

Lanthanides and actinides. Annual survey of their organometallic chemistry covering the year 1993¹

Joachim Richter, Frank T. Edelmann*

Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Magdeburg, Germany

Received 15 February 1995

Contents

1. Introduction	373
2. Lanthanides	373
3. Actinides	427

Keywords: Lanthanides; Actinides

1. Introduction

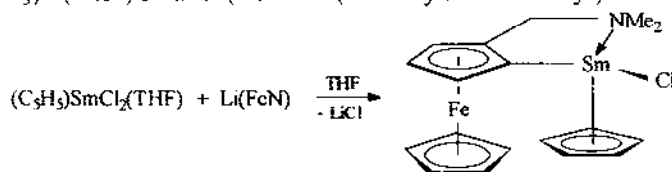
This review has been restricted to compounds of the lanthanides and actinides containing M–C bonds as defined by section 29 of Chemical Abstracts. The prelanthanides Sc, Y, and La have been included because of their similar size and charge to the lanthanides. Abstracts of papers presented at conferences, dissertations, and patents have mostly been excluded.

2. Lanthanides

2.1. Cyclopentadienyl and cyclopentadienyl-like compounds

2.1.1. Mono(cyclopentadienyl) compounds

Jacob, Pavlik and Edelmann [1] reported the synthesis of the thermally stable, heterobimetallic organolanthanide compounds $(C_5H_5)Sm(FcN)Cl$ and $(C_5Me_5)Y(FcN)Cl$ and $(FcN=2-(dimethylaminomethyl)ferrocenyl)$ by reaction of



¹ No reprints available for previous annual survey see *Coord. Chem. Rev.*, 141 (1995) 1.

* Corresponding author.

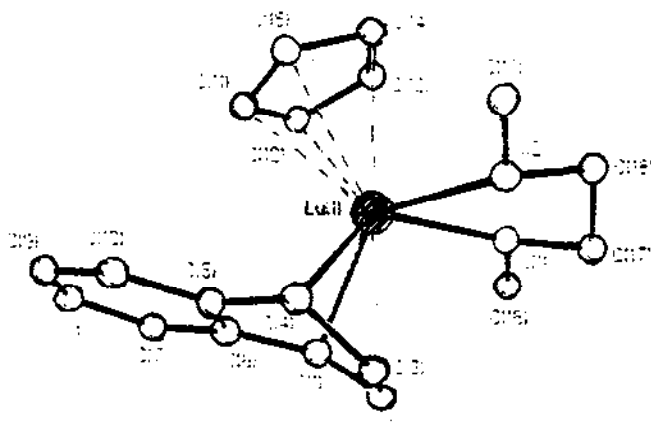
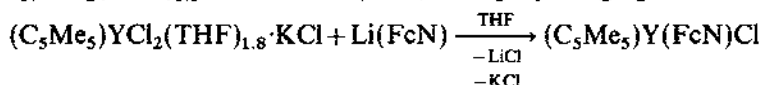


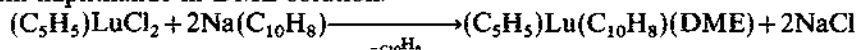
Fig. 1.

the corresponding cyclopentadienyl rare-earth chlorides $(C_5H_5)SmCl_2(THF)$ and $(C_5Me_5)YCl_2(THF)_{1.8} \cdot KCl$ with $Li(FcN)$ as organylating agent.



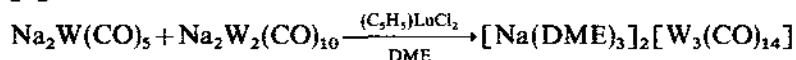
The compounds were characterized by elemental analysis, IR, 1H NMR, ^{13}C NMR and UV VIS spectra as well as by measuring the magnetic moments and by mass spectrometry.

Bochkarev et al. [2] published the synthesis and structure (Fig. 1) of the complex $(C_5H_5)Lu(C_{10}H_8)(DME)$ which was prepared by reaction of $(C_5H_5)LuCl_2$ with sodium naphthalide in DME solution.

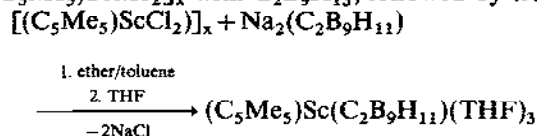


The naphthalene moiety in the complex is bent about the C(1)–C(4) plane with a dihedral angle of 148° . The Lu–C($C_{10}H_8$) bond lengths as well as the redistribution of C–C bond distances in the coordinated naphthalene ring suggest $2\eta^1:\eta^2$ -interaction of the lutetium atom with the naphthalene moiety.

The unexpected formation of the trinuclear tungsten carbonyl cluster $[Na(DME)_3]_2[W_3(CO)_{14}]$ after the treatment of $(C_5H_5)LuCl_2$ with an equimolar mixture of $Na_2W(CO)_5$ and $Na_2W_2(CO)_{10}$ in DME was reported by Voskoboynikov et al. [3].



Bercaw et al. [4] reported the synthesis of the scandium dicarbollide complex $(C_5Me_5)Sc(C_2B_9H_{11})(THF)_3$ by reactions of $[(C_5Me_5)ScCl_2]_x$ with $Na_2(C_2B_9H_{11})$ or $[(C_5Me_5)ScMe_2]_x$ with $C_2B_9H_{13}$, followed by treatment with THF.



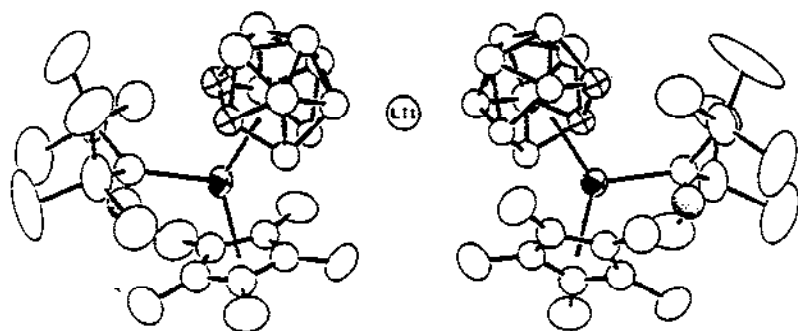
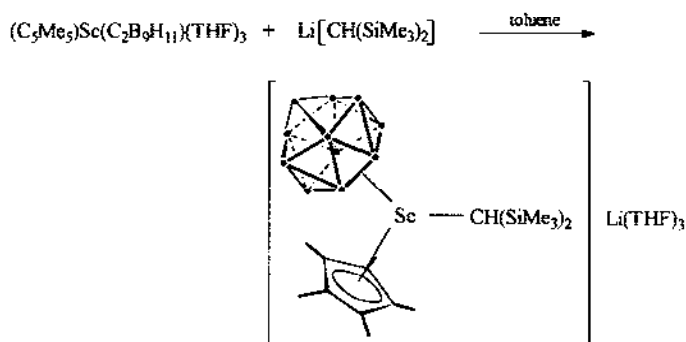


Fig. 2.

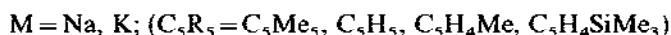
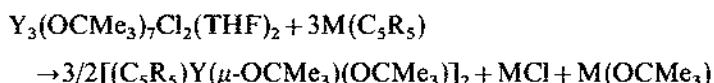
Alkylation of $(C_5Me_5)Sc(C_2B_9H_{11})(THF)_3$ with $LiCH(SiMe_3)_2$ yields $[(C_5Me_5)Sc(C_2B_9H_{11})\{CH(SiMe_3)_2\}][Li(THF)_3]$, and $[(C_5Me_5)Sc(C_2B_9H_{11})\{CH(SiMe_3)_2\}]_2Li[Li(THF)_3]$, which is obtained by its recrystallisation from pentane/toluene, has been characterized structurally (Fig. 2).



This alkyl derivative reacts slowly with H_2 to yield the unreactive scandium hydride dimer $[(C_5Me_5)(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$. Recrystallisation from toluene affords a crystalline form with less coordinated THF, $[(C_5Me_5)(C_2B_9H_{11})ScH]_2[Li(THF)_2(C_6H_5CH_3)_{3/2}]$, whose structure reveals that the two anionic $[(C_5Me_5)(C_2B_9H_{11})ScH]$ fragments are held together by reciprocal B–H dative bonds from the dicarbollide ligand to the electron deficient scandium. The potential of pentamethylcyclopentadienyl-dicarbollide derivatives of scandium to serve as efficient α -olefin polymerisation catalysts was also discussed.

Evans and co-workers [5] showed that the reaction of $Y_3(OR')_7Cl_2(THF)_2$ ($R' = CMe_3$) with alkali metal cyclopentadienyl reagents, $M(C_5R_5)$ ($M = Na, K$) in toluene disrupts the trimetallic structure of the starting material and forms the halide-free bimetallic compounds $[(C_5R_5)Y(\mu-OR')(OR')]_2$ ($C_5R_5 = C_5Me_5, C_5H_5, C_5H_4Me, C_5H_4SiMe_3$). $[(C_5Me_5)Y(\mu-OR')(OR')]_2$ and $[(C_5H_4SiMe_3)Y(\mu-OCMe_3)(OCMe_3)]_2$ were also obtained from the reaction of $YCl_3(THF)_x$ with two equivalents

of NaOCMe_3 and one equivalent of $\text{M}(\text{C}_5\text{R}_5)$ in toluene solution at reflux temperature.



X-ray crystallographic data for $[(\text{C}_5\text{Me}_5)\text{Y}(\mu\text{-OCMe}_3)(\text{OCMe}_3)]_2$ (Fig. 3), $[(\text{C}_5\text{H}_5)\text{Y}(\mu\text{-OCMe}_3)(\text{OCMe}_3)]_2$ (Fig. 4) and $[(\text{C}_5\text{H}_4\text{SiMe}_3)\text{Y}(\mu\text{-OCMe}_3)(\text{OCMe}_3)]_2$ (Fig. 5) reveal that structurally analogous complexes are formed in these reactions despite the different substituents on the cyclopentadienyl rings. In each of these three complexes the two C_5H_5 ligands are arranged in a *cis* orientation around a

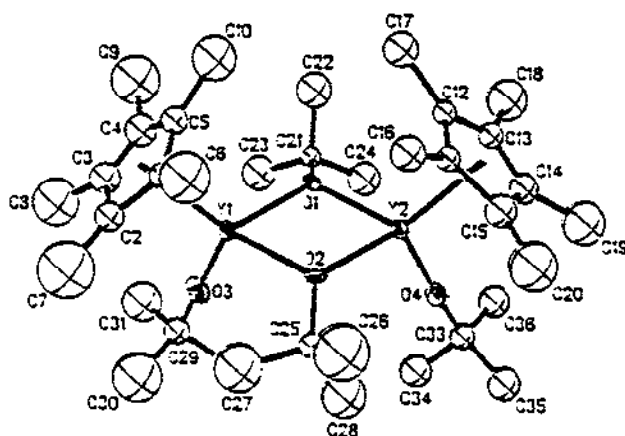


Fig. 3.

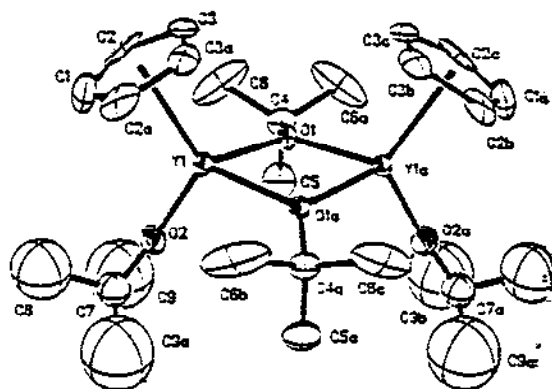


Fig. 4.

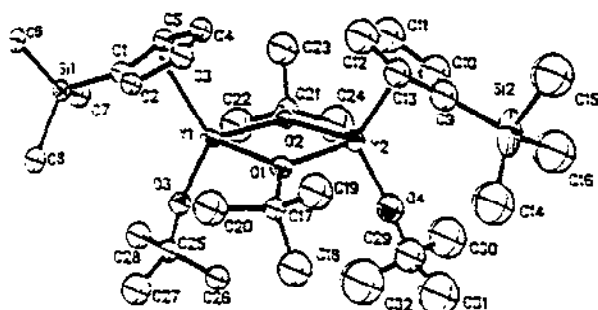


Fig. 5.

$(\text{Me}_3\text{CO})\text{Y}(\mu\text{-OCMe}_3)\text{Y}(\text{OCMe}_3)$ central core which has similar metrical parameters in each compound.

The compounds $[(\text{C}_5\text{R}_5)\text{Y}(\mu\text{-OCMe}_3)(\text{OCMe}_3)]_2$ ($\text{C}_5\text{R}_5 = \text{C}_5\text{H}_5$, $\text{C}_5\text{H}_4\text{Me}$, $\text{C}_5\text{H}_4\text{SiMe}_3$) react with $\text{LiCH}_2\text{SiMe}_3$ to unexpectedly lose $\text{Li}(\text{C}_5\text{R}_5)$ instead of LiOCMe_3 . Crystallisation of the reaction product from $[(\text{C}_5\text{H}_5)\text{Y}(\mu\text{-OCMe}_3)(\text{OCMe}_3)]_2$ and $\text{LiCH}_2\text{SiMe}_3$ in the presence of DME yields the cyclopentadienyl-free alkoxide complex $(\text{Me}_3\text{CO})\text{Y}(\mu\text{-OCMe}_3)_3\text{Li}_5(\mu^3\text{-OCMe}_3)_2(\text{THF})(\mu\text{-OCH}_2\text{CH}_2\text{OMe})_2$ (Fig. 6). This compound can be viewed as a $(\text{Me}_3\text{CO})\text{Y}(\mu\text{-OCMe}_3)[(\mu\text{-OCMe}_3)_2\text{Li}(\text{THF})]$ unit connected to a Li_4O_4 cube which has oxygen donor atoms provided by bridging *tert*-butoxide ligands and two bidentate ligands formally derived from DME by loss of a methyl group.

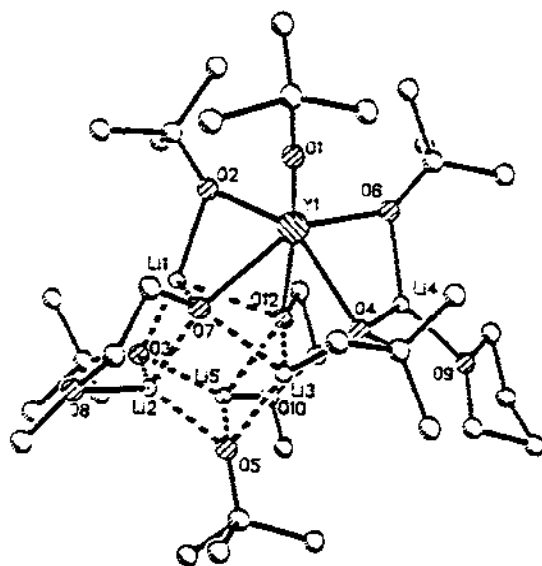
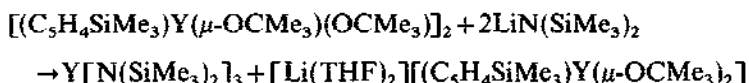


Fig. 6.

In the reaction of $[(C_5H_4SiMe_3)Y(\mu-OCMe_3)(OCMe_3)]_2$ with $LiCH_2SiMe_3$, the cyclopentadienyl component is recovered in a crystalline form as the polymeric, supersandwich metallocene, $[Li(\mu,\eta^5,\eta^5-C_5H_4SiMe_3)]_n$. $[(C_5H_4SiMe_3)Y(\mu-OCMe_3)(OCMe_3)]_2$ reacts with $LiN(SiMe_3)_2$ by a ligand redistribution pathway to form $[Li(THF)_2][[(C_5H_4SiMe_3)Y(\mu-OCMe_3)_2]]$.

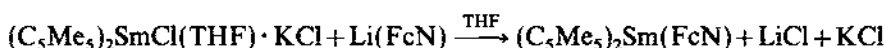


The crystal structure of $[Li(THF)_2][[(C_5H_4SiMe_3)_2Y(\mu-OCMe_3)_2]]$ was also reported (Fig. 7).

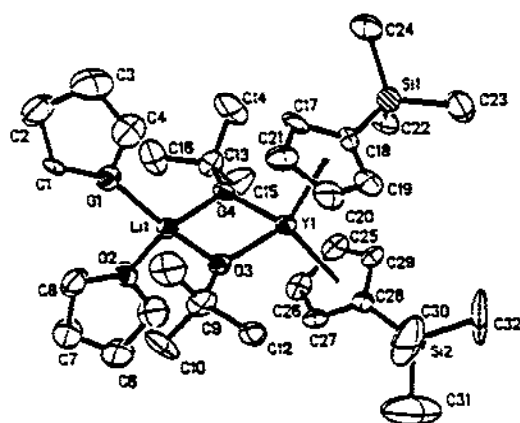
Wu et al. [6] published the synthesis of $(C_5H_5)HoCl_2(THF)_3$ by a one-pot reaction of $HoCl_3$ with C_5H_6 and sodium (1:5:1 molar ratio) in THF. The compound was characterized by elemental analysis, IR and MS spectra, and X-ray crystallography showing that it is monomeric in both the vapor and solid state. The holmium atom displays a distorted octahedral geometry, being coordinated by one C_5H_5 ring centroid, three THF molecules and two chloride ions.

2.1.2. Bis(cyclopentadienyl) compounds

Jacob, Pavlik and Edelman [1] reported the synthesis of the heterobimetallic compound $(C_5Me_5)_2Sm(FcN)$ by reaction of $(C_5Me_5)_2SmCl(THF) \cdot KCl$ with $Li(FcN)$ ($FcN = 2$ -(dimethylaminomethyl)ferrocenyl) in THF solution.



Wu et al. [7] reported the formation and crystal structure of $(C_5H_5)_2Yb(NO_2)(THF)$. This compound was obtained by reaction of $(C_5H_5)_2YbCl$ with $NaNO_2$ in THF at room temperature. The crystal structure (Fig. 8) shows that the central ytterbium atom is connected to two η^5 -bonded cyclopentadienyl ligands



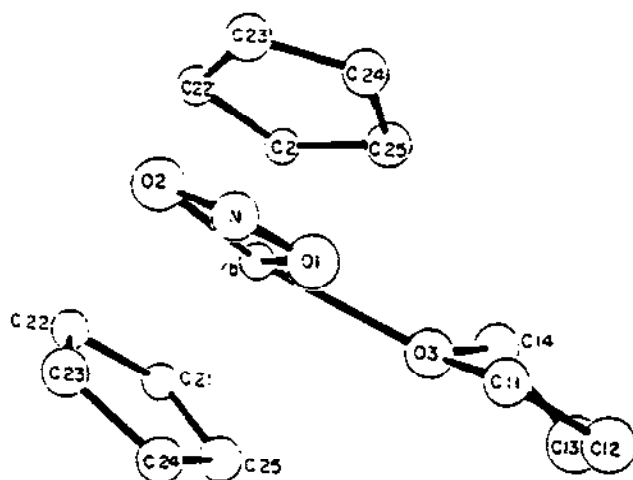
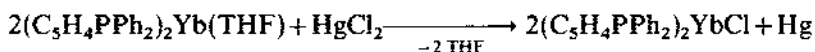


Fig. 8.

and three oxygen atoms (one from the coordinated THF molecule and the other two from the chelating nitrite ligand) in a distorted octahedral arrangement. The average Yb–C(C₅H₅) distance is 2.64 Å. Yb–O(THF) and Yb–O(NO₂) distances are 2.31 Å and 2.38 Å.

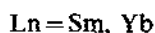
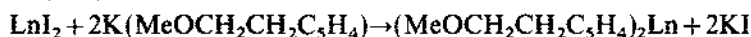
The compound loses the coordinated THF molecule readily on heating under vacuum to give the dimeric complex [(C₅H₅)₂Yb(NO₂)₂]₂. The compounds have been characterized by elemental analysis, IR spectroscopy, and mass spectrometry.

Deacon et al. [8] prepared (C₅H₄PPh₂)₂YbCl by reaction of (C₅H₄PPh₂)₂Yb(THF) with HgCl₂ in THF or toluene.



An X-ray crystal structure of the compound (Figs. 9 and 10) revealed the presence of two independent chloride-bridged dimers with uncoordinated Ph₂P groups and pseudo-tetrahedral coordination (two η⁵-C₅H₄PPh₂ and two μ-Cl ligands) at ytterbium. The dimers differ in the arrangement (*syn*, *anti*) of the PPh₂ groups.

Qian et al. [9] published the synthesis of solvent-free (MeOCH₂CH₂C₅H₄)₂Sm and (MeOCH₂CH₂C₅H₄)₂Yb by the reaction of K(MeOCH₂CH₂C₅H₄) with LnI₂ (Ln = Sm, Yb) in a 2:1 molar ratio in THF.



The crystal structure of (MeOCH₂CH₂C₅H₄)₂Yb(THF) was also published (Fig. 11). The compound crystallizes in monomeric units with the coordination number nine. The two ring centroids of the 2-methoxyethyl-cyclopentadienyl rings, the two oxygen atoms of the ether groups on the rings and the oxygen atom of the THF ligand form a distorted bipyramidal coordination polyhedron around the central ytterbium ion.

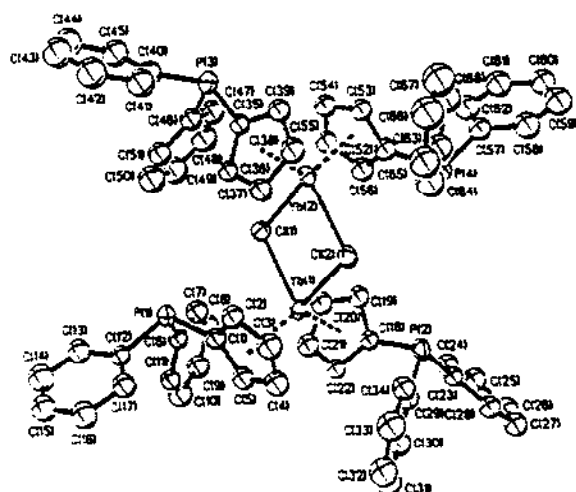


Fig. 9.

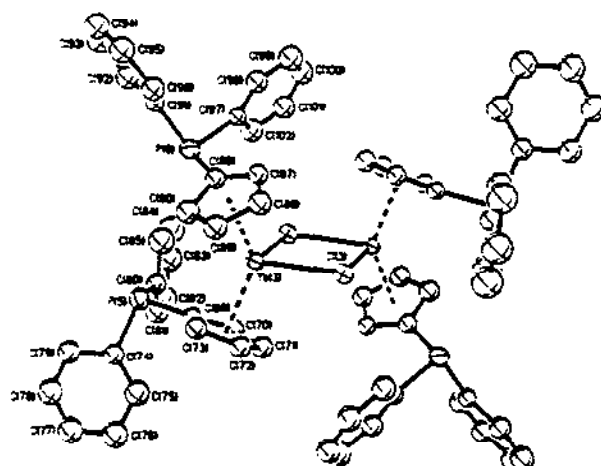
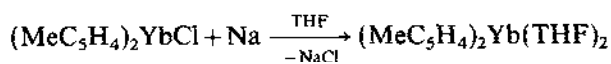


Fig. 10.

Shen et al. [10] reported the synthesis and crystal structure of $(\text{MeC}_5\text{H}_4)_2\text{Yb}(\text{DME})$ (Fig. 12), which was prepared by the reduction of the corresponding chloride $(\text{MeC}_5\text{H}_4)_2\text{YbCl}$ with metallic sodium in THF and crystallized from DME.



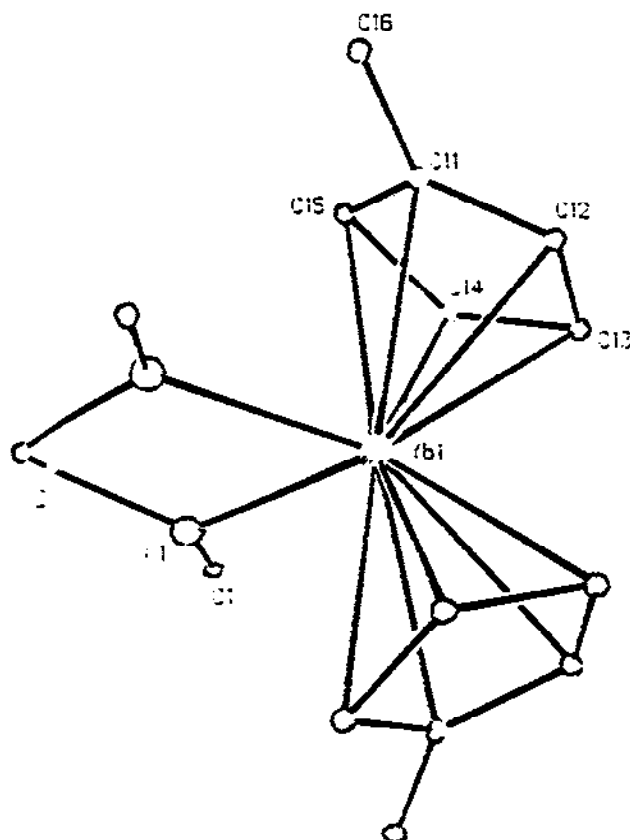
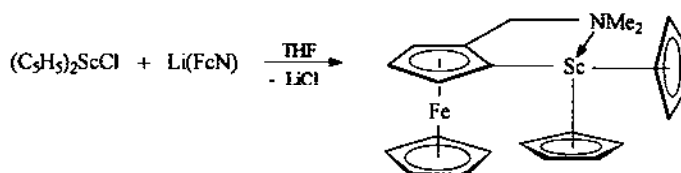


Fig. 12.

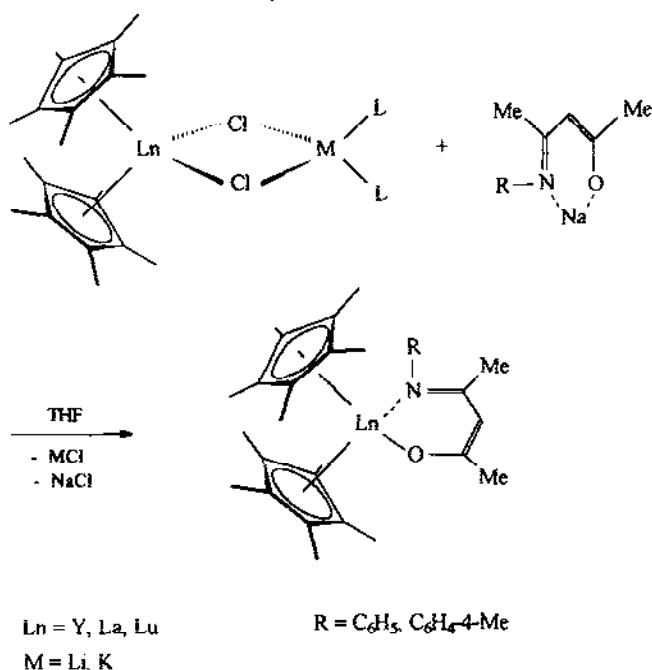
Thiele et al. [12] observed the formation of $(C_5H_5)_2Sc(FcN)$ in the reaction of $(C_5H_5)_2ScCl$ with $Li(FcN)$ ($FcN = 2\text{-(dimethylaminomethyl)ferrocenyl}$) in THF.



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

The same authors [13] also described the synthesis of the monomeric iminoacetylacetonate complexes $(\eta^5\text{-C}_5\text{Me}_5)_2Ln(OCMe=CHCMe=NR)$ ($Ln = Y, La, Lu$; $R = Ph, MeC_6H_4$) by reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2Ln(\mu\text{-Cl})_2ML_2$ ($Ln = Y, La, Lu$; $M = Li, K$;

L = Et₂O, DME) with Na(OCMe=CHCMe=NR) (R = Ph, MeC₆H₄). The compounds were characterized by IR, NMR and mass spectrometry.



In the case of the lanthanum complex (η^5 -C₅Me₅)₂La(OCMe=CHCMe=NC₆H₄Me) the chelating structure was confirmed by an X-ray structure analysis (Fig. 13). The lanthanum atom forms with the iminoacetylacetonate ligand a six-membered chelate ring.

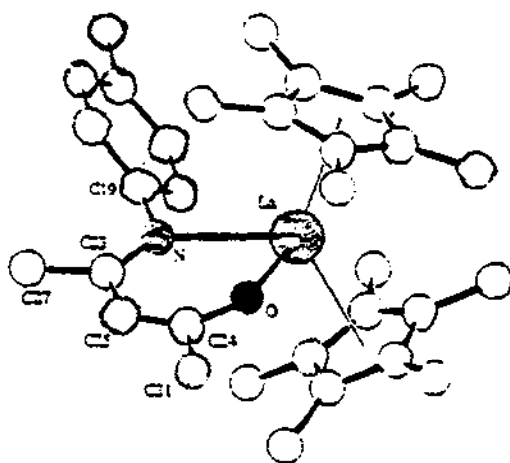
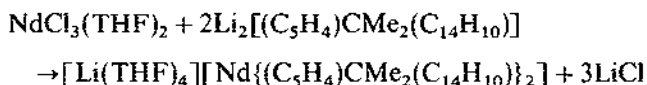


Fig. 13.

The formation of the "ate" complex $[\text{Li}(\text{THF})_4][\text{Nd}\{(\text{C}_5\text{H}_4)\text{CMe}_2(\text{C}_{14}\text{H}_{10})\}_2]$ from neodymium trichloride and two equivalents of the lithium salt of 9-(cyclopentadienyl)-1-methylethyl)-9,10-dihydroanthracene was published by Chauvin et al. [14].



The compound has been characterized by elemental analysis and its crystal structure (Fig. 14). The neodymium atom is situated in a tetrahedral environment. It is η^5 -bonded to the two cyclopentadienyl rings and σ -bonded to the C(10) atoms of the dihydroanthracene moieties.

Roitershtein et al. [15] reported the formation of the organolutetium derivatives $(\text{C}_5\text{H}_5)\text{Lu}(\text{C}_{14}\text{H}_{10})(\text{THF})_2$ and $[\text{Na}(\text{diglyme})_2][(\text{C}_5\text{H}_5)_2\text{Lu}(\text{C}_{14}\text{H}_{10})]$ by the interaction of $(\text{C}_5\text{H}_5)\text{LuCl}_2(\text{THF})_3$ and $(\text{C}_5\text{H}_5)_2\text{LuCl}$ with dianionic $\text{Na}_2(\text{C}_{14}\text{H}_{10})$ or radical-ionic $\text{Na}(\text{C}_{14}\text{H}_{10})$ sodium anthracene adducts. The decrease in the electron density of the anthracene ligand upon coordination to the lutetium atom is demonstrated by NMR and UV spectroscopy. The crystal structure of $[\text{Na}(\text{diglyme})_2][(\text{C}_5\text{H}_5)_2\text{Lu}(\text{C}_{14}\text{H}_{10})]$ was established by an X-ray diffraction study (Fig. 15). An interesting feature of this structure is the conformation of the coordinated anthracene dianion: the central six-membered ring of the ligand has lost its aromatic character and acquired a boat conformation.

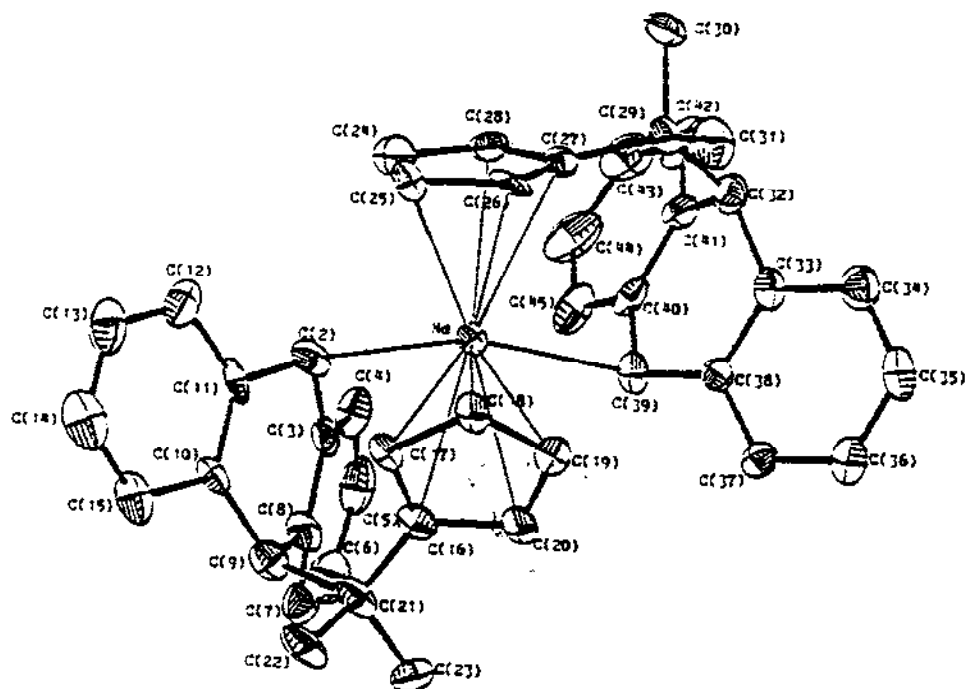
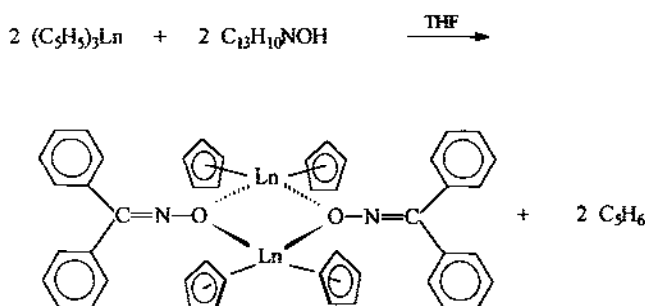


Fig. 14.

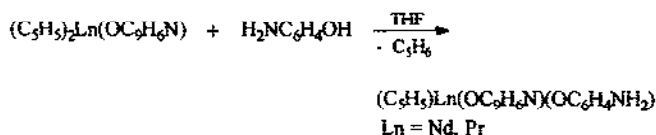
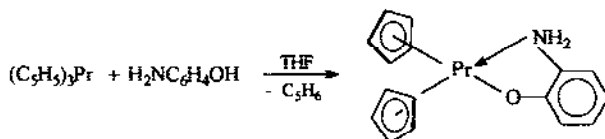
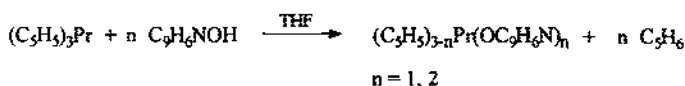
The complex adopts a geometry which has a molecular two-fold rotation axis perpendicular to the Sm_2Cl_2 plane and a crystallographic inversion center. Both methyl groups of each $(\text{C}_5\text{H}_4\text{Me})_2\text{Sm}$ unit are located on the side opposite of the THF ligands, which are *trans* to each other, and the four $\text{C}_5\text{H}_4\text{Me}$ rings define a square plane. The Sm–Cl distances are 2.759 Å and 2.819 Å, the Sm–centroid ($\text{C}_5\text{H}_4\text{Me}$) distances are 2.437 Å and 2.458 Å.

Wang et al. [17] reported the synthesis of $[(\text{C}_5\text{H}_5)_2\text{Ln}(\text{ONC}_{13}\text{H}_{10})]_2$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$) by the reaction of $(\text{C}_5\text{H}_5)_3\text{Ln}$ with benzo-phenoneoxime in THF:



The relatively air stable complexes are dimeric with oxygen-bridged bonds. They have been characterized by elemental analyses as well as by IR and MS data.

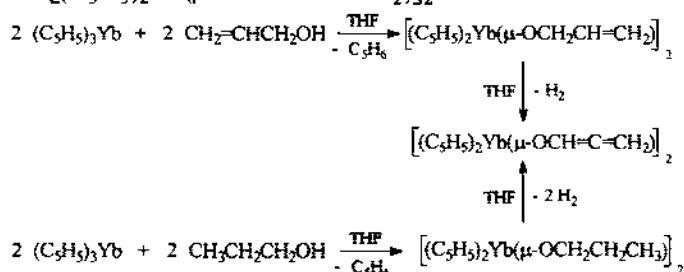
Xu et al. [18] described the reaction of $(\text{C}_5\text{H}_5)_3\text{Pr}$ with 8-hydroxyquinoline ($\text{C}_9\text{H}_6\text{NOH}$) or 2-aminophenol ($\text{H}_2\text{NC}_6\text{H}_4\text{OH}$) in THF to give the thermally stable complexes $(\text{C}_5\text{H}_5)_2\text{Pr}(\text{OC}_9\text{H}_6\text{N})$, $(\text{C}_5\text{H}_5)\text{Pr}(\text{OC}_9\text{H}_6\text{N})_2$ and $(\text{C}_5\text{H}_5)_2\text{Pr}(\text{OC}_6\text{H}_4\text{NH}_2)$. Also reported is the synthesis of the mixed-ligand organolanthanide complexes $(\text{C}_5\text{H}_5)\text{Ln}(\text{OC}_9\text{H}_6\text{N})(\text{OC}_6\text{H}_4\text{NH}_2)$ ($\text{Ln} = \text{Pr}, \text{Nd}$) by reacting $(\text{C}_5\text{H}_5)_2\text{Ln}(\text{OC}_9\text{H}_6\text{N})$ with 2-aminophenol in THF.



The structures of the complexes were verified by elemental analyses, IR, MS and XPS spectra and molecular weight determinations, indicating that they are mono-

meric. The $\text{OC}_6\text{H}_5\text{N}$ and $\text{OC}_6\text{H}_4\text{NH}_2$ ligands interact with the metal in a chelating fashion to form an intramolecular five-membered ring.

The same authors [19] also described the reaction of $(\text{C}_5\text{H}_5)_3\text{Yb}$ with $\text{HOCH}_2\text{CH}=\text{CH}_2$ and $\text{HOCH}_2\text{CH}_2\text{CH}_3$ in THF at room temperature to give the complexes $[(\text{C}_5\text{H}_5)_2\text{Yb}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_3)]_2$ and $[(\text{C}_5\text{H}_5)_2\text{Yb}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_3)]_2$, which are dehydrogenated in refluxing THF solution to yield the complex $[(\text{C}_5\text{H}_5)_2\text{Yb}(\mu\text{-OCH}=\text{C}=\text{CH}_2)]_2$.



The crystal structure of $[(\text{C}_5\text{H}_5)_2\text{Yb}(\mu\text{-OCH}=\text{C}=\text{CH}_2)]_2$ (Fig. 17) shows that the complex is dimeric with oxygen atoms as bridging groups.

Evans et al. [20] described the synthesis and structure of the mono-THF-solvated organosamarium(II) complexes $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})$ and $[\text{C}_5\text{H}_2(\text{SiMe}_3)_3]\text{Sm}(\text{THF})$. The latter was prepared by reaction of $\text{SmI}_2(\text{THF})$ with $\text{K}[\text{C}_5\text{H}_2(\text{SiMe}_3)_3]$ and $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ in THF solution (Figs. 18 and 19). In these bent metallocenes, the THF oxygen atoms do not adopt the sterically least crowded positions and lie off the plane defined by the two ring centroids and samarium by 1.54 Å for $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})$ and by 0.85 Å for $[\text{C}_5\text{H}_2(\text{SiMe}_3)_3]\text{Sm}(\text{THF})$.

Tilley et al. [21] prepared the scandocene complexes $(\text{C}_5\text{H}_5)_2\text{Sc}[\text{Si}(\text{SiMe}_3)_3](\text{THF})$, $(\text{C}_5\text{H}_5)_2\text{Sc}[\text{Si}(\text{SiMe}_3)_2\text{Ph}](\text{THF})$, $(\text{C}_5\text{H}_5)_2\text{Sc}[\text{Si}^t\text{BuPh}_2](\text{THF})$,

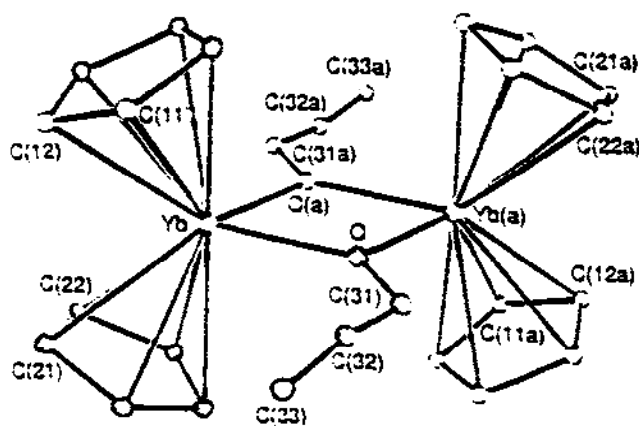


Fig. 17.

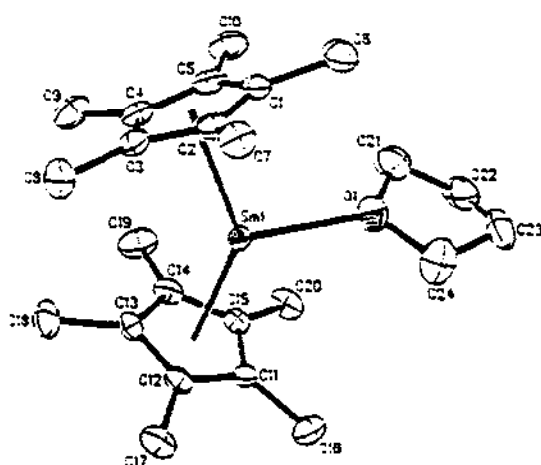


Fig. 18.

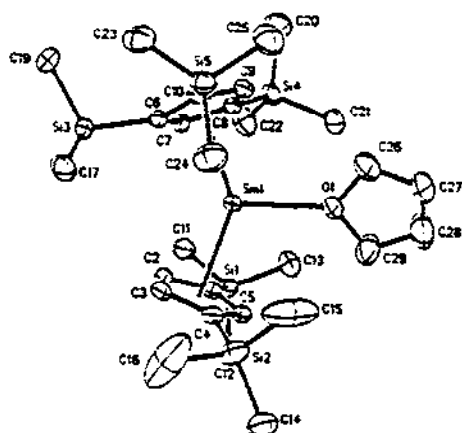
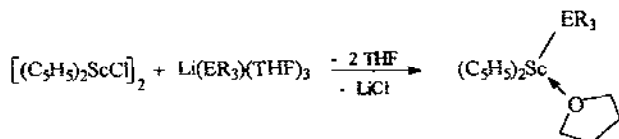


Fig. 19.

$(C_5H_5)_2Sc[SiPh_3](THF)$ and $(C_5H_5)_2Sc[Ge(SiMe_3)_3](THF)$ by addition of the appropriate silyl- or germyllithium reagents to $[(C_5H_5)_2ScCl]_2$ in THF.



$ER_3 = Si(SiMe_3)_3, Si(SiMe_2)Ph, Si^iBuPh_2, SiPh_3, Ge(SiMe_3)_3$

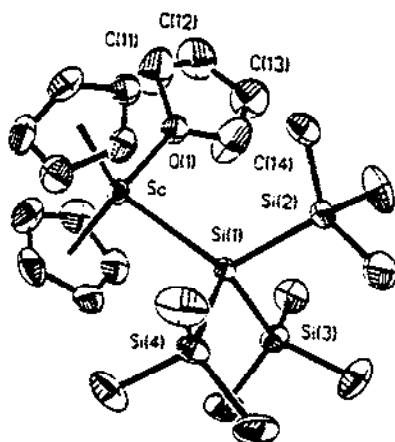
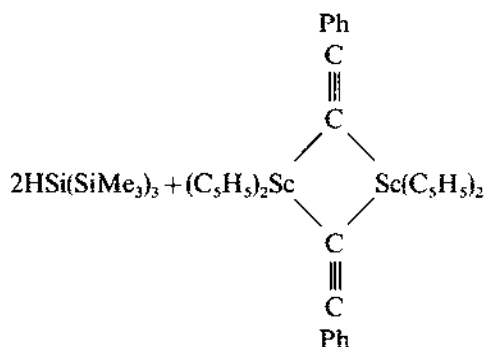


Fig. 20.

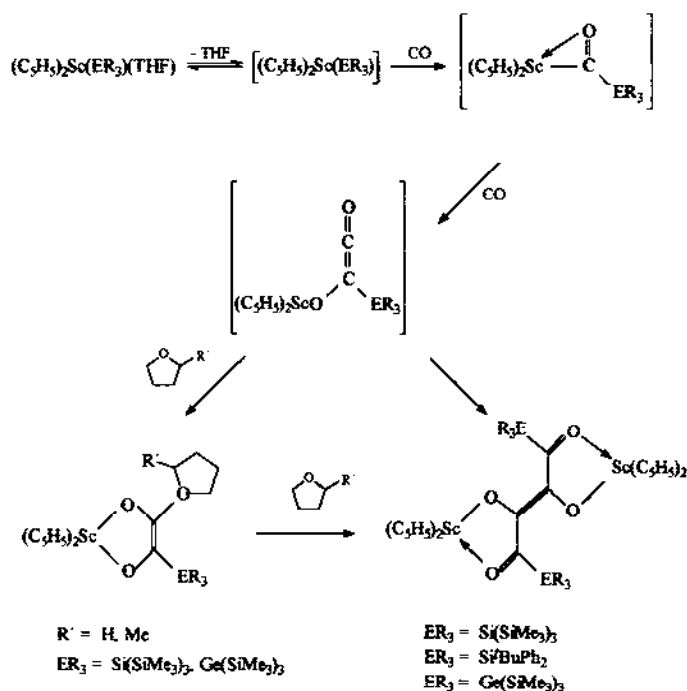
The crystal structure of $(C_5H_5)_2Sc[Si(SiMe_3)_3](THF)$ (Fig. 20) revealed no unusual distortions in the molecule and a Sc–Si bond length of 2.86 Å. The Sc–centroid (C_5H_5) distances are 2.21 Å and 2.20 Å.

These unusually reactive d^0 silyl complexes polymerize ethylene. $(C_5H_5)_2Sc[Si(SiMe_3)_3](THF)$ reacts with phenylacetylene via σ -bond metathesis to give $HSi(SiMe_3)_3$ and the known acetylide $[(C_5H_5)_2Sc(C\equiv CPh)]_2$.

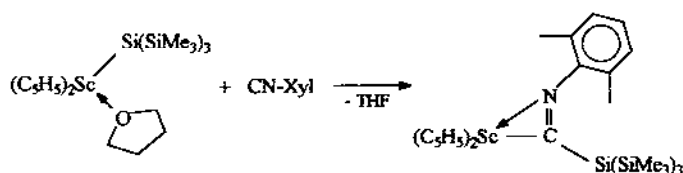


The complexes $(C_5H_5)_2Sc[Si(SiMe_3)_3](THF)$, $(C_5H_5)_2Sc[Si^tBuPh_2](THF)$ and $(C_5H_5)_2Sc[Ge(SiMe_3)_3](THF)$ react with CO via CO–CO coupling processes, to give the scandoxyketene derivatives $(C_5H_5)_2ScO(R_3E)(C=C=O)$, which are trapped as the adducts $(C_5H_5)_2Sc[O(L)C(ER_3)CO]$ ($ER_3 = Si(SiMe_3)_3$, $Ge(SiMe_3)_3$; $L = Me-THF$, THF , PMe_2Ph). In nonpolar media carbonylations of $(C_5H_5)_2Sc[Si(SiMe_3)_3](THF)$, $(C_5H_5)_2Sc[Si^tBuPh_2](THF)$ and $(C_5H_5)_2Sc$

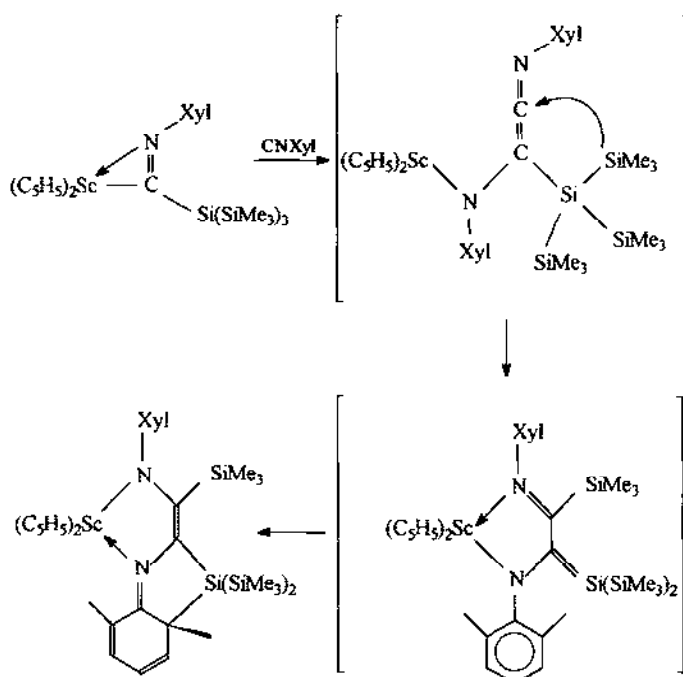
$[\text{Ge}(\text{SiMe}_3)_3](\text{THF})$ afford the enedione diolate structures $[(\text{C}_5\text{H}_5)_2\text{Sc}(\text{OC}(\text{ER}_3)\text{CO})_2]$ ($\text{ER}_3 = \text{Si}(\text{SiMe}_3)_3$, Si^tBuPh_2 , $\text{Ge}(\text{SiMe}_3)_3$).



The insertion of 2,6-xylylisocyanide (CN-Xyl) into the Sc–Si bond of $(\text{C}_5\text{H}_5)_2\text{Sc}[\text{Si}(\text{SiMe}_3)_3](\text{THF})$ provides the stable η^2 -iminosilaacyl complex $(\text{C}_5\text{H}_5)_2\text{Sc}[\eta^2\text{-CN(Xyl)Si}(\text{SiMe}_3)_3]$, which reacts with $\text{PhC}\equiv\text{CH}$ to afford $[(\text{C}_5\text{H}_5)_2\text{Sc}(\text{C}\equiv\text{CPh})_2]$ and the formimidoyl silane $\text{HC}(=\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Si}(\text{SiMe}_3)_3$.



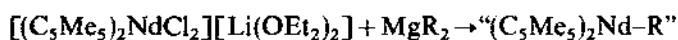
The complex $(\text{C}_5\text{H}_5)_2\text{Sc}[\eta^2\text{-CN(Xyl)Si}(\text{SiMe}_3)_3]$ reacts with a second equivalent of CN-Xyl to form $\{(\text{C}_5\text{H}_5)_2\text{ScN(Xyl)C}(\text{SiMe}_3)=\text{C}-\text{N}=\text{CCMe}=\text{CHCH}=\text{CHCMe}[\text{Si}(\text{SiMe}_3)_2]\}$.



Bosnich et al. [22] studied the molecular geometry of $[M(C_5Me_5)_2]$ ($M = Sm, Eu, Yb$). A molecular mechanics force field was applied to minimize the structures of these complexes. It was found that van der Waals attractive forces between C_5Me_5 -rings cause all of the molecules to be bent. The calculated and observed structures correspond to a high degree. The difference in energy between the bent and linear geometries is small, and it has been predicted that the bis(pentaisopropylcyclopentadienyl)complexes of these metals should be linear.

Ye et al. [23] published the synthesis and crystal structure of $(C_5H_5)_2Yb(CH_3COCHCOCF_3)$ (Fig. 21) by reaction of $(C_5H_5)_3Yb$ with $CH_3COCH_2COCF_3$ in THF. The ytterbium atom is η^5 -coordinated to two cyclopentadienyl ligands and chelated with the two oxygen atoms of the 1,1,1-trifluoroacetylacetonato ligand.

Mortreux and co-workers [24] showed that the direct alkylation of the neodymium complex $[(C_5Me_5)_2NdCl_2][Li(OEt)_2]$ by butylethyl-magnesium gives rise to the production of efficient homogeneous catalytic species for ethylene polymerisation with a very high productivity.



The polymers are highly linear, vinyl terminated, and possess narrow molecular weight distributions ($M_w/M_n = 2$). The observed molecular weights are strongly dependent on the reaction temperature and ethylene pressure. The catalytic system

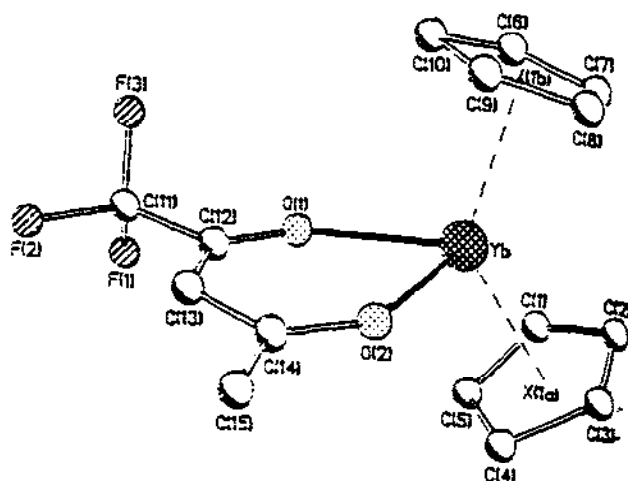


Fig. 21.

is shown to be more active than classical Ti/Mg heterogeneous catalysts, and even more stable at high temperatures and pressures.

The formation of stable adducts by treatment of $[(C_5Me_5)_2NdCl_2][Li(OEt_2)_2]$ and $[(C_5Me_5)_2NdMeCl][Li(OEt_2)_2]$ with phosphine oxides was described by Dormond et al. [25]. The authors also investigated the coordination of bifunctional ligands $OPPh_2CH(R)PPh_2$ to several neodymium derivatives by 1H and ^{31}P NMR studies.

Fischer et al. [26] reported the synthesis and crystal structure of the complexes $[(C_5H_5)_2Yb(\mu-OCH_2CH=CHCH_3)]_2$ and $[(C_5H_4CH_3)_2Yb(\mu-OCH(CH_2)_3O)]_2$ (Figs. 22 and 23) by reaction of $[(C_5H_5)_2Yb(C_2H_2(N^iBu)_2)]_n$ and

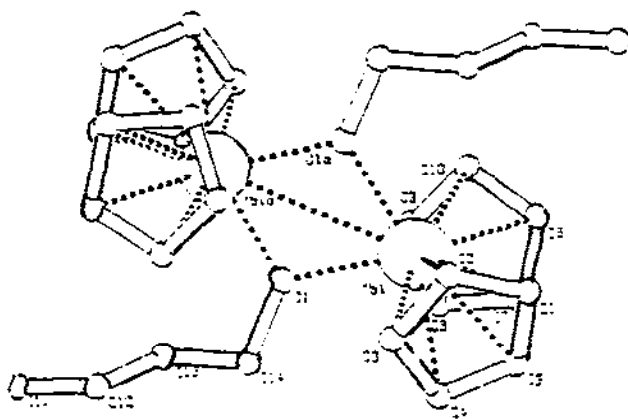
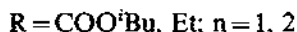
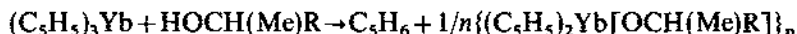


Fig. 22.

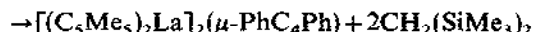
The complexes are oxygen-bridged dimers. The average Yb–C(C₅H₅) and Yb–O distances in [(C₅H₅)₂Yb(μ-OCH₂CH=CHCH₃)]₂ are 2.65 Å and 2.21 Å, the Yb···Yb distance is 3.53 Å. In [(C₅H₄CH₃)₂Yb(μ-OCH(CH₂)₃O)]₂ the average Yb–C(C₅H₅) and Yb–O distances are 2.658 Å and 2.26 Å, the Yb···Yb distance is 3.72 Å.

The reactions of (C₅H₅)₃Yb with (R)-(+)-, (S)-(-)-isobutyl lactate or (S)-(+)-2-butanol in a molar ratio of 1:1 to afford the new bis(cyclopentadienyl)ytterbium(III)alkoxides (C₅H₅)₂Yb[OCH(Me)(Et)] and {(C₅H₅)₂Yb[OCH(Me)COO^tBu]}₂ were also described by Fischer et al. [27]. The compounds were characterized by ¹H NMR spectroscopy.



The single crystal X-ray analysis of {(C₅H₅)₂Yb[OCH(Me)COO^tBu]}₂ reveals a particularly rigid dinuclear framework (Fig. 24). The Yb1–centroid(C₅H₅) distances are 2.383 Å and 2.39 Å, the Yb2–centroid(C₅H₅) distances are 2.383 Å and 2.385 Å. The chiral complex {(C₅H₅)₂Yb[OCH(Me)COO^tBu]}₂ displays notable *f-f*-circular dichroism (*f-f*-CD), the *f-f*-absorption range of the likewise chiral complex (C₅H₅)₂Yb[OCH(Me)(Et)] with a less rigid configuration is devoid of any CD effects.

Marks et al. [28] described the reaction of (C₅Me₅)₂La[CH(SiMe₃)₂] with PhC≡CH at room temperature to yield the coupled product [(C₅Me₅)₂La]₂(μ-PhC₄Ph) and CH₂(SiMe₃)₂.



The reaction of (C₅Me₅)₂La[CH(SiMe₃)₂] with ^tBuC≡CH at 0 °C yields the uncoupled dimer [(C₅Me₅)₂La(C≡C^tBu)]₂, which, in toluene solution at 50 °C and

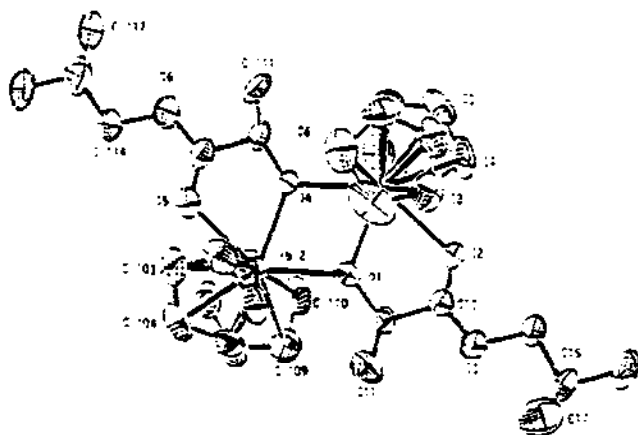
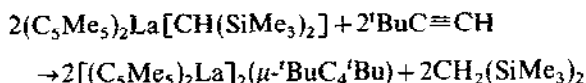


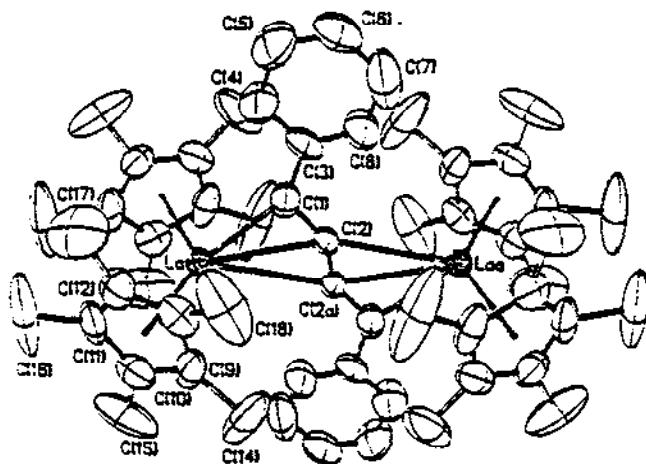
Fig. 24.

60 °C, undergoes clean unimolecular conversion to the coupled dimer $[(C_5Me_5)_2La]_2(\mu\text{-}^iBuC_4^iBu)$.



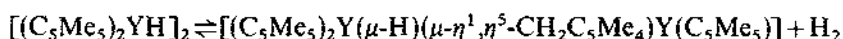
The crystal structures of $[(C_5Me_5)_2La]_2(\mu\text{-}PhC_4Ph)$ (Fig. 25) and $[(C_5Me_5)_2La]_2(\mu\text{-}^iBuC_4^iBu)$ (Fig. 26) were also described. The average La-centroid(C_5Me_5) distance in $[(C_5Me_5)_2La]_2(\mu\text{-}PhC_4Ph)$ is 2.80 Å and 2.85 Å in $[(C_5Me_5)_2La]_2(\mu\text{-}^iBuC_4^iBu)$.

The room-temperature luminescence and photolysis of a series of organoscandium complexes with the general formula $(C_5Me_5)_2ScX$ (X represents a σ -donating ligand)



was studied by Thompson and Bocarsly [29]. The authors performed semiempirical molecular orbital calculations for $(C_5Me_5)_2ScX$ ($X=Cl, I, Me$) using the INDO/S method. The calculations indicate a large amount of metal and ligand orbital mixing in these d^0 complexes, with the lowest unoccupied molecular orbitals consisting principally of Sc d-orbitals admixing with the (C_5Me_5) π -orbitals. The highest-occupied molecular orbital for the chloride derivative contains primarily (C_5Me_5) character, while that of the iodide species is mostly halogen in nature. The presence of a lone pair on X is requisite for room-temperature emission to occur, as evidenced by the observation of luminescence for $X=Cl^-, I^-$, and NPh and by the lack of luminescence from $(C_5Me_5)_2ScMe$ or $(C_5Me_5)_2Sc(CH_2Ph)$, under identical conditions.

Teuben et al. [30] reported several C–H activation reactions with $[(C_5Me_5)_2YH]_2$. Thermolysis of $[(C_5Me_5)_2YH]_2$ in octane, cyclohexane or benzene leads to formation of the thermodynamically favored product $[(C_5Me_5)_2Y(\mu-H)(\mu-\eta^1, \eta^5-CH_2C_5Me_4)Y(C_5Me_5)]$.



The molecular structure of this compound was determined by X-ray diffraction (Fig. 27). One yttrium atom (Y2) is surrounded by two intact C_5Me_5 ligands, forming a normal $(C_5Me_5)_2YH$ moiety. The other yttrium atom is η^5 -bonded to both a normal C_5Me_5 and a tetramethylfulvene ligand, giving also a $(C_5Me_5)_2Y$ -like structure.

With deuterated aromatic solvents fast H/D exchange takes place between the solvent and hydride ligands of $[(C_5Me_5)_2YH]_2$, without intermediate metalation of solvent molecules. Metalation of benzene and toluene is possible when the generated hydrogen gas is removed quickly, leading to the compounds $(C_5Me_5)_2YPh$ and

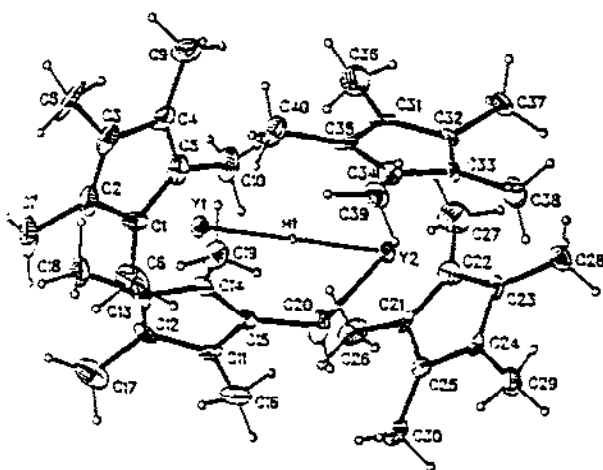
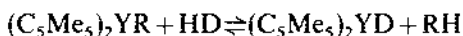
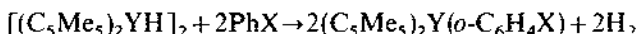


Fig. 27.

$(C_5Me_5)_2Y(CH_2Ph)$. This process is much slower than the H/D scrambling reaction, and formation of $[(C_5Me_5)_2Y(\mu-H)(\mu-\eta^1, \eta^5-CH_2C_5Me_4)Y(C_5Me_5)]$ competes. The authors proposed that the H/D exchange with benzene and toluene and the formation of $(C_5Me_5)_2YPPh$ and $(C_5Me_5)_2Y(CH_2Ph)$ proceed through different σ -bond metathesis pathways.



With aromatic molecules PhX ($X=OMe, SMe, NMe_2, CH_2NMe_2, PMe_2, PPh_2=CH_2$) *ortho*-metalation of the phenyl group is the dominant reaction, although formation of $[(C_5Me_5)_2Y(\mu-H)(\mu-\eta^1, \eta^5-CH_2C_5Me_4)Y(C_5Me_5)]$ was also observed ($X=NMe_2, CH_2NMe_2$).



The crystal structure of $(C_5Me_5)_2Y(o-C_6H_4PPh_2=CH_2)$ (Fig. 28) was also reported. The most interesting part is a chelating five-membered ring $Y-C21-C22-P-C39$ which is located in the plane bisecting the angle between the two C_5Me_5 ligands. Four of the chelate ring atoms ($Y, C21, C22, C39$) are coplanar within 0.02 Å, and the phosphorus atom is 0.34 Å out of this plane.

Reactions of the early lanthanide hydrocarbyls $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$ ($Ln = Ce, La$) with terminal alkynes $HC\equiv CR$ ($R = Me, ^iBu$) to produce the oligomeric

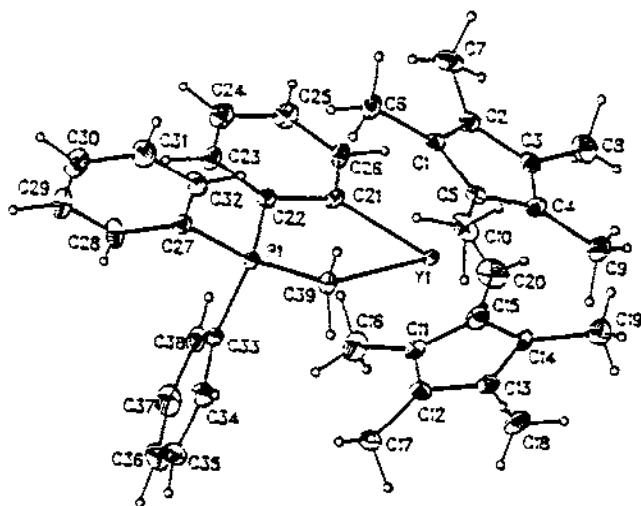


Fig. 28.

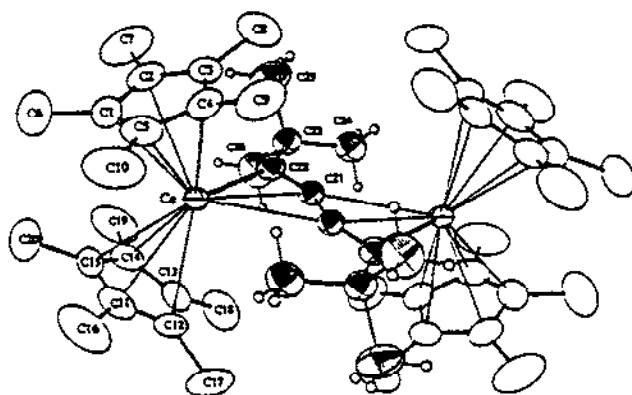
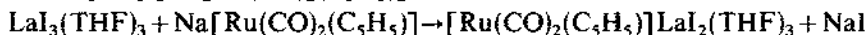
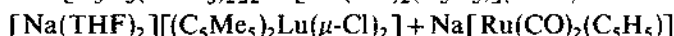
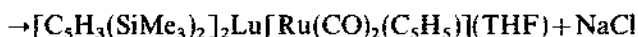
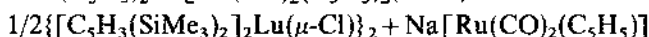
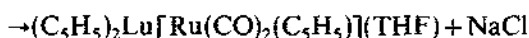
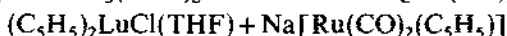


Fig. 30.

$(C_5H_5)_2LuCl(THF)$, $\{[C_5H_3(SiMe_3)_2]_2Lu(\mu-Cl)\}_2$, $[Na(THF)_2][(C_5Me_5)_2Lu(\mu-Cl)_2]$ and $LaI_3(THF)_3$ with the salt $Na[Ru(CO)_2(C_5H_5)]$.



The structure of $(C_5H_5)_2Lu[Ru(CO)_2(C_5H_5)](THF)$ has been established by X-ray crystal structure analysis (Fig. 31). The complex is the first example of a compound characterized by X-ray diffraction in which there is a direct lanthanide–metal bond (Lu–Ru 2.955 Å) without additional bridging ligands. According to IR and NMR evidence the Ln–Ru bond in all new complexes is stable in solution.

The reactivity of the compounds towards HCl, H_2O , $HgCl_2$, iPr_2CO , MeI, H_2 , CO, $PhMeSiH_2$ and $Me_3SiC\equiv CSiMe_3$ has also been investigated. Reactions of $[C_5H_3(SiMe_3)_2]_2Lu[Ru(CO)_2(C_5H_5)](THF)$ with HCl and H_2O yield $\{[C_5H_3(SiMe_3)_2]_2Lu(\mu-Cl)\}_2$ and $\{[C_5H_3(SiMe_3)_2]_2Lu(\mu-OH)\}_2$, the structures of which have been determined by X-ray analysis (Figs. 32 and 33). Both compounds possess similar dimeric structures with a pair of bridging ligands Cl or OH, respectively. Average distances are 2.62 Å for Lu–Cl and 2.26 Å for Lu–O.

¹³⁹La spectroscopy has been used for studying Schlenk type equilibria for both the cyclopentadienyl complexes $(C_5H_5)_3La$, $(C_5H_5)_2LaI$, and $\{[C_5H_3(SiMe_3)_2]_2Lu(\mu-Cl)\}_2$ and the bimetallic complexes $X_2La[Ru(CO)_2(C_5H_5)]$ ($X = C_5H_5$, $[C_5H_3(SiMe_3)_2]$).

The C–C bond formation which occurs when two $(PhC\equiv C)$ ligands on $(C_5Me_5)_2Sm$ -containing organosamarium complexes are coupled to form the $(PhC-C\equiv C-C\equiv CPh)^{2-}$ trienediyl ligand in $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-PhC-C\equiv C-C\equiv CPh)$ has been investigated by Evans et al. [33]. The generality of

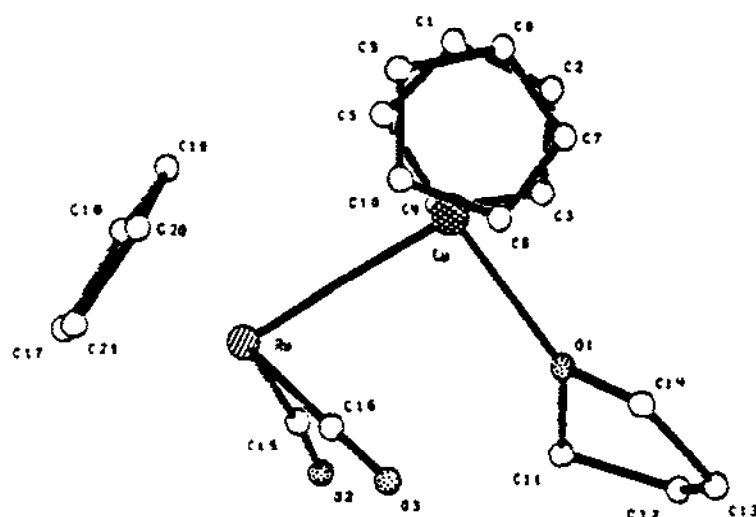


Fig. 31.

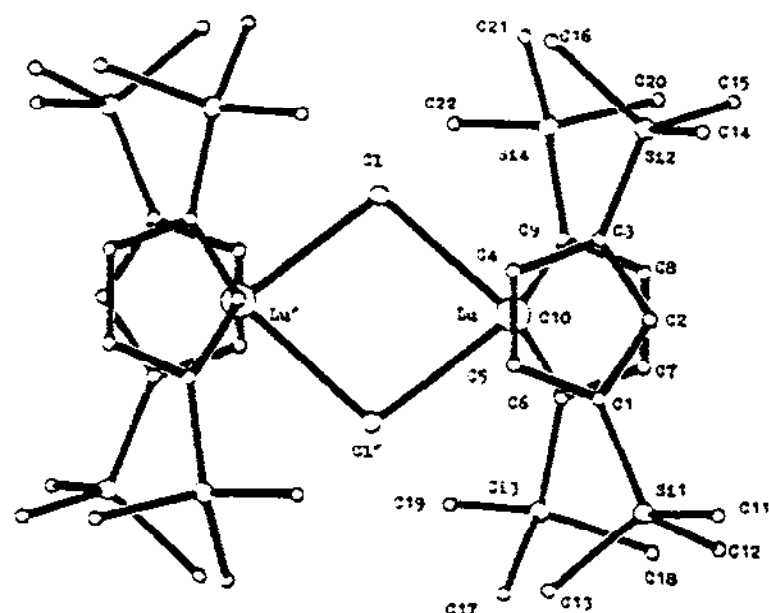


Fig. 32.

the reactions which form $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-PhC\equiv C\equiv CPh)$, namely the reactions of $[(C_5Me_5)_2Sm(\mu-H)]_2$ and $(C_5Me_5)_2Sm$ with $HC\equiv CPh$ and the thermolysis of $(C_5Me_5)_2Sm(C\equiv CPh)(THF)$, has been probed by examining the reactivity of a variety of lanthanide alkynide system. The bis(alkynide) complexes $[(C_5Me_5)_2Ln(\mu-C\equiv CPh)_2K]_n$ ($Ln = Ce, Nd, Sm$) do not undergo the coupling reaction, but trienediyl

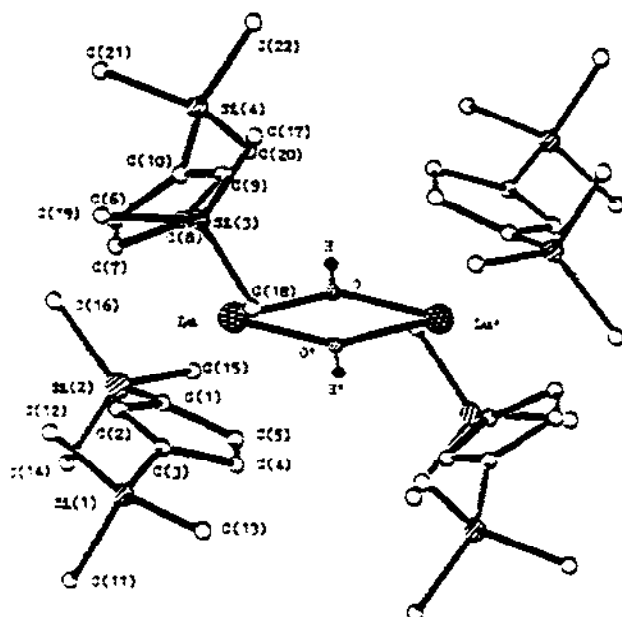
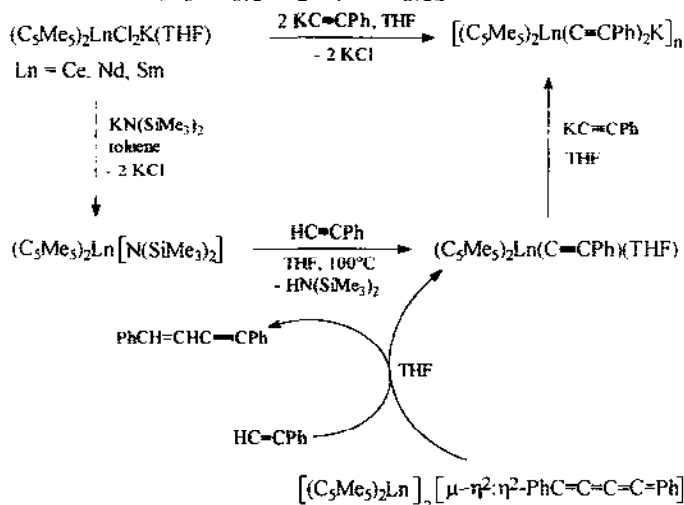


Fig. 33.

complexes have been obtained by thermolysis of $(C_5Me_5)_2Ce(C\equiv CPh)(THF)$ and $(C_5Me_5)_2Nd(C\equiv CPh)(THF)$. These compounds were synthesized by metathetical reactions between $(C_5Me_5)_2Ln[N(SiMe_3)_2]$ and $HC\equiv CPh$.



The coupled trienediyl products $[(C_5Me_5)_2Sm]_2[\mu-\eta^2:\eta^2-Ph(CH_2)_2C\equiv C\equiv C\equiv C-(CH_2)_2Ph]$ and $[(C_5Me_5)_2Sm]_2[\mu-\eta^2:\eta^2-Me_2CH(CH_2)_2C\equiv C\equiv C\equiv C(CH_2)_2CHMe_2]$ have also been obtained by treatment of $(C_5Me_5)_3Sm$ with $HC\equiv C(CH_2)_2Ph$ and $HC\equiv C(CH_2)_2CHMe_2$, respectively. The NMR spectra and crystal structures of these

products show agostic interactions involving methylene groups. The reaction of $[(C_5Me_5)_2Sm(\mu-H)]_2$ with $HC\equiv CMe_3$ generates the loosely associated dimeric alkynide $[(C_5Me_5)_2Sm(C\equiv CMe_3)]_2$ and the unusual insertion product $(C_5Me_5)_2Sm[Me_3CCH=CC(CMe_3)=CH_2]$. The authors used X-ray crystallography to definitively identify several of the products and synthetic precursors. In $[(C_5Me_5)_2Sm(\mu-C\equiv CPh)_2K]_n$ (Fig. 34), the two C_5Me_5 ring centroids and the two alkynide α -carbon atoms define a distorted tetrahedron around samarium. The potassium atom is bound to both alkynide ligands of one molecular unit and to a C_5Me_5 ligand of the adjacent molecule to generate a polymeric species. The amide ligand in $(C_5Me_5)_2Sm[N(SiMe_3)_2]$ (Fig. 35) is attached symmetrically to the $(C_5Me_5)_2Sm$ unit so that the two ring centroids, the amide nitrogen, and the samarium are coplanar to within 0.05 Å.

Each alkynide ligand in a monomeric unit of $[(C_5Me_5)_2Sm(C\equiv CMe_3)]_2$ (Fig. 36)

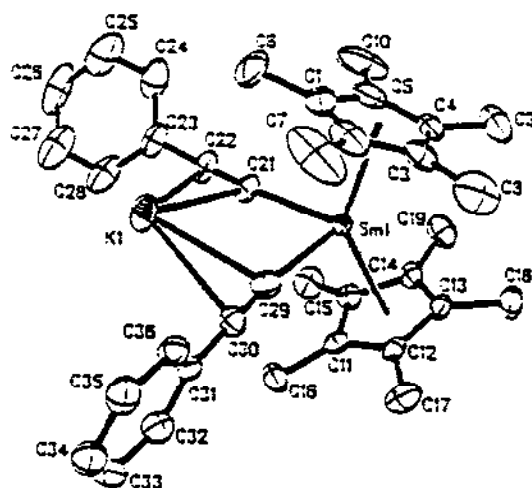


Fig. 34.

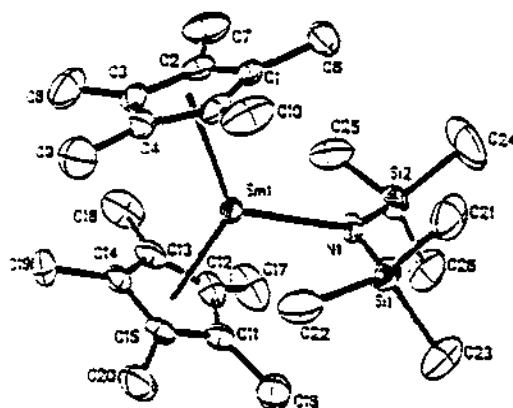


Fig. 35.

is attached asymmetrically to the $(C_5Me_5)_2Sm$ unit so that samarium lies 0.38 Å out of the plane defined by the two ring centroids and the alkynide α -carbon atoms. A methyl group from the C_5Me_5 ligand of another monomer is oriented toward samarium at a distance of 3.006 Å to generate a loosely linked dimeric structure. In $(C_5Me_5)_2Sm[Me_3CCH=CC(CMe_3)=CH_2]$, (Fig. 37), a 1,3-di-tert-butyl-1,3-butadien-2-yl ligand is coordinated to a $(C_5Me_5)_2Sm$ fragment via a 2.484 Å Sm–C bond. In $[(C_5Me_5)_2Sm]_2[\mu-\eta^2:\eta^2-Ph(CH_2)_2C=C=C=C(CH_2)_2Ph]$ (Fig. 38), the eight-carbon chain of the trienediyl unit and the two samarium atoms are coplanar to within 0.09 Å. The two shortest Sm–C distances connecting a $(C_5Me_5)_2Sm$ unit to the ligand are 2.483 Å and 2.689 Å. A methylene group is oriented toward each $(C_5Me_5)_2Sm$ unit at a distance of 3.748 Å.

Andersen et al. [34] prepared the dimeric compound $[(C_5H_4CMe_3)_2Ce(\mu-Me)]_2$ from $(C_5H_4CMe_3)_3Ce$ or $[(C_5H_4CMe_3)_2Ce(\mu-SCHMe_2)]_2$ and MeLi in hydrocarbon solvents. The X-ray structure analysis of the complex (Fig. 39) shows that the methyl

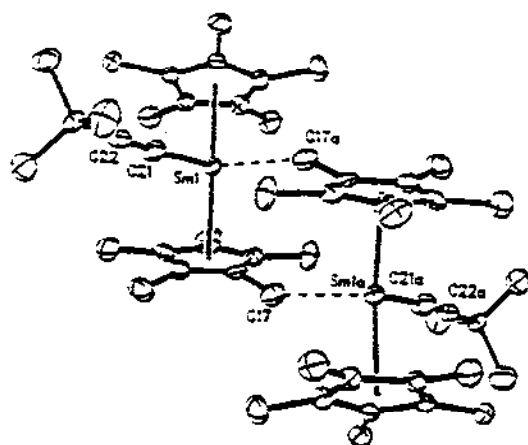


Fig. 36.

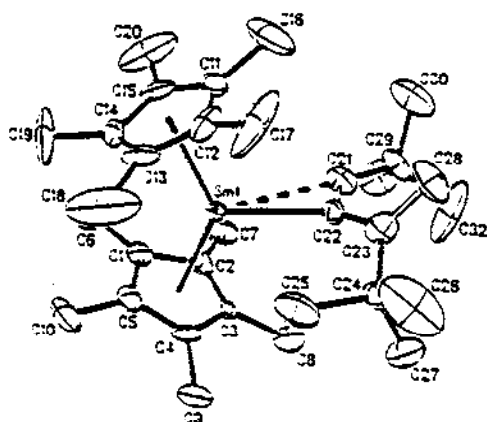
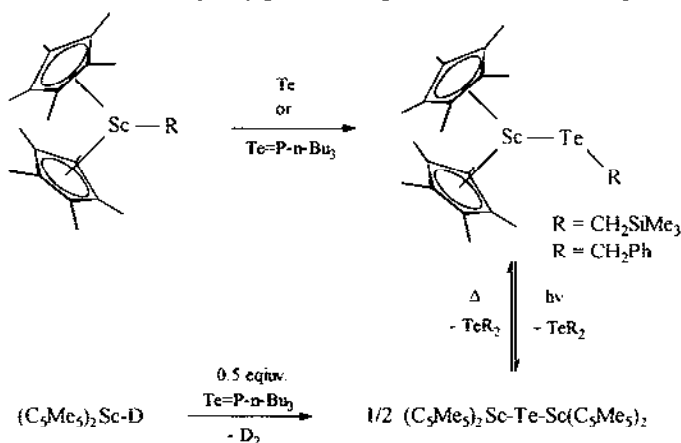


Fig. 37.

$(C_5Me_5)_2Sc(\mu\text{-}Te)Sc(C_5Me_5)_2$ and TeR_2 was irradiated using a UV lamp.



The crystal structure of $(C_5Me_5)_2Sc(\mu\text{-}Te)Sc(C_5Me_5)_2$ was also published (Fig. 40). The Sc–Te distance is 2.75 Å and the Sc–Te–Sc angle is 172.1°. These data, coupled with allene-like orientation of the C_5Me_5 -rings about the Sc–Te–Sc unit, suggest significant π -bonding between scandium and tellurium.

Chen et al. [36] reported the reactions of $Na(C_5H_4C_5H_9)$ (C_5H_9 =cyclopentyl) with $LnCl_3$ (Ln =Nd, Sm, Er, Yb) in a 2:1 molar ratio in THF to yield the new complexes $(C_5H_4C_5H_9)_2LnCl(THF)$ (Ln =Nd, Sm) and $(C_5H_4C_5H_9)_2LnCl$ (Ln =Er, Yb). Dimeric structures were revealed for $[(C_5H_4C_5H_9)_2SmCl(THF)]_2$ and $[(C_5H_4C_5H_9)_2ErCl]_2$ by X-ray crystallography.

Yasuda [37] prepared lactone polymers in a high yield by ring opening polymerization of lactones using $(C_5R_5)_aLnX_b$ (R =H, alkyl, $SiMe_3$; Ln =Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu; X =halogen except F; $a, b=1$ or 2, $a+b=3$) as catalysts.

The same author [38] described the polymerization of methylmethacrylate by $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ in toluene to give poly(methylmethacrylate) with extremely low polydispersity. $(C_5Me_5)_2Yb(Me)(THF)$ and $(C_5Me_5)_2Lu(Me)(THF)$ as well as $AlMe_3$ adducts of organolanthanides(III) such as $(C_5Me_5)_2Yb(\mu\text{-}Me)_2(AlMe_2)$, $(C_5Me_5)_2Y(\mu\text{-}Me)_2(AlMe_2)$, and $(C_5Me_5)_2Lu(\mu\text{-}Me)_2(AlMe_2)$ behaved in a fashion

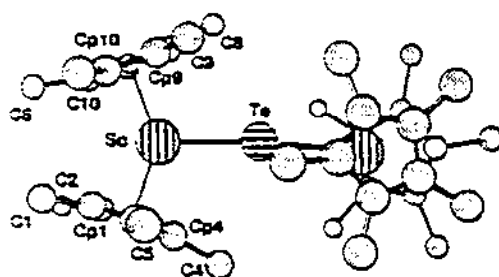


Fig. 40.

similar to that of $[(C_5Me_5)_2Sm(\mu-H)]_2$. Organolanthanide(II) complexes such as $(C_5Me_5)_2Yb(THF)_2$, $(C_5Me_5)_2Sm(THF)_2$, and $(Ind)_2Yb(THF)_2$ also start the living polymerization although their initiator efficiencies are much lower (35%) than those obtained by organolanthanide(III) complexes (>90%).

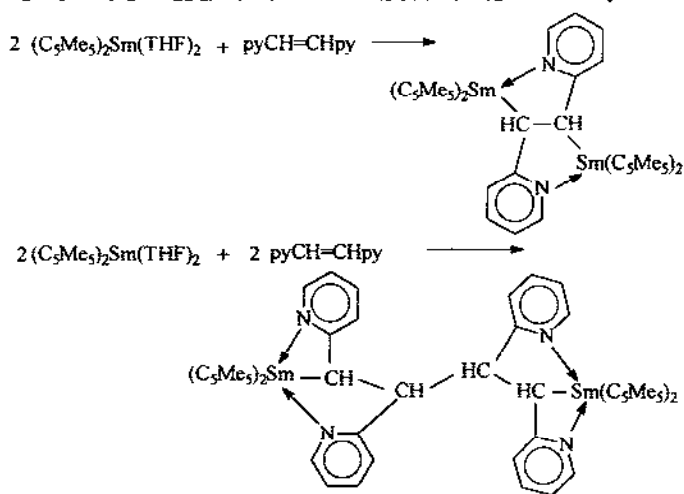
Lueken et al. [39] investigated the crystal structure of $[(C_5H_5)_2Tb(\mu-Br)]_2$ X-ray diffraction and measured its magnetic susceptibility. The complex is isomorphous with $[(C_5H_5)_2Sc(\mu-Cl)]_2$. The magnetic properties were compared with the prediction of various models, starting from cubic crystal fields and isotropic intramolecular exchange interactions, followed by extension to lower crystal field symmetry and anisotropic contributions to the spin coupling.

Shen et al. [40] reported the synthesis and crystal structure of $[(C_5H_4^tBu)_2Gd(\mu-Cl)]_2$ by reaction of $GdCl_3$ with $Na(C_5H_4^tBu)$ in THF. The compound exists as a chloride-bridged dimer.

Ziegler et al. [41] carried out electron density calculations on $(C_5H_5)_2Sc-R$ ($R = H, Me, Et, Pr, \text{vinyl}, \text{acetylide}$). Geometry optimizations revealed an agostic interaction for $R = Et$, whereas Me and Pr are bonded to the metal center without agostic interactions. The σ -bond metathesis reaction proceeds from an adduct between $(C_5H_5)_2Sc-R$ and $H-R'$ via a kite-shaped four-center transition state with a $Sc-R-H-R'$ core to an adduct between $(C_5H_5)_2Sc-R'$ and $H-R$. The activation energies increase with the number of vinyl and methyl groups in the $Sc-R-H-R'$ core as the directional σ -orbitals on these groups are unable to maintain optimal interactions with both neighbors in the $Sc-R-H-R'$ core.

Chamberlain et al. [42] accomplished selective hydrogenation of conjugated di-olefin polymers, especially copolymers with alkenylaromatic hydrocarbons, by treatment of the polymers with hydrogen in the presence of a catalyst comprising $(C_5Me_5)_2LnR$ ($R = H, \text{alkyl}, \text{aryl}$) and an alkali metal promoter.

Evans et al. [43] reported the formation of $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2\text{-pyCH=CHpy})$ by reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1,2-bis(2-pyridyl)ethylene in 80% yield if the reaction stoichiometry is 2:1. Combination of the same reagents in a 1:1 molar ratio formed $[(C_5Me_5)_2Sm]_2[\mu-\eta^3:\eta^3\text{-1,2,3,4-(py)}_4\text{C}_4\text{H}_4]$ in 78% yield.



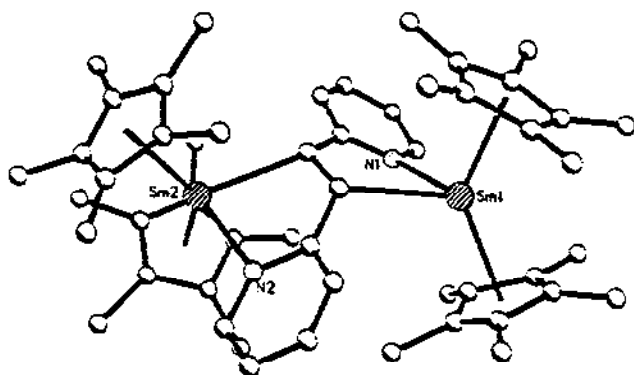


Fig. 41.

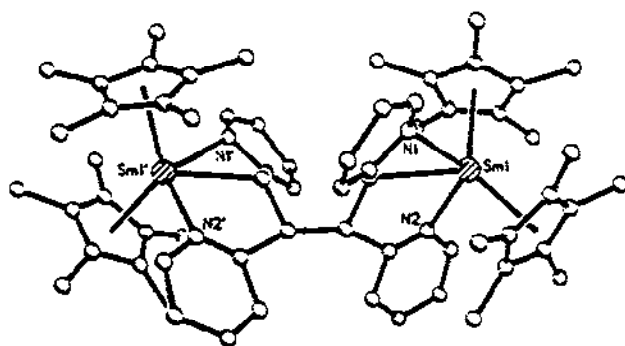
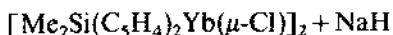
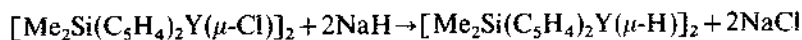


Fig. 42.

The compounds were characterized by X-ray crystallography (Figs. 41 and 42). Both complexes can also be interconverted either by reacting $\text{pyCH}=\text{CHpy}$ with $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-pyCH-CHpy})$ or by treatment of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ with $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2[\mu\text{-}\eta^3\text{:}\eta^3\text{-1,2,3,4-(py)}_4\text{C}_4\text{H}_4]$.

2.1.3. Bridged cyclopentadienyl compounds

Fischer and Paolucci [44] reported the synthesis of $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-H})]_2$ and $(\mu\text{-H})(\mu\text{-Cl})[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Yb}(\text{THF})]_2$ by reaction of $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Ln}(\mu\text{-Cl})]_2$ ($\text{Ln} = \text{Yb}, \text{Y}$) with NaH in THF.



The complexes have been investigated mainly by mass spectrometry (MS). An X-ray crystallographic study of $(\mu\text{-H})(\mu\text{-Cl})[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Yb}(\text{THF})]_2$ shows the complex to be dimeric with metal bridging $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2$ ligands and one THF ligand on

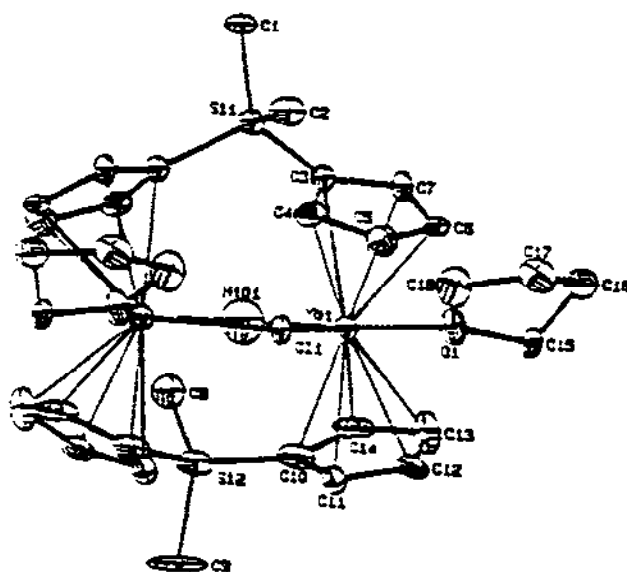
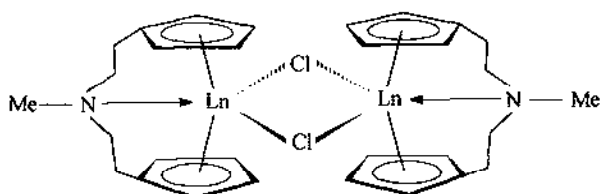
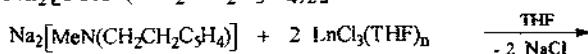


Fig. 43.

each Yb atom, one chlorine and one hydrogen bridging the two Yb atoms (Fig. 43). The unit cell contains two different dimers each of which is accompanied by one additional THF molecule.

Qian et al [45] described the synthesis of $[\text{MeN}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnCl}]_2$ ($\text{Ln} = \text{Y}, \text{Yb}, \text{Sm}, \text{Nd}$) in high yields by treatment of anhydrous $\text{LnCl}_3(\text{THF})_n$ ($n = 0, 3$ or 4) with $\text{Na}_2[\text{MeN}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2]$.

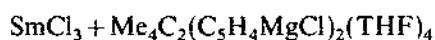


$\text{Ln} = \text{Y}, \text{Yb}, \text{Sm}, \text{Nd}$
 $n = 0, 3, 4$

The compounds were fully characterized by elemental analyses, MS, IR and ^1H NMR. Their spectroscopic data indicate that these complexes are chloride-bridged dimers and the two amine-linked cyclopentadienyl rings coordinate to the metal in a chelating fashion with intramolecular coordination of the nitrogen atom to the metal.

The bimetallic compound $\{[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{SmClMgCl}_2(\text{THF})_4\}_2$ has been syn-

thesized by Chen et al. [46] by reaction of $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4\text{MgCl})_2(\text{THF})_4$ with SmCl_3 in THF.



The crystal structure of the compound (Fig. 44) shows a symmetrical centre and a

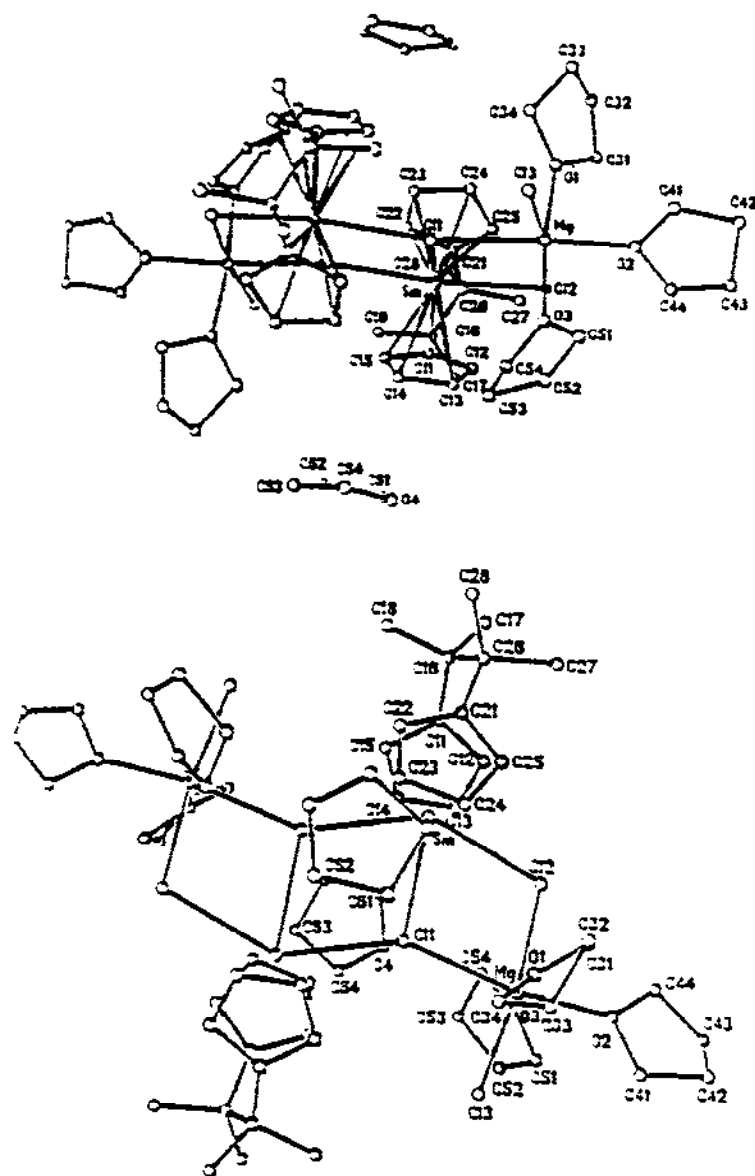
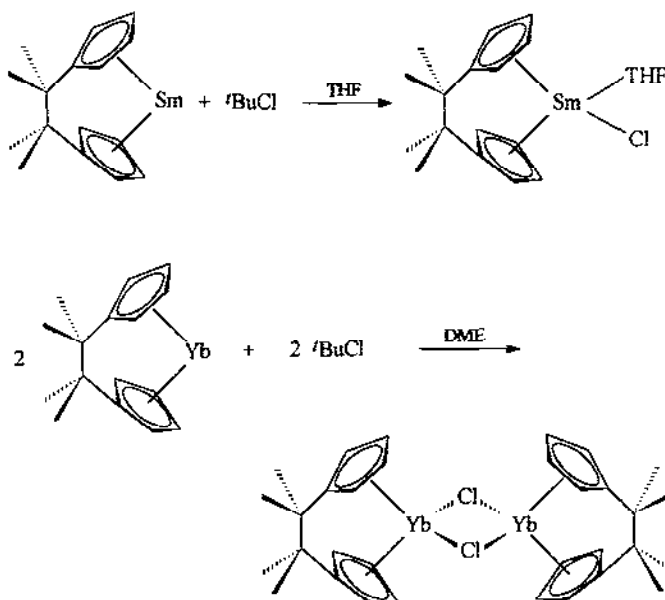


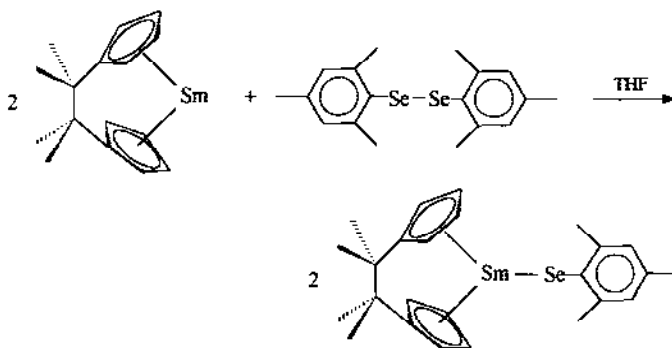
Fig. 44.

quadrilateral formed by Sm, Mg and two chlorine atoms. Two centroids of the cyclopentadienyls, bridged by a tetramethylethylene group, form with three bridging chlorine atoms a pseudo-trigonal bipyramid around Sm. Three oxygen atoms of THF and three chlorine atoms constitute a distorted octahedron around Mg.

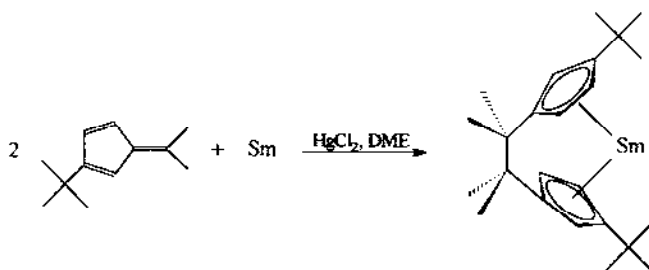
The derivative chemistry of the complexes $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Sm}$ and $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Yb}$ was described by Edelmann et al. [47]. Oxidation of $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Yb}$ with $^t\text{BuCl}$ affords the chloro-bridged binuclear ytterbium(III) complex $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Yb}(\mu\text{-Cl})_2]$. In contrast, treatment of $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Sm}$ with $^t\text{BuCl}$ yields the mononuclear derivative $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{SmCl}(\text{THF})$.



An organosamarium(III) selenolate, $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Sm}(\text{SeMes})$, was prepared from $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Sm}$ and dimesityldiselenide via reductive cleavage of the Se–Se bond. Similarly, the dithiocarbamates and dithiophosphates $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Ln}(\text{S}_2\text{CNMe}_2)$ and $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Ln}[\text{S}_2\text{P}(\text{OMe})_2]$ ($\text{Ln} = \text{Sm}, \text{Yb}$) have been obtained by treatment of $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Ln}$ ($\text{Ln} = \text{Sm}, \text{Yb}$) with the corresponding disulphides.



2-*t*-Butyl-6,6-dimethylfulvene reacts with samarium metal to give the *ansa*-samarocene(II) complex $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_3'\text{Bu})_2]\text{Sm}$ [47].



The compounds were fully characterized by NMR, IR and mass-spectrometry and elemental analysis.

2.1.4. *Tris(cyclopentadienyl) compounds*

$(\text{C}_5\text{H}_5)_3\text{Sm}(\text{NCMe})_2$, hitherto unknown in pure form, has been chemically stabilized by Amberger et al. [48] by doping a $(\text{C}_5\text{H}_5)_3\text{La}(\text{NCMe})_2$ matrix with $(\text{C}_5\text{H}_5)_3\text{Sm}(\text{NCMe})_2$. The absorption spectra of $(\text{C}_5\text{H}_5)_3\text{La}_{0.8}\text{Sm}_{0.2}(\text{NCMe})_2$, $(\text{C}_5\text{H}_5)_3\text{La}(\text{NCMe})_2$ and $(\text{C}_5\text{H}_5)_3\text{Sm}(\text{NCMe})_2$ as well as the luminescence spectra of $(\text{C}_5\text{H}_5)_3\text{La}_{0.8}\text{Sm}_{0.2}(\text{NCMe})_2$ and $(\text{C}_5\text{H}_5)_3\text{Sm}(\text{NCMe})_2$ have been measured. From these data the truncated crystal field (CF) splitting patterns of $(\text{C}_5\text{H}_5)_3\text{La}_{0.8}\text{Sm}_{0.2}(\text{NCMe})_2$ and $(\text{C}_5\text{H}_5)_3\text{Sm}(\text{NCMe})_2$ were derived.

Single crystals of various ester adducts derived from $\text{tris}(\eta^5\text{-cyclopentadienyl})\text{lanthanides}$ $[(\text{C}_5\text{H}_5)_3\text{Ln}]$; $\text{Ln} = \text{La, Pr, Sm, Tb, Er, Tm}$ have been isolated by the same authors [49] and were inspected by polarizing microscopy. The crystal and molecular structures of the butylacetate (BA) adduct derived from $(\text{C}_5\text{H}_5)_3\text{La}$ were determined by X-ray diffraction (Fig. 45). The La–centroid(C_5H_5) distances are 2.589 Å, 2.595 Å and 2.587 Å. The La–O1(BA) distance is 2.516 Å. Selected regions of the α -, σ -, and π -absorption spectra of $(\text{C}_5\text{H}_5)_3\text{La}$ and $(\text{C}_5\text{H}_5)_3\text{Pr}$ were also discussed.

Pires de Matos et al. [58] prepared the tetramethylurea adducts of $\text{tris}(\text{cyclopentadienyl})\text{lanthanide(III)}$ complexes $(\text{C}_5\text{H}_5)_3\text{Ln}(\text{TMU})$ ($\text{Ln} = \text{La, Ce, Nd, Sm, Eu, Yb}$; $\text{TMU} = 1,1,3,3\text{-tetramethylurea}$) by addition of stoichiometric amounts of $\text{Me}_2\text{NC}(\text{O})\text{NMe}_2$ to $(\text{C}_5\text{H}_5)_3\text{Ln}(\text{THF})$ in hexane. The structures of $(\text{C}_5\text{H}_5)_3\text{Ce}(\text{TMU})$ and $(\text{C}_5\text{H}_5)_3\text{Nd}(\text{TMU})$ were determined by single crystal X-ray diffraction analyses. The two compounds are isomorphous. The metal center is tetrahedrally coordinated.

The magnetic data and the results of low temperature absorption, luminescence and magnetic circular dichroism spectra of 4-methoxy-substituted lanthanide (III) $\text{tris}[N,N'\text{-bis}(\text{trimethylsilyl})]\text{benzamidates}$ $[(\text{MeOC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2)_3\text{Ln}]$ ($\text{Ln} = \text{Eu, Pr}$) and of adducts derived from $\text{tris}(\eta^5\text{-cyclopentadienyl})\text{europium(III)}$ $[(\text{C}_5\text{H}_5)_3\text{EuX}]$; $\text{X} = \text{CNC}_6\text{H}_{11}, \text{THF}$ were published by Amberger, Edelmann and Edelstein [50]. In the case of $(\text{C}_5\text{H}_5)_3\text{Eu}(\text{CNC}_6\text{H}_{11})$, $(\text{C}_5\text{H}_5)_3\text{Eu}(\text{THF})$, and $[(\text{MeOC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2)_3\text{Eu}]$ the ^{151}Eu Mössbauer spectra were also recorded. On the basis of the optical measurements the truncated crystal field (CF) splitting

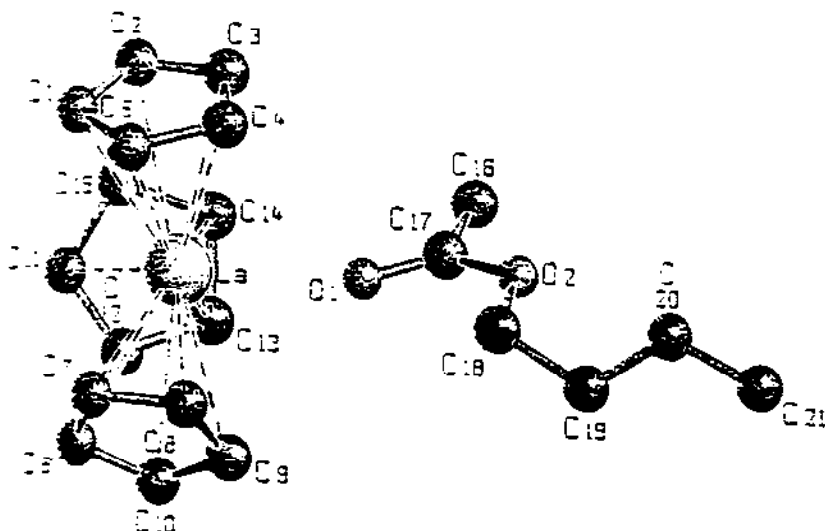
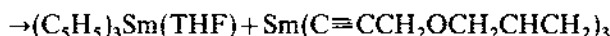
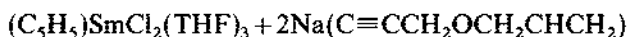


Fig. 45.

patterns of $[(\text{MeOC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2)_3\text{Eu}]$ and $[(\text{MeOC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2)_3\text{Pr}]$ were derived. The parameters of an empirical Hamiltonian were fitted to the experimentally derived splitting patterns. The parameters obtained suggest that the benzamidine ligand may be considered to a certain extent as an electronic equivalent to the C_5H_5 ligand in case of Ln central ions with small electron affinity. The C_5H_5 ligand, however, causes unusual physical properties which cannot be explained on the basis of an Eu^{3+} central ion which is surrounded by three C_5H_5 ligands.

Ye et al. [51] reported that the reaction of $(\eta^5\text{-C}_5\text{H}_5)_3\text{SmCl}_2(\text{THF})_3$ with $\text{Na}(\text{C}\equiv\text{CCH}_2\text{OCH}_2\text{CHCH}_2)$ in 1:2 molar ratio in THF results in the formation of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Sm}(\text{THF})$.



A crystal structure of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Sm}(\text{THF})$ (Fig. 46) shows the THF molecule coordinated to the samarium atom with a Sm–O distance of 2.52 Å. The Sm–C(cyclopentadienyl) bond lengths range from 2.70 Å to 2.80 Å and average 2.74 Å.

Schumann et al. [52] reported the synthesis of the homoleptic complexes $(\text{C}_5\text{Me}_4\text{H})_3\text{Ln}$ (Ln = La, Sm, Tb) by treatment of LnCl_3 with $\text{Na}(\text{C}_5\text{Me}_4\text{H})$. In contrast to compounds with C_5Me_5 as ligand it is possible to synthesize rare earth

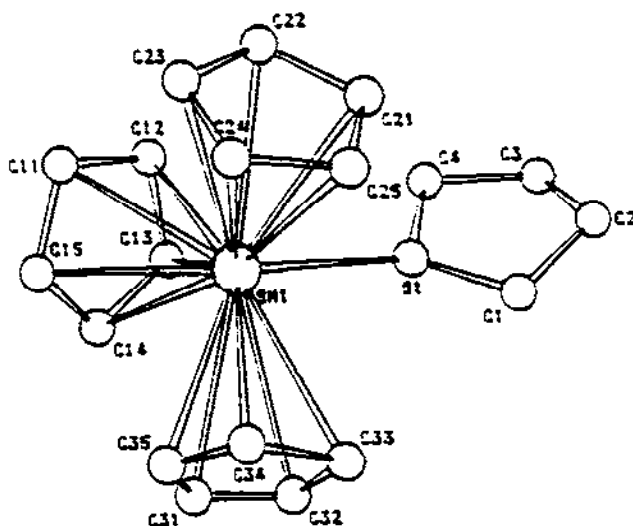
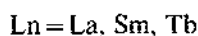
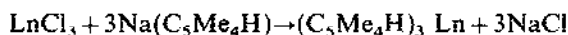


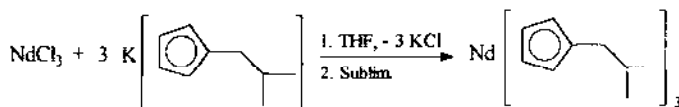
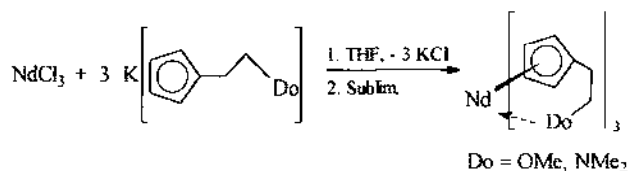
Fig. 46.

tris(cyclopentadienyl)complexes with C_5Me_4H as ligand by a classical metathetical route.



The crystal structure of $(C_5Me_4H)_3Tb$ has been determined (Fig. 47). The average Tb–centroid(C_5Me_4H) distance is 2.44 Å.

Herrmann et al. [53] reported the reaction of $NdCl_3$ with $K(C_5H_4CH_2CH_2Do)$ ($Do = OMe, NMe_2$) in THF to yield the sublimable homoleptic complexes $(C_5H_4CH_2CH_2OMe)_3Nd$ and $(C_5H_4CH_2CH_2NMe_2)_3Nd$. Under the same conditions, $K(tBuC_5H_4)$ yields the adduct $(tBuC_5H_4)_3Nd(THF)$, which is obtained solvent-free by thermal treatment.



The silylamide route was applied to synthesize the homoleptic neopentylcyclopentadienyl derivative $[C_5H_4CH_2CMe_3]_3Nd$. The alkyl-substituted complexes, particu-

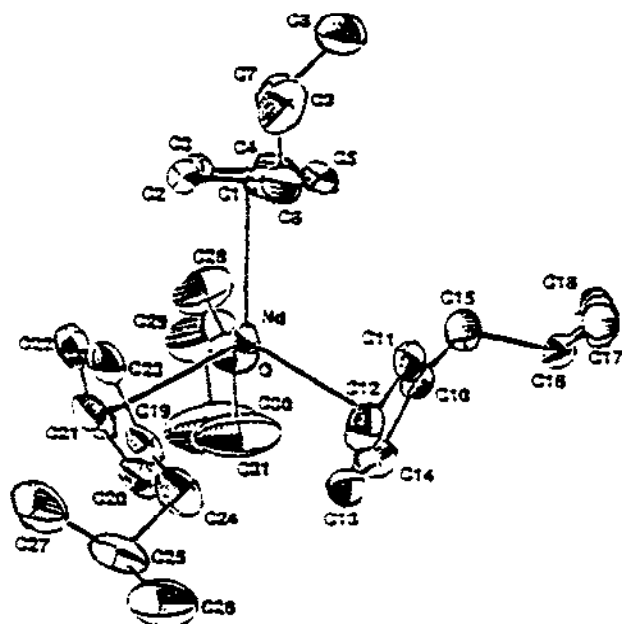


Fig. 48.

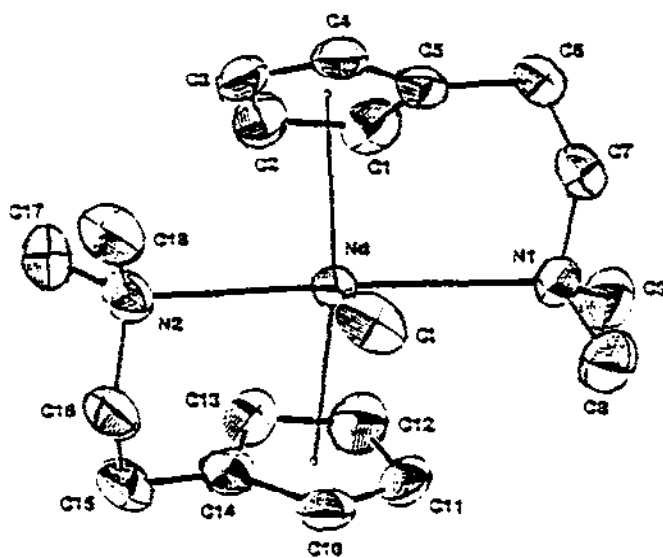


Fig. 49.

Greenwald et al. [56] developed several new source materials for doping AlGaAs films. The authors compared $(C_5H_5)_3Er$ to $Er[N(SiMe_3)_2]_3$ for purity, kinetics and doping of germanium films deposited from $GeMe_4$ in a hydrogen atmosphere. $(C_5H_5)_3Er$ left large amounts of carbon in pure metal films, and in the germanium

film, at low pressure and temperatures up to 850 °C. $\text{Er}[\text{N}(\text{SiMe}_3)_2]_3$ decomposed without incorporating carbon, nitrogen or silicon in the deposited film.

Different III–V compound semiconductors were doped with Yb, Er, and Tm using atmospheric pressure metal–organic CVD by Scholz et al. [57]. Best results were obtained using the novel isopropyl–cyclopentadienyl complexes $(\text{C}_5\text{H}_4\text{C}_3\text{H}_7)_3\text{Ln}$ ($\text{Ln} = \text{Yb}, \text{Er}, \text{Tm}$) as precursors which have an acceptable vapor pressure and can be used as liquids at bubbler temperatures of 60–90 °C. Only Yb was found to occupy a regular lattice site in InP, whereas the other lanthanides show complex optical spectra because of their incorporation as different centers and clusters.

Yoshida et al. [59] prepared quartz glass doped with rare earth elements by thermal decomposition of porous glass preforms containing dopants (Ge, P, B, Al, Ni) and lanthanide cyclopentadienyl complexes.

Fragalà and Marks [60] investigated the electronic structure of the alkoxide complex $(\text{C}_5\text{H}_5)_3\text{Ce}(\text{OR})$ by He I and He II UV photoelectron spectroscopy combined with SCF X α -DVM calculations.

2.1.5. Compounds with cyclooctatetraenyl and cyclopentadienyl ligands

The reactions of $[(\text{C}_8\text{H}_8)\text{Ln}(\mu\text{-Cl})(\text{THF})_n]_2$ ($\text{Ln} = \text{Y}, \text{La}, \text{Pr}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Er}, \text{Lu}; n = 1, 2$) with $\text{Na}(\text{C}_5\text{Me}_4\text{H})$ in THF to yield the complexes $(\text{C}_8\text{H}_8)\text{Ln}(\text{C}_5\text{Me}_4\text{H})(\text{THF})_x$ ($\text{Ln} = \text{Y}, \text{La}, \text{Pr}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Er}, \text{Lu}; x = 1\text{--}2$) were reported by Schumann et al. [61]. The crystal structures of $(\text{C}_8\text{H}_8)\text{La}(\text{C}_5\text{Me}_4\text{H})(\text{THF})_2$ (Fig. 50) and $(\text{C}_8\text{H}_8)\text{Lu}(\text{C}_5\text{Me}_4\text{H})(\text{THF})_2$ (Fig. 51) were also described.

The average $\text{La}-(\text{C}_5\text{H}_5)(\text{centroid})$ and $\text{La}-(\text{C}_8\text{H}_8)(\text{centroid})$ distances are 2.57 Å and 2.09 Å.

The average $\text{Lu}_1-(\text{C}_5\text{H}_5)(\text{centroid})$ and $\text{Lu}_1-(\text{C}_8\text{H}_8)(\text{centroid})$ distances were reported to be 2.21 Å and 1.62 Å, the $\text{Lu}_2-(\text{C}_5\text{H}_5)(\text{centroid})$ and $\text{Lu}_2-(\text{C}_8\text{H}_8)(\text{centroid})$ distances are 2.23 Å and 1.65 Å.

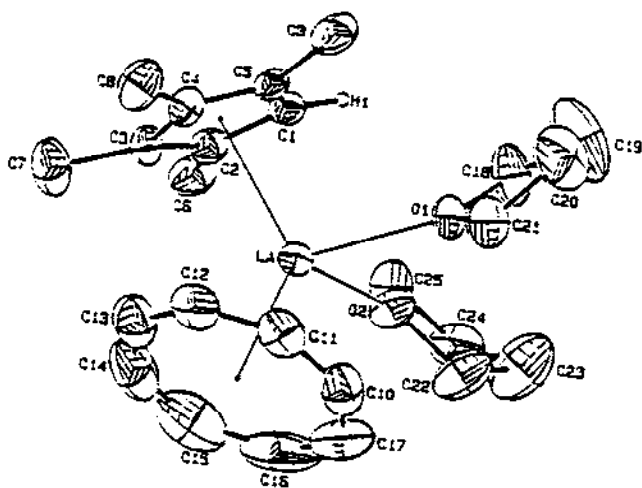


Fig. 50.

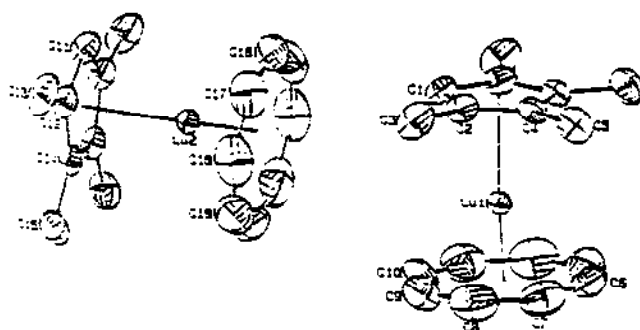
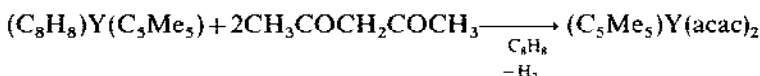
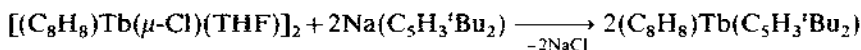
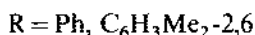
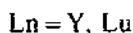
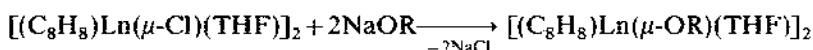


Fig. 51.

2.1.6. Compounds with cyclooctatetraenyl, porphyrine and other ligands

Schumann et al. [62] published the reaction of $[(C_8H_8)Ln(\mu-Cl)(THF)]_2$ with NaOR to give the dinuclear cyclooctatetraenyl alkoxides $[(C_8H_8)Ln(\mu-OR)(THF)]_2$ ($Ln = Y, Lu$; $R = Ph, C_6H_3Me_2-2,6$). The reactions of $[(C_8H_8)Ln(\mu-Cl)(THF)]_2$ ($Ln = Y, Lu, Tb$) with $Li[OC^tBu_3]$, $Na(OSiPh_3)$ and $Na(C_5H_3^tBu_2)$ result in the formation of $(C_8H_8)Ln(OC^tBu_3)(THF)$, $(C_8H_8)Ln(OSiPh_3)(THF)$ ($Ln = Y, Lu$) and $(C_8H_8)Tb(C_5H_3^tBu_2)$. Treatment of $(C_8H_8)Y(C_5Me_5)$ with acetylacetone yields $(C_5Me_5)Y(acac)$. The compounds were characterized by NMR and mass-spectroscopy.



The crystal structures of $[(C_8H_8)Y(\mu-OPh)(THF)]_2$ and $(C_8H_8)Tb(C_5H_3^tBu_2)$ are depicted in Fig. 52 and Fig. 53. The Y_1-Y_2 distance in the dimeric complex $[(C_8H_8)Y(\mu-OPh)(THF)]_2$ is 3.69 Å, the $Y_1-O_1(Ph)$ and $Y_1-O_2(Ph)$ distances are 2.36 Å and 2.29 Å, the $Y_2-O_1(Ph)$ and $Y_2-O_2(Ph)$ distances are 2.25 Å and 2.26 Å and the $Y_1-(C_8H_8)(\text{centroid})$ and $Y_2-(C_8H_8)(\text{centroid})$ distances are 1.77 Å and 1.85 Å. In the monomeric compound $(C_8H_8)Tb(C_5H_3^tBu_2)$ the $Tb-(C_8H_8)(\text{centroid})$ and $Tb-(C_5H_3^tBu_2)(\text{centroid})$ distances are 1.40 Å and 1.42 Å, respectively.

Five series of mono(cyclooctatetraenyl) lanthanide(III) half-sandwich complexes have been synthesized by Edelman et al. [63]. The compounds $(C_8H_8)Ln(HBpz_3)$, $(C_8H_8)Ln[HB(3,5-Me_2pz)_3]$, $(C_8H_8)Ln\{(C_5H_5)Co[P(O)(OEt)_2]_3\}$, $(C_8H_8)Ln[Ph_2P(NSiMe_3)_2](THF)$, and $(C_8H_8)Ln[MeOC_6H_4C(NSiMe_3)_2](THF)$ ($Ln = Ce, Pr, Sm, Nd$; $pz = \text{pyrazol-1-yl}$) are readily accessible through metathetical reactions of $[(C_8H_8)Ln(\mu-Cl)(THF)]_2$ with the appropriate anionic ligands.

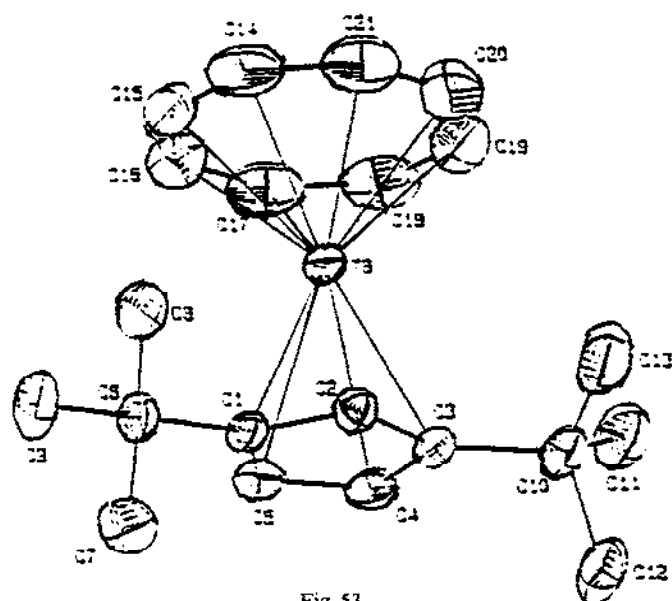
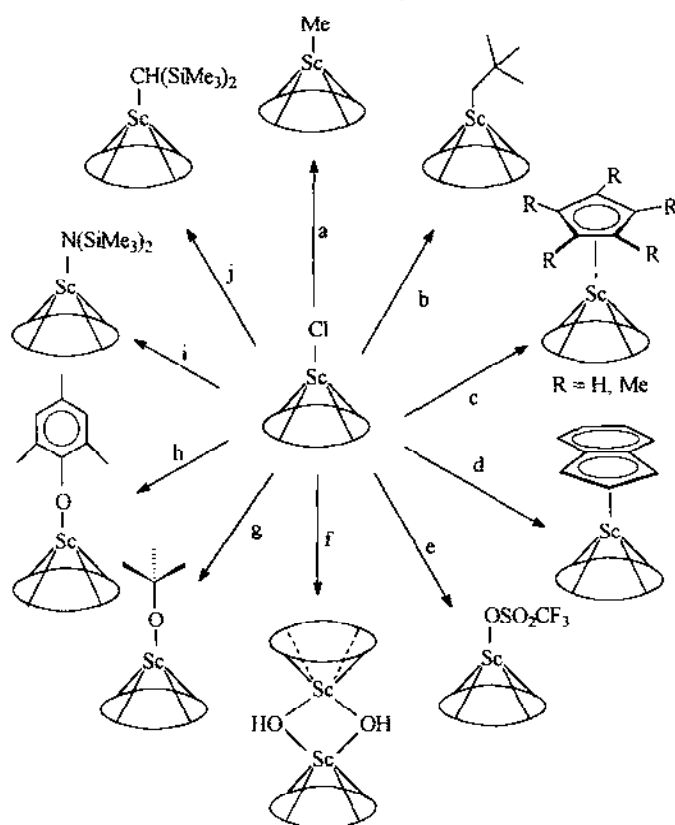


Fig. 53.



Conditions: (a) Me_2Mg in toluene; (b) Np_2Mg in toluene (Np=neopentyl); (c) $\text{Na}(\text{C}_3\text{H}_5)$ in THF, $\text{Li}(\text{C}_5\text{Me}_5)$ in THF, $\text{Li}(\text{C}_5\text{Me}_4\text{H})$ in THF; (d) $\text{Na}(\text{Ind})$ in THF; (e) TMSOTf in toluene (Tf=triflate); (f) H_2O in CH_2Cl_2 ; (g) LiOCMe_3 in toluene; (h) $\text{LiO}(\text{Me}_3\text{C}_6\text{H}_2)$ in toluene; (i) $\text{NaN}(\text{SiMe}_3)_2$ in toluene; (j) $\text{LiCH}(\text{SiMe}_3)_2$ in toluene.

Three of these complexes have been structurally characterized by X-ray crystallography. $[(\text{OEP})\text{ScMe}]_2 \cdot (\text{CH}_2\text{Cl}_2)$ (Fig. 54) and $(\text{OEP})\text{Sc}[\text{CH}(\text{SiMe}_3)_2]$ (Fig. 55)

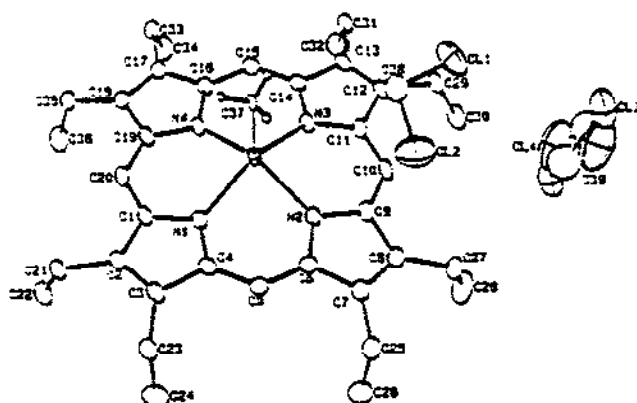


Fig. 54.

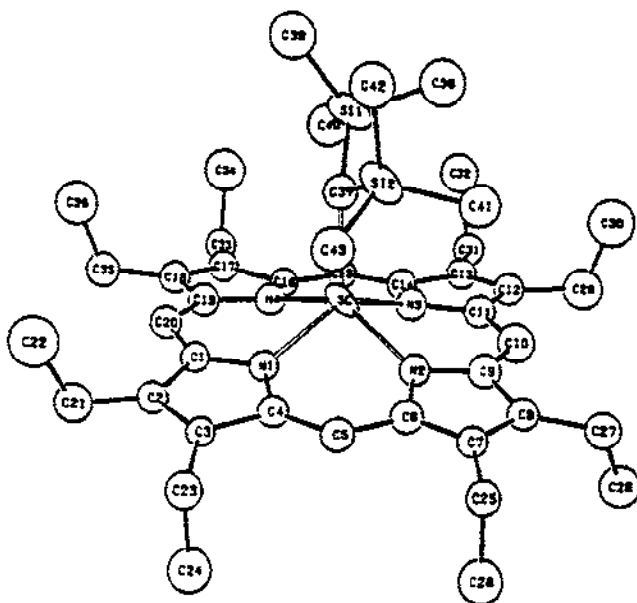


Fig. 55.

were obtained by recrystallization from CH_2Cl_2 . The (OEP)ScMe molecule in $[(\text{OEP})\text{ScMe}]_2(\text{CH}_2\text{Cl}_2)$ features a scandium coordinated in a regular square pyramidal fashion with Sc–N distances of 2.151–2.158 Å. The scandium sits atop a planar N_4 ring at a distance of 0.66 Å. The OEP ligand as a whole is slightly domed and ruffled. The Sc–C(Me) distance is 2.246 Å. The Sc–N bond lengths in $(\text{OEP})\text{Sc}[\text{CH}(\text{SiMe}_3)_2]$ are similar to those of the methyl derivative, ranging from 2.142 to 2.146 Å, and the Sc is displaced from the N_4 plane slightly more than in the methyl derivative (0.71 Å). The Sc–C bond length is 2.243 Å. The crystal structure of $(\text{OEP})\text{Sc}(\text{C}_9\text{H}_7)$ (Fig. 56) consists of well-separated molecules. The indenyl ring is bound in an η^5 -fashion. The average Sc–centroid(C_9H_7) distance is 2.232 Å, and the average bond length between the scandium and the nitrogens of the core is 2.182 Å. The scandium sits 0.78 Å above the mean plane containing the four core nitrogens.

The σ -alkyls react with ketones and CO_2 to yield alkoxides and acetates, respectively. Additional derivatives with $\text{R} = \text{OCMe}_3$, $\text{O}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)$, $\text{N}(\text{SiMe}_3)_2$, and triflate have also been prepared. Hydrolysis of these complexes yields the dimeric bridging hydroxide $[(\text{OEP})\text{Sc}(\mu\text{-OH})]_2$ which has also been crystallographically characterized (Fig. 57). The Sc– N_4 plane distance is 0.84 Å, and the Sc–O distances are 2.084 Å and 2.072 Å.

2.1.7. Cyclopentadienyl-like compounds

Xu et al. [18] published the reaction of $(\text{C}_9\text{H}_7)_3\text{Pr}(\text{THF})$ with 8-hydroxyquinoline ($\text{C}_9\text{H}_6\text{NOH}$) or 2-aminophenol ($\text{H}_2\text{NC}_6\text{H}_4\text{OH}$) in THF to give the thermally stable complexes $(\text{C}_9\text{H}_7)_2\text{Pr}(\text{OC}_9\text{H}_6\text{N})$, $(\text{C}_9\text{H}_7)\text{Pr}(\text{OC}_9\text{H}_6\text{N})_2$ and $(\text{C}_9\text{H}_7)_2\text{Pr}(\text{OC}_6\text{H}_4\text{NH}_2)$. Also reported was the synthesis of the mixed-ligand organolanthanide complexes

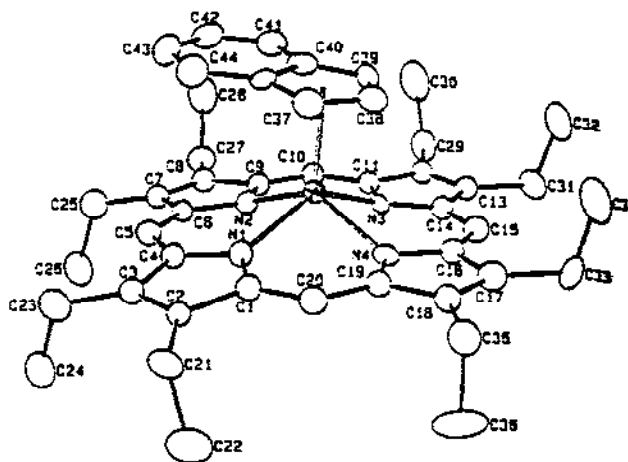


Fig. 56.

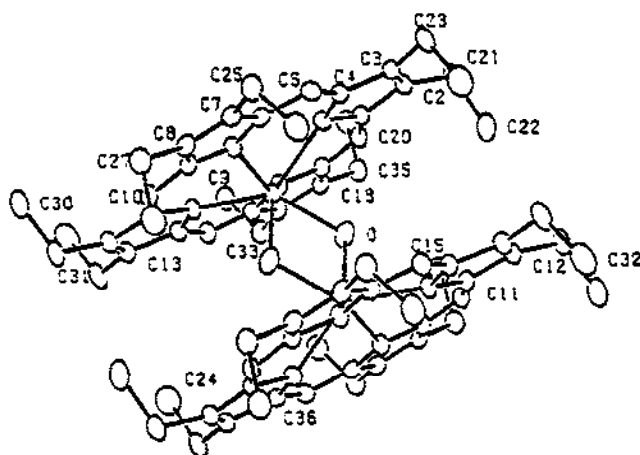
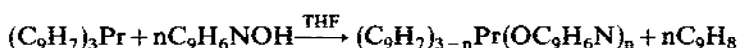
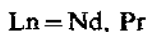
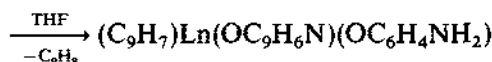
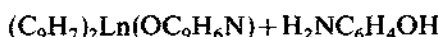
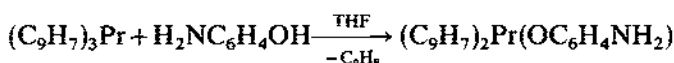


Fig. 57.

$(C_9H_7)Ln(OC_9H_6N)(OC_6H_4NH_2)$ ($Ln = Pr, Nd$) by reacting $(C_9H_7)_2Ln(OC_9H_6N)$ with 2-aminophenol in THF.

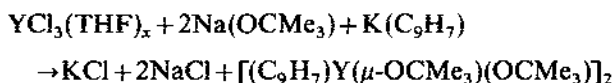


$$n = 1, 2$$



The structures of the complexes were verified by elemental analyses, IR, MS, and XPS spectra and molecular weight determinations, indicating that they are monomeric. The OC_9H_6N and $OC_6H_4NH_2$ ligands chelate with the metal to form an intramolecular five-membered ring.

Evans et al. [5] described the synthesis and crystal structure (Fig. 58: Y -centroid(C_9H_7) = 2.416 Å; Y - Y = 3.510 Å; Y -O(μ -OCMe₃) = 2.241 Å, 2.205 Å, 2.247 Å, 2.203 Å) of the dimeric indenyl complex $[(C_9H_7)Y(\mu$ -OCMe₃)(OCMe₃)]₂ by reaction of $YCl_3(THF)_x$ with Na(OCMe₃) and K(C_9H_7) in toluene at reflux.



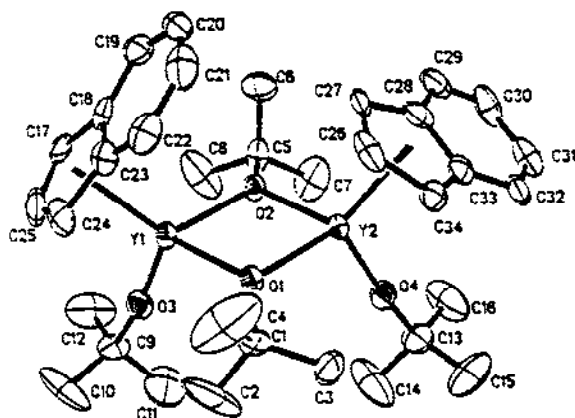
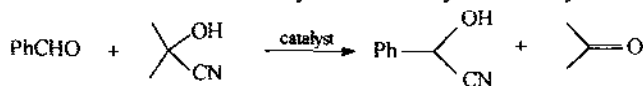


Fig. 58.

2.2. Compounds without supporting cyclopentadienyl ligands

2.2.1. Alkoxides

Inoue et al. [65] showed that a rapid transhydrocyanation from acetone cyanohydrin to several aldehydes and ketones takes place in the presence of a catalytic amount of $\text{Ln}(\text{O}^i\text{Pr})_3$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Sm}, \text{Yb}$) to provide the corresponding cyanohydrins. In the case of benzaldehyde the catalytic activity of $\text{Yb}(\text{O}^i\text{Pr})_3$ is very high.



catalyst: $\text{La}(\text{O}^i\text{Pr})_3$, $\text{Ce}(\text{O}^i\text{Pr})_3$, $\text{Sm}(\text{O}^i\text{Pr})_3$, $\text{Yb}(\text{O}^i\text{Pr})_3$

Oehme et al. [66] studied the stereospecific polymerization of butadiene with a neodymium octoate/diethylaluminium chloride/triethylaluminium catalyst in *n*-heptane. The neodymium octoate was prepared by the reaction of neodymium acetate with 2-ethyl-caproic acid. The concentration of the three catalyst components was varied and the optimum ratio was used for the copolymerization of butadiene/isoprene. The results of the determination of conversion, microstructure, and molecular weight of the polymers are also illustrated.

Wu et al. [67] studied the solid state CP/MAS ^{89}Y NMR spectra of a series of air-sensitive yttrium-alkoxide complexes with a chemical shift range of over 1000 ppm. The effects of variable power level, contact time, and spinning rate were described. Spectra obtained on mono-, di-, and polymetallic samples which had been characterized by X-ray crystallography show a direct correlation between the number of unique solid state environments. The crystal structure of $\text{Y}_3(\mu^3\text{-OCMe}_3)(\mu^3\text{-Br})(\mu^3\text{-OCMe}_3)_3(\text{OCMe}_3)_3\text{Br}(\text{THF})_2$ (Fig. 59) shows a triangle of three yttrium atoms with three $(\mu\text{-OCMe}_3)$ ligands on each edge and a $(\mu\text{-OCMe}_3)$ and a $(\mu\text{-Br})$ ligand above and below the plane of the metals. One yttrium is ligated by a terminal (OCMe_3) and a terminal bromide ligand, whereas the other two metals are each ligated by one terminal *t*-butoxide ligand and one THF.

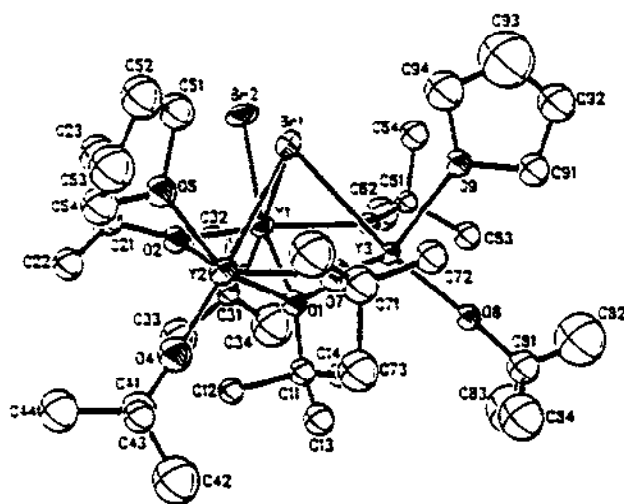


Fig. 59.

2.2.2. Alkyl and arene compounds

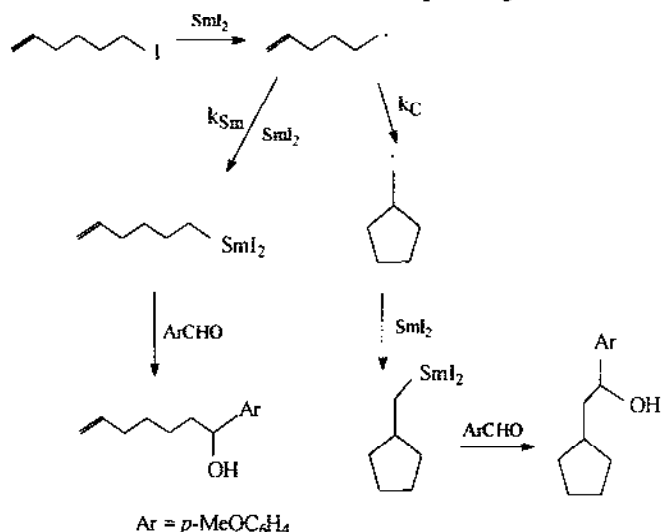
Siegbahn et al. [68] studied covalent ligand effects in the oxidative addition of methane and of molecular hydrogen to second-row transition-metal complexes including yttrium. The reaction energies and barrier heights have been determined. The entire sequence of second-row transition metals from yttrium to palladium has also been studied. The results were analyzed in terms of promotion energies, loss of exchange energies, as well as steric and other electronic repulsion effects.

Calculations including electron correlation of all the valence electrons for the activation of the C–H bond in ethylene by second row transition metals including yttrium have been performed by the same authors [69]. The resulting binding energies for vinyl hydride products were compared to previously calculated binding energies for π -coordinated ethylene complexes. The product energies and the barrier heights for the ethylene reaction were also compared to previous results for the corresponding methane reaction. It was found that the product binding energies are larger and the barrier heights for C–H activation lower for the ethylene reaction.

The same author studied the Ziegler–Natta insertion into a metal–alkyl bond for the second-row transition metal atoms including yttrium, without additional ligands and with two hydride ligands added [70]. For yttrium the barrier height for the olefin insertion into the metal–alkyl bond is about 15 kcal mol^{-1} higher than for insertion into the metal–hydride bond. The origin of this difference is the directional character of the methyl bond in contrast to the hydride bond.

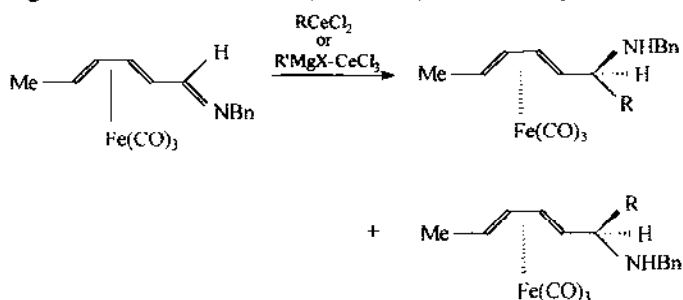
Siegbahn and Svensson [71] presented a systematic investigation of the geometry optimization step in studies of the energetics of reactions involving second-row transition metal complexes. The systems studied are products of the oxidative addition between metal hydrides and methane from yttrium to palladium. The results are put in perspective by a consideration of the overall accuracy obtainable in the final energy evaluation step at the optimized geometries.

Curran et al. [72] determined the first bimolecular rate constants for the reduction of a primary alkyl radical by SmI_2 by using a hexenyl radical clock. Rate constants varied from 5×10^5 to $7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, depending on the amount of HMPA present.



Bandow et al. [73] reported a high yield synthesis of endohedral lanthanofullerenes via lanthanum carbide by a newly developed fullerene arc generator equipped with an anaerobic sampling apparatus. The yield of the lanthanofullerene La@C_{82} increased by a factor of 10 or more, when LaC_2 -enriched composite carbon rods were used for the generation of soot instead of hydrooxidized or oxidized lanthanum composite rods. The compound is characterized by ESR and by the powder X-ray diffraction method.

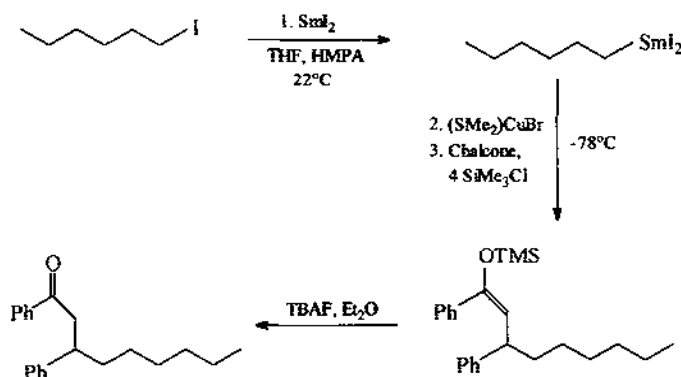
Iwata et al. [74] described the stereoselective nucleophilic addition of organocerium reagents such as RCeCl_2 or RMgBr/CeCl_3 ($\text{R} = \text{Ph}, \text{Me}$) to the 1-imino-*E,E*-butadiene-iron tricarbonyl complex $(\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{NBn})\text{Fe}(\text{CO})_3$, resulting in two diastereomeric (1*RS*,2*RS*)-amine complexes.



$\text{R} = \text{Me}, \text{Ph}, n\text{-Bu}$

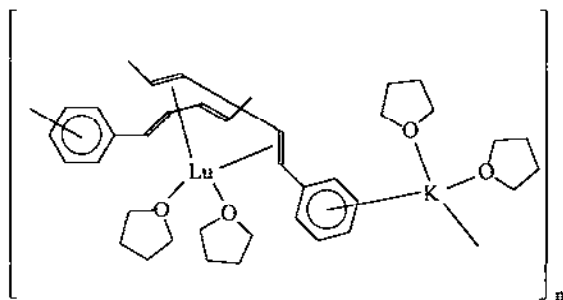
$\text{R}' = \text{Me}, \text{Ph}, \text{allyl}$

Wipf et al. [75] showed that Me_3SiCl accelerates the conjugate addition of in situ prepared organosamarium reagents to α,β -unsaturated carbonyl compounds and nitriles in the presence of HMPA and catalytic amount of Cu(I) salts. HMPA is also necessary for the in situ preparation of the organosamarium species from alkyl halide and SmI_2 . In the absence of Cu(I) salts, 1,2-additions of organosamarium reagents to carbonyl groups are also dramatically accelerated by $\text{Me}_3\text{SiCl/HMPA}$.



Beletskaya et al. [76] described the reaction of $\text{C}_5\text{H}_{11}\text{C}\equiv\text{CMe}$ with MeYbI and MeI to yield the dimeric compound $\text{C}_5\text{H}_{11}\text{CMe}=\text{CMeCMe}=\text{CMe}-\text{C}_5\text{H}_{11}$, two cyclobutenes $[-(\text{C}_5\text{H}_{11})\text{CMeCMe}_2\text{C}(\text{C}_5\text{H}_{11})=\text{C}(\text{Me})-]$ and $[-(\text{C}_5\text{H}_{11})\text{CMeCHMeC}(\text{C}_5\text{H}_{11})=\text{C}(\text{Me})-]$, and $\text{C}_5\text{H}_{11}\text{CMe}=\text{CMeCH}=\text{CMe}-\text{C}_5\text{H}_{11}$. The reaction of $\text{C}_5\text{H}_{11}\text{C}\equiv\text{CSiMe}_3$ with MeYbI and MeI yields *cis*- and *trans*- $\text{C}_5\text{H}_{11}(\text{Me})\text{C}=\text{C}(\text{Me})\text{C}_5\text{H}_{11}$ and $\text{CH}_2\text{CH}(\text{CH}_2)_3\text{CMe}=\text{CHSiMe}_3$. Treatment of $\text{PhC}\equiv\text{CSiMe}_3$ with MeYbI followed by MeI gives *cis*- and *trans*- $\text{PhCMe}=\text{CMe}(\text{SiMe}_3)$.

Bochkarev et al. [77] reported the synthesis and crystal structure of the lutetium 1,4-butadiene complex $\text{K}(\text{THF})_2(\mu\text{-Ph}_2\text{C}_4\text{H}_4)_2\text{Lu}(\text{THF})_2$.



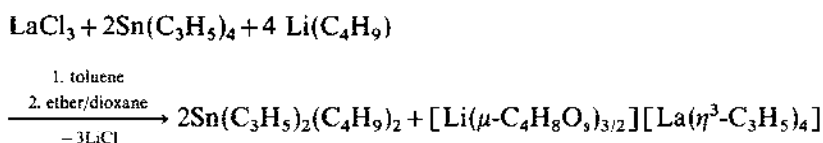
The lutetium atom is linked to two tetrahapto-coordinated 1,4-diphenyl-1,3-butadiene ligands and two THF molecules. The average $\text{Lu}-\text{C}(\eta^4)$ distance is 2.523 Å. In the crystal, endless one-dimensional chains are formed due to the fact that K is linked η^6 -coordinatively to two Ph rings of the diphenylbutadiene ligands in the neighboring molecules.

2.2.3. Carbonyl compounds

Fournier [78] reported the results of density functional calculations on the most stable high-spin and low-spin states of MCO, where M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu. The ground state was found to be high spin for scandium, and the Sc–CO binding energy was estimated to be 9 kcal mol⁻¹. The calculated CO harmonic stretch frequencies generally overestimate the observed values, but follow a similar trend. The CO bond lengths, CO stretching frequencies, and metal–CO bond strengths all correlate well with the extent of π -back donation. These correlations hold only within either the group of all high-spin states, or the group of low-spin states. Thus, there are no simple trends in the calculated properties of ground state MCO complexes.

2.2.4. Allyl compounds

The synthesis of the complex $[\text{Li}(\mu\text{-C}_4\text{H}_8\text{O}_2)_{3/2}][\text{La}(\eta^3\text{-C}_3\text{H}_5)_4]$ by reaction of LaCl_3 , $\text{Sn}(\text{C}_3\text{H}_5)_4$ and $\text{Li}(\text{C}_4\text{H}_9)$ in toluene was reported by Taube and Schumann et al. [79]. The compound could be obtained as crystals in the form of the dioxane adduct from ether solution.



Characterization of the compound was achieved by elemental analysis, ¹H NMR, ¹³C NMR and IR spectroscopy as well as X-ray crystal structure analysis (Fig. 60). The π -bonded allyl groups are coordinated to the lanthanum with tetrahedral distortion. The lithium ions form wavy layers and each is bridged by three dioxane molecules. There is also a weak interaction with one terminal C-atom of one allyl group. Under standard conditions the complex has a moderately catalytic effect on the 1,4-*trans* polymerization of butadiene in toluene.

3. Actinides

3.1. Cyclopentadienyl and cyclopentadienyl-like compounds

3.1.1. Bis(cyclopentadienyl) compounds

Andersen et al. [34] prepared the bridged methyl compound $[(\text{C}_5\text{H}_4\text{CMe}_3)_2\text{U}(\mu\text{-Me})]_2$ by reaction of $(\text{C}_5\text{H}_4\text{CMe}_3)_3\text{U}$ with MeLi. The compound is unstable in the gas phase and in benzene solution and rearranges to give $(\text{C}_5\text{H}_4\text{CMe}_3)_3\text{U}$ and other materials.

Hauchard et al. [80] studied the voltammetric behavior of $(\text{C}_5\text{H}_5)_2\text{U}(\text{BH}_4)_2$ and $(\text{C}_5\text{H}_5)_3\text{U}(\text{BH}_4)$ at a Pt conventional microelectrode or at a Pt ultramicroelectrode in an $\text{NBu}_4\text{PF}_6/\text{THF}$ medium. The results showed that both compounds

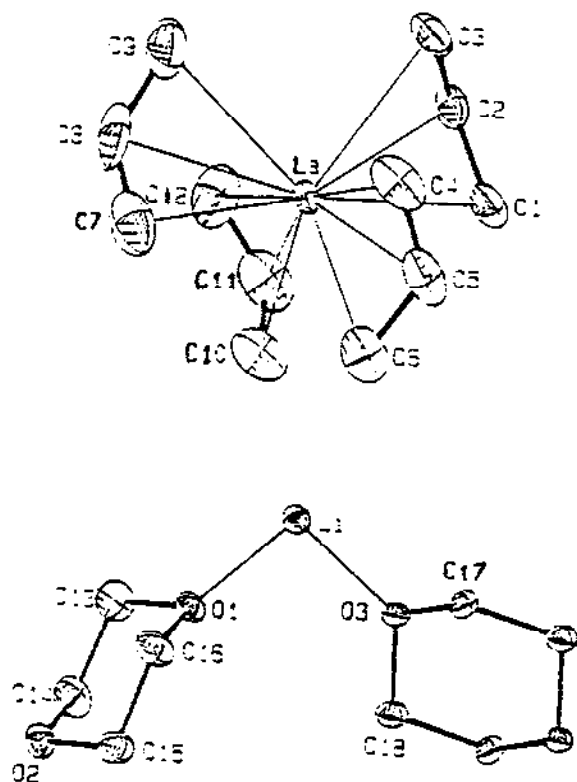
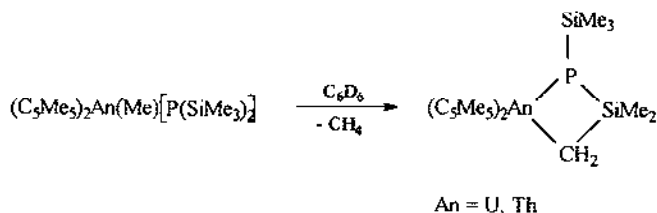


Fig. 60.

were reduced, according to a rapid one-electron process to afford the stable species $(C_5H_5)_2U(BH_4)_2^-$ and $(C_5H_5)_3U(BH_4)^-$. It was possible to stabilize $(C_5H_5)_2U(BH_4)_2$ for a few hours at low temperatures (below 250 K) or in pure THF.

Burns et al. [81] synthesized the actinide diorganophosphido complexes $(C_5Me_5)_2U[P(SiMe_3)_2]Cl$, $(C_5Me_5)_2Th[P(SiMe_3)_2]Cl$, $(C_5Me_5)_2U[P(SiMe_3)_2]Me$ and $(C_5Me_5)_2Th[P(SiMe_3)_2]Me$ by reaction of $(C_5Me_5)_2AnCl_2$ or $(C_5Me_5)_2AnCl(Me)$ ($An=U, Th$) with $K[P(SiMe_3)_2]$ in THF. Thermal decomposition of $(C_5Me_5)_2U[P(SiMe_3)_2]Me$ and $(C_5Me_5)_2Th[P(SiMe_3)_2]Me$ results in the formation of the metallacyclic complexes $(C_5Me_5)_2U[P(SiMe_3)SiMe_2CH_2]$ and $(C_5Me_5)_2Th[P(SiMe_3)SiMe_2CH_2]$, accompanied by the liberation of methane.



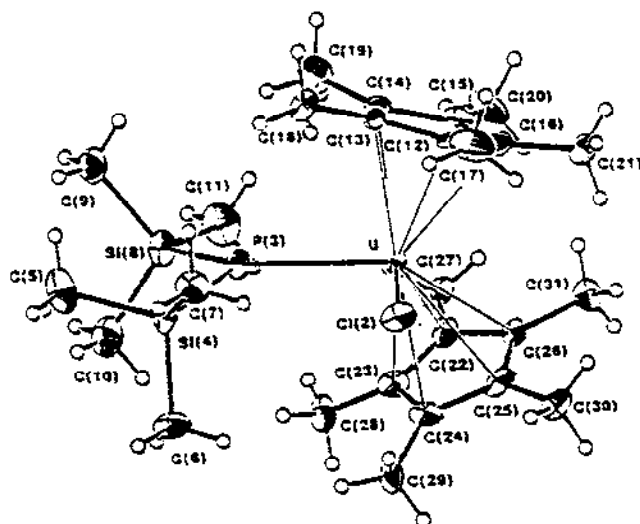


Fig. 61.

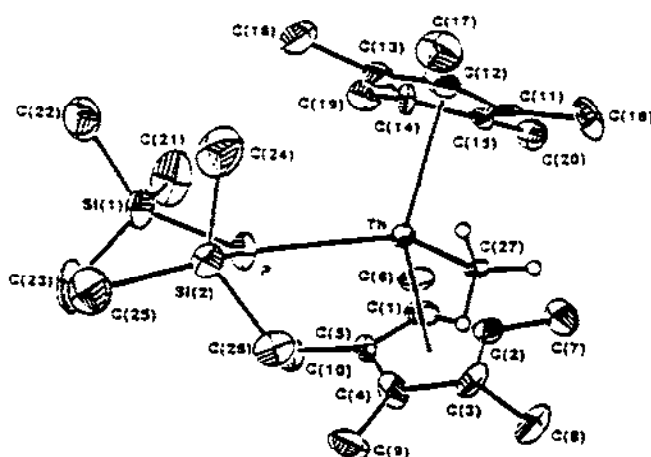


Fig. 62.

The structures of $(C_5Me_5)_2U[P(SiMe_3)_2]Cl$ (Fig. 61), $(C_5Me_5)_2Th[P(SiMe_3)_2]Me$ (Fig. 62) and $(C_5Me_5)_2U[P(SiMe_3)SiMe_2CH_2]$ (Fig. 63) were determined by X-ray diffraction. The steric repulsion of the pentamethylcyclopentadienyl rings in $(C_5Me_5)_2U[P(SiMe_3)_2]Cl$ and $(C_5Me_5)_2Th[P(SiMe_3)_2]Me$ results in a compression of the phosphorus–metal–X angle ($X=Cl$ or Me) as compared to tetrahedral values ($P-U-Cl=93.92^\circ$; $P-Th-Me=94.8^\circ$). The $U-Cl$ distance in $(C_5Me_5)_2U[P(SiMe_3)_2]Cl$ is 2.570 \AA and the $Th-C(Me)$ distance in $(C_5Me_5)_2Th[P(SiMe_3)_2]Me$ is 2.510 \AA . The coordination geometry about the phosphorus is approximately planar in both complexes, with angle sums of 357.7° and 355.2° around the phosphorus. Both

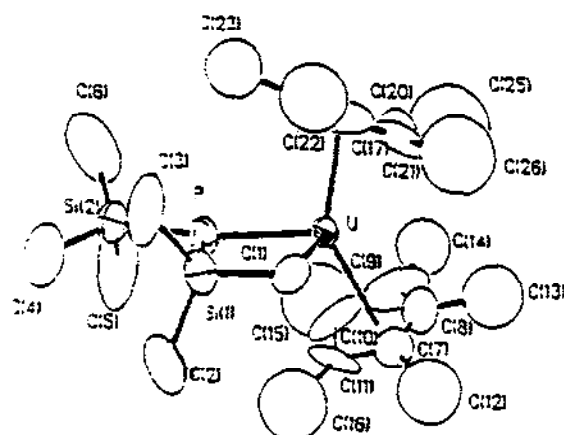


Fig. 63.

structures exhibit nonbonding contacts between one silylphosphide methyl group and two methyl substituents of the cyclopentadienyl rings, as well as between a different methyl group and the "X" ligand. This restricts further rotation and leads to inequivalent signals in the ^1H NMR spectra of both compounds. The $\text{U}-\text{C}(\text{CH}_2)$ distance in $(\text{C}_5\text{Me}_5)_2\text{U}[\text{P}(\text{SiMe}_3)\text{SiMe}_2\text{CH}_2]$ is 2.415 Å.

Marks and coworkers [82] reported the reaction of $(\text{C}_5\text{Me}_5)_2\text{ThMe}_2$ with the bis(dicarbollide) complexes $[\text{HNEt}_3][\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]$ and $[\text{HNEt}_3][\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})_2]$ in toluene to yield the salt-like species $[(\text{C}_5\text{Me}_5)_2\text{ThMe}]^+[\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$ and $[(\text{C}_5\text{Me}_5)_2\text{ThMe}]^{2+}[\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})_2]^{2-}$. The crystal structure of $[(\text{C}_5\text{Me}_5)_2\text{ThMe}]^{2+}[\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})_2]^{2-}$ (Fig. 64) reveals tight ion-pairing with three

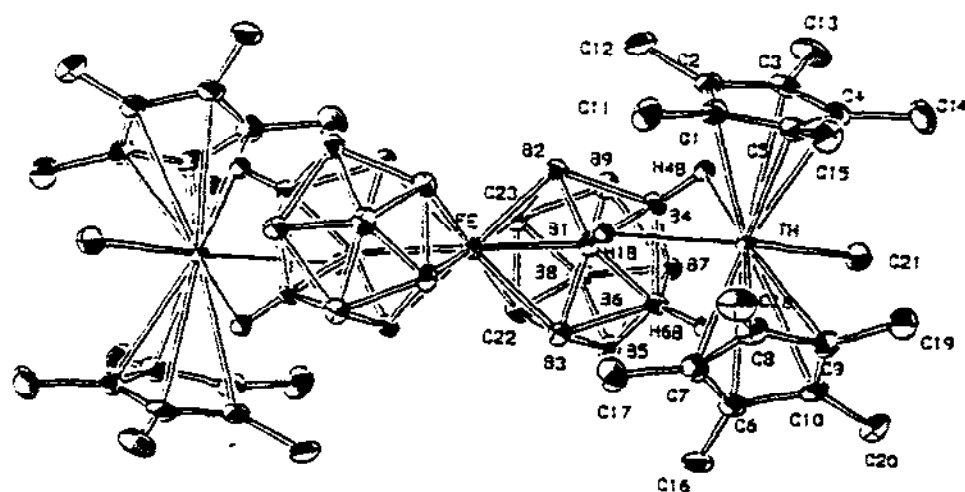
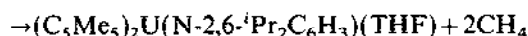
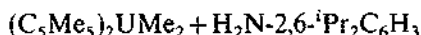
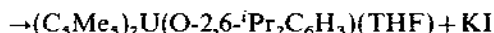
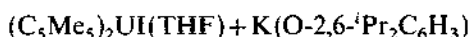


Fig. 64.

close Th–H–B bridging interactions (2.42 Å, 2.50 Å, 2.67 Å). The high level of Th coordinative saturation explains the chemical inertness of $[(C_5Me_5)_2ThMe]^+$ $[Co(B_9C_2H_{11})_2]^-$ and $[(C_5Me_5)_2ThMe]^{2+}$ $[Fe(B_9C_2H_{11})_2]^{2-}$.

The reaction of $(C_5Me_5)_2Th(CH_2SiMe_3)_2$ with $[HNEt_3][Co(B_9C_2H_{11})_2]$ affords $[(C_5Me_5)_2Th(CH_2SiMe_3)]^+$ $[Co(B_9C_2H_{11})_2]^-$, which undergoes hydrogenolysis to yield $[(C_5Me_5)_2ThH]^+$ $[Co(B_9C_2H_{11})_2]^-$.

Burns et al. [83] reported the synthesis of $(C_5Me_5)_2U(O-2,6-^iPr_2C_6H_3)(THF)$ and $(C_5Me_5)_2U(N-2,6-^iPr_2C_6H_3)(THF)$ by reaction of $(C_5Me_5)_2UI(THF)$ or $(C_5Me_5)_2UMe_2$ with $K(O-2,6-^iPr_2C_6H_3)$ or $H_2N-2,6-^iPr_2C_6H_3$ in THF.



Reactions of $(C_5Me_5)_2U(N-2,6-^iPr_2C_6H_3)(THF)$ and $(C_5Me_5)_2U(O-2,6-^iPr_2C_6H_3)(THF)$ with C_5H_5NO afforded $(C_5Me_5)_2U(N-2,6-^iPr_2C_6H_3)(O)$ and $(C_5Me_5)_2U(O-2,6-^iPr_2C_6H_3)(O)$, respectively. These compounds represent the first high-valent organouranium complexes containing terminal monooxo functional groups. The crystal structures of $(C_5Me_5)_2U(O-2,6-^iPr_2C_6H_3)(O)$ (Fig. 65) and $(C_5Me_5)_2U(N-2,6-^iPr_2C_6H_3)(O)$ (Fig. 66) were also reported. The U–C(centroid) distances in $(C_5Me_5)_2U(O-2,6-^iPr_2C_6H_3)(O)$ are 2.712 Å and 2.811 Å, the $(C_5Me_5)(centroid)$ –U– $(C_5Me_5)(centroid)$ angle is 134.1°.

The U–C(centroid) distances in $(C_5Me_5)_2U(N-2,6-^iPr_2C_6H_3)(O)$ are 2.730 Å and 2.805 Å, the $(C_5Me_5)(centroid)$ –U– $(C_5Me_5)(centroid)$ angle is 135.9°.

3.1.2. Tris(cyclopentadienyl) compounds

Ephritikhine et al. [84] prepared the uranium(III) nitrile complexes $(C_5H_5)_3U(NCR)$ (R = Me, nPr , iPr , tBu) by treatment of $(C_5H_5)_3U(THF)$ with the corresponding nitrile.

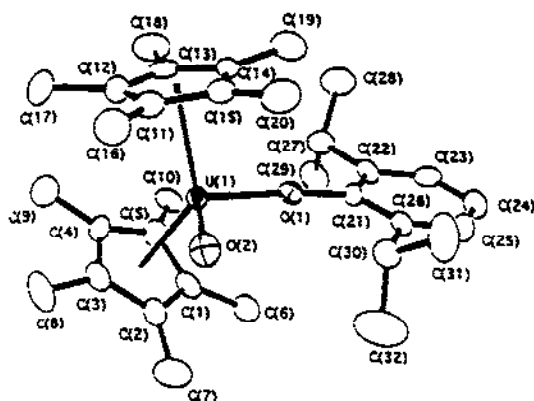


Fig. 65.

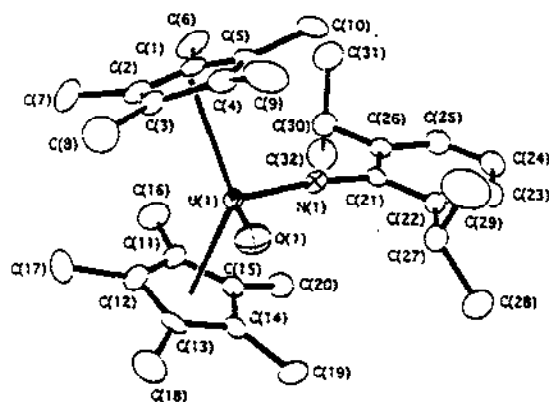
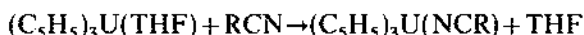


Fig. 66.



Reaction of $(\text{C}_5\text{H}_5)_3\text{U}(\text{THF})$ with benzonitrile at room temperature or thermolysis of the adducts $(\text{C}_5\text{H}_5)_3\text{U}(\text{NCMe})$ and $(\text{C}_5\text{H}_5)_3\text{U}(\text{NC}^n\text{Pr})$ afforded an equimolar mixture of the uranium(IV) compounds $(\text{C}_5\text{H}_5)_3\text{U}(\text{CN})$ and $(\text{C}_5\text{H}_5)_3\text{U}(\text{R})$ ($\text{R} = \text{Me}, {}^n\text{Pr}, \text{Ph}$). The crystal structures of $(\text{C}_5\text{H}_5)_3\text{U}(\text{NC}^n\text{Pr})$ (Fig. 67) and $(\text{C}_5\text{H}_5)_3\text{U}(\text{NC}^i\text{Pr})$ (Fig. 68) have also been published. The two molecules have a similar geometry; the three C_5H_5 ligands and the nitrile ligand form a distorted tetrahedron around uranium. The average U–C distances are 2.81 Å in $(\text{C}_5\text{H}_5)_3\text{U}(\text{NC}^n\text{Pr})$ and 2.76 Å in $(\text{C}_5\text{H}_5)_3\text{U}(\text{NC}^i\text{Pr})$. The metal–ring centroid distances range from 2.51 Å to 2.582 Å and the single uranium–nitrogen bond lengths are 2.61 Å in $(\text{C}_5\text{H}_5)_3\text{U}(\text{NC}^n\text{Pr})$ and 2.551 Å in $(\text{C}_5\text{H}_5)_3\text{U}(\text{NC}^i\text{Pr})$.

Fragalà and Marks [60] investigated the electronic structure of the alkoxide complexes $(\text{C}_5\text{H}_5)_3\text{U}(\text{OR})$ and $(\text{C}_5\text{H}_5)_3\text{Th}(\text{OR})$ by He I and He II UV photoelectron spectroscopy combined with SCF X α -DVM calculations. Fully relativistic Dirac–Slater calculations were also carried out for the thorium complex. The nonrelativistic calculations indicate that metal–ligand interactions involving the highest energy ligand orbitals involve primarily metal 5f orbitals while 6d admixtures are found for lower energy orbitals. The M–O bonding is both σ and π in nature and involves primarily metal 6d orbitals. The fully relativistic calculations show that metal d contributions are underestimated at the nonrelativistic level. Such deviations do not alter the overall description of the metal–ligand bonding.

Comparative relativistic effective core potential ab initio calculations for both Th(IV) and U(IV) $(\text{C}_5\text{H}_5)_3\text{AnL}$ ($\text{L} = \text{Me}, \text{BH}_4$) complexes were reported by the same authors [85]. The C_5H_5 –An bonding appears to be dominated by metal 6d orbitals interacting with ligand π_2 orbitals. The stability of the An–Me bonding depends on interactions involving metal 6d $_z^2$ -based orbitals directed along the An–Me vector.

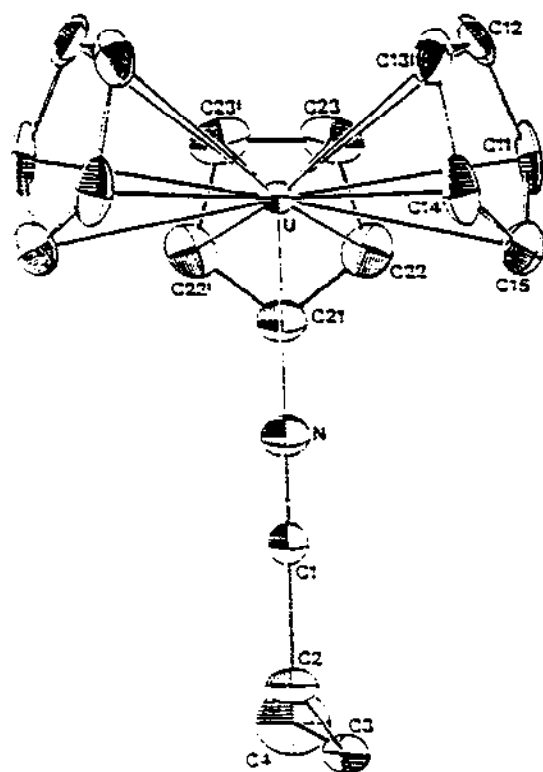
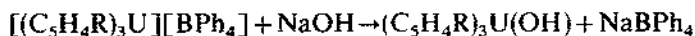
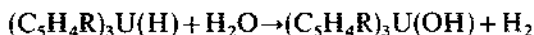


Fig. 67.

The BH_4 ligand interactions are mediated by d_{xz} and d_{yz} atomic orbitals, which are even better suited for favorable overlap and for greater metal–ligand π covalency.

Bond disruption enthalpies have been determined by Goffart et al. for the complexes $(\text{C}_9\text{H}_6\text{SiMe}_3)_3\text{Th-H}$, $(\text{C}_9\text{H}_6\text{SiMe}_3)_3\text{Th-D}$ and $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Th-H}$ [86]. The thermodynamic data were obtained by iodinolysis batch titration calorimetry. The calculated enthalpy values for $(\text{C}_9\text{H}_6\text{SiMe}_3)_3\text{Th-H}$, $(\text{C}_9\text{H}_6\text{SiMe}_3)_3\text{Th-D}$ and $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Th-H}$ in toluene are 264 kJ mol^{-1} , 276 kJ mol^{-1} and 274 kJ mol^{-1} , respectively.

Ephritikhine et al. [87] prepared the U(IV) hydroxo-complexes $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U(OH)}$ and $(\text{C}_5\text{H}_4\text{'Bu})_3\text{U(OH)}$, either by hydrolysis of the corresponding hydrides or by treatment of the cationic compounds $[(\text{C}_5\text{H}_4\text{R})_3\text{U}][\text{BPh}_4]$ ($\text{R} = \text{SiMe}_3$, 'Bu) with sodium hydroxide.



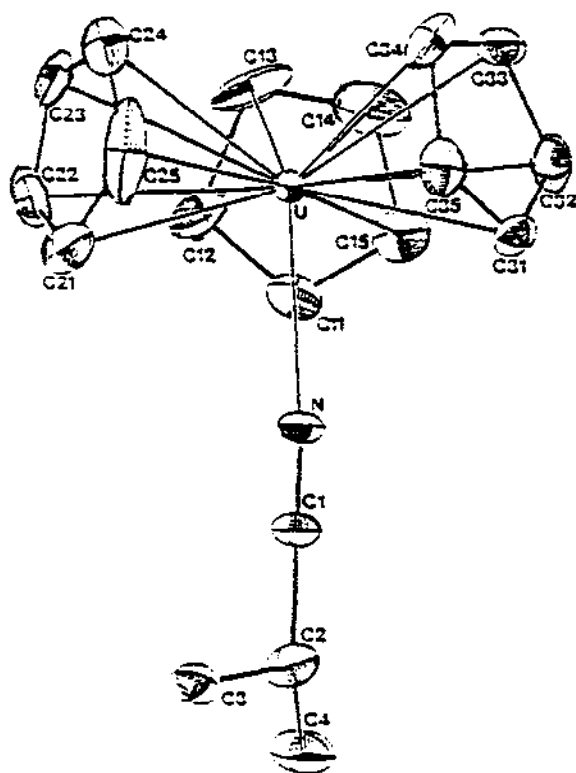
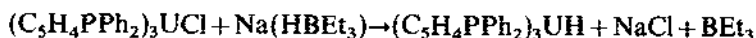


Fig. 68.

Reaction of $(C_5H_4SiMe_3)_3U(OH)$ with $(C_5H_4SiMe_3)_3U(H)$ gave the μ -oxo derivative $(\mu-O)[(C_5H_4SiMe_3)_3U]_2$ and thermolysis of the hydroxo complexes afforded the trinuclear compounds $[(C_5H_4SiMe_3)_2U(\mu-O)]_3$ and $[(C_5H_4^tBu)_2U(\mu-O)]_3$. The crystal structure of $[(C_5H_4SiMe_3)_2U(\mu-O)]_3$ was also published (Fig. 69). The U–O bond lengths range from 2.05 Å to 2.12 Å. These relative short distances and the ring planarity reflect the strong π bonding between the metal and oxygen atoms. The U–C(centroid) distances range from 2.49 Å to 2.51 Å. The $SiMe_3$ substituents of two adjacent cyclopentadienyl rings are staggered and remote from the metal centre.

Baudry et al. [88] prepared the diphenylphosphinocyclopentadienyl complex $(C_5H_4PPh_2)_3UCl$ by reaction of UCl_4 with three equivalents of $(C_5H_4PPh_2)Ti$ in toluene. $(C_5H_4PPh_2)_3UCl$ reacts with $Na(HBEt_3)$ to yield $(C_5H_4PPh_2)_3UH$ which has been isolated and characterized.



The bimetallic complexes $[(C_5H_4PPh_2)_2Mo(CO)_4][(C_5H_4PPh_2)UX]$ ($X = Cl, NEt_2, BH_4$) were also synthesized, and electrochemical measurements showed a significant

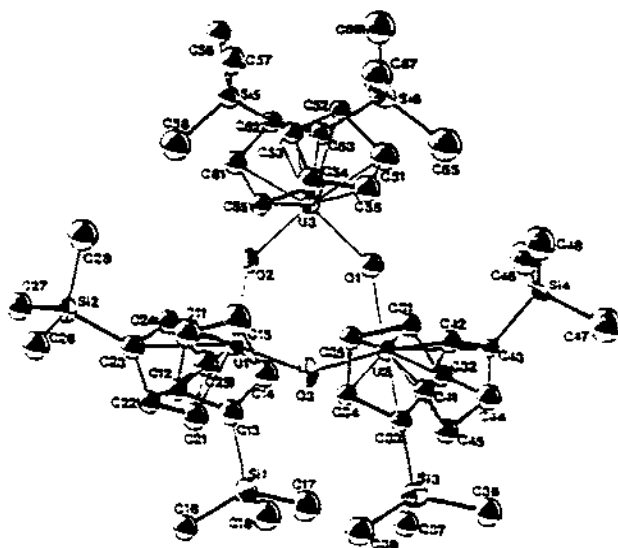
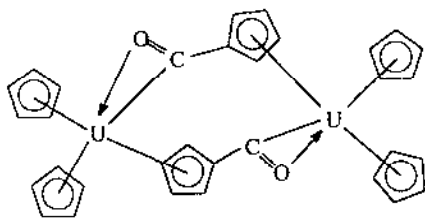


Fig. 69.

decrease in the electron density on the uranium atom after coordination to the molybdenum moiety.

Leonov et al. [89] investigated reactions of tetrakis(η^5 -cyclopentadienyl)uranium with CO and CO₂. Interaction occurred by a migratory insertion mechanism of gas molecules into the uranium–carbon bond. Treatment of (C₅H₅)₄U with CO in benzene affords the dinuclear complex [(C₅H₅)₂U(C₅H₄CO)]₂.



Andersen et al. [90] described the reaction of (C₅H₄Me)₃U(^{*i*}Bu) with C₆F₆ or PhCF₃ in toluene to give (C₅H₄Me)₃UF in quantitative yields as the first example of intermolecular C–F activation of a saturated fluorocarbon by a neutral d- or f-transition metal complex.

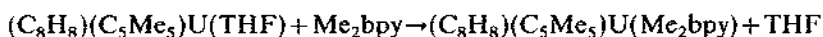
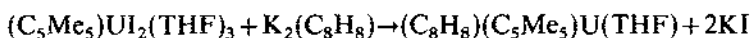
Kanellakopulos et al. [91] determined the crystal structure of (C₅H₅)₃U(NCS). The uranium atom is surrounded by three η^5 -cyclopentadienyl rings and by one thiocyanate N atom in a distorted tetrahedral configuration. The average U–C(centroid) distances are 2.73 Å. These distances do not appear to be influenced by the nature of the basic ligand. The U–N bond length is 2.34 Å.

3.1.3. Tetrakis(cyclopentadienyl) compounds

Kanellakopoulos et al. [92] also investigated the crystal structure of $(C_5H_5)_4Th$ by single-crystal X-ray diffraction. The average Th–C(centroid) distance of 2.606 Å is in agreement with the predicted distance of 2.588 Å, and is larger than the corresponding distance of the uranium analog (2.538 Å). The temperature dependence of the dipole moment of $(C_5H_5)_4Th$, $(C_5Me_5)_4Th$ and $(C_5Me_5)_4U$ in benzene solution was also discussed with respect to the molecular structures of these complexes.

3.1.4. Compounds with cyclooctatetraenyl and cyclopentadienyl ligands

Burns et al. [93] described the synthesis of the mixed-ring uranium(III) complex $(C_8H_8)(C_5Me_5)U(THF)$ by reaction of $(C_5Me_5)UI_2(THF)_3$ with $K_2(C_8H_8)$ in THF. Reaction of $(C_8H_8)(C_5Me_5)U(THF)$ with 4,4'-dimethyl-2,2'-bipyridine (Me_2bpy) in toluene yields the 10-coordinate complex $(C_8H_8)(C_5Me_5)U(Me_2bpy)$.



The crystal structure of $(C_8H_8)(C_5Me_5)U(Me_2bpy)$ was also described (Fig. 70). The average U–C(C_5Me_5 -centroid) and U–C(C_8H_8 -centroid) distances are 2.49 Å and 2.01 Å. The U–N1 and U–N2 distances are 2.429 Å and 2.423 Å.

3.2. Compounds without supporting cyclopentadienyl ligands

3.2.1. Compounds with cyclooctatetraenyl ligands

The uranium(V) complexes $(C_8H_8)U(NEt_2)_3$ and $[(C_8H_8)U(NEt_2)_2(THF)][BPh_4]$ as well as the uranium(IV) compounds $(C_8H_8)U(NEt_2)_2$ and $[(C_8H_8)U(NEt_2)(THF)_2][BPh_4]$ have been prepared by Ephritikhine et al. [94].

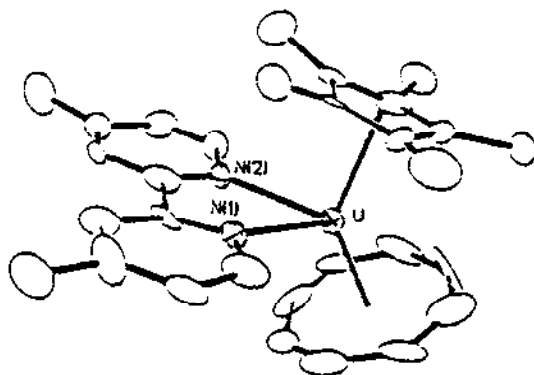
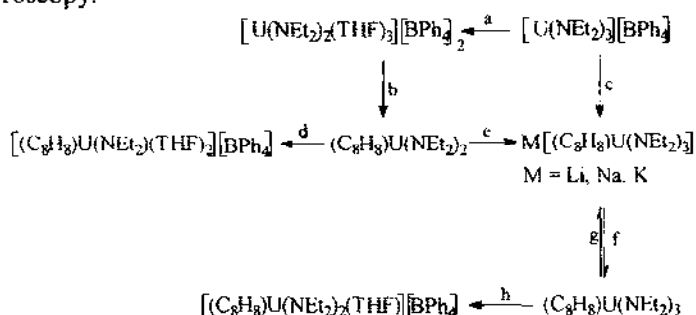


Fig. 70.

The compounds have been characterized by elemental analyses and ^1H NMR spectroscopy.



Reagents and conditions: (a) $\text{NEt}_3\text{HBPh}_4$; (b, c) $\text{K}_2(\text{C}_8\text{H}_8)$; (d) $\text{NEt}_3\text{HBPh}_4$; (e) LiNEt_2 ; (f) tBPh_4 ; (g) $\text{Na}(\text{Hg})$; (h) $\text{NEt}_3\text{HBPh}_4$. All reactions in THF at 20°C , except (a) at 65°C .

References

- [1] K. Jacob, I. Pavlik and F.T. Edelmann, Zur Kenntnis von 2-(Dimethylaminomethyl)ferrocenyl-Verbindungen des Samariums und Yttriums. *Z. anorg. allg. Chem.*, 619 (1993) 1957–1961.
- [2] A. Protchenko, L.N. Zakharov, M.N. Bochkarev and Y. Struchkov, Synthesis and characterization of the naphthalene complex $(\text{C}_8\text{H}_5)\text{Lu}(\text{C}_{10}\text{H}_8)(\text{DME})$, *J. Organomet. Chem.*, 447 (1993) 209–212.
- [3] I.P. Beletskaya, A.Z. Voskoboynikov, E. Chuklanova and A. Kisin, Metallocarbonylates of lanthanides. Unexpected formation of the trinuclear cluster $[\text{Na}(\text{DME})_3]_2[\text{W}_3(\text{CO})_{14}]$, *J. Organomet. Chem.*, 454 (1993) 1–3.
- [4] G.C. Bazan, W. Schaefer and J.E. Bercaw, Pentamethylcyclopentadienyl-dicarbollide derivatives of scandium, *Organometallics*, 12 (1993) 2126–2130.
- [5] W.J. Evans, T.J. Boyle and J.W. Ziller, Synthesis, structure, and reactivity of dimeric mono(cyclopentadienyl)yttrium bis(tert-butoxide) complexes: $[(\text{C}_5\text{R}_5)\text{Y}(\mu\text{-OCMe}_3)(\text{OCMe}_3)]_2$ ($\text{C}_5\text{R}_5 = \text{C}_5\text{Me}_5$, C_5H_5 , $\text{C}_3\text{H}_4\text{Me}$, $\text{C}_3\text{H}_4\text{SiMe}_3$ and C_9H_7), *Organometallics*, 12 (1993) 3998–4009.
- [6] Z. Xu, X. You, X. Zhou, H. Wang and Y. Yang, Synthesis and crystal structure of monocyclopentadienyl holmium dichloride tris(tetrahydrofuran), *Polyhedron*, 12 (1993) 795–800.
- [7] Z. Xu, X. You, H. Wang, Z. Wu, X. Zhou, F. Sheng and J. Hu, Synthesis and X-ray crystal structure of the cyclopentadienyl nitrito complex of ytterbium(III), $(\text{C}_5\text{H}_5)_2\text{Yb}(\text{NO}_2)(\text{THF})$, *J. Organomet. Chem.*, 455 (1993) 93–97.
- [8] G.B. Deacon, G.D. Fallon and C.M. Forsyth, The synthesis and X-ray crystal structure of $\text{di}[\mu\text{-chlorobis}(\text{diphenylphosphino-}\eta^5\text{-cyclopentadienyl})\text{ytterbium(III)}]$, *J. Organomet. Chem.*, 462 (1993) 183–190.
- [9] D. Deng, C. Qian, F. Song, Z. Wang, G. Wu and P. Zheng, Synthesis of bis(2-methoxyethyl-cyclopentadienyl) divalent organolanthanides ($\text{Ln} = \text{Sm, Yb}$) and molecular structure of solvated $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb}(\text{THF})$, *J. Organomet. Chem.*, 443 (1993) 79–83.
- [10] T. Jiang, Q. Shen, Y. Lin and S. Jin, Synthesis and molecular structure of $(\text{C}_3\text{H}_4\text{Me})_2\text{Yb}(\text{DME})$ and its catalytic activity for the polymerization of methyl methacrylate, *J. Organomet. Chem.*, 450 (1993) 121–124.
- [11] P. Jutzi, J. Dahlhaus and M. Kristen, Intramolekulare Basenkoordination je nach Bedarf: Der 1-(Dimethylaminoethyl)-2,3,4,5-tetramethyl-cyclopentadienyl-Ligand in der Komplexchemie von s-, p-, d- und f-Block-Elementen, *J. Organomet. Chem.*, 450 (1993) C1–C3.
- [12] K.-H. Thiele and H. Baumann, Cyclopentadienyl-2-(dimethylaminomethyl)ferrocenyl-Verbindungen elektronenarmer 3d-Elemente, *Z. anorg. allg. Chem.*, 619 (1993) 1111–1114.

- [13] K.-H. Thiele, A. Scholz, J. Scholz and U. Böhme, Iminoacetylacetonat-Komplexe der Lanthanoide: Synthese, Eigenschaften und Struktur, *Z. Naturforsch.*, 48b (1993) 1753–1759.
- [14] Y. Chauvin, S. Heyworth, H. Olivier, F. Robert and L. Saussine, Synthesis and structural determination of a neodymium(III) complex derived from 9-(cyclopentadienyl)-1-methylethyl-9,10-dihydroanthracene, *J. Organomet. Chem.*, 455 (1993) 89–92.
- [15] D.M. Roitherstein, L. Rybakova, E. Petrov, A. Ellern and M. Yu, Lutetium complexes with an anthracene dianion ligand. Molecular structure of $[\text{Na}(\text{diglyme})_2][(\text{C}_5\text{H}_5)_2\text{Lu}(\text{C}_{14}\text{H}_{10})]$, *J. Organomet. Chem.*, 460 (1993) 39–45.
- [16] W.J. Evans, R. Keyer and J. Ziller, Tetrahedral versus square planar arrangement of cyclopentadienyl ligands in bimetallic organosamarium complexes. X-ray crystal structure of $[(\text{C}_5\text{H}_5\text{Me})_2\text{Sm}(\mu\text{-Cl})(\text{THF})]_2$, *J. Organomet. Chem.*, 450 (1993) 115–120.
- [17] X. Weng, X. Shen and B. Du, Synthesis and characterization of cyclopentadienyl lanthanide derivatives containing benzophenone-oximate ligands, *Synth. React. Inorg. Met.-Org. Chem.*, 23 (1993) 419–433.
- [18] Z. Wu, Z. Xu and X. You, Synthesis and study on thermal stability of cyclopentadienyl (or indenyl) early lanthanide complexes involving 8-quinolino and *o*-aminophenolato chelate ligands, *Synth. React. Inorg. Met.-Org. Chem.*, 23 (1993) 155–1169.
- [19] Z. Wu, Z. Xu, X. You, X. Zhou, Y. Xing and Z. Jin, Dehydrogenation of organolanthanide alkoxides and X-ray crystal structure of reaction product $[(\text{C}_5\text{H}_5)_2\text{Yb}(\mu\text{-OCH}=\text{C}=\text{CH}_2)]_2$, *J. Chem. Soc., Chem. Commun.* (1993) 1494–1495.
- [20] W.J. Evans, G. Kociok-Köhn, S. Foster, J. Ziller and R. Doedens, Synthesis and structure of mono-THF solvates of bis(cyclopentadienyl)samarium(II) complexes: $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})$ and $[\text{C}_5\text{H}_2(\text{SiMe}_3)_3][\text{C}_5\text{H}_3(\text{SiMe}_3)_2]\text{Sm}(\text{THF})$, *J. Organomet. Chem.*, 444 (1993) 61–66.
- [21] B. Campion, R. Heyn and T.D. Tilley, Synthesis and reactions of silyl and germyl derivatives of scandocene. Structure of $(\text{C}_5\text{H}_5)_2\text{Sc}[\text{Si}(\text{SiMe}_3)_3](\text{THF})$, *Organometallics*, 12 (1993) 2584–2590.
- [22] T. Hollis, J. Burdett and B. Bosnich, Why are bis(pentamethylcyclopentadienyl) complexes, $[(\text{C}_5\text{Me}_5)_2\text{M}]$, of calcium, strontium, barium, samarium, europium, and ytterbium bent?, *Organometallics*, 12 (1993) 3385–3386.
- [23] Z. Ye, Y. Yu, S. Wang and X. Jin, Structural investigation of the organolanthanide di- η^5 -cyclopentadienyl-1,1,1-trifluoroacetylacetonato ytterbium, *J. Organomet. Chem.*, 448 (1993) 91–93.
- [24] X. Olonde, A. Mortreux and F. Petit, A useful method for the synthesis of neodymocene homogeneous catalysts for ethylene polymerization, *J. Mol. Catal.*, 82 (1993) 75–82.
- [25] M. Visseaux, A. Dormond and D. Baudry, Chimie organométallique des lanthanides: étude en RMN ^1H et ^{31}P de la coordination de composés du néodyme avec les ligands bifonctionnels $\text{OPPh}_2\text{CH}(\text{R})\text{PPh}_2$, *Bull. Soc. Chim. Fr.*, 130 (1993) 173–184.
- [26] G. Massarweh and R.D. Fischer, Umlagerung von Tetrahydrofuran im Lanthanoid-Organyl: die Kristall- und Molekülstrukturen von Bis(cyclopentadienyl)ytterbium(III)(μ -n-buten-2-olat) und Bis(methylcyclopentadienyl)ytterbium(III)(μ - η^2 : η^1 -tetrahydrofuran-2-olat), *J. Organomet. Chem.*, 444 (1993) 67–74.
- [27] J. Stehr and R.D. Fischer, Bis(cyclopentadienyl)ytterbium(III)-Alkoxide mit jeweils einem dissymmetrischen Ligandenatom: Molekülbau und chiroptische Effekte, *J. Organomet. Chem.*, 459 (1993) 79–86.
- [28] C.M. Forsyth, S. Nolan and C. Stern, T.J. Marks, Alkyne coupling reactions mediated by organolanthanides. Probing the mechanism by metal and alkyne variation, *Organometallics*, 12 (1993) 3618–3623.
- [29] B.W. Pfennig, M.E. Thompson and A.B. Bocarsly, Luminescent d^0 scandocene complexes: photophysical studies and electronic structure calculations on $(\text{C}_5\text{Me}_5)_2\text{ScX}$ ($\text{X}=\text{Cl}$, I , Me), *Organometallics*, 12 (1993) 649–655.
- [30] M. Booi, B.-J. Deelman, R. Duchateau, D. Postma, A. Meetsma and J.H. Teuben, C-H activation of arenes and substituted arenes by the yttrium hydride $[(\text{C}_5\text{Me}_5)_2\text{YH}]_2$: competition between C_5Me_5 ligand metalation, arene metalation, and H/D exchange. Molecular structures of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-H})(\mu\text{-}\eta^1, \eta^3\text{-CH}_2\text{C}_5\text{Me}_4)\text{Y}(\text{C}_5\text{Me}_5)$ and $(\text{C}_5\text{Me}_5)_2\text{Y}(\text{o-C}_6\text{H}_4\text{PPh}_2\text{CH}_2)$, *Organometallics*, 12 (1993) 3531–3540.

- [31] H.J. Heeres, J. Nijhoff and J.H. Teuben, Reversible carbon-carbon formation in organolanthanide systems. Preparation and properties of lanthanide acetylides $[(C_5Me_5)_2Ln(CCR)]_n$ and their rearrangement products $[(C_5Me_5)_2Ln]_2(\mu-\eta^2-\eta^2-RC_4R)$ ($Ln = La, Ce, R = \text{alkyl}$), *Organometallics*, 12 (1993) 2609–2632.
- [32] I.P. Beletskaya, A. Voskoboynikov, E. Chuklanova and N. Kirillova, Bimetallic lanthanide complexes with lanthanide-transition metal bonds. Molecular structure of $(THF)(C_5H_5)_2LuRu(CO)_2(C_5H_5)$. The use of ^{139}La NMR spectroscopy, *J. Am. Chem. Soc.*, 115 (1993) 3156–3166.
- [33] W.J. Evans, R. Keyer and J. Ziller, Investigation of organolanthanide-based carbon-carbon bond formation: synthesis, structure, and coupling reactivity of organolanthanide alkynide complexes, including the unusual structures of the trienediyl complex $[(C_5Me_5)_2Sm]_2[\mu-\eta^2-\eta^2-Ph(CH_2)_2C \equiv C \equiv C(CH_2)_2Ph]$ and the unsolvated alkynide $[(C_5Me_5)_2Sm(CCCMe_3)]_2$, *Organometallics*, 12 (1993) 2618–2633.
- [34] S. Stults, R.A. Andersen and A. Zalkin, Preparation of $[(C_5H_4CMe_5)_2M(\mu-Me)_2]$ ($M = Ce$ or U) and the crystal structure of the cerium derivative, *J. Organomet. Chem.*, 462 (1993) 175–182.
- [35] W.E. Piers, L. MacGillivray and M. Zaworotko, Reversible interconversion of permethylscandocene tellurolates and tellurides. X-ray crystal structure of $[(C_5Me_5)_2Sc]_2(\mu-Te)$, *Organometallics*, 12 (1993) 4723–4725.
- [36] J. Jin, Z. Jin, G. Wei and W. Chen, Syntheses of cyclopentyl-cyclopentadienyl lanthanide complexes $(C_5H_9C_5H_4)_2LnCl(THF)_n$ and crystal structures of $[(C_5H_9C_5H_4)_2LnCl(THF)]_2$ and $[(C_5H_9C_5H_4)_2ErCl]_2$, *Chin. Sci. Bull.*, 38 (1993) 526–527.
- [37] H. Yasuda, Preparation of lactone polymers at low temperature without depolymerization and thermal decomposition, *Jpn. Kokai Tokkyo Koho JP 05, 247, 184* [93, 247, 184].
- [38] H. Yasuda, H. Yamamoto, M. Yamashita and K. Yokota, Synthesis of high molecular weight poly(methylmethacrylate) with extremely low polydispersity by the unique function of organolanthanide(III) complexes, *Makromolecules*, 26 (1993) 7134–7143.
- [39] J. Schmitz, H. Schilder and H. Lucken, Structural chemistry and magnetism of dicyclopentadienide halides of lanthanides. Dicyclopentadienylterbium bromide dimer, $[(C_5H_5)_2TbBr]_2$, *J. Alloys Comp.*, 200 (1993) 195–204.
- [40] S. Song, S. Jin, Y. Lin and Q. Shen, Synthesis and crystal structure of bis(tert-butylcyclopentadienyl)gadolinium chloride $(C_5H_4^tBu)_2GdCl$, *Yingyong Huaxue*, 10 (1993) 80–82.
- [41] T. Ziegler, E. Folga and A. Berces, A density functional study on the activation of hydrogen-hydrogen and hydrogen-carbon bonds by $(C_5H_5)_2ScH$ and $(C_5H_5)_2ScMe$, *J. Am. Chem. Soc.*, 115 (1993) 636–646.
- [42] L. Chamberlain, C. Gibler, R.A. Kemp, S. Wilson and T.F. Brownscombe, Process and catalyst for selective hydrogenation of conjugated diolefin polymers, U.S. Patent 5,177,155.
- [43] W.J. Evans, R. Keyer, G. Rabe, D. Drummond and J. Ziller, The reactivity of $(C_5Me_5)_2Sm(THF)_2$ with bis(2-pyridyl)ethene including the synthesis of $[(C_5Me_5)_2Sm]_2(\mu-\eta^2-\eta^2-pyCHCHpy)$ from $[(C_5Me_5)_2Sm]_2[\mu-\eta^3-\eta^3-1,2,3,4-(py)_4C_4H_4]$ by reductive C-C bond cleavage, *Organometallics*, 12 (1993) 4664–4667.
- [44] K. Qiao, R.D. Fischer and G. Paolucci, Mass spectrometry of organo-rare earth ($M = Y, Yb$) hydrides containing the $Me_2Si(C_5H_4)_2$ ligand, and crystal structure of the new complex $(\mu-H)(\mu-Cl)[Me_2Si(\eta^5-C_5H_4)Yb(THF)]_2$, *J. Organomet. Chem.*, 456 (1993) 185–194.
- [45] C. Qian and D. Zhu, Synthesis and characterization of N-containing ring-linked biscyclopentadienyl lanthanide and yttrium chlorides, *J. Organomet. Chem.*, 445 (1993) 79–84.
- [46] C. Sun, G. Wei, Z. Jin and W. Chen, Synthesis and crystal structure of $\{[Me_2C_2(C_5H_5)_2SmClMgCl_2(THF)_2]THF\}_2$, *J. Organomet. Chem.*, 453 (1993) 61–64.
- [47] F.T. Edelmann, M. Rieckhoff and I. Haiduc, ansa-Metallocenderivate des Samariums und Ytterbiums mit "weichen" Donorliganden, *J. Organomet. Chem.*, 447 (1993) 203–208.
- [48] H. Schulz, H. Reddmann and H.-D. Amberger, Absorptions- und lumineszenzspektroskopische Charakterisierung von optisch verdünntem $(C_5H_5)_3Sm(NCCH_3)_2$, *J. Organomet. Chem.*, 461 (1993) 69–74.
- [49] H. Schulz and H.-D. Amberger, Esteraddukte des Grundkörpers $Tris(\eta^5\text{-cyclopentadienyl})\text{-lanthan(III)}$: Ideale Wirtsgitter für einkristallographische Untersuchungen von Lanthanoid-Ionen in metallorganischer Umgebung, *J. Organomet. Chem.*, 443 (1993) 71–78.

- [50] C. Hagen, H. Reddmann, H.-D. Amberger, F.T. Edelmann, U. Pegelow, G. Shalimoff and N.M. Edelstein, Ist der *N,N'*-Bis(trimethylsilyl)benzamidinato-Ligand im Falle von Lanthanoid-Zentralionen ein elektronisches Äquivalent zum η^5 -Cyclopentadienyl-Liganden?, *J. Organomet. Chem.*, 462 (1993) 69–78.
- [51] S. Wang, Y. Yu, Z. Ye, C. Qian and X. Huang, The formation and molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Sm}(\text{THF})$, *J. Organomet. Chem.*, 464 (1993) 55–58.
- [52] H. Schumann, M. Glanz and H. Hemling, Tris(tetramethyl-cyclopentadienyl)komplexe der Lanthanoide, *J. Organomet. Chem.*, 445 (1993) C1–C3.
- [53] W.A. Herrmann, R. Anwender, F. Munck and W. Scherer, Alkyl- und Donor-substituierte Cyclopentadienyl-Komplexe des Neodyms, *Chem. Ber.*, 126 (1993) 331–337.
- [54] C. Qian, B. Wang, D. Deng and X. Jin, Synthesis of mixed tris-cyclopentadienyl lanthanide complexes, $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OCH}_3)\text{Ln}(\text{C}_5\text{H}_5)_2$, containing one intramolecular coordination bond. Crystal structure of $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OCH}_3)\text{Y}(\text{C}_5\text{H}_5)_2$, *Polyhedron*, 12 (1993) 2265–2269.
- [55] D.W. Langer, Y. Li, X. Fang and V. Conn, MOCVD growth and properties of erbium doped gallium arsenide, *Mater. Res. Soc. Symp. Proc.*, 301 (1993) 15–20.
- [56] A.C. Greenwald and U.W. Lay, MOCVD erbium sources, *Mater. Res. Soc. Symp. Proc.*, 301 (1993) 21–26.
- [57] F. Scholz, J. Weber, K. Pressel and A. Doernen, MOVPE of rare earth doped III-V semiconductors, *Mater. Res. Soc. Symp. Proc.*, 301 (1993) 3–13.
- [58] A. Domingos, N. Marques, A. Pires de Matos, M.G. Silva-Valenzuela and L.B. Zinner, Tetramethylurea adducts of the tricyclopentadienyl lanthanide complexes, *Polyhedron*, 12 (1993) 2545–2549.
- [59] N. Edakawa, H. Yoshida, K. Kama and M. Taya, Manufacture of quartz glass doped with rare earth elements, *Jpn. Kokai Tokkyo Koho JP 05, 279, 050* [93, 279, 050].
- [60] A. Gulino, S. Di Bella, I. Fragalà, M. Casarin, A. Seyam and T.J. Marks, A comparative fully relativistic/nonrelativistic first-principles X α -DVM and photoelectron spectroscopic investigation of electronic structure in homologous 4f and 5f tris(η^5 -cyclopentadienyl)metal(IV) alkoxide complexes, *Inorg. Chem.*, 32 (1993) 3873–3879.
- [61] H. Schumann, M. Glanz, J. Winterfeld and H. Hemling, Cyclooctatetraenyl(tetramethylcyclopentadienyl)-Komplexe der Lanthanoide, *J. Organomet. Chem.*, 456 (1993) 77–83.
- [62] H. Schumann, J. Winterfeld, R.D. Köhn, L. Esser, J. Sun and A. Dietrich, Synthese und Struktur neuer Monocyclooctatetraenyl-Komplexe von Yttrium, Terbium und Lutetium, *Chem. Ber.*, 126 (1993) 907–912.
- [63] U. Kilmann and F.T. Edelmann, Neue Cyclooctatetraenyl-lanthanid(III)-Komplexe, *J. Organomet. Chem.*, 444 (1993) C15–C17.
- [64] J. Arnold, C. Hoffmann, D. Dawson and F. Hollander, Preparation, characterization, and reactivity of scandium octaethylporphyrin complexes. X-ray crystal structures of $(\text{OEP})\text{ScCH}_3$, $(\text{OEP})\text{ScCH}(\text{SiMe}_3)_2$, $(\text{OEP})\text{Sc}(\eta^5\text{-C}_9\text{H}_7)$, and $[(\text{OEP})\text{Sc}]_2(\mu\text{-OH})_2$, *Organometallics*, 12 (1993) 3645–3654.
- [65] H. Ohno, A. Mori and S. Inoue, Lanthanoid(III) alkoxides as novel catalysts for a rapid transhydrocyanation from acetone cyanohydrin to aldehydes and ketones, *Chem. Lett.*, 375–378. (1993)
- [66] A. Oehme, U. Gebauer and K. Gehrke, Homopolymerization and copolymerization of butadiene with a neodymium catalyst, *J. Mol. Catal.*, 82 (1993) 83–91.
- [67] J. Wu, T. Boyle, J. Shreeve, J. Ziller and W.J. Evans, CP/MAS ^{89}Y NMR spectroscopy: a facile method for characterizing yttrium-containing solids, *Inorg. Chem.*, 32 (1993) 1130–1134.
- [68] P.E.M. Siegbahn, M. Blomberg and M. Svensson, The effects of covalent ligands on the oxidative addition reaction between second-row transition-metal atoms and methane, *J. Am. Chem. Soc.*, 115 (1993) 4191–4200.
- [69] P.E.M. Siegbahn, M. Blomberg and M. Svensson, A theoretical study of the activation of the C-H bond in ethylene by second-row transition metal atoms, *J. Am. Chem. Soc.*, 115 (1993) 1952–1958.
- [70] P.E.M. Siegbahn, The Ziegler-Natta olefin insertion reaction into a metal-alkyl bond for second-row transition metal atoms, *Chem. Phys. Lett.*, 205 (1993) 290–300.

- [71] P.E.M. Siegbahn and M. Svensson, Geometry optimization for second-row transition metal complexes, *Chem. Phys. Lett.*, 216 (1993) 147–154.
- [72] E. Hasegawa and D.P. Curran, Rate constants for the reactions of primary alkyl radicals with SmI_2 in THF/HMPA, *Tetrahedron Lett.*, 34 (1993) 1717–1720.
- [73] S. Bandow, H. Shinohara, Y. Saito, M. Ohkohchi and Y. Ando, High yield synthesis of lanthanofullerenes via lanthanum carbide, *J. Phys. Chem.*, 97 (1993) 6101–6103.
- [74] Y. Takemoto, J. Takeuchi and C. Iwata, Absolutely diastereoselective 1,2-nucleophilic addition of organometallic reagents to imines using diene-iron tricarbonyl chirality, *Tetrahedron Lett.*, 34 (1993) 6069–6072.
- [75] P. Wipf and S. Venkatraman, Transmetalation reactions of organosamarium reagents. Chlorosilane-accelerated copper-catalyzed conjugate additions, *J. Org. Chem.*, 58 (1993) 3455–3459.
- [76] V.K. Kalinin, E. Kazimirschuk, S.V. Vitt and I.P. Beletskaya, Carbolanthanation of internal alkynes, *Dokl. Akad. Nauk.*, 329 (1993) 449–451.
- [77] A.A. Trifonov, L.N. Zakharov, M.N. Bochkarev, A. Shestakov and Y. Struchkov, Synthesis, crystal and electronic structure of bis(tetrahydrofuran)potassiumbis(cis-1,4-diphenyl-1,3-butadiene)-bis(tetrahydrofuran)lutetium, *Metalloorg. Khim.*, 6 (1993) 363–371.
- [78] R. Fournier, Theoretical study of the monocarbonyls of first-row transition metal atoms, *J. Chem. Phys.*, 99 (1993) 1801–1815.
- [79] R. Taube, H. Windisch, F.H. Görlitz and H. Schumann, Darstellung und Kristallstruktur des Tetra(allyl)lanthanat(III)-Komplexes $[\text{Li}(\mu\text{-C}_3\text{H}_5\text{O}_2)_3/2][\text{La}(\eta^3\text{-C}_3\text{H}_5)_4]$, eines Katalysators für die stereospezifische Butadienpolymerization, *J. Organomet. Chem.*, 445 (1993) 85–91.
- [80] D. Hauchard, M. Cassir, J. Chivot, D. Baudry and M. Ephritikhine, Electrochemical study of uranium(IV) and (III) organometallic compounds in tetrahydrofuran by means of conventional microelectrodes and ultramicroelectrodes. Application to borohydride compounds and study of the stability of $(\text{C}_5\text{H}_5)_2\text{U}(\text{BH}_4)_2$, *J. Electroanal. Chem.*, 347 (1993) 399–407.
- [81] S.W. Hall, J. Huffman, M. Miller, L. Avens, C.J. Burns, D. Arney, A. England and A. Sattelberger, Synthesis and characterization of bis(pentamethylcyclopentadienyl)uranium(IV) and -thorium(IV) compounds containing the bis(trimethylsilyl)phosphide ligand, *Organometallics*, 12 (1993) 752–758.
- [82] X. Yang, W. King, M. Sabat and T.J. Marks, Cationic actinide metallocene alkyls and hydrides. Metal bis(dicarbollides) as counterions, *Organometallics*, 12 (1993) 4254–4258.
- [83] D. Arney and C.J. Burns, Synthesis and structure of high-valent organouranium complexes containing terminal monooxo functional groups, *J. Am. Chem. Soc.*, 115 (1993) 9840–9841.
- [84] R. Adam, C. Villiers, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, Synthesis, structure and oxidative addition reactions of triscyclopentadienyluranium(III) nitrile complexes, *J. Organomet. Chem.*, 445 (1993) 99–106.
- [85] S. Di Bella, A. Gulino, G. Lanza, I.L. Fragalà and T.J. Marks, An investigation of the electronic structure of some tris(η^5 -cyclopentadienyl)thorium(IV) and -uranium(IV) complexes by relativistic effective core potential ab initio calculations and gas-phase UV photoelectron spectroscopy, *J. Phys. Chem.*, 97 (1993) 11673–11676.
- [86] X. Jemine, J. Goffart, M. Ephritikhine and J. Fuger, Organo-f-element thermochemistry. Thorium-ligand bond disruption enthalpies in $[(\text{CH}_3)_3\text{SiC}_5\text{H}_6]_3\text{ThX}$ ($\text{X}=\text{H}$ or D) and in $[(\text{CH}_3)_3\text{SiC}_5\text{H}_4]_3\text{ThH}$ complexes, *J. Organomet. Chem.*, 448 (1993) 95–98.
- [87] J.-C. Berthet, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, Synthesis of the triscyclopentadienyl(hydroxo)uranium(IV) complexes $[\text{U}(\text{C}_5\text{H}_4\text{R})_3(\text{OH})]$ ($\text{R}=\text{SiMe}_3$ or t-Bu) and their transformation into μ -oxo bridged derivatives. Crystal structure of the trinuclear compound $[\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3(\mu\text{-O})_3]$, *J. Organomet. Chem.*, 460 (1993) 47–53.
- [88] D. Baudry, A. Dormond and A. Hafid, Synthèse et réactivité du tris(diphénylphosphinocyclopentadiényl)chlorouranium. L'anneau diphénylphosphinocyclopentadiényl: un ligand électroniquement pauvre, *New J. Chem.*, 17 (1993) 465–470.
- [89] M.R. Leonov and G.V. Solov'yova, Reaction of tetracyclopentadienyl-uranium with carbon oxides, *Metalloorg. Khim.*, 6 (1993) 198–201.
- [90] M. Weydert, R. Andersen and R. Bergman, Reactions of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{t-Bu})$: Intermolecular fluorine atom abstraction from fluorocarbons including saturated perfluorocarbons, *J. Am. Chem. Soc.*, 115 (1993) 8837–8838.

- [91] M. Spirllet, J. Rebizant, C. Apostolidis and B. Kanellakopulos, Structure of tris(η^5 -cyclopentadienyl)uranium thiocyanate, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C49 (1993) 929–931.
- [92] R. Maier, B. Kanellakopulos, C. Apostolidis, D. Meyer and J. Rebizant, Molecular structure of the 4f and 5f elements. V. Crystal and molecular structure of tetrakis(η^5 -cyclopentadienyl)thorium(IV) and the temperature dependence of its electrical dipole, *J. Alloys Comp.*, 190 (1993) 269–271.
- [93] A. Schake, L. Avens, C.J. Burns, D.L. Clark, A. Sattelberger and W. Smith, Synthesis of mixed-ring organoactinide complexes. 2. $(C_8H_8)(C_5Me_5)U(THF)$ and its 4,4'-dimethyl-2,2'-bipyridine derivative, *Organometallics*, 12 (1993) 1497–1498.
- [94] J.-C. Berthet and M. Ephritikhine, New reactions of uranium amide complexes leading to pentavalent and cationic derivatives, *J. Chem. Soc., Chem. Commun.* (1993) 1566–1567.