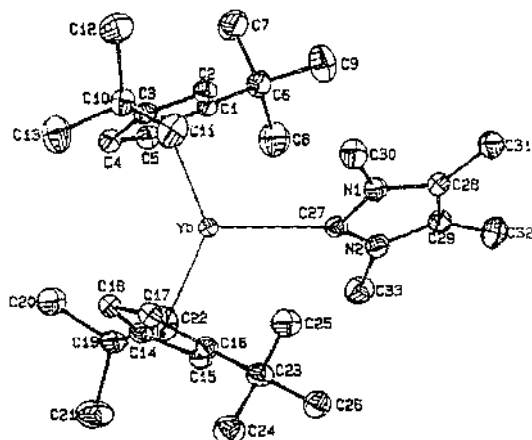
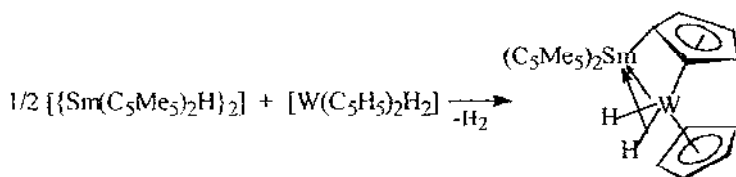




Scheme 21.

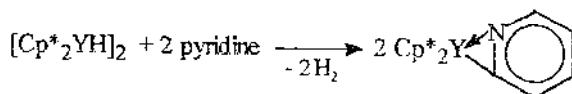
The silyl complexes $\text{Cp}^*_2\text{LnSiH}(\text{SiMe}_3)_2$ are monomeric in pentane solution but in the solid state they contain an intermolecular $\text{Ln}\cdots\text{CH}_3\cdots\text{Si}$ interaction. The σ -bond metathesis reaction proceeds via a second-order autocatalytic process catalysed by $[\text{Cp}^*_2\text{LnH}]_2$. The above-mentioned reactions of $[\{\text{Ln}(\text{C}_5\text{Me}_5)_2\text{H}\}_2]$ ($\text{Ln} = \text{Y}, \text{Sm}$) with $[\text{W}(\text{C}_2\text{H}_5)_2\text{H}_2]$ (Scheme 22) were also discussed in the work. The borohydride complexes $\text{Cp}^*_2\text{Ln}(\eta^2\text{-H}_2\text{BMes}_2)$ ($\text{Mes} = \text{mesityl}$, $\text{Ln} = \text{Sm}, \text{Y}$) were synthesized from $[\text{Cp}^*_2\text{LnH}]_2$ and $[\text{HBMes}_2]_2$.



Fig. 35. Molecular structure of $(C_5H_5)_2Yb \cdot \overline{CN(Me)CMe-CMeN(Me)}$.

Scheme 22.

Teuben and coworkers [48] reported the synthesis and properties of $Cp^*_2Y(2\text{-pyridyl})$ ($Cp^* = C_5Me_5$). The complex was obtained from $[Cp^*_2YH]_2$ and pyridine.



This compound reacts with hydrogen and Lewis bases (THF, Et_2O , pyridine) as well as with alkenes, alkynes and carbon monoxide (Scheme 23).

The structure of the CO insertion complex $[Cp^*_2Y]_2[\mu-\eta^2:\eta^2-OC(NC_5H_4)_2]$ (Fig. 37) consists of two normal bent Cp^*_2Y units that are bridged by a $\mu-\eta^2:\eta^2$ -dipyridyl ketone fragment. The product of ethylene insertion $Cp^*_2YCH_2CH_2(2\text{-NC}_5H_4)$ gave σ -bond metathesis with pyridine to form

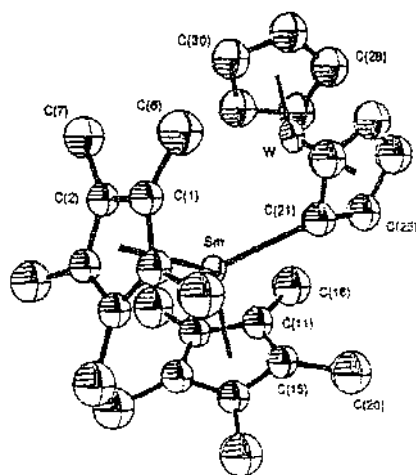


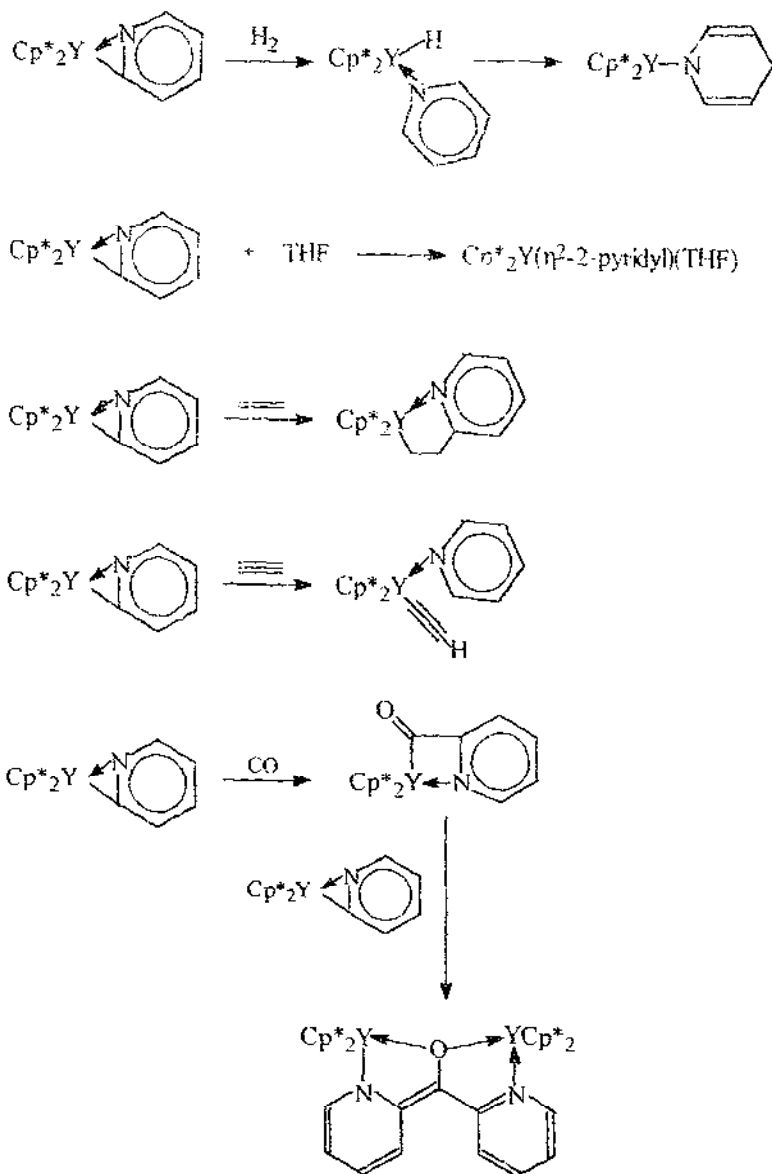
Fig. 36. Molecular structure of $[(C_5Me_5)_2Ln(\mu-\eta^1, \eta^5-C_5H_5)(\mu-H)_2W(C_5H_5)]$.

2-ethylpyridine and $Cp^*Y(2\text{-pyridyl})$. The complex $Cp^*YCH_2CH_2(2\text{-NC}_5H_4)$ decomposes to the isomers $Cp^*Y[2\text{-NC}_5H_3(6\text{-Et})]$ and $Cp^*YCHMe(2\text{-NC}_5H_4)$ at 80°C .

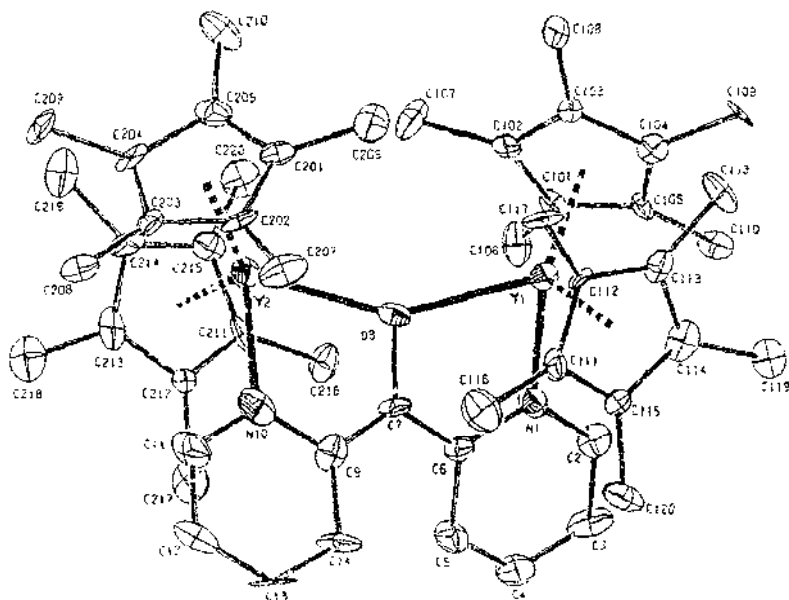
Marks and coworkers [49] investigated the bis(polymethylcyclopentadienyl)lanthanide hydrocarbyl complexes $Cp'_2LnCH(SiMe_3)_2$ and $Me_2SiCp''_2LnCH(SiMe_3)_2$ ($Cp' = \eta^5\text{-(CH}_3)_5C_5$; $Cp'' = \eta^5\text{-(CH}_3)_4C_5$; $Ln \approx La, Ce, Nd, Sm, Lu$) by relativistic *ab initio* and DV-*X α* calculations and gas-phase UV photoelectron spectroscopy. The investigations revealed that the lanthanide–ligand bonding interactions are dominated by the metal 5d orbitals. The metal 4f orbitals are only marginally involved in the bonding. The ionization from the $Ln\text{-}\sigma$ bonding orbital represents the lowest-energy, nearly constant PE feature followed by $Ln\text{-}Cp$ ionization in the He I spectra. Metal f^1 ionizations, observed in the He II spectra of the Ce, Nd, Sm and Lu complexes, were interpreted on the basis of the states generated upon ionization of the f^n ground states. They had either the form of low intensity onset features for Ce, Nd and Sm complexes, or of intense structures in the 16–17 eV range in the spectrum of the Lu compound. Trends in the $4f^1$ ionizations are consistent with a gradual energetic stabilization of 4f orbitals across the lanthanide series. Metal 4f orbitals appear core-like in character in the f^{14} Lu complex.

2.2.3. Tris(cyclopentadienyl) complexes

Chen et al. [50] published the syntheses and crystal structures of $(\eta^5\text{-C}_5H_5)_3Ln(THF)$ ($Ln \approx Ce, Er$). The reaction of $(NH_4)_2Ce(NO_3)_6$ with C_5H_5Na in THF led to the Ce(III) complex $(C_5H_5)_3Ce(THF)$. The authors also made an attempt to obtain a cyclooctadienyl bis(cyclopentadienyl)erbium complex by the reaction

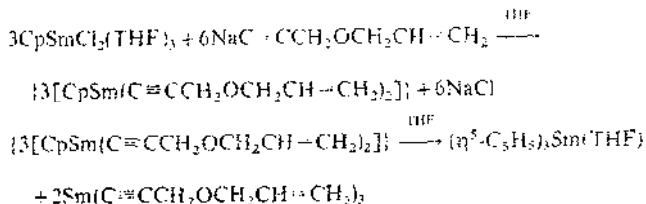


Scheme 23.

Fig. 37. Molecular structure of $[\text{Cp}^*\text{Y}]_2[\mu\text{-}\eta^5\text{:}\eta^5\text{-OC}(\text{C}_6\text{H}_5)_2]$.

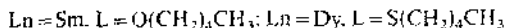
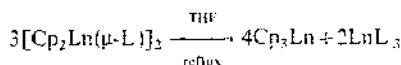
of $\text{ErCl}_3 \cdot 4\text{THF}$ with $\text{C}_5\text{H}_{11}\text{K}$ and with $\text{C}_5\text{H}_5\text{Na}$, but the reaction gave $(\text{C}_5\text{H}_5)_3\text{Er}(\text{THF})$ only. The complex $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ce}(\text{THF})$ and the analogous erbium complex are not isostructural, but $(\eta^5\text{-C}_5\text{H}_5)_3\text{Er}(\text{THF})$ is isostructural with known $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}(\text{THF})$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Dy}, \text{Y}$ and Lu).

Wang et al. [51] reported the formation and molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Sm}(\text{THF})$. The complex was obtained from the reaction of $(\eta^5\text{-C}_5\text{H}_5)_3\text{SmCl}_2(\text{THF})_3$ with $\text{NaC}\equiv\text{CCH}_2\text{OCH}_2\text{CH}=\text{CH}_2$ in THF.



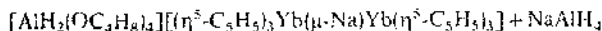
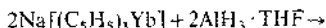
The molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Sm}(\text{THF})$ has a coordination sphere of three η^5 -cyclopentadienyl ligands and one tetrahydrofuran to form a distorted tetrahedron around the Sm atom.

This structure, as well as the structure of $(C_5H_5)_3Dy(THF)$, was also reported by Wu et al. [52]. The complexes were obtained by refluxing $[Cp_2SmO(CH_2)_4CH_3]_2$ and $[Cp_2DyS(CH_2)_4CH_3]_2$ ($Cp = C_5H_5$) in THF.



The complexes are isostructural with the known complexes $Cp_3Ln(THF)$ ($Ln = La, Pr, Nd, Gd$ and Lu).

Kujazhansky et al. [53] reported the synthesis and structure of the complex $[AlH_2(OC_4H_9)_4][(\eta^5-C_5H_5)_3Yb(\mu-Na)Yb(\eta^5-C_5H_5)_3]$, which was obtained by the reaction of $Na[(C_5H_5)_3Yb]$ with aluminium hydride in THF.



The structure (Fig. 38) consists of the anion $[(\eta^5-C_5H_5)_3Yb(\mu-Na)Yb(\eta^5-C_5H_5)_3]^-$ and the cation $[AlH_2(OC_4H_9)_4]^+$. In the cation the Al atom has an

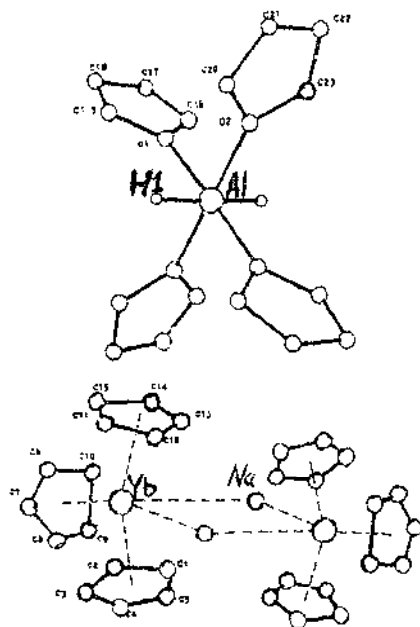


Fig. 38. Molecular structure of $[AlH_2(OC_4H_9)_4][(\eta^5-C_5H_5)_3Yb(\mu-Na)Yb(\eta^5-C_5H_5)_3]$.

octahedral environment with bond angles close to 90° . The anion contains two $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Yb}]^-$ fragments and the Na^+ ion bound by ionic interactions. The $\text{Yb}\cdots\text{Na}$ distance (3.54(1) Å) is sufficiently large that the interaction can be considered as a purely ionic one.

Depaoli et al. [16] described the europium-151 Mössbauer spectra of several organoeuropium(III) compounds including $(\eta^5\text{-C}_5\text{H}_5)_3\text{Eu}(\text{THF})$. The europium-151 Mössbauer spectrum of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Eu}(\text{THF})$ revealed a weak but definite covalent interaction between the 4f orbitals of Eu(III) and the ligands.

Ren et al. [54] reported the synthesis and X-ray structure of an organolanthanum complex $[(^i\text{BuCp})_3\text{LaClLi}(\text{THF})_3]$. The compound was obtained by the reaction of $\text{LaCl}_3 \cdot 2\text{LiCl}$ with two equivalents of $^i\text{BuCpNa}$ in THF. In the structure the central La^{3+} is coordinated to three $^i\text{BuCp}$ groups and one chloride to form a distorted tetrahedron (Fig. 39). The two units $(^i\text{BuCp})_3\text{La}$ and $\text{Li}(\text{THF})^+$ are connected by a single chloride bridge.

2.2.4. Bridged cyclopentadienyl complexes

Sun et al. [55] published the synthesis and crystal structure of $[\text{Me}_4\text{C}_2\text{Cp}_2\text{SmCl}(\text{THF})_2]_2$. The complex was synthesized by the reaction of SmCl_3 with the $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_5\text{MgCl})_2(\text{THF})$ in THF. The structure of $[\text{Me}_4\text{C}_2\text{Cp}_2\text{SmCl}(\text{THF})_2]_2$ is dimeric (Fig. 40). Two Sm atoms are bridged by two chlorine atoms to form two unsymmetrical $\text{Sm}-\text{Cl}$ bonds ($\text{Sm}-\text{Cl}$ distance is 2.78, 2.84 Å). The two Cp rings are in eclipsed conformation.

Paolucci et al. [56] reported the synthesis of new bis(cyclopentadienyl)lanthanide chlorides (Scheme 24). The compounds were characterized by elemental analyses, IR, MS, ^1H NMR and X-ray photoelectron spectroscopy. The reaction of two equivalents of $\text{PrCl}_3(\text{THF})_2$ and three equivalents of $\text{Na}_2[\text{1,6-(CH}_2\text{C}_5\text{H}_4)_2\text{C}_4\text{H}_5\text{N}]$

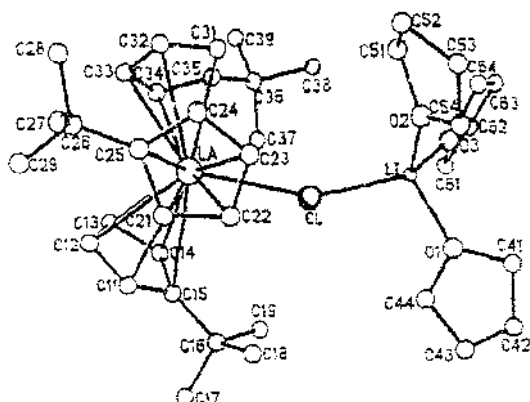
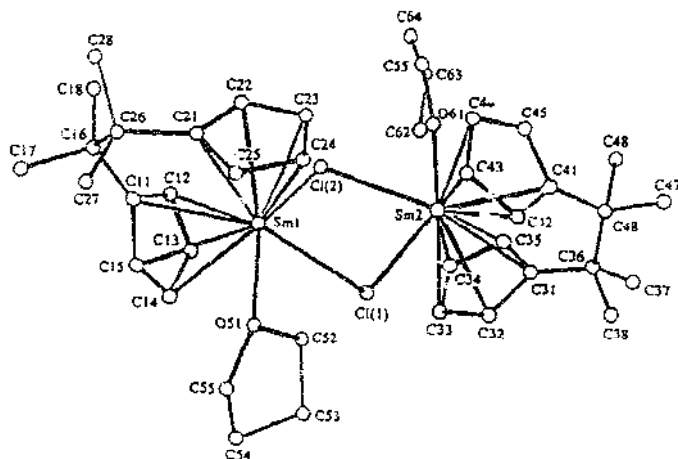
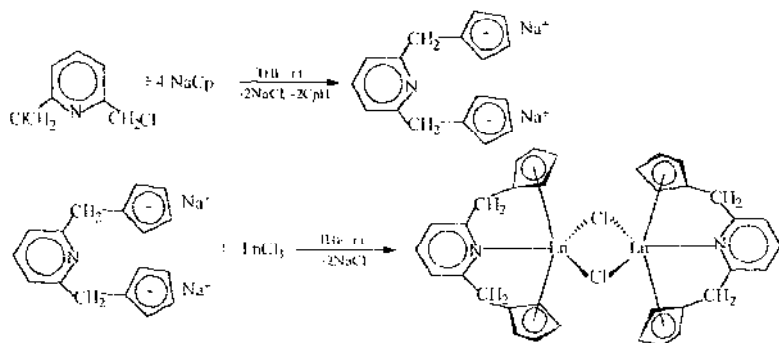


Fig. 39. Molecular structure of $[(^i\text{BuCp})_3\text{LaClLi}(\text{THF})_3]$.

Fig. 40. Molecular structure of $[\text{Me}_3\text{C}_5\text{Cp}_2\text{SmCl}(\text{THF})]_2$.

Ln = Y, Pr, Nd, Sm, Dy, Er, Yb, or Lu.

Scheme 24.

led to the complex, which according to elemental analysis, has the formula $[(2,6-(\text{CH}_2\text{C}_5\text{H}_4)_2\text{C}_5\text{H}_3\text{N})_3\text{Pr}_2]$. Some preliminary studies of the catalytic properties of the bis(cyclopentadienyl)lanthanide chlorides in the reduction of hex-1-ene by LiAlH_4 were also carried out.

Gräper et al. [57] described the new lanthanocenophanes $[\{\text{OMe}_2\text{SiC}_5\text{H}_4\}_2\text{PrCl}(\text{THF})]_x$ ($x=1$ or 2) and $[\{\text{OMe}_2\text{SiC}_5\text{H}_4\}_2\text{YbCl}]_2$. The

complexes were synthesized by the reaction of the potassium salt of 1,1,3,3-tetramethyl-1,3-dicyclopentadienyl disiloxane with PrCl_3 or YbCl_3 . According to the X-ray structure determination the complex $[\{\text{OMe}_2\text{SiC}_5\text{H}_4\}_2\text{YbCl}]_2$ is a Cl-bridged dimer. In the molecule of $[\{\text{OMe}_2\text{SiC}_5\text{H}_4\}_2\text{YbCl}]_2$ the ring-bridging $-\text{Me}_2\text{SiOSiMe}_2-$ group is positioned asymmetrically with respect to the Cl-Yb-Cl plane. The Yb-Cp(cent.) distances are 229.0(7) and 228.1(7) Å.

Qian and Zhu [58] published the synthesis of a series of furan-bridged bis(cyclopentadienyl) lanthanide (Yb, Sm or Nd) and yttrium (Scheme 25) complexes.

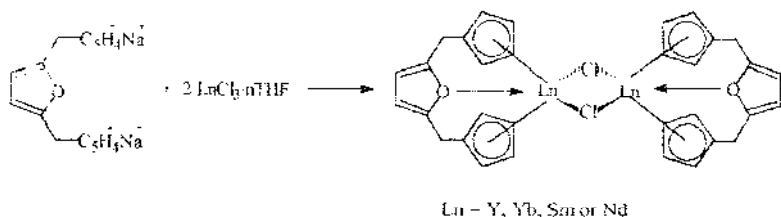
The compounds were characterized by elemental analyses, MS, IR and ^1H NMR. The reactivity of organolanthanide hydrides generated in situ from the $[\text{Ln}(\text{C}_5\text{H}_5)_2\text{Cl}]\cdot\text{NaH}$ system was studied. The authors come to the conclusion that the reactivity can be tuned not only by varying the ligands but also by taking advantage of the lanthanide contraction. The goal of acquiring more reactive organolanthanide hydrides can be achieved by selecting the appropriate ligands and using the early lanthanide metals.

Piers et al. [59] investigated the insertion of elemental tellurium into the scandium-carbon bonds of the *ansa*-scandocene alkyl(*meso*-(CH_3)₂Si[(1-C₄H₉)C₅H₅]₂; Sc(CH_2SiMe_3)(DpScR). The chemical procedures are summarized in Scheme 26.

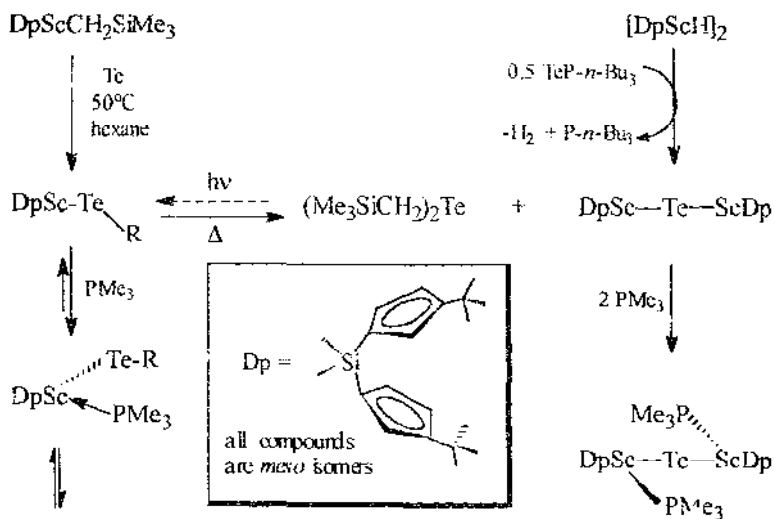
The dimeric telluride DpSc-Te-ScDp was characterized by X-ray analysis as the benzene solvate of its bis(trimethylphosphine) adduct $\text{DpSc}(\text{PMe}_3)\text{-Te-Sc}(\text{PMe}_3)\text{Dp}$ (Fig. 41). The asymmetric unit of the complex consists of two independent half-molecules (the Te atom is on an inversion centre), which differ only slightly in conformation. The Sc-Te-Sc coordination is, as a consequence, precisely linear, with a mean Sc-Te bond distance of 2.875(5) Å.

Schumann et al. [60] reported the synthesis and characterization of the $[(^t\text{BuC}_5\text{H}_3)\text{SiMe}_2(\text{C}_5\text{Me}_4)]\text{Ln}(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)_2$ ($\text{Ln} = \text{La, Lu}$) (Scheme 27) and the chiral tris(cyclopentadienyl) complexes $[(^t\text{BuC}_5\text{H}_3)\text{SiMe}_2(\text{C}_5\text{Me}_4)]\text{Ln}(\text{C}_5\text{Me}_5\text{H})(\text{THF})$ ($\text{Ln} = \text{La, Nd}$) (Scheme 27).

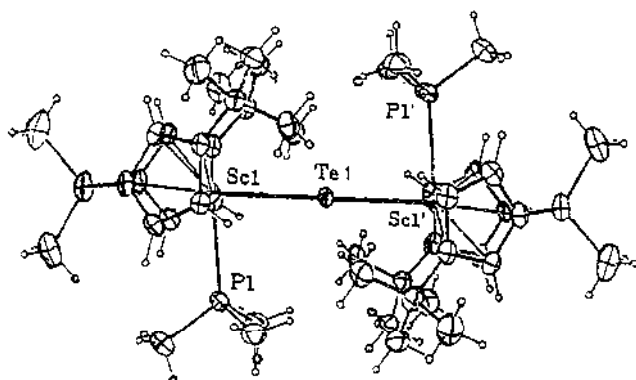
According to X-ray analysis, in the structure of $[(^t\text{BuC}_5\text{H}_3)\text{SiMe}_2(\text{C}_5\text{Me}_4)]\text{-La}(\text{C}_5\text{Me}_5\text{H})(\text{THF})$ the La atom adopts a distorted tetrahedral arrangement, which is formed by the three cyclopentadienyl rings and one THF molecule (Fig. 42). This complex, as well as the other complexes, were characterized also by their ^1H and ^{13}C NMR and MS spectra.

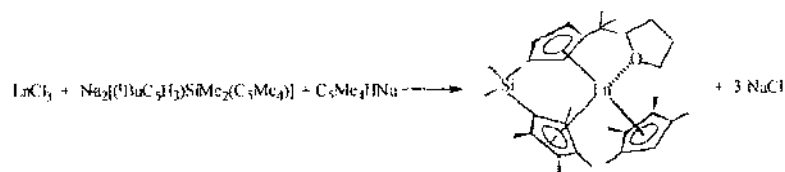
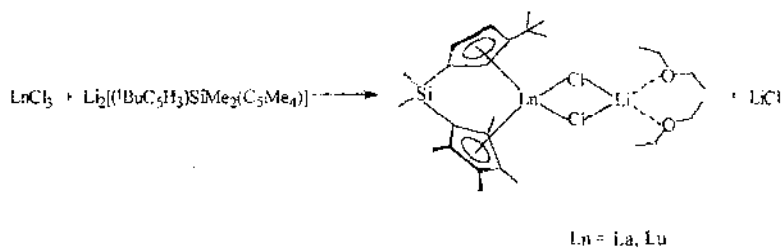


Scheme 25.



Scheme 26.

Fig. 41. Molecular structure of $\text{DpSc(PMe}_3)_2\text{Te-Sc(PMe}_3)_2\text{Dp}$ ($\text{Dp} = \text{meso-(CH}_3)_2\text{Si}[(1\text{-C}_6\text{H}_4\text{-C}_6\text{H}_3)_2]$).



Scheme 27.

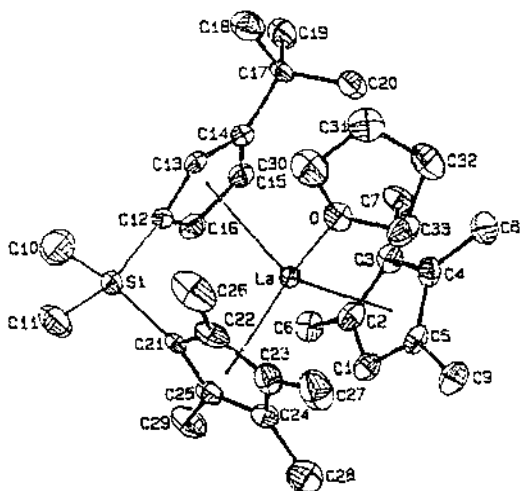
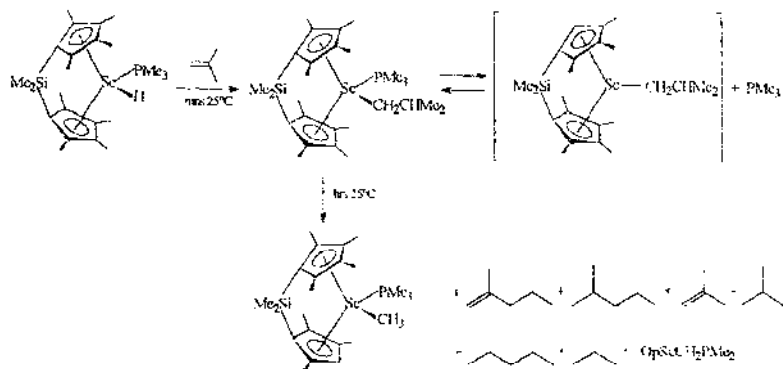
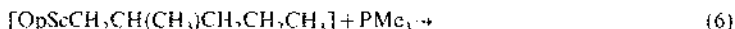
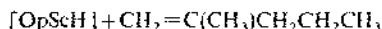
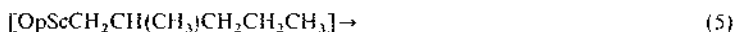
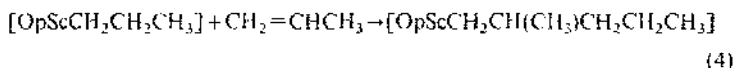
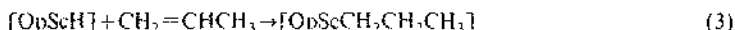
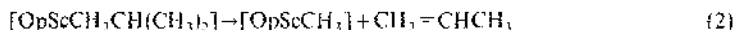
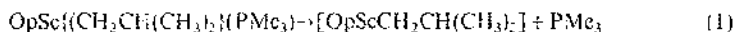


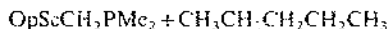
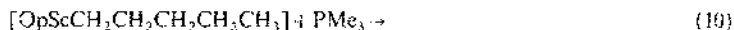
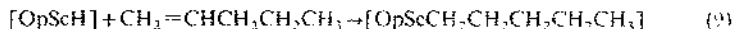
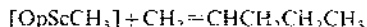
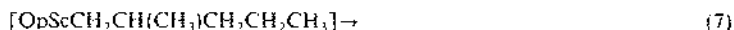
Fig. 42. Molecular structure of $[(^t\text{BuC}_5\text{H}_3)\text{SiMe}_2(\text{C}_5\text{Me}_4)]\text{La}(\text{C}_5\text{Me}_4\text{H})(\text{THF})$.

Hajela and Bercaw [61] reported that the reaction of permethylscandocene complex $\text{OpSc}(\text{H})(\text{PMe}_3)$ ($\text{Op} = \{(\eta^5\text{-C}_5\text{Me}_5)_2\text{SiMe}_2\}$) with isobutene produced $\text{OpSc}\{(\text{CH}_2\text{CH}(\text{CH}_3)_2)\}(\text{PMe}_3)$, which slowly decomposed to afford the $\text{OpSc}(\text{CH}_3)(\text{PMe}_3)$ along with isobutene, 2-methylpentane, isobutene, 2-methyl-1-pentene, propane and *n*-pentane (Scheme 28).

A transient observed in the reaction sequence has been unambiguously characterized as $\text{OpSc}(\text{CH}_2\text{CH}_2\text{CH}_3)(\text{PMe}_3)$. The two C_6 products, 2-methylpentane, 2-methyl-1-pentene and *n*-pentane, were formed according to Eqs. (1)–(10).

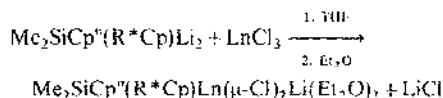


Scheme 28.



β -Ethyl migration is not observed for the derivative $\text{OpSc}\{\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_3\}(\text{PMe}_3)$, obtained from reaction of 2-ethyl-1-butene with $\text{OpSc}(\text{H})(\text{PMe}_3)$.

Marks and coworkers [62] described the synthesis, characterization, and configurational interconversions of chiral, C_1 -symmetric organolanthanide halides, amides, and hydrocarbyls. The $\text{Me}_2\text{Si}(\text{Cp}^*(\text{H}))(\text{R}^*\text{CpH})$ ancillary ligands and the corresponding dilithium derivatives were obtained according to the Scheme 29. The chiral $\text{Me}_2\text{SiCp}^*(\text{R}^*\text{Cp})\text{Ln}(\mu\text{-Cl})_2\text{Li}(\text{ether})_2$ complexes were synthesized by transmetalation of $\text{Me}_2\text{SiCp}^*(\text{R}^*\text{Cp})\text{Li}_2$ with the appropriate lanthanide trichloride.

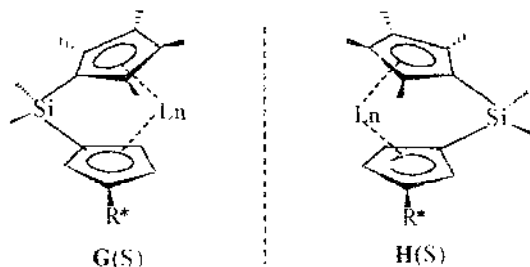


$\text{R}^* = (+)\text{-neomenthyl}$, $\text{Ln} = \text{La}$, Nd , Sm , Y , Lu ;

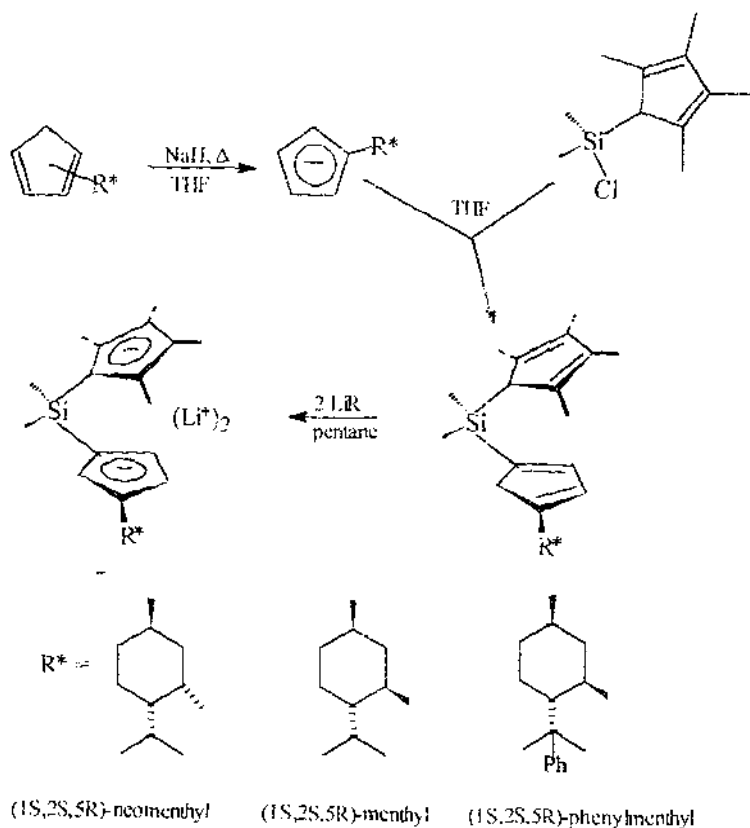
$\text{R}^* = (-)\text{-menthyl}$, $\text{Ln} = \text{Sm}$, Y , Lu ;

$\text{R}^* = (-)\text{-phenylmenthyl}$, $\text{Ln} = \text{Y}$

The mono-DME adducts can be prepared by the analogous reaction in the presence of DME. Diastereomers produced are epimeric with respect to the orientation of the chiral auxiliary on the Cp group relative to the lanthanide centre (**G**, **H**):

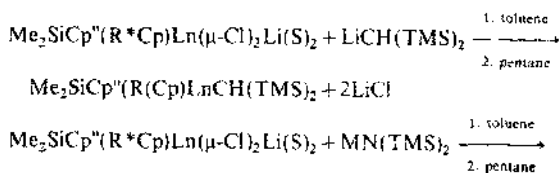


The molecular structure of $(\text{R})\text{-Me}_2\text{SiCp}^*[(+)\text{-neomenthyl}]\text{Cp}\text{Lu}(\mu\text{-Cl})_2\text{Li}(\text{ether})_2$ is shown in Fig. 43. The X-ray diffraction analysis reveals a single



Scheme 29.

planar chiral configuration of the diastereotopic, chirally substituted Cp group, i.e. the (*R*)-configuration. Chiral organolithianthene hydrocarbyls and amides were prepared according to the following equations:



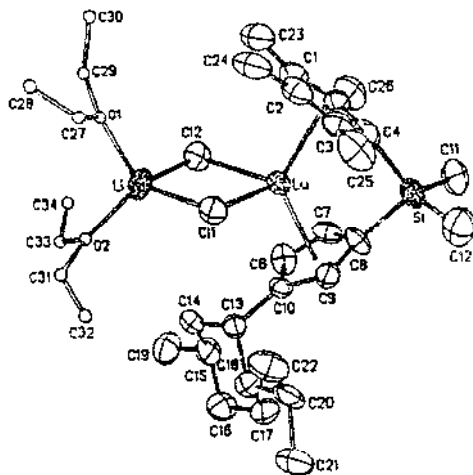
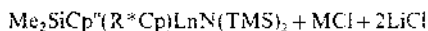


Fig. 43. Molecular structure of $(R)\text{-Me}_2\text{SiCp}''[(+)\text{-neomenthylCp}]\text{Lu}(\mu\text{-Cl})_2\text{Li(ether)}_2$.

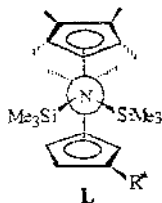
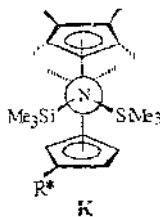
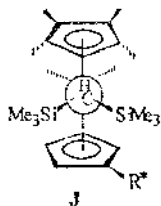
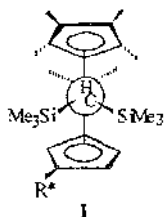


$\text{R}^* = (+)\text{-neomenthyl}$, $\text{Ln} = \text{La}$, Nd , Sm , Y , Lu ;

$\text{R}^* = (-)\text{-menthyl}$, $\text{Ln} = \text{Sm}$, Y , Lu ;

$\text{R}^* = (-)\text{-phenylmenthyl}$, $\text{Ln} = \text{Y}$

The spectroscopic data supported solution structures **I**, **J** and **K**, **L** for the pair of hydrocarhyl and amido complexes respectively:



The reactions of $(R)\text{-Me}_2\text{SiCp}''[(+)\text{-neomenthylCp}]\text{Lu}(\mu\text{-Cl})_2\text{Li(ether)}_2$ with the other alkylating reagents were also investigated.

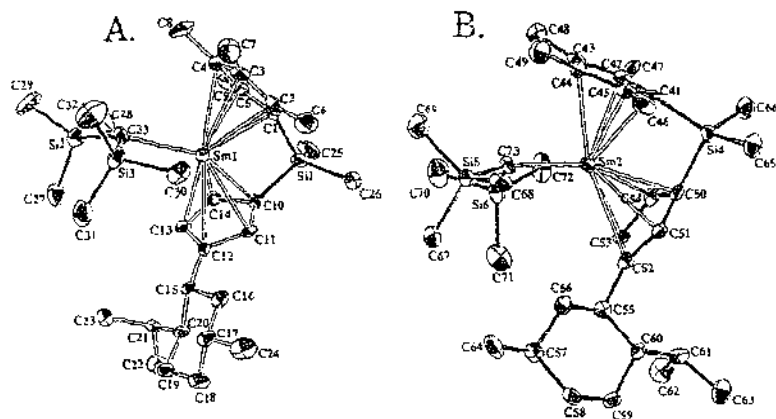
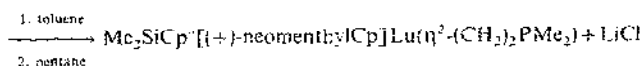
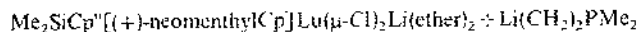
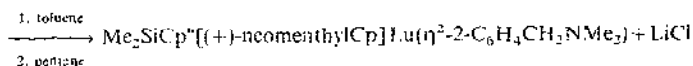
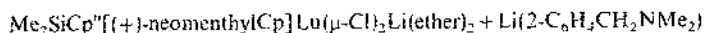
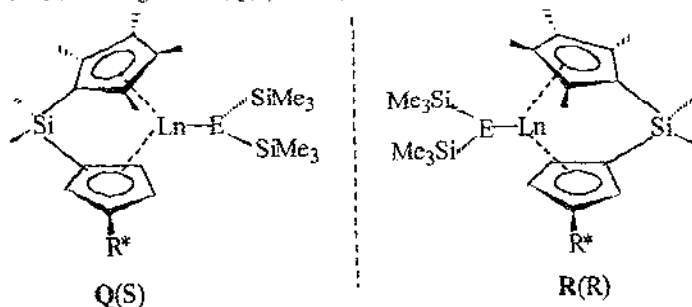


Fig. 44. Structure of $(R)\text{-Me}_2\text{SiCp}^*[(+)\text{-menthylCp}]\text{SmCH}(\text{TMS})_2$.



Low-temperature single crystal X-ray structural determinations were carried out on selected hydrocarbyl ($\text{E}=\text{CH}$) and anide ($\text{F}=\text{N}$) complexes to establish the absolute configuration ($\text{Q}(\text{S})$ and $\text{R}(\text{R})$):



X-ray analyses of $(R)\text{-Me}_2\text{SiCp}^*[(+)\text{-menthylCp}]\text{LnCH}(\text{TMS})_2$ complexes ($\text{Ln} \approx \text{Y, Sm}$) showed that each unit cell contains two crystallographically independent molecules (A and B) with the same planar chiral (R)-configurations (Fig. 44).

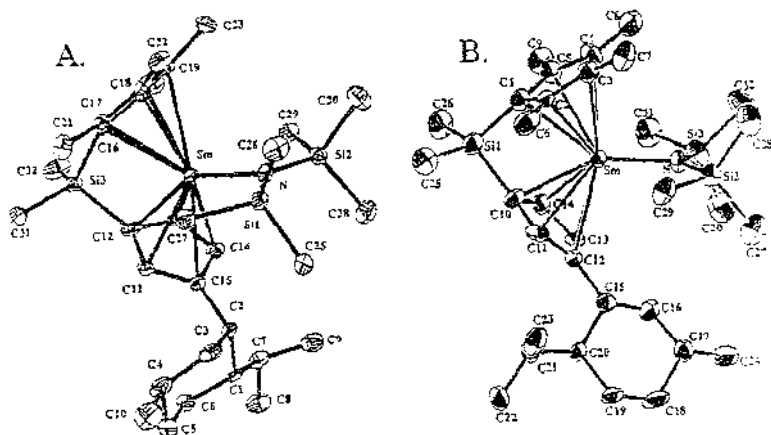
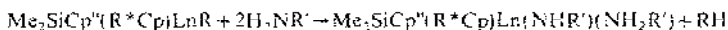


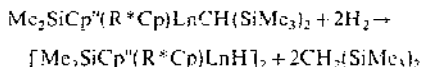
Fig. 45. Molecular structures of $(S)\text{-Me}_2\text{SiCp}''[(+)\text{-neomenthylCp}]\text{SmN}(\text{TMS})_2$ (A) and $(S)\text{-Me}_2\text{SiCp}''[(−)\text{-menthylCp}]\text{SmN}(\text{TMS})_2$ (B).

Diffraction analyses of $(S)\text{-Me}_2\text{SiCp}''[(+)\text{-neomenthylCp}]\text{SmN}(\text{TMS})_2$ (A) and $(S)\text{-Me}_2\text{SiCp}''[(−)\text{-menthylCp}]\text{SmN}(\text{TMS})_2$ (B) indicate the (S) -configuration in both complexes (Fig. 45), while analysis of $\text{Me}_2\text{SiCp}''[(−)\text{-menthylCp}]\text{YN}(\text{TMS})_2$ indicated the (R) -configuration in the two independent molecules.

The hydrocarbonyl and amide complexes $\text{Me}_2\text{SiCp}''(\text{R}^*\text{Cp})\text{LnR}$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$, $\text{N}(\text{SiMe}_3)_2$, $\eta^2\text{-2-C}_6\text{H}_4\text{CH}_2\text{NMe}_2$, $\eta^2\text{-(CH}_2)_2\text{PMe}_2$) are protolyzed by alkylamines, presumably forming organolanthanide amide–amine adducts.



The $\text{Me}_2\text{SiCp}''(\text{R}^*\text{Cp})\text{LnCH}(\text{SiMe}_3)_2$ complexes also undergo hydrogenolysis of the $\text{E}(\text{TMS})_2$ group, affording $\text{CH}_2(\text{SiMe}_3)_2$ and a hydrido complex.



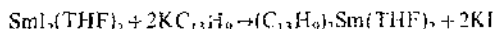
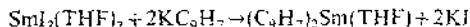
Thus the work has presented the first systematic study of the synthetic, spectroscopic and structural properties of chiral organolanthanides.

2.3. Cyclopentadienyl-like complexes

2.3.1. Indenyl and fluorenyl complexes

Evans et al. [63] published the synthesis and structures of indenyl and fluorenyl complexes of $\text{Sm}(\text{II})$, which were prepared by the reactions between the

$\text{SmI}_2(\text{THF})_2$ and the corresponding potassium salts in THF.



After crystallization of $(\text{C}_9\text{H}_7)_2\text{Sm}(\text{THF})$ from THF, crystals of the trisolvate $(\text{C}_9\text{H}_7)_2\text{Sm}(\text{THF})_3$ were obtained. The crystallographic data for the latter complex were not complete owing to decomposition of the crystal during the X-ray diffraction experiment.

According to the X-ray structure the fluorenyl complex $(\text{C}_{13}\text{H}_9)_2\text{Sm}(\text{THF})_2$ is an eight-coordinate disolvated complex (Fig. 46). The average Sm-C(ring) distance is 2.90(7) Å. Several bond distances and angles in the $(\text{C}_{13}\text{H}_9)_2\text{Sm}(\text{THF})_2$ suggest that the effective steric bulk of the fluorenyl ligand is less than that provided by the C_5Me_5 ligand.

2.3.2. Heterocycles

Jubb and Gambarotta [64] described the preparation of a low-valent samarium macrocyclic complex and its reaction with dinitrogen to form a tetralithium hydrazide salt (Scheme 30).

The X-ray crystal structure determination of $[(\text{THF})_2\text{Li}(\text{OEPG})\text{Sm}]_2(\text{N}_2\text{Li}_4)$ has shown a dimeric complex where two $(\text{THF})_2\text{Li}(\text{OEPG})\text{Sm}$ units are bridged by a planar N_2Li_4 moiety placed on a symmetry centre (Fig. 47). The crystal structure indicated that the molecule arises from the aggregation of two $(\text{THF})_2\text{Li}(\text{OEPG})\text{Sm}$ units, formally containing Sm(III), with an N_2Li_4 unit. The magnetic moment of 2.72 μ_B per dimeric complex was also as expected for a Sm(III) species.

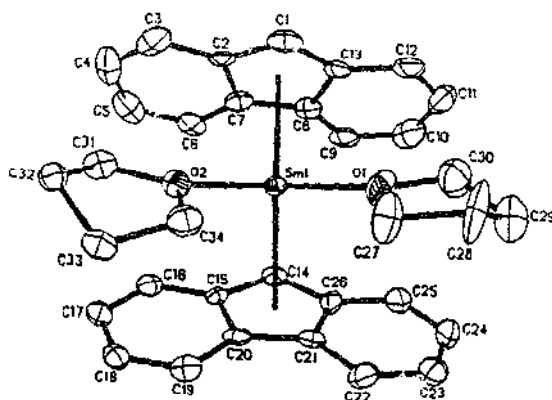
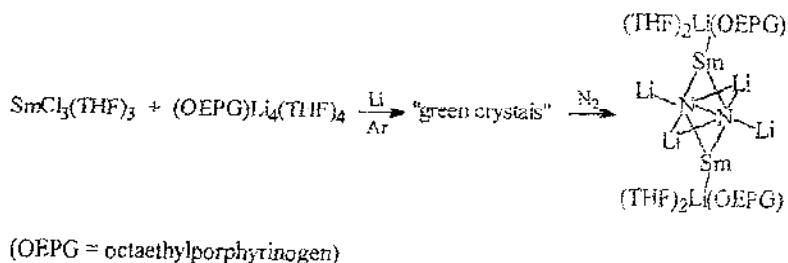
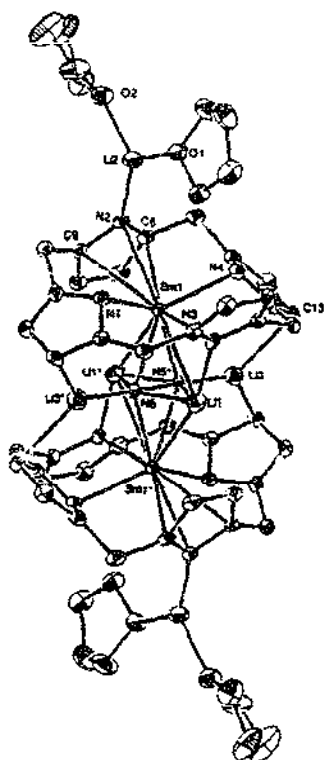


Fig. 46. Molecular structure of $(\text{C}_{13}\text{H}_9)_2\text{Sm}(\text{THF})_2$.

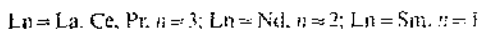
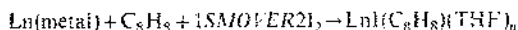


Scheme 30.

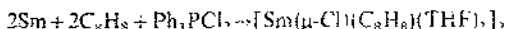
Fig. 47. Structure of $[\text{Li}(\text{THF})_2\text{Li}(\text{OEPG})\text{Sm}]_2\text{Li}_4$ (OEPG = octaethylporphyrinogen).

2.4. Complexes with cyclooctatetraenyl ligands

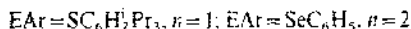
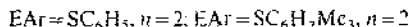
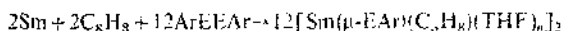
Mashima et al. [65] published a preparation of monocyclooctatetraenyl-lanthanide complexes from metallic lanthanides and oxidants. The iodo(cyclooctatetraenyl) complexes of lanthanides $\text{Ln}(\eta^8\text{-cot})(\text{THF})_n$ (cot = C_8H_8 ; Ln = La, Ce, Pr, $n=3$; Ln = Nd, $n=2$; Ln = Sm, $n=1$) have been prepared by the one-pot reaction of metallic lanthanides with cyclooctatetraene in the presence of an equimolar amount of iodine in THF.



Bromo- and chloro-bridged binuclear complexes of samarium, $[\text{Sm}(\mu\text{-X})(\text{cot})(\text{THF})_2]_2$ ($\text{X} = \text{Br, Cl}$), were also prepared by the reaction of samarium metal with cyclooctatetraene in the presence of 1,2-dibromoethane or Ph_3PCl_2 .



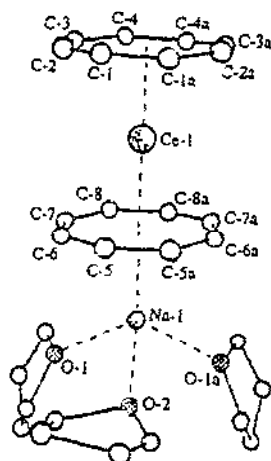
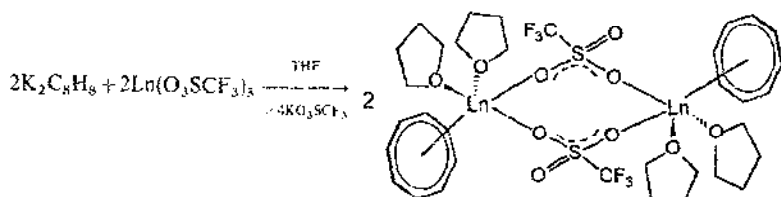
Reaction among Sm, COT, and diphenyl disulphide in THF in the presence of a catalytic amount of iodine afforded $[\text{Sm}(\mu\text{-SPh})(\text{COT})(\text{THF})_2]_2$. Similarly, $[\text{Sm}(\mu\text{-SC}_6\text{H}_2\text{Me}_3\text{-2,4,6})(\text{COT})(\text{THF})_2]_2$ and $[\text{Sm}(\mu\text{-SC}_6\text{H}_2\text{Pr}_3\text{-2,4,6})(\text{COT})(\text{THF})_2]_2$ were prepared. A benzeneselenolate complex $[\text{Sm}(\mu\text{-SePh})(\text{COT})(\text{THF})_2]_2$ was also prepared by the same procedure.



The molecular structure of $[\text{Sm}(\mu\text{-SePh})(\text{COT})(\text{THF})_2]_2$ was studied by X-ray diffraction (Fig. 48). The samarium atom has a pseudo square pyramidal and four-legged piano-stool geometry coordinated by one planar C_8H_8 ring, two bridging selenium atoms, and two oxygen atoms of THF. The Sm_2Se_2 unit is exactly planar, and two bridging selenium ligands are in a distorted trigonal-planar geometry. The Sm-Se bond distances are 3.015(2) and 3.174(2) Å.

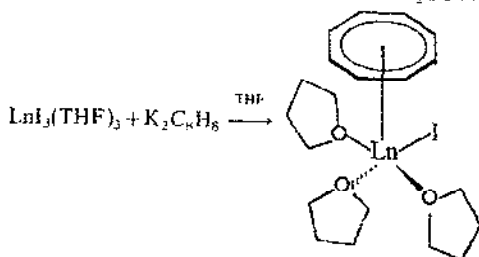
Edelmann and coworkers [66] prepared $[\text{Li}(\text{THF})_4][\text{Ce}(\text{COT})_2]$ and $(\text{THF})_3\text{-Na}(\mu\text{-COT})\text{Ce}(\text{COT})$ ($\text{COT} = \eta^8\text{-cyclooctatetraenyl}(2-)$) complexes. The complex $[\text{Li}(\text{THF})_4][\text{Ce}(\text{COT})_2]$ was obtained as a by-product from $[(\text{COT})\text{Ce}(\mu\text{-Cl})(\text{THF})_2]_2$ and $\text{LiCH}(\text{SiMe}_3)_2$ in THF. The structure consists of separated ions' pairs (Fig. 49). In the anion $[\text{Ce}(\text{COT})_2]^-$ the central Ce atom is coordinated by two $\eta^8\text{-cyclooctatetraenyl}$ rings to form a sandwich. The Ce(1)-COT(centroid) distance is 204.3(4) Å. In the cation $[\text{Li}(\text{THF})_4]^+$ the Li has tetrahedral arrangement, which is formed by the coordination of four THF molecules.

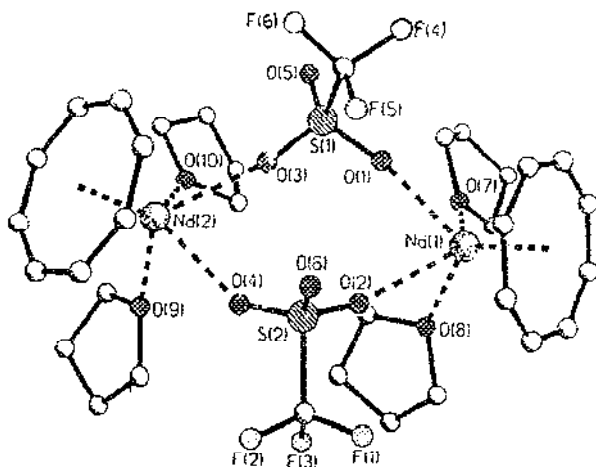
The complex $(\text{THF})_3\text{Na}(\mu\text{-COT})\text{Ce}(\text{COT})$ was separated from the reaction of $[(\text{COT})\text{Ce}(\mu\text{-Cl})(\text{THF})_2]_2$ with $\text{t-BuN}=\text{CH}-\text{CH}=\text{Nt-Bu}$ in THF. In the structure of $(\text{THF})_3\text{Na}(\mu\text{-COT})\text{Ce}(\text{COT})$ (Fig. 50), cerium and sodium are bound by the bridge-

Fig. 50. Structure of $(\text{THF})_3\text{Na}(\mu\text{-COT})\text{Ce}(\text{COT})$.

The structure of $[(\text{COT})\text{Nd}(\mu\text{-O}_3\text{SCF}_3)(\text{THF})_2]_2$ consists of dimeric molecules with two bridging triflate-anions between two Nd atoms (Fig. 51). The Nd(1)–COT(1)(centroid) distance is 193.5(2) pm, the average Nd–O distance for triflate ligands is 248.6(3) pm.

The monomeric iodides $(\text{COT})\text{Ln}(\text{I})(\text{THF})_3$ ($\text{Ln} = \text{Nd}, \text{Sm}$) were synthesized by the reaction of lanthanide triiodides with K_2COT :

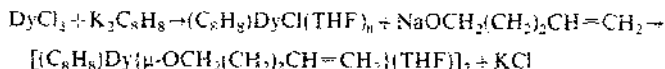


Fig. 51. Molecular structure of $[(\text{COT})\text{Nd}(\mu\text{-O}_3\text{SCF}_3)(\text{THF})_2]_2$.

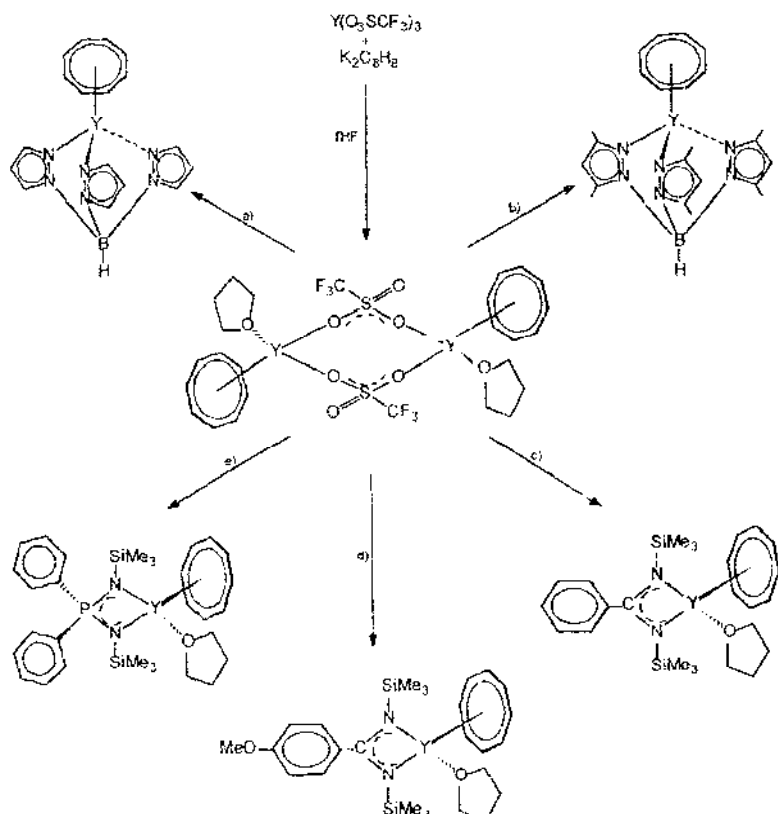
The neodymium derivative $(\text{COT})\text{Nd}(\text{I})(\text{THF})_3$ is isostructural with the previously described $(\text{COT})\text{Ce}(\text{I})(\text{THF})_3$. The Nd-I distance is 328.7(1) pm.

Kilmann and Edelmann [68] also reported the synthesis of some yttrium half-sandwich cyclooctatetraenyl complexes. The complex $[(\text{COT})\text{Y}(\mu\text{-O}_3\text{SCF}_3)(\text{THF})]_2$ was obtained from $\text{Y}(\text{O}_3\text{SCF}_3)_3$ and K_2COT in THF. Reaction of $[(\text{COT})\text{Y}(\mu\text{-O}_3\text{SCF}_3)(\text{THF})]_2$ with pyrazolylborate anions gave the monomeric half-sandwich complexes $(\text{COT})\text{Y}(\text{HBpz}_3)$ and $(\text{COT})\text{Y}[\text{HB}(3,5\text{-Me}_2\text{pz})_3]$. The yttrium benzanidates $(\text{COT})\text{Y}[\text{MeOC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]\text{THF}$ and $(\text{COT})\text{Y}[\text{CF}_3\text{C}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]\text{THF}$ were prepared similarly. The treatment of $[(\text{COT})\text{Y}(\mu\text{-O}_3\text{SCF}_3)(\text{THF})]_2$ with $[\text{Li}][7\text{-Ph-N-SiMe}_3]$ led to the yttrium phosphazene derivative $(\text{COT})\text{Y}[\text{Ph}_2\text{P}(\text{N-SiMe}_3)_2]\text{THF}$. All synthetic procedures are shown in the Scheme 31. The new organoyttrium complexes have been characterized by elemental analyses and spectroscopic methods, including ^{89}Y NMR spectroscopy.

Zhang et al. [69] published the synthesis and crystal structure of $[(\text{C}_8\text{H}_8)\text{Dy}(\mu\text{-OCH}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2)(\text{THF})]_2$. The complex $[(\text{C}_8\text{H}_8)\text{Dy}(\mu\text{-OCH}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2)(\text{THF})]_2$ was synthesized by the reaction of DyCl_3 and $\text{K}_2\text{C}_8\text{H}_8$ in THF, followed by the addition of $\text{NaOCH}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2$.



The complex has a dimeric structure (Fig. 52). Each dysprosium is coordinated by one C_8H_8 ligand, one THF and two bridging $\text{OCH}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2$ groups. The average Dy-C(C_8H_8 ring) distance is 2.593(6) Å.



Scheme 31

Kilimann et al. [70] published the synthesis of some Ce(III), Ce(IV) and U(IV) cyclooctatetraenyl complexes. The reaction of the dilithium salt of 1,4-bis(trimethylsilyl)cyclooctatetraene with anhydrous cerium trichloride led to the anionic sandwich complex, which was immediately converted to the neutral Ce(IV) derivative by oxidation with excess of silver iodide (Scheme 32).

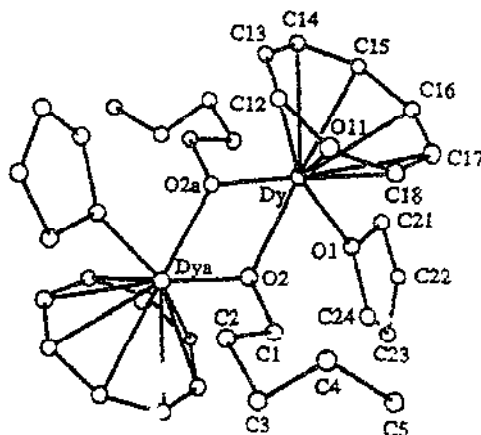
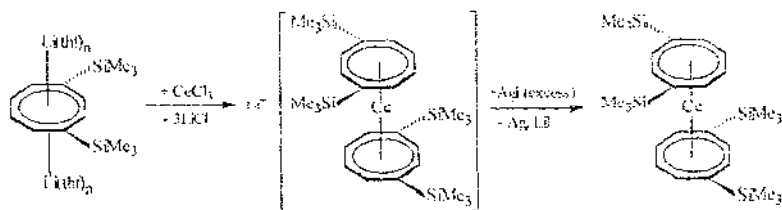


Fig. 52. Molecular structure of $[(C_6H_5)_2Dy\{\mu-OCH_2(CH_2)_2CH_3\}-CH_3](THF)_2$.

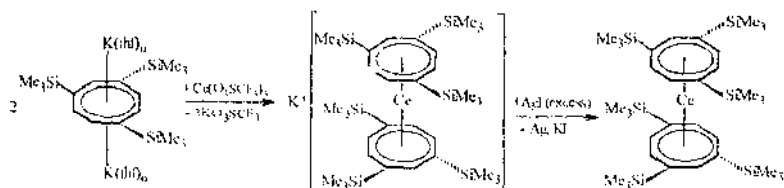


Scheme 32.

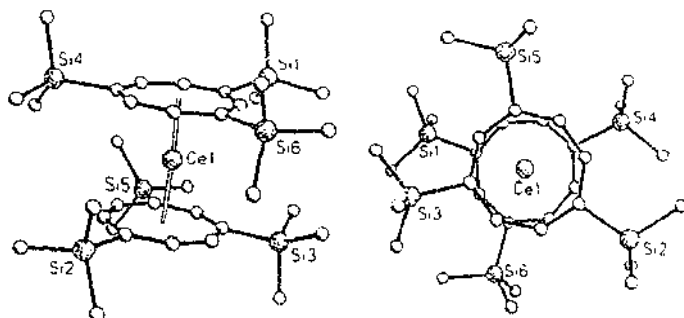
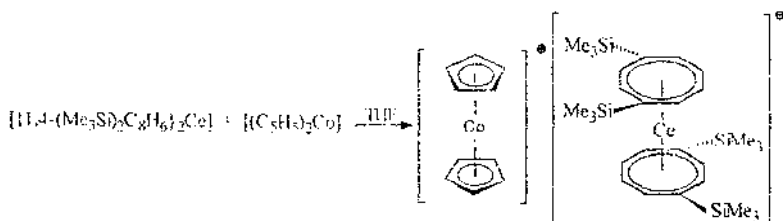
One more Ce(IV) sandwich complex was prepared by the reaction between the dipotassium salt of the 1,3,6-tris(trimethylsilyl)cyclooctatetraene and cerium triflate followed by oxidation of the ionic intermediate by AgI (Scheme 33).

The structure of the latter complex was studied by X-ray diffraction. In the structure (Fig. 53) the two annulene rings are η^8 -coordinated to the Ce atom. The Ce1-C distances range from 267.0 to 275.1 pm. The two C_8 -rings are not coplanar: the ring-centroid-Ce-ring-centroid angle is 176.1° .

A redox reaction of $[1.44-(Me_3Si)_6C_8H_6]Ce^+$ with cobaltocene afforded a novel Ce(III) ionic complex, in which both the cation and the anion are sandwich complexes (Scheme 34).



Scheme 33.

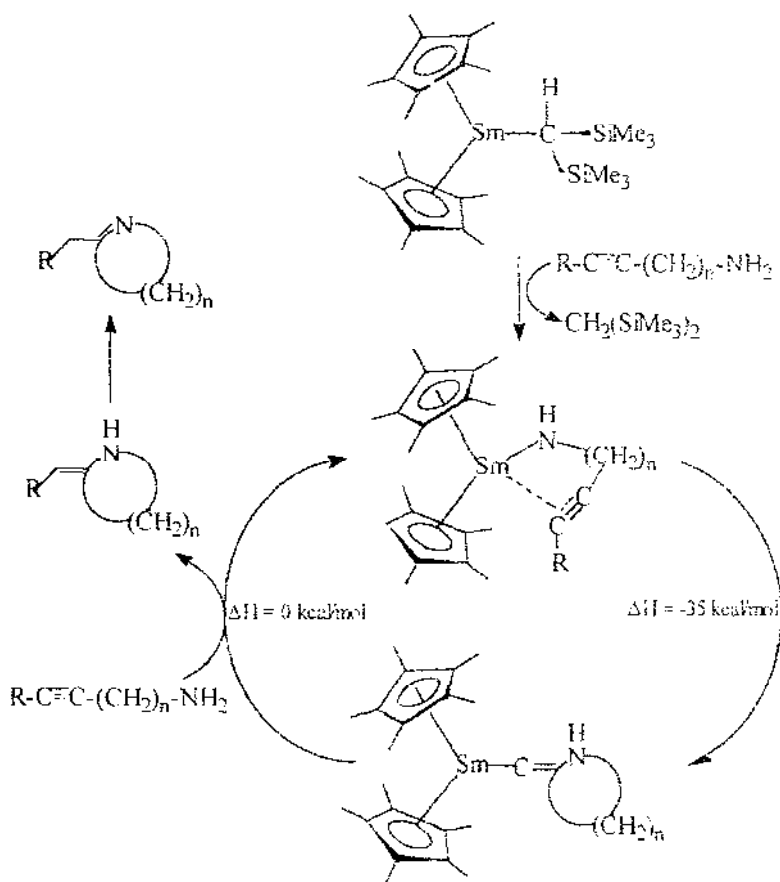
Fig. 53. Molecular structure of $[\text{11.3.6-(Me}_3\text{Si)}_2\text{C}_6\text{H}_3]_2\text{Ce}]$.

Scheme 34.

2.5. Organolanthanide catalysis

Li et al. [71] showed that the complex $(\eta^5\text{-Me}_5\text{C}_5)_2\text{SmCH}(\text{TMS})_2$ serves as a precatalyst for the efficient and regiospecific hydroamination cyclization of aliphatic and aromatic aminoalkynes $\text{RC}\equiv\text{C}(\text{CH}_2)_n\text{NH}_2$ to yield the corresponding heterocycles (Scheme 35).

Marks and coworkers [72] investigated the C_1 -symmetric $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{C}_5\text{H}_3\text{R})\text{-LnE}(\text{SiMe}_3)_2$ ($\text{Ln}=\text{La, Nd, Sm, Y, Lu}$; $\text{E}=\text{N, CH}$;

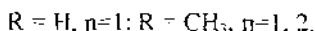
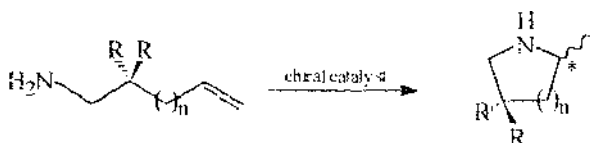


Scheme 35

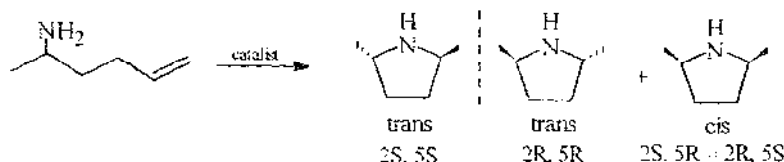
R* = chiral auxiliary) complexes as precatalysts for the efficient regio- and enantioselective hydroamination-cyclization of the aminoenynes 1-aminopent-4-ene, 2-aminohex-5-ene, 2,2-dimethyl-1-aminopent-5-ene, and 2,2-dimethyl-1-aminohex-5-ene to yield the corresponding heterocycles (Scheme 36).

The (+)-ncomenthyl precatalysts (Ln = Nd, Sm) effect the cyclization of 2-aminohex-5-ene to *trans*-2,5-dimethylpyrrolidine in greater than 95% diastereoselectivity at 25 °C (Scheme 37).

The authors supposed that the basic mechanism for the present asymmetric aminoenyne hydroamination/cyclization by the chiral organolanthanides is ana-



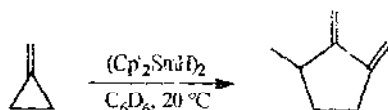
Scheme 36.



Scheme 37.

logous to the mechanism proposed for the achiral Cp^*_2Ln -catalysed process (Scheme 38).

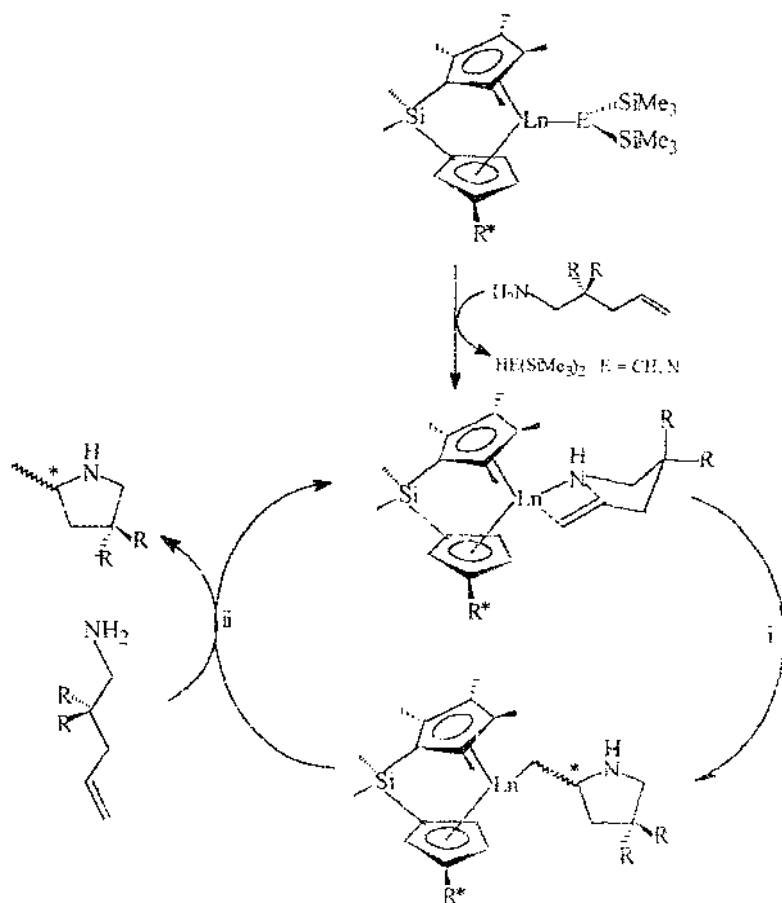
Yang et al. [73] reported on efforts to broaden the scope of polymerization/copolymerization using efficiently prepared methylenecyclopropane and organolanthanide catalysts of the type $[(\eta^5-C_5Me_5)_2LnH]_2$ ($Ln = Lu, Sm$). The homopolymerization of methylenecyclopropane in the presence of $[(\eta^5-C_5Me_5)_2LuH]_2$ proceeds cleanly to afford ring-opened, *exo*-methylene product. However, polymer yields are low and the polymerization process ceases before monomer consumption is complete. The larger Sm^{+3} ion effects catalytic methylenecyclopropane dimerization to yield the known 1,2-dimethylene-3-methylcyclopentane.



A probable mechanism for the reaction invokes β -H elimination and the intermediacy of a 1,3-diene fragment (Scheme 39).

Evans and Katsumata investigated the polymerization of ϵ -caprolactone [74] and copolymerization of ethylene carbonate and ϵ -caprolactone [75] by samarium complexes. Some characteristics of the catalysts are shown in Tables 1 and 2.

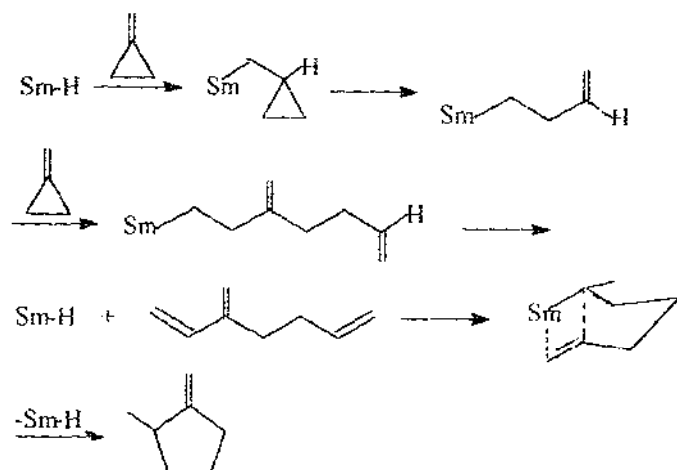
A variety of $Sm(II)$ complexes generate a ring-opening polymerization system with ϵ -caprolactone in reactions which initially involve oxidation of the metal. The $(C_5Me_5)_2-Sm(THF)_x$ reaction has been shown to be an active polymerization system which maintains activity after all of the initial batch of monomer is consumed [74].



Scheme 38.

Ethylene carbonate can be incorporated into a caprolactone polymer using a Sm(II) catalyst precursor to form rubbery polymer with up to 22% ethylene carbonate content [75].

Taube and Windisch [24] reported the catalysis of butadiene polymerization by the complexes $[\text{Li}(\text{C}_4\text{H}_8\text{O}_2)][\eta^5\text{-Cp}^*\text{La}(\eta^5\text{-C}_5\text{H}_5)_3]$ ($\text{Cp}^* = \text{C}_5\text{H}_5$, C_5Me_5 , C_6H_5) in toluene under standard conditions with moderate activity and high *trans* selectivity. The results are presented in Table 3.



Scheme 39.

Table 1

Polymerization of ϵ -caprolactone by divalent samarium complexes [74]

Sm(II) complex	Solvent	Time	Yield (wt.%)	M_n	M_w/M_n
$(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$	toluene	1 min	15	9000	1.4
		5 min	61	18000	1.7
		1 h	99	63000	1.4
		6 h	98	29000	2.5
	THF	5 min	70	31000	1.5
	THF	1 h	98	56000	1.3
$(\text{C}_5\text{Me}_5)_2\text{Sm}$	toluene	5 min	55	17000	1.5
$(\text{C}_9\text{H}_7)_2\text{Sm}(\text{THF})_2$	THF	5 min	98	34000	1.7
$(\text{C}_{13}\text{H}_9)_2\text{Sm}(\text{THF})_2$	THF	5 min	94	24000	1.6
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sm}(\text{THF})_2$	toluene	1 min	99	17000	3.0

Onozawa et al. [76] revealed that a wide variety of aldehydes are efficiently dimerized to esters by a catalytic amount of $(\text{C}_5\text{Me}_5)_2\text{LnCH}(\text{SiMe}_3)_2$ ($\text{Ln} = \text{Nd}, \text{La}$).

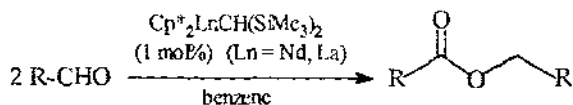


Table 2

Ethylene carbonate (EC), ϵ -caprolactone (CL) copolymerization by divalent samarium complexes [75]

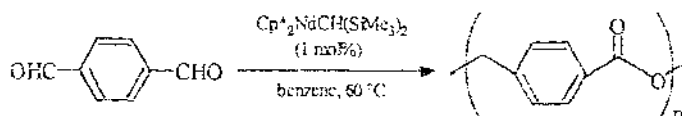
Catalyst	Solvent	EC:CL	Time (h)	Yield (wt.%)	GPC		EC content (mol%)	
					M_n	M_w/M_n	Calc	Found
$(C_5Me_5)_2Sm(THF)_2$	toluene	100:100	1	12	6000	1.9		22
			6	34	43000	2.0		22
			24	68	82000	1.9	21	22
			48	70	82000	1.8	23	22
	THF	100:100	24	94	95000	1.9	13	11
			6	30	19000	1.7		12
$(C_9H_7)_2Sm(THF)_2$	THF	100:100	6	14	18000	1.9		19
$(C_{13}H_9)_2Sm(THF)_2$	THF	100:100	6	63	28000	2.3	13	14
$[(Me_2Si)_2N]_2Sm(THF)_2$	toluene	100:100	1	30	7000	4.7		23

Table 3

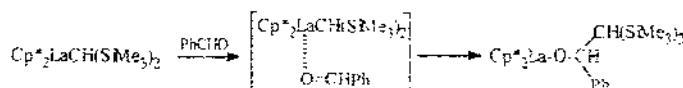
Results of butadiene polymerization catalyzed by the complexes $[Li(C_4H_8O_2)][\eta^5-Cp^*Lam^2-C_5H_5]_2$ ($Cp^* = C_5H_5$ (1), C_5Me_5 (2), C_9H_7 (3))

Catalyst	1	1	1	2	3
Temperature (°C)	25	50	50	50	50
Time of the reaction (h)	14	3	4	4	4
Yield (%)	74	43	25	57	74
Turnover number (mol C_4H_6 / (mol Li) h^{-1})	102	284	308	284	265
1,4- <i>trans</i> -Polybutadiene (%)	73	74	74	82	56
1,4- <i>cis</i> -Polybutadiene (%)	11	19	18	12	30
1,4-Polybutadiene (%)	16	7	8	6	14

The neodymium catalyst was applied to polyester synthesis starting with dialdehydes.



A stoichiometric reaction of the lanthanum complex with benzaldehyde indicated the intermediacy of alkoxo complexes in the catalysis.

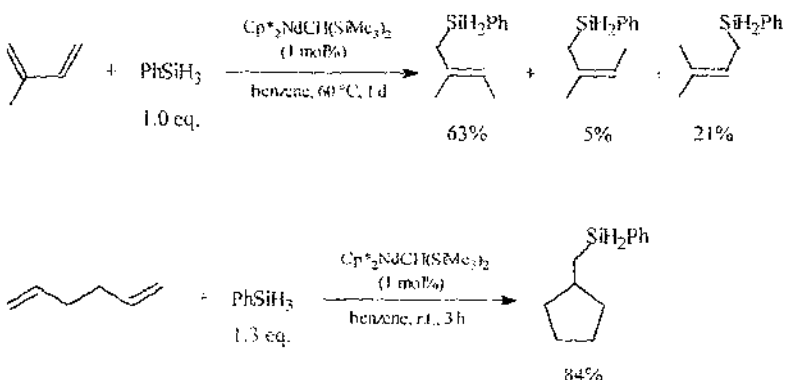


The same authors [77] also reported the hydrosilylation of dienes catalysed by $\text{Cp}^*_2\text{NdCH}(\text{SiMe}_3)_2$ (Scheme 40).

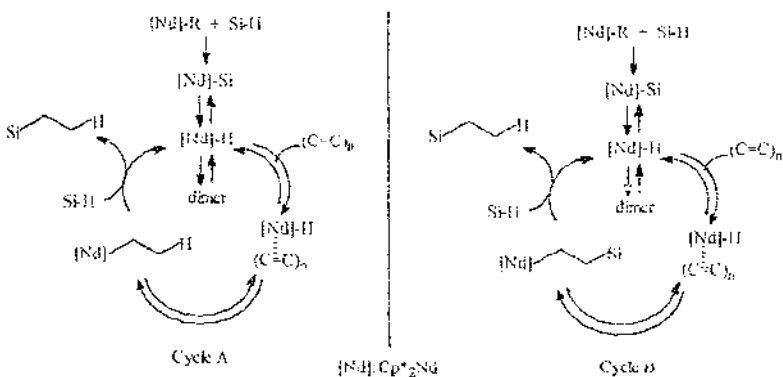
Two different catalytic cycles are possible for the hydrosilylation: one involving a hydridometal species as a key intermediate and the other being based on silylmetallacyclopentane species (Cycles A and B, Scheme 41).

In contrast, hydrosilylation of 1,5- and 1,6-dienes proceeded through intramolecular C-C bond formation to give (silylmethyl)cyclopentanes.

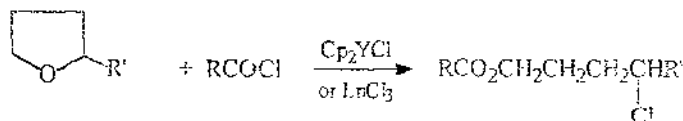
Qian et al. [78] published the regioselective acylative cleavage of cyclic ethers catalysed by 1% Cp^*_2YCl or 10% LnCl_3 ($\text{Ln} = \text{Y}, \text{Yb}, \text{Er}, \text{Gd}, \text{Pr}, \text{Ce}, \text{La}$). Heavy rare earth trichlorides were much more catalytically active than the lighter ones.



Scheme 40.



Scheme 41.



Yasuda [79] reported the preparation of lactone polymers at low temperature by ring-opening polymerization of lactones using the cyclopentadienyl complexes $(\text{C}_5\text{R}_5)_n\text{LnX}_h$ ($\text{R} = \text{H, Alk, SiMe}_3$; $\text{Ln} = \text{Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$; $\text{X} = \text{Cl, Br}$; $a + b = 3$) as catalysts.

Geerts [80] patented a catalytic system consisting of $\text{Cp}_n\text{YX}_{2-n}\text{ML}$ ($\text{Cp} = \text{C}_5\text{H}_5$ or C_5Me_5 ; $\text{X} = \text{halogen}$; $\text{M} = \text{alkali metal}$; $\text{L} = \text{electron donor ligand}$; $n = 1, 2$) and an alkali or alkaline earth metal alkyl as cocatalyst. For example, ethylene was polymerized by using $(\text{Me}_5\text{C}_5)_2\text{Y}(\mu\text{-Cl})_2\text{K}(\text{THF})_2$ as catalyst and BuLi as cocatalyst in the presence of H_2 .

Yokota [81] published catalysts containing organoaluminium compounds, Lewis bases and (substituted) dicyclopentadienyl lanthanides for preparation of polyolefins with controlled molecular weight. The polymerization of ethylene at 3 atm in PhMe in the presence of bis(pentamethylcyclopentadienyl)butyltetramethylaluminum and THF -trimethylaluminum complex produced polyethylene with $M_w = 2670$ and $M_w/M_n = 2.17$.

Schaverien [21,22] reported the α -olefin and diene polymerization catalysed by the yttrium complexes $[\text{Y}(\text{C}_5\text{Me}_5)(\text{OC}_6\text{H}_3\text{Bu}_2)(\mu\text{-H})]_2$ and $[\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr})]_2(\mu\text{-H})(\mu\text{-C}_6\text{H}_4\text{CH}_2\text{R})$. The compounds are single-component catalysts for the polymerization of α -olefins. Dissolution of $[\text{Y}(\text{C}_5\text{Me}_5)(\text{OC}_6\text{H}_3\text{Bu}_2)(\mu\text{-H})]_2$ in 1-hexene led to slow polymerization to yield poly(1-hexene) with $M_w = 15\,700$, $M_n = 9400$, $M_w/M_n = 1.67$. The complex also cyclopolymerized the nonconjugated diene 1,5-hexadiene to afford poly(methylene-1,3-cyclopentane).

Hajela and Bercaw [61] investigated the model Ziegler-Natta olefin polymerization system $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_5)_2]\text{Sc}(\text{CH}_2\text{CH}(\text{CH}_3)_2)(\text{PMc}_3)$. The authors reported the competitive chain transfer by β -hydrogen and β -methyl elimination for the system.

Woo et al. [82,83] carried out nonlocal density functional (DF) calculations on the insertion of ethylene into the metal- CH_3 bond of Kaminsky-type metallocenes including Cp_2ZrCH_3 . The DF calculations revealed that the insertion into the bis-Cp systems proceeds with 14 kJ mol^{-1} for Cp_2ZrCH_3 . This barrier is marginally influenced by going from the charged species $\text{Cp}_2\text{-Zr}^+\text{CH}_3^-$ to the neutral d^0 system Cp_2ZrCH_3 .

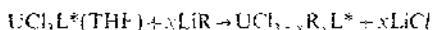
Bierwagen et al. [84] reported investigations of the geometries of the isoelectronic model complexes $\text{X}_2\text{M}^+-\text{R}$ including the complexes where $\text{M} \approx \text{Sc}$, $\text{X} = \text{Cl}$ or $(\eta^5\text{-C}_5\text{H}_5)$ and $\text{R} = \text{H, CH}_3, \text{SiH}_3$. The Sc compounds strongly prefer a planar configuration that is related to the electronic configuration of $\text{Sc } (4s)^1(3d)^1$. The results suggested that $[(\eta^5\text{-C}_5\text{H}_5)_2\text{CMe}]^+(\eta^5\text{-fluorenyl})\text{Sc}^-\text{R}$ would not catalyze syndiotactic polymerization under these conditions.

3. Actinides

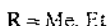
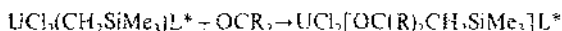
3.1. Actinides complexes without supporting cyclopentadienyl ligands

3.1.1. Alkyl complexes

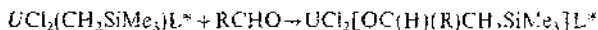
Domingos et al. [85] published the synthesis of the tetravalent uranium hydrocarbyl compounds $\text{UCl}_2[\text{CH}(\text{SiMe}_3)_2]\text{L}^*$ ($\text{L}^* = \text{HB}(3,5\text{-i-Pr}_2\text{-C}_6\text{H}_3)_2$) and $\text{UCl}_{1-x}[\text{CH}_2(\text{SiMe}_3)_x]\text{L}^*$ by salt metathesis from $\text{UCl}_4\text{L}^*(\text{THF})$ and the appropriate lithium alkyls:



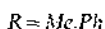
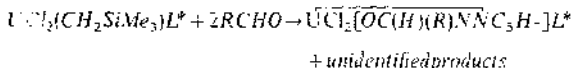
Reaction of $\text{UCl}_2(\text{CH}_2\text{SiMe}_3)\text{L}^*$ with stoichiometric amounts of ketones gave tertiary alkoxide derivatives as a result of insertion of the ketone into the U-C bond:



Reaction of $\text{UCl}_2(\text{CH}_2\text{SiMe}_3)\text{L}^*$ with acetaldehyde and benzaldehyde led to the corresponding $\text{UCl}_2[\text{OC}(\text{H})(\text{R})\text{CH}_2\text{SiMe}_3]\text{L}^*$ ($\text{R} = \text{Me, Ph}$).



When $\text{UCl}_2(\text{CH}_2\text{SiMe}_3)\text{L}^*$ reacted with two equivalents of aldehydes the reaction gave some different products:



The molecular structure of $\text{UCl}_2[\text{OC}(\text{H})(\text{Me})\text{CH}_2\text{SiMe}_3]\text{L}^*$ consists of monomeric units with the uranium atom in a distorted-octahedral environment (Fig. 54). The U-O distance is 2.05(2) Å, the average U-Cl and U-N bond distances are 2.61(1) Å and 2.48(2) Å respectively.

The structures of $\text{UCl}_2[\text{OC}(\text{H})(\text{R})\text{NNC}_5\text{H}_5]\text{L}^*$ ($\text{R} = \text{Me}$ (Fig. 55), Ph) and $\text{UCl}_2[\text{OC}(\text{Me})_2\text{NNC}_5\text{H}_5]\text{L}^*$ consist of discrete molecules. In the structures the uranium atom is seven-coordinate and displays capped-octahedral geometry.

3.1.2. Complexes with phosphine ligands

Edwards et al. [86] studied the reaction of $\text{Th}[\text{P}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2]_4$ with carbon monoxide, which led to the compound $\text{Th}\{\text{OC}[\text{P}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2]_2\}_2$. The molecule contains ten-coordinate thorium bonded to two di-anionic diphospha-secondary alkoxy ligands generated as a result of CO insertion (Fig. 56). Only two CO molecules

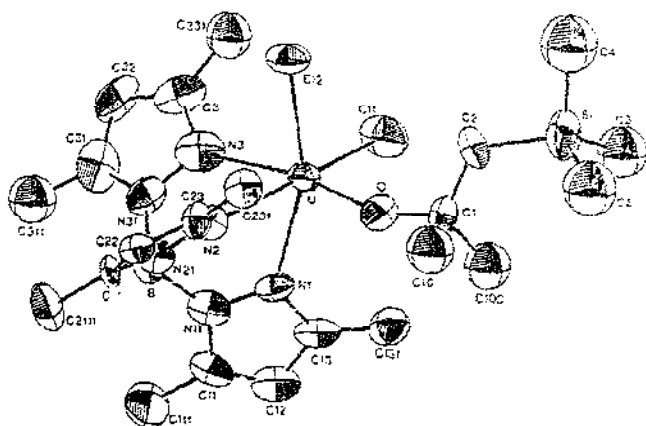


Fig. 54. Molecular structure of $\text{UCl}_2[\text{OC}(\text{H})(t\text{-Me})\text{CH}_2\text{SiMe}_3]\text{L}^* \cdot \text{L}^*$, $\text{L}^* = \text{HBr}(3,5\text{-Me}_2\text{pz})_2$.

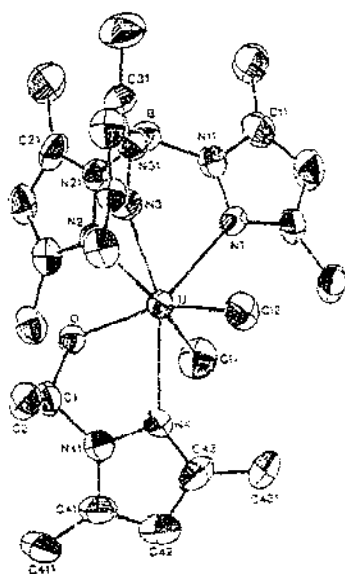
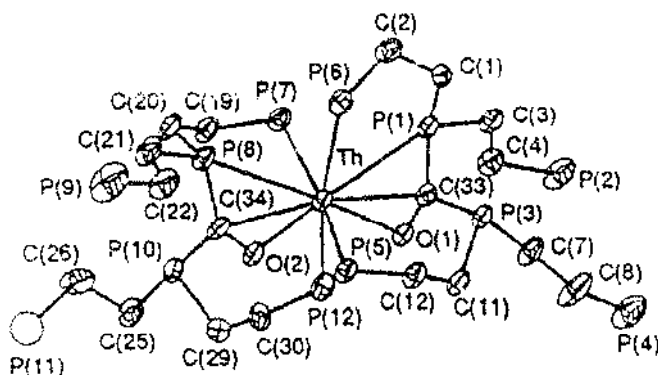


Fig. 55. Molecular structure of $\text{UCl}_2[\text{OC}(\text{H})(\text{N} \equiv \text{N})\text{C}(\text{Br})_2]\text{L}^* \cdot \text{L}^*$, $\text{L}^* = \text{HBr}(3,5\text{-Me}_2\text{pz})_2$.

Fig. 56. Molecular structure of $\text{Th}\{\text{OC}[\text{P}(\text{CH}_2\text{CH}_1)\text{PMe}_2]_2\}_{12}$.

have inserted, each between two metal phosphide bonds, thereby coupling two phosphido phosphorus atoms at each CO carbon atom generating two new tertiary phosphines with concomitant formal reduction of the CO bond order from 3 to 1. Each P_2CO unit is η^3 -bonded to the thorium atom with one of the phosphorus atoms coordinated to thorium. Although the geometry of the ten-coordinate thorium atom cannot be described in terms of any idealized polyhedron, if each $\eta^3\text{-PCO}$ unit is considered to occupy one coordination site then the geometry is distorted trans-octahedral.

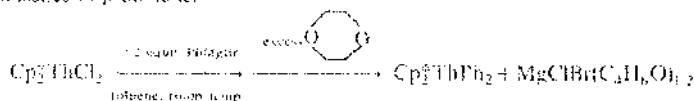
3.2. Cyclopentadienyl complexes

3.2.1. Mono- and bis(cyclopentadienyl) complexes

Grades et al. [87] prepared several mono- and bis(pentamethylcyclopentadienyl) borohydrides of uranium (Scheme 42).

The complex $[\text{UCl}(\text{Me})_2(\text{BH}_4)_2]$ has been characterized by an X-ray crystal structure analysis (Fig. 57). The molecule adopts a pseudo-tetrahedral bent-sandwich configuration. The U-B and the average U-C bond distances are 2.58(3) Å and 2.74(3) Å respectively.

Englund et al. [88] reported new syntheses of $\text{Cp}_2^*\text{ThPh}_2$ and $\text{Cp}_2^*\text{Th}(\text{Me})(\text{aryl})$ derivatives. The complex $\text{Cp}_2^*\text{ThPh}_2$ was obtained from $\text{Cp}_2^*\text{ThCl}_2$ and PhMgBr in the presence of *p*-dioxane.



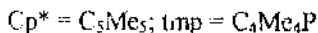
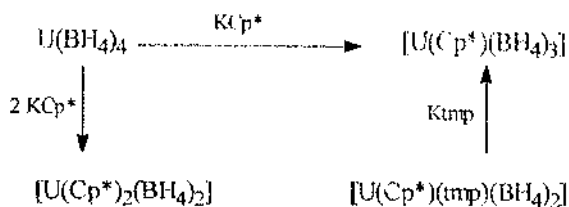
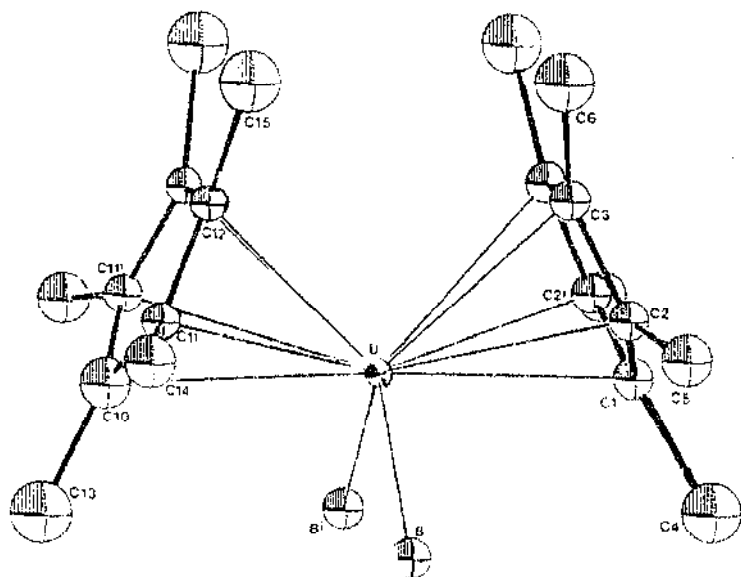
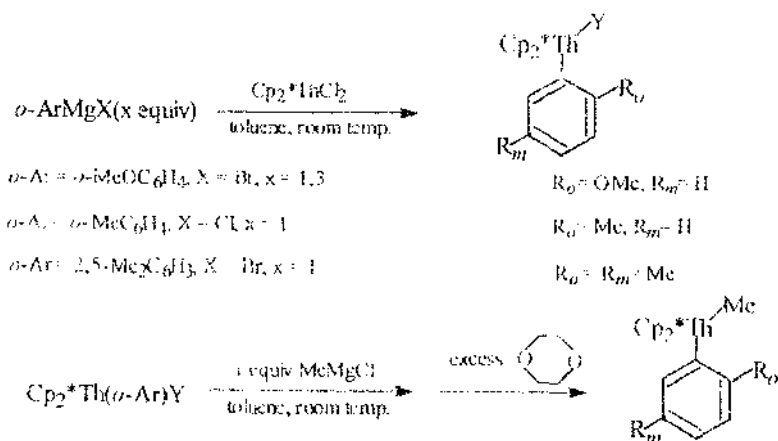


Fig. 42.

Fig. 57. Molecular structure of $[\text{Cp}^*_2\text{CMe}_4(\text{BH}_4)_2]$.

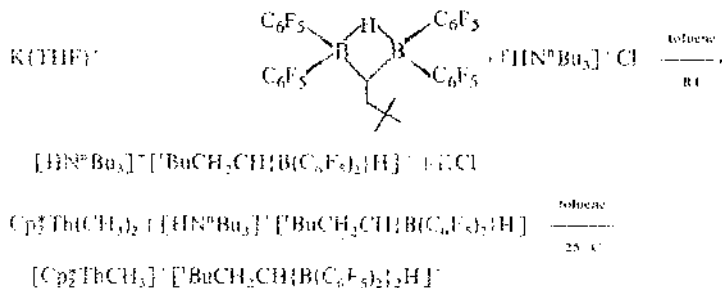
The aryl-hydride intermediates and the respective methyl-aryl complexes $\text{Cp}^*_2\text{Th}(\text{Me})(o\text{-Ar})$ ($o\text{-Ar} = o\text{-MeOC}_6\text{H}_4$, $o\text{-MeC}_6\text{H}_4$ and $2,5\text{-Me}_2\text{C}_6\text{H}_3$) were prepared according to Scheme 43.

The tolyl and xylyl derivatives exists as pairs of rotamers in solution. The halide exchange was observed in the preparation of the aryl hydride complexes when aryl-magnesium bromides were employed.

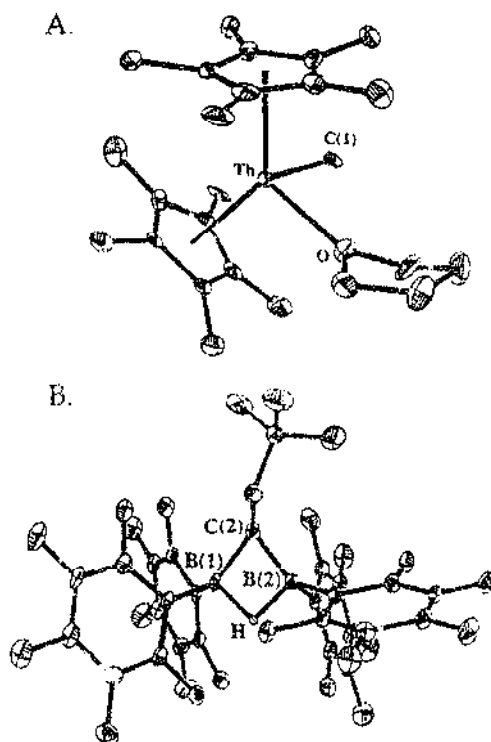


Scheme 43

Jin et al. [89] reported the synthesis and properties of the cationic metallocene complex $\text{Cp}_2^*\text{ThCH}_3^+ [\text{tBuCH}_2\text{CH}[\text{B}(\text{C}_6\text{F}_5)_2]_2\text{H}]^-$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$). The complex was obtained by the protolytic reaction of the $[\text{HN}^+\text{Bu}_3]^- [\text{tBuCH}_2\text{CH}[\text{B}(\text{C}_6\text{F}_5)_2]_2\text{H}]^-$ with $\text{Cp}_2^*\text{Th}(\text{CH}_3)_2$.



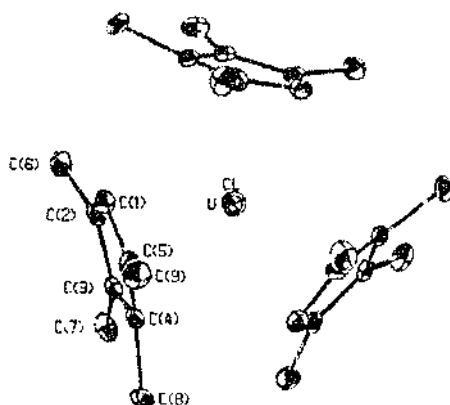
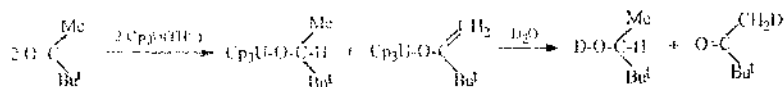
The mono-THF adduct $[\text{Cp}_2^*\text{Th}(\text{CH}_3)\text{THF}]^+ [\text{tBuCH}_2\text{CH}[\text{B}(\text{C}_6\text{F}_5)_2]_2\text{H}]^-$ has been characterized by X-ray diffraction. The complex consists of well-separated $\text{Cp}_2^*\text{Th}(\text{CH}_3)\text{THF}^+$ and $[\text{tBuCH}_2\text{CH}[\text{B}(\text{C}_6\text{F}_5)_2]_2\text{H}]^-$ ions (Fig. 58). The cation adopts a 'bent metallocene' geometry with the angle $\text{Cp}^*\text{ThCp}^* = 137.1^\circ$ and with the distances $\text{Th}-\text{C}(1) = 2.433(7)$, $\text{Th}-\text{O}(1) = 2.455(4)$, $\text{Th}-\text{C}_{\text{avg}}(\text{av}) = 2.486 \text{ \AA}$. The dinuclear anion contains an essentially planar four-membered ring with significant steric screening of the $\mu\text{-H}$ functionality. The average $\text{B}-\text{C}(\text{aryl})$ distance of $1.62 \text{ \AA}$ in the anion is shorter than in typical $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3$ complexes ($1.64\text{--}1.66 \text{ \AA}$).

Fig. 58. Structure of $[Cp^*ThCl_2(THF)]^+ [B(C_6F_5)_4]^-$

3.2.2. Tris(cyclopentadienyl) complexes

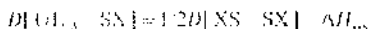
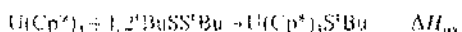
Cloke et al. [90] reported the synthesis of tris(tetramethylecyclopentadienyl) derivatives of the uranium and thorium $[MCl(\eta-C_5Me_5H)_3]$ ($M=U, Th$) from $[Li(C_5Me_5H)]$ and the appropriate MCl_4 in THF. The products have been characterized by variable-temperature NMR studies and the uranium complex by X-ray crystallography. In the molecular structure of $[UCl(\eta-C_5Me_5H)_3]$ (Fig. 59) the U-Cl vector lies on a crystallographic three-fold axis; the average U-C(Cp) lengths are 2.79 Å.

Ephritikhine and co-workers [91] reported the reaction of saturated ketones $RCOCH_2R'$ with the trivalent uranium complex $Cp_3U(THF)$ ($Cp = \eta-C_5H_5$) (Scheme 44). The reaction gave an equimolar mixture of the complexes $Cp_3U[OC^dR(CH_2R')]$ and $Cp_3U[OCR(-CH_2R')]$. The hydrolysis of the compounds with deuterium oxide afforded respectively the O-deuterated pinacolyl alcohol and the pinacolone.

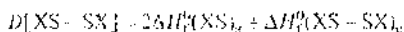
Fig. 39. Molecular structure of $[1,1'\text{-Cl}(\eta^5\text{-Ind})_2\text{U}_2]$.

Scheme 44.

Ephritikhine and coworkers [92] also calculated the 'absolute' bond disruption enthalpies $[D(\text{U}-\text{S})]$, neglecting solvent effects and possible U-U interaction in U_2U from the oxidative addition reaction by batch-titration solution calorimetry in toluene.

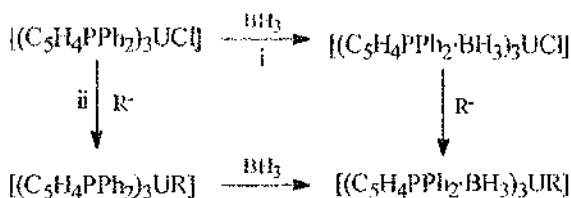


The disruption enthalpy of the sulphur-sulphur bond was given by the expression:



The derived values were as follows (kJ mol^{-1}): 252 ± 8 (Cp^* , Et), 266 ± 9 (Cp^* , Et), 158 ± 8 (Cp^* , ^tBu) and 158 ± 8 (Ind * , Et).

Baudry et al. [93] investigated the reactivity of U-H and U-C bonds in electron-poor cyclopentadienyluranium complexes. The organouranium complexes $[(\text{C}_5\text{H}_4\text{PPh}_2)_3\text{Bf}(\text{O})_2\text{UX}]$ (X = Cl, Me) were synthesized according to Scheme 45 (i) addition of borane and subsequent reaction of the intermediate borane adduct with $\text{Na}[\text{HBEt}_3]$ or LiMe ; (ii) addition of three equivalents of borane to the methyl derivative or to the hydride $[(\text{C}_5\text{H}_4\text{PPh}_2)_3\text{UH}]$.



Scheme 45

The complexes $[(C_5H_4PPh_2)_3UX]$ ($X = Me, H$) were converted finally into the complex $[(C_5H_4PPh_2 \cdot BH_3)_3UBH_4]$ according to Scheme 46.

The complexes $[(C_5H_4PPh_2 \cdot BH_3)_3UCl]$ and $[(C_5H_4PPh_2 \cdot BH_3)_3UBH_4]$ were easily reduced by sodium amalgam to afford the neutral complex $[(C_5H_4PPh_2 \cdot BH_3)_3U]$.

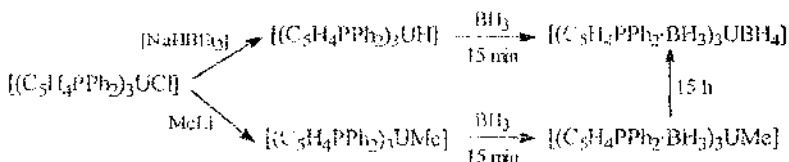
3.2.3. Cyclopentadienyl-like complexes

Arhigie et al. [94] published the ionic complexes $[K(18\text{-crown-6})][(NEt_2)_3U(\mu-\eta^7, \eta^7-C_7H_7)U(NEt_2)_3]$ and $[U(BH_4)_2(OC_4H_9)_2][(BH_4)_3U(\mu-\eta^7, \eta^7-C_7H_7)U(BH_4)_3]$. The $[(NEt_2)_3U(\mu-\eta^7, \eta^7-C_7H_7)U(NEt_2)_3]^-$ anion was formed by treatment of the amide complex $[U(NEt_2)_3]$ with $K[C_7H_9]$. Subsequent treatment of the product with 18-crown-6 leads to $[K(18\text{-crown-6})][(NEt_2)_3U(\mu-\eta^7, \eta^7-C_7H_7)U(NEt_2)_3]$.

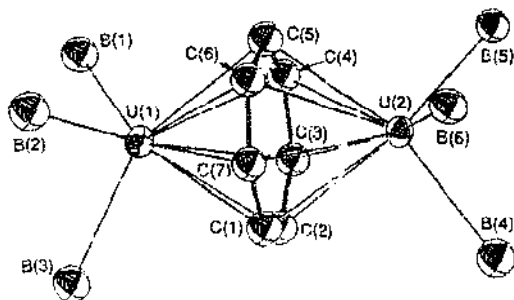
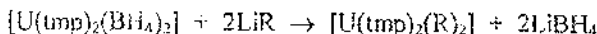
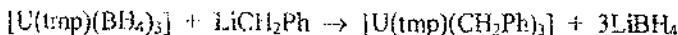
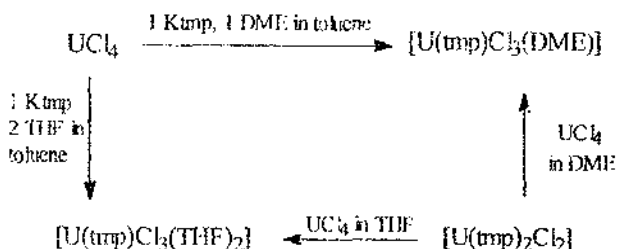
The reaction between $[U(BH_4)_4]$ and $K[C_7H_9]$ gave $K[(BH_4)_3U(\mu-\eta^7, \eta^7-C_7H_7)U(BH_4)_3]$ and the concomitant product $[U(BH_4)_3]$. Recrystallization of the mixture from THF-pentane led to the crystals of $[U(BH_4)_2(OC_4H_9)_2][(BH_4)_3U(\mu-\eta^7, \eta^7-C_7H_7)U(BH_4)_3]$. The structure is composed of discrete cation-anion pairs. In the anion (Fig. 60) each uranium atom has a distorted tetrahedral environment formed by the bridging C-H₇ ligand and three BH_4 groups. In the cation $[U(BH_4)_2(OC_4H_9)_2]^+$ the U atom is in a quite perfect pentagonal-bipyramidal arrangement with the tridentate boron hydride ligands in apical position.

Grados et al. [87] also published the syntheses of mono- and bis(tetramethylphospholyl)uranium complexes $[U(tmp)Cl_2(L)_2]$ ($tmp = C_4Me_4P$, $L = THF$ or $L_2 = \text{dimethoxyethane}$), $[U(tmp)X_3]$ ($X = BH_4$, CH_2Ph), $[U(tmp)_2X_2]$ ($X = Cl$, BH_4 , alkyl) or alkoxide; (Scheme 47).

The complex $[U(tmp)Cl_2(DMF)]$ was characterized by X-ray crystallography in



Scheme 46

Fig. 60. Structure of anion $[\text{U}(\text{BH}_4)_3(\text{ump})\text{Cl}_3] \cdot n \cdot \text{C}_6\text{H}_5\text{H} \cdot n(\text{BH}_4)_3$.

Scheme 47.

the structure of $[\text{U}(\text{tmp})\text{Cl}_3(\text{DME})]$ (Fig. 61) the coordination geometry around uranium is mer pseudo-octahedral with the tmp-ligand and one oxygen atom of the DME molecule in trans axial positions, while the other oxygen and three chlorine atoms, which are coplanar within $\pm 0.07(1)$ Å, constitute the equatorial plane.

The tetramethylphospholyl complexes were compared with their above-mentioned pentamethylcyclopentadienyl analogues (Scheme 42). Although the structures of tetramethylphospholyl uranium(IV) complexes and their pentamethylcyclopentadienyl counterparts are quite similar, the different electronic effects of C_5Me_5 and tmp ligands are manifested in the coordinating and redox properties of the complexes.

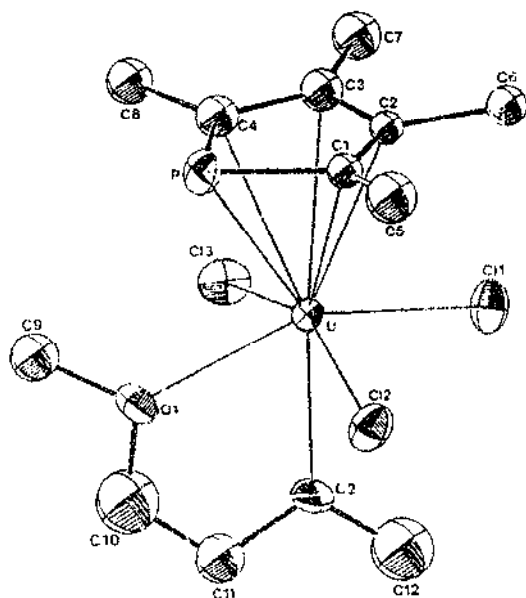


Fig. 61. Molecular structure of $[U(tmp)Cl_3(DME)]$ ($tmp = C_4Me_4P$).

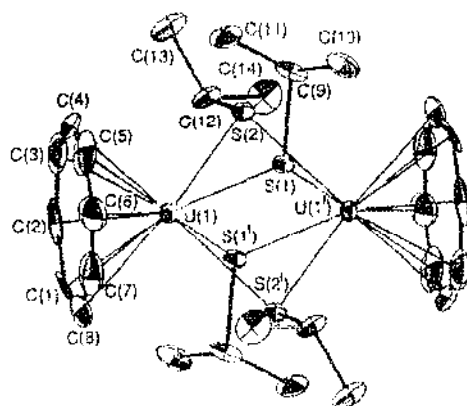
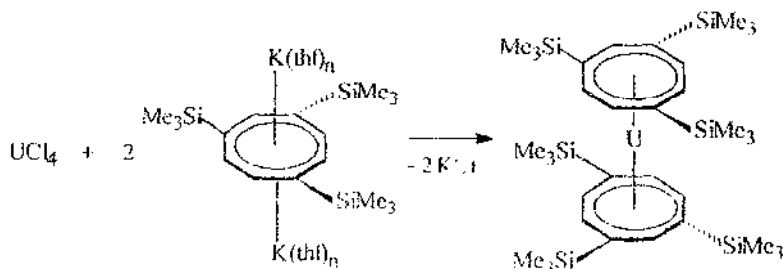
3.3. Complexes with cyclooctatetracycl ligands

Leverd et al. [95] described the complexes $[U(COT)(SR)_2]$ ($R = nBu, iPr, tBu$), which were obtained by treating $[U(COT)(BH_4)_2]$ with an excess of the corresponding thiol RSH or $NaSR$ in toluene. The complex $[U(COT)(S^iPr)_2]$ is built up of two monomeric units which are bridged by four S^iPr groups (Fig. 62). Each uranium atom is five-coordinate in a quite perfect square-pyramidal arrangement, if COT is considered as a mono-dentate ligand. The $U-S^iPr$ distances range from 2.806(3) to 2.895(3) Å. The reaction of the $[U(COT)(BH_4)_2]$ with $Na^+S^tBu^-$ led to the anionic species $[U(COT)(S^tBu)_2]^-$, for example $[Na(tbf)][U(COT)(S^tBu)_2]$.

Edelmann and coworkers [70] reported a uranium sandwich complex with the 1,3,6- $(Me_3Si)_3C_8H_3$ ligand, which was obtained by the reaction of UCl_4 with two equivalents of the dipotassium salt of the ligand (Scheme 48).

3.4. Organouranilic catalysis

Jia et al. [89] reported the highly active catalyst for ethylene polymerization and 1-hexene hydrogenation $[Cp^*ThCH_3]^+ [tBuCH_2CH(B(C_6F_5)_2)_2H]^-$ ($Cp^* = \eta^5-$

Fig. 62. Molecular structure of $[U(COT)_2(SiPr)_2]$.

Scheme 43.

C_4Me_5). At 25 °C, the activity of the compound was $5.8(1.1) \times 10^6$ g of linear polyethylene $(mol\ Th)^{-1} h^{-1} atm^{-1}$; $Nr \approx 58(11) s^{-1}$.

Samsel [96] patented actinide metallocene catalysts for the chain growth reaction of an α -olefin on an aluminum alkyl. A mixture of 15 mg $(\eta^5-C_5Me_5)_2ThCl_2$, 200 μl undecene, 5 ml Et_3Al and 5 ml PhMe was charged with ethylene to 160 psig, was heated 10 min at 70 °C, then reacted with 1 ml Me-aluminoxane for 30 min; 2 ml Me-aluminoxane was added to the mixture in two portions to give an Al alkyl with C_{4-22} alkyl groups.

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