Chem. Rev. **1995,** *95,* 865–986

Synthesis, Structure, and Reactivity of Organometallic π-Complexes of the Rare Earths in the Oxidation State Ln^{3+} with Aromatic Ligands

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Received June 9, 1994 (Revised Manuscript Received February 6, 1995)

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I. Introduction

Less than 20 years ago organometallic compounds of the rare earth metals were a curiosity. Apart from some cyclopentadienyl derivatives, prepared in analogy with ferrocene to complete the system of sandwich compounds within the periodic table, only very few significant contributions had been made to f-element organometallic chemistry. That changed after the availability of modern preparative and analytical techniques made it possible to handle these compounds, which are all extremely sensitive to oxygen and water. Beginning in the late 1970s the chemistry of these fascinating organometallic compounds developed, first with the discovery of several classes of compounds with the rare earth elements in their principal oxidation state Ln^{3+}, then later extended to the elements in their oxidation states Ln^0, Ln^{2+}, and Ln^{4+}. These organometallic compounds have been characterized and used as reagents in organic synthesis and as very active catalysts.

The research in this field has been extensively reviewed. There are three books,[1] several comprehensive review articles,[2] and a lot of specialized reviews on the structure,[3] bonding energeties,[4] magnetic properties,[5] NMR,[6] photoelectron spectroscopy,[7] UV spectroscopy,[8] and chemiluminescence.[9] This article will not review the application of organolanthanide compounds as reagents in organic synthesis and catalysis since this topic was reviewed very recently in this journal.[10] Attention should be made to annual surveys covering the recent research in organolanthanide chemistry, which have appeared since 1964.[11]

The extensive development of this area of chemistry during the last decade renders a comprehensive

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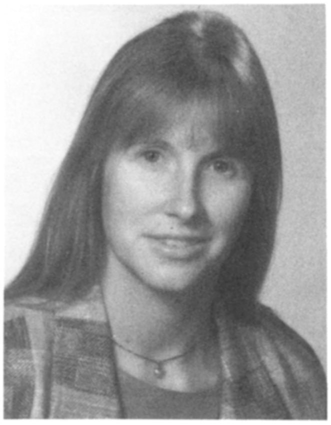
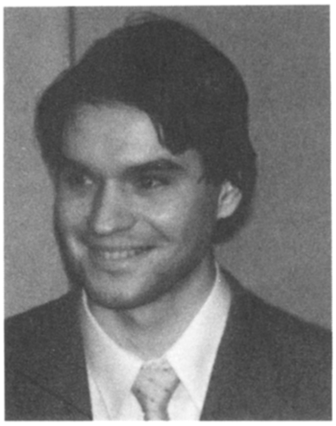
Herbert Schumann was born in Coburg, Germany, in 1935. He received his degree Diplom-Chemiker in 1961 and Dr. rer. nat. in 1962 at the Ludwigs-Maximilians Universität München under the direction of Max Schmidt. He spent three years at the Universität Marburg and two years at the Universität Würzburg Germany as Wissenschaftlicher Assistent until he obtained his Habilitation to Privatdozent in Würzburg in 1967. In 1970 he took over the chair of Inorganic Chemistry at the Technische Universität Berlin. In 1992 he was a Lady Davies Professor at the Hebrew University of Jerusalem.



Juliane A. Meese-Marktscheffel was born in Berlin-Wilmersdorf, Germany, in 1964. She studied chemistry at the Technische Universität Berlin, from 1983 to 1988 as scholar of the Studienstiftung des deutschen Volkes, and was granted the Klaus Koch award. She received her Ph.D. with Professor Herbert Schumann in 1991 doing research on organolanthanide chemistry. During her doctorate she was a scholar of the Fonds der Chemischen Industrie as well as a member of the Graduiertenkolleg "Synthese und Strukturaufklärung niedermolekularer Verbindungen". In 1992/1993 she joined the research group of Professor John W. Gilje at the University of Hawaii as a postdoctoral Alexander von Humboldt fellow, where she focused on alkoxide and siloxide precursors of ceramic films. Just recently, Dr. Meese-Marktscheffel was given the Carl-Ramsauer award by AEG (Daimler-Benz) for her outstanding thesis.



Lothar Esser was born in Berlin, Germany, in 1964. He received his Diploma in Inorganic Chemistry at the Technische Universität Berlin in 1988. He continued graduate school und the supervison on Professor H. Schumann and was an exchange student at the University of Oklahoma in Norman in 1989 with Professor D. van der Helm. In 1992 he receiced the degree Dr. rer. nat. from the Technische Universität Berlin. He is currently a postdoctoral fellow with Professor Deisenhofer at the Howard Hughes Medical Institute in Dallas.

review the field impossible, like was done eight years ago.[2k] Therefore this review focuses only on organometallic compounds of the rare earths, which includes the group 3 elements scandium, yttrium, and lutetium as well as the 4f-elements lanthanum to ytterbium, in the oxidation state Ln^{3+}, and it reviews two important aspects of this area of chemistry: the most successful methods for their preparation and their molecular structure. Although one review from 1984[2j] deals with all rare earth organometallic compounds known up to this date, the present article will include this material in the tables for completeness. Spectroscopic data are not discussed in detail, but mentioned in the tables of compounds. In this review article the types of compounds have been numbered in several cases for ease of identification; lower case letters after the numbers signify the respective metal that is present: **a** stands for Sc, **b** for Y, **c** for La and the lanthanide elements **d** through **i** for the elements Ce through Eu, then **k** for Gd through **r** for Lu. Ln signifies Sc, Y, La through Lu. All other abbreviations are given in the list of abbreviations.

II. Cyclopentadienyl Rare Earth Compounds

A. Tris(cyclopentadienyl) Rare Earth Complexes

The organometallic chemistry of the rare earth metals began with the synthesis of their tris(cyclopentadienyl) derivatives. Their early discovery[12] together with their ready availability and moderate sensitivity toward moisture and air made them one of the best investigated classes within the organo rare earth compounds.

1. Cyclopentadienyl Derivatives

Nearly exactly in the middle of this century Wilkinson and Birmingham[12a,b] reported the synthesis of a series of tris(cyclopentadienyl)lanthanide complexes from the metathesis of anhydrous lanthanide trichlorides with a 5-fold molar excess of sodium cyclopentadienide in THF. They isolated the pure, THF-free compounds **1** after high vacuum sublimation above 200 °C according to eq 1:

$$LnCl_3 + 3NaC_5H_5 \xrightarrow{THF} \underset{\mathbf{1}}{(C_5H_5)_3Ln} + 3NaCl \quad (1)$$

Ln = Sc (**1a**), Y (**1b**), La (**1c**), Ce (**1d**), Pr (**1e**), Nd (**1f**), Sm (**1h**), Gd (**1k**), Dy (**1m**), Er (**1o**), Yb (**1q**)

The same compounds and also the missing tris(cyclopentadienyl) species of the four smaller lanthanide metals $(C_5H_5)_3Tb$ (**1l**), $(C_5H_5)_3Ho$ (**1n**), $(C_5H_5)_3Tm$ (**1p**), and $(C_5H_5)_3Lu$ (**1r**) were obtained analogously from the $LnCl_3$ and NaC_5H_5[13,14] or KC_5H_5 [14] in ether or benzene (eq 2):

$$\mathrm{LnCl_3 + 3MC_5H_5} \xrightarrow{\mathrm{Et_2O\ or\ benzene}} \underset{\mathbf{1}}{\mathrm{(C_5H_5)_3Ln}} + \mathrm{3MCl} \qquad (2)$$

Ln = Tb (**1l**), Ho (**1n**), Tm (**1p**), Lu (**1r**);
M = K or Na

Later on Tsutsui et al. succeeded in preparing the thermally sensitive $(C_5H_5)_3Eu$ (**1i**) following eq 1 or by reacting THF solutions of $(C_5H_5)EuCl_2(THF)_3$ with 2 equiv of NaC_5H_5.[15] The radioactive derivative $(C_5H_5)_3Pm$ (**1g**) was obtained for the first time after neutron bombardment of **1f** and a subsequent β-decay process (eq 3);[16] further evidence for the existence of **1g** has been obtained by doping experiments of **1e** with ^{147}Pm:[17]

$$\underset{\mathbf{1f}}{^{150}\mathrm{Nd(C_5H_5)_3}} \xrightarrow{(\mathrm{n},\,\gamma)} {}^{151}\mathrm{Nd(C_5H_5)_3} \xrightarrow{\beta} \underset{\mathbf{1g}}{^{151}\mathrm{Pm(C_5H_5)_3}} \qquad (3)$$

Using molten $(C_5H_5)_2Be$[18] as a cyclopentadienyl transfer reagent and as a solvent represents another route to tris(cyclopentadienyl)lanthanides, specifically **1g**, which also can be made like all the other $(C_5H_5)_3Ln$ compounds using $(C_5H_5)_2Mg$ and $LnCl_3$,[18] LnF_3,[19,20] or LnI_3.[19] More recently discovered methods are the transmetalation between rare earth metal powders and C_5H_5Tl[21−24] or $(C_5H_5)_2Hg$,[23a,25−27] and the ligand exchange reactions between $Ln(C_6F_5)_n$ ($n = 2$, 3) and C_5H_6,[23a,28] and the oxidation of $(C_5H_5)_2Eu$ or $(C_5H_5)_2Yb$ with C_5H_5Tl or $(C_5H_5)_2Hg$.[21,22,23] Finally it should be mentioned that the reaction between excess of NaC_5H_5 and $(pyH)_2[CeCl_6]$ does not result in the formation of $(C_5H_5)_4Ce$,[29] but yields $(C_5H_5)_3Ce$ (**1d**).[30]

Nearly all the tris(cyclopentadienyl) compounds of the rare earth elements have been investigated by X-ray crystallography. The unsaturated character of the complexes **1** is reflected in their formation of polymeric structures. For instance, the samarium derivative **1h** crystallizes in two different polymeric chains along with severely disordered cyclopentadienyl ligands.[31,32a] Unexpectedly, both the scandium complex **1a**[33] and the lutetium compound **1r**[34] (Figure 1) are isostructural. They crystallize in chains $[(C_5H_5)_2Ln(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_5H_5)]_\infty$ in which $(C_5H_5)_2Ln$ units are bridged in a monohapto fashion by two other C_5H_5 ligands.

On the other hand, La (**1c**) (Figure 2), Pr (**1e**),[35] and Nd (**1f**)[36] form polymeric zigzag chains of distinct $(C_5H_5)_2Ln(\mu\text{-}\eta^5\text{:}\eta^x\text{-}C_5H_5)$ units (La $x = 2$,[32a] 1;[32b] Pr $x = 1{-}2$; Nd $x = 1$) involving two nonequivalent terminal cyclopentadienyl ligands. The effective coordination numbers of the lanthanides increase from nine in the hypothetical monomers to either 10 or 11 in the polymeric species.

1b[37], **1o**,[38] and **1p**[38] are isomorphous because of the similarity of their ionic radii. The compounds show coordinatively saturated molecules containing three η^5-C_5H_5 ligands around the metal atoms, which form polymeric chains via van der Waals interactions between monomeric units. However, in spite of the very similar ionic radii of Yb^{3+} and Lu^{3+}, **1q**[39] is strictly a monomer, unlike the polymeric **1r** (note that only two C_5H_5 groups are η^5), with D_{3h} idealized symmetry, resulting in an effective coordination number 9 for Yb. These unexpected differences in the structure of tris(cyclopentadienyl)lanthanides are largely due to steric effects caused by the difference sizes of the respective rare earth elements: the larger metal centers try to attain as high a coordination number as possible, consistent with tolerable intramolecular repulsions. The smaller rare earths have lower coordination numbers due to the increase in intramolecular ligand−ligand repulsions as the metal size decreases.[40]

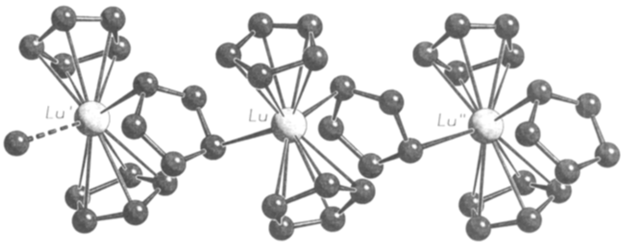


Figure 1. Structure of $(C_5H_5)_3Lu$ (**1r**) in the crystal.[34]

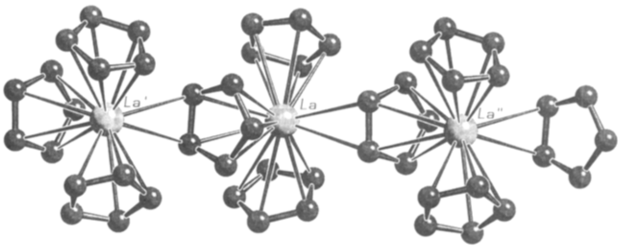


Figure 2. Structure of $(C_5H_5)_3La$ (**1c**) in the crystal.[32a]

All compounds of type **1** are air and moisture sensitive. The bonds between the three negatively charged cyclopentadienyl ligands and the rare earth metal ions in the oxidation state Ln^{3+} is assumed to be predominantly electrostatic, a conclusion derived from several spectroscopic studies, e.g. refs 1b, 2f, 12b, and 91. Except for the europium derivative **1i**, all complexes **1** have a high thermal stability. **1h**, **1i**, and **1q** can be reduced reversibly at platinum, gold, and mercury electrodes to give the Ln^{2+} species $[(C_5H_5)_3Ln]^-$.[92] In general, tris(cyclopentadienyl)lanthanides show very similar chemical behavior, e.g. with regard to their solubility in organic and inorganic solvents.[12b,35,38] They hydrolyze in water, forming the corresponding lanthanide hydroxides and cyclopentadiene. The first step of this reaction, the 1:1 complex with water $(C_5H_5)_3Ln(OH_2)$, has been detected recently.[93] With alcohols they decompose to give lanthanide alkoxides and cyclopentadiene; with $FeCl_2$ ferrocene is formed quantitatively.[12b,94]

Because of their strong Lewis acidity, most tris(cyclopentadienyl)lanthanides coordinate one or even two solvent molecules (eq 4). Several complexes of **1b−f** and **1h−r** with H_2O,[93] THF (**2**),[3e,f,g,21−23,25,26,38,52a,b,60−62,73,84−87,90,95−116] methyltetrahydrofuran,[52a,68,73,115,117,118] acetone,[52b] $MeCO_2Me$,[119,121c] $MeCO_2Bu$ (**3**),[118,120,121a,c] DMSO,[52b] $OS(Me)C_6H_4Me$-4 (**4**),[121b] $OS(CH_2py\text{-}2)C_6H_4Me$-4,[121b] tetrahydrothiophene,[90] NH_3,[12b,86−88,96] Et_2NH,[119] Bu_2NH,[119] NEt_3,[90] pyrrole,[90] methylpyrrole,[65] py (**5**),[23,24,65,85,86] picoline,[119] pyrazine (**6**),[3e,110,122] phen,[123] (−)-nicotine,[65] DMF,[52b] and various primary, secondary, and tertiary organophosphines,[52a,b,72,86,89,90,96] have been prepared and investigated by several spectroscopic methods. Special attention should be drawn to the complexes of **1** with the nitriles NCMe (**7**),[23,52a,61,62,73,89,119,121,124−127]

NCEt (**8**),[124,128,129] NCPr,[124] NC^{i}Pr,[124] NC^{t}Bu,[124,125] NCPh,[89] NCC$_6$H$_4$Me-4,[89,124] NCC$_6$H$_4$Cl-4,[89] and the isonitrile ^{c}C$_6$H$_{11}$NC (**9**),[52a,60,65,68,85,86,96,117,130–139] which

$$\underset{\mathbf{1}}{\mathrm{(C_5H_5)_3Ln}} + n\mathrm{LB} \rightarrow \mathrm{(C_5H_5)_3Ln(LB)}_n \qquad (4)$$

LB = H_2O, THF (**2**), MeTHF, MeCO$_2$Me, MeCO$_2$Bu (**3**), OS(Me)C$_6$H$_4$Me-4 (**4**), OS(CH$_2$py-2)C$_6$H$_4$Me-4, SC$_4$H$_8$, NH$_3$, Et$_2$NH, Bu$_2$NH, NEt$_3$, NHC$_4$H$_8$, MeNC$_4$H$_8$, py (**5**), Mepy, N$_2$C$_4$H$_4$ (**6**), phen, nicotine, ^{c}C$_6$H$_{11}$PH$_2$, PhPH$_2$, (^{c}C$_6$H$_{11}$)$_2$PH, Ph$_2$PH, PEt$_3$, PBu$_3$, P(^{c}C$_6$H$_{11}$)$_3$, PPh$_3$, PPhMe$_2$, PBu$_2$Cl, NCMe (**7**) (n = 1, 2), NCEt (**8**) (n = 1, 2), NCPr (n = 2), NC^{i}Pr (n = 2), NC^{t}Bu NCPh, NCC$_6$H$_4$Me, NCC$_6$H$_4$Cl, CN^{c}C$_6$H$_{11}$ (**9**) (n = 1, 2)

have been the target of extensive structural and spectroscopic investigations (e.g. ^{139}La-NMR of **1c** in different coordinating solvents and other basic ligands[6c,52a,b]) to find out the influence of the f-electrons on the ligand field parameters of these complexes.

Single-crystal X-ray structure determinations of the THF and other Lewis base adducts **2b**,[98] **2c**,[98] **2e**,[103] **2f**,[101,103] **2k** (Figure 3),[97] **2m**,[114,116] **2q**,[108] **2r**,[105] **5f**,[24] **5h**,[24] (C$_5$H$_5$)$_3$Sm(NCCD$_3$),[140a] **7m** (n = 1),[121] **8c** (n = 1),[128,140b] **8e** (n = 1),[128] **8q** (n = 1),[128] **9e** (n = 1),[123] **3**,[121] and **4** [121b] show these compounds to be monomeric with three η^5-C$_5$H$_5$ systems and the Lewis base coordinated via O, N, S, P, or C in the case of the isonitriles. Using structural criteria the bonding character of these organolanthanides is described best via an ionic model.[3c] Geometrical approaches to the coordination numbers are discussed by the cone-packing model.[3b,e,f]

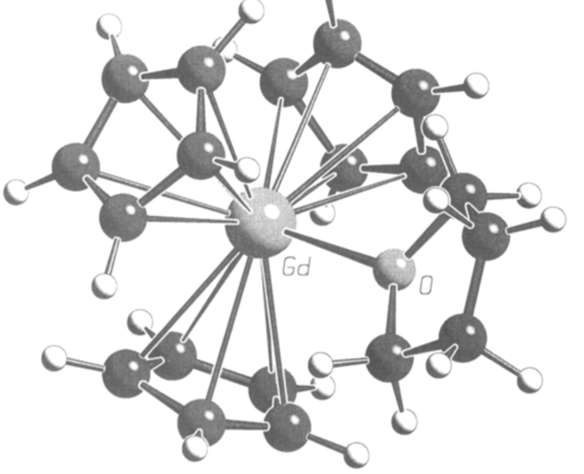


Figure 3. Structure of (C$_5$H$_5$)$_3$Gd(THF) (**2k**) in the crystal.[97]

Pyrazine coordinates two (C$_5$H$_5$)$_3$Yb units as shown in the X-ray structure of **6q** (Figure 4),[122] and the complexes of various **1** with two nitrile ligands show a trigonal bipyramidal structure with the nitrile ligands occupying the axial positions as in **7c**,[124] **7d**,[124] **7e**,[124] and **8c** (Figure 5).[128,140b]

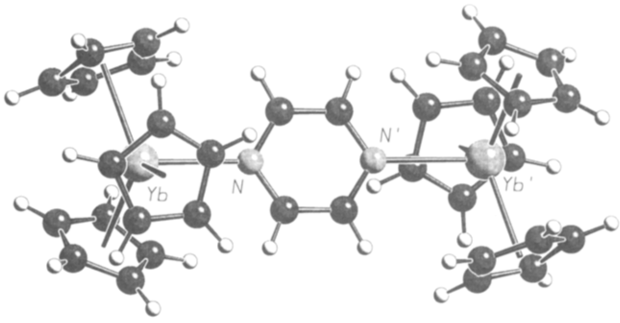


Figure 4. Structure of (C$_5$H$_5$)$_3$Yb(NC$_4$H$_4$N)Yb(C$_5$H$_5$)$_3$ (**6q**) in the crystal.[122]

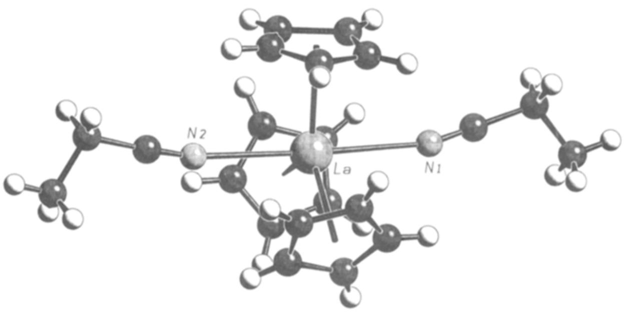


Figure 5. Structure of (C$_5$H$_5$)$_3$La(NCEt)$_2$ (**8c**) in the crystal.[128]

The Lewis acidity of **1** together with the distinct oxophilicity of the lanthanides results in the formation of complexes with transition metal carbonyls and nitrosyls. Their IR spectra give evidence for isocarbonyl and isonitrile coordination.[141,142] Even phosphorus ylides like Ph$_3$PCH$_2$ react with **1r** to give the zwitterionic complex (C$_5$H$_5$)$_3$LuCH$_2$PPh$_3$.[143]

Dry ammonium cerium(IV) nitrate (NH$_4$)$_2$[Ce(NO$_3$)$_6$] is reduced by excess NaC$_5$H$_5$ to yield **1d** together with the first formal tetrakis(cyclopentadienyl) derivative of a trivalent rare earth metal (**10d**) (eq 5).[109] IR and NMR spectra, but no X-ray structural investigations, are in accordance with a [(η^5-C$_5$H$_5$)$_3$Ln(μ-η^1-C$_5$H$_5$)Na(THF)$_n$] formulation for the complexes; **10c**, **10e**, and **10f** are also available from LnCl$_3$ and 4 equiv of NaC$_5$H$_5$.[113]

$$\mathrm{(NH_4)_2[Ce(NO_3)_6]} \xrightarrow{\mathrm{NaC_5H_5}} \underset{\mathbf{2d}}{\mathrm{(C_5H_5)_3Ce(THF)}} + \underset{\mathbf{10d}}{\mathrm{[Na(THF)][Ce(C_5H_5)_4]}} \qquad (5)$$

Nucleophilic substitution of **10d** with alkyl, aryl, acyl, and organometallic halides shows that the σ-bonded C$_5$H$_5$ group can be transferred preferentially to these substrates.[109,113,144] Furthermore **10d** reacts with equimolar amounts of I$_2$ forming [Na(THF)][(C$_5$H$_5$)$_3$CeI].[109] The X-ray structural analysis of [Li(DME)$_3$][(C$_5$H$_5$)$_3$NdPh], prepared in a similar fashion, reveals three π-bonded cyclopentadienyl ligands and one σ-bonded phenyl group in a distorted tetrahedral arrangement.[145,146a,b] Quasi tetrahedral complexes [Bu$_4$N]$^+$[(C$_5$H$_5$)$_3$LnX]$^-$ (Ln = La,[146c] X = Br, I; Ln = Pr,[147] X = NCS) and (C$_5$H$_5$)$_3$Yb-F-U(C$_5$H$_5$)$_3$,[148] are also formed during the reactions of **1** with [Bu$_4$N]X (X = Br, I, NCS) or (C$_5$H$_5$)$_3$UF, respectively.

Ionic, binuclear organolanthanides containing an anion bridging two tris(cyclopentadienyl)lanthanide units (eq 6) are also known. Fischer et al.[52a,119] postulated, on the basis of NMR experiments orga-

Table 1. Spectroscopic and Other Data of Tris(cyclopentadienyl)lanthanide Compounds

compound	Ln		color, characterization, etc.
$(C_5H_5)_3Ln$	Sc	**1a**	straw,[12a,b] X-ray,[33] NMR,[6c,41,45] IR,[42] Raman,[43] MS,[41,44] melt./dec.,[12a,b] elec. d.,[45] thermo. d.[44,46,47]
	Y	**1b**	pale yellow,[12a,b] X-ray,[37] Raman,[48] MS,[44,49,50] melt./dec.,[12a,b] elec. d.,[45] thermo. d.;[44,46,47,51] complex with H_2O: colorless;[93] with THF (**2b**): white, X-ray, melt./dec.,[98] bond angles;[3e,3f] with $^{c}C_6H_{11}NC$ (**9b**): UV,[96] NMR, IR, melt./dec.[130]
	La	**1c**	colorless,[12a,b] X-ray,[32] NMR,[32,52a,b] IR,[52c] Raman,[43] UV,[54] fluores.,[53] MS,[44,49,50,55,56] melt./dec.,[12a,b] elec. d.,[45,57] thermo. d.;[44–47,58,59] complex with THF (**2c**): white, X-ray, melt./dec.,[98] light yellow,[103] colorless,[146c] NMR,[52a,115,146c] UV, electr. d.,[115] IR,[100] bond angles;[3e,3f] with 3THF: melt./dec.;[25] with MeTHF: NMR,[52a,115] UV, electr. d.;[115] with $MeCO_2Bu$ (**3c**): X-ray, UV;[121c] with NCMe (**7c**): white, IR,[124] NMR;[52a,52b,125] with 2NCMe (**7c**): X-ray, IR,[124] UV, lumines.,[694] NMR;[6c,52a,124,125] with NCEt (**8c**): X-ray,[128,140b] NMR;[124] with 2NCEt (**8c**): X-ray,[128] NMR;[124] with 2NCPr;[124] with 2NC^{i}Pr: NMR;[124] with NC^{t}Bu: colorless, NMR, IR;[125] with $^{c}C_6H_{11}NC$ (**9c**): NMR, IR, melt./dec.;[130] with $^{c}C_6H_{11}CN$: colorless, melt./dec.,[125] NMR;[6c,52a,125] with acetone: NMR; with DMSO: NMR; with DMF: NMR; with $OP(OMe)_3$: NMR,[52b] with $OP(OEt)_3$: colorless, IR, NMR, dip.[696]
	Ce	**1d**	orange,[12a,b,40,687] UV,[60,62] lumines.,[61] MS,[44,49,50] melt./dec.,[12a,b,30] magn. d.,[12b,30,62] elec. d.,[45,62,63] thermo. d.;[44,47,50,58,59] complex with THF (**2d**): brown,[103,693] tan,[112] X-ray,[112,693] NMR,[112] IR,[22,100] UV,[62] luminescence,[61] magn. d.;[109] with NCMe (**7d**): NMR, IR,[124] UV;[62] with 2NCMe (**7d**): X-ray, NMR, IR,[124] lumines.;[61] with $^{c}C_6H_{11}NC$ (**9c**): IR, melt./dec.,[130] NMR,[85,130] UV,[62] with $OP(OEt)_3$: yellow, IR, NMR, dip.[696]
	Pr	**1e**	pale green,[12a,b,687] X-ray,[35] powder diffr.,[18,64] NMR,[65] UV–vis,[12b,66,68] Raman,[43,48] MS,[44,49,50,55,56,67] melt./dec.,[12a,b] magn. d.,[12b] elec. d.,[45,63,66,68] thermo. d.;[44,46,47,58,59,69] complex with THF (**2e**): greenish, X-ray,[103] UV,[60,107] IR,[100] bond angles;[3e,f] with MeTHF: UV;[68,117,118] with $MeCO_2Bu$ (**3e**): X-ray,[121a] UV;[118,120,121c] with $OS(Me)C_6H_4Me$-4 (**4e**): X-ray, NMR, UV;[121b] with $MeCO_2Me$: NMR,[119] UV;[121c] with $OS(CH_2py\text{-}2)C_6H_4Me$-4: X-ray, NMR, UV;[121b] with $NHEt_2$: NMR; with $NHBu_2$: NMR; with picoline: NMR;[119] with (−)-nicotine: NMR;[65] with NCMe (**7e**): IR,[124] NMR,[119,124] UV;[126] with 2NCMe (**7e**): X-ray, NMR, IR;[124] UV;[126] with NCEt (**8e**): X-ray;[128] with NC^{t}Bu: NMR;[124] with $^{c}C_6H_{11}NC$ (**9e**): light green,[131] X-ray,[132] NMR,[54,119,130,131] IR,[130] bond angles,[3e] UV,[68,117,134] lumines., magn. d.,[135] with $OP(OEt)_3$: green, IR, NMR, dip.[696]
	Nd	**1f**	blue,[12a,b,687] X-ray,[36] NMR,[65] IR,[42] Raman,[43] UV–vis,[66,70–73] MS,[44,49,50,55,56,74] melt./dec.,[12a,b,16] magn. d.,[12b] elec. d.,[45,63,73] thermo. d.;[44,47,50,55,58,59,69,75] complex with THF (**2f**): pale yellow,[101] light purple,[103] X-ray,[101,103] light blue,[106,23b] NMR[106,115] MS,[22] IR,[22,23b,100,103] UV,[23b,73,115] elec. d.,[100,115] magn. d,[115] bond angles;[3e,f] with MeTHF: NMR, magn. d., elec. d,[115] UV;[73,115] with methylpyrrole: NMR;[65] with py (**5f**): X-ray,[24] light blue, NMR, MS, IR, UV;[23a] with phen: red brown, IR, melt./dec.;[123] with (−)-nicotine: NMR;[65] with NCMe (**7f**): blue, MS, IR,[23a] UV;[23a,73] with 2NCMe (**7f**): UV;[127] with $^{c}C_6H_{11}NC$ (**9f**): violet, magn. d.,[96] IR, melt./dec.,[96,130] NMR,[65,130] UV,[136] with $OP(OEt)_3$: blue-violet, IR, NMR, dip,[696] with CH_2PMePh_2: purple, X-ray, NMR, IR, melt./dec.[772]
	Pm	**1g**	yellow orange, powder diffr., vis,[18] γ-spectrum[16]
	Sm	**1h**	orange,[12a,b] X-ray,[31,688] powder diffr.,[18] NMR,[28] IR,[15] Raman,[43] UV–vis,[18,76] lumines.,[77–79] MS,[44,49,50,74,80] melt./dec.,[12a,b,76] magn. d.,[12b,76] elec. d.,[45,63] thermo. d.;[44,47,50,52d,58,59] complex with THF (**2h**): yellow,[22,23b,26,106] melt./dec.;[3] X-ray;[3,4] NMR,[106] IR,[22,23b,689] UV, MS;[22,690] with 2THF: melt./dec.;[25] $OS(Me)C_6H_4Me$-4 (**4h**): NMR, UV;[121b] with py (**5h**): X-ray,[24] yellow, NMR, IR, UV, MS;[23a] with NCMe (**7h**): X-ray,[140a] yellow, MS,[23a] UV,[23a,694] IR;[23a,124] luminesc.;[694] with 2NCMe: UV, luminesc.;[694] with $^{c}C_6H_{11}NC$ (**9h**): NMR, melt./dec.,[130] IR,[124,130] UV, magn. d.,[137] with $OP(OEt)_3$: orange, IR, NMR, dip,[696] with CH_2PMePh_2: yellow, X-ray, NMR, IR, melt./dec.[773]
	Eu	**1i**	brown, IR,[15] lumines.,[77,79] melt./dec.,[15] mag. d.;[15] complex with THF (**2i**): brown,[95] NMR,[23c] UV, luminesc., magn. d.[691] Möβb.;[5,6,692] with 2THF: melt./dec.;[25] with py (**5i**): orange, NMR, IR, MS, UV;[23a] with $^{c}C_6H_{11}NC$ (**9i**): IR, melt./dec.,[130] NMR;[85,130,138] UV, luminesc., magn. d., Möβb.,[691] with $OP(OEt)_3$: brown, IR, NMR, dip.[696]
	Gd	**1k**	pale yellow,[12a,b] powder diffr.,[18] UV–vis,[53,54] Raman,[43,48] PE,[81] MS,[44,49,50] melt./dec.,[12a,b] magn. d.,[12b] elec. d.,[45,63,81] thermo. d.;[44,47,50,58,59] complex with THF (**2k**): X-ray,[3c,97] IR,[22] bond angles;[3e,f] with $^{c}C_6H_{11}NC$ (**9k**): NMR, IR, melt./dec.,[130] with $OP(OEt)_3$: white, IR, NMR, dip.[696]
	Tb	**1l**	colorless,[14] powder diffr.,[18] IR,[14] Raman,[48] MS,[44,49,50] melt./dec.,[14] magn. d.,[14] thermo. d.;[44,47,50,51] complex with THF (**2l**): dark green,[96] lumines.;[69,104] with $MeCO_2Bu$ (**3f**): UV;[121c] with NCMe (**7l**): X-ray,[121a] UV;[73] with $^{c}C_6H_{11}NC$ (**9l**): colorless,[96,139] melt./dec.,[96,130,139] IR,[96] NMR,[130] magn. d.,[96] with $OP(OEt)_3$: white, IR, NMR, dip.[696]
	Dy	**1m**	yellow,[12b] Raman,[43] UV,[73] MS,[44,49,50] melt./dec.,[12b] magn. d.,[12b] elec. d.,[45,63,73] thermo. d.;[44,47,50,51] complex with THF (**2m**): X-ray,[114,116,690] MS;[690] with $^{c}C_6H_{11}NC$ (**9m**): NMR, IR, melt./dec.,[13] with $OP(OEt)_3$: ivory, IR, NMR, dip.[696]
	Ho	**1n**	yellow,[14] powder diffr.,[69] NMR,[65] UV–vis,[14,60] Raman,[48] MS,[44,49,50,67] melt./dec.,[14] magn. d.,[14] thermo. d.;[44,47,50,51,67,69] complex with H_2O: pale yellow, X-ray;[93] with $^{c}C_6H_{11}NC$ (**9n**): yellow,[96,139] melt./dec.,[96,130,139] NMR,[65,130] IR,[96,130] magn. d.,[96] with $OP(OEt)_3$: beige, IR, NMR, dip.[696]
	Er	**1o**	pink,[12b] X-ray,[38] IR,[12b,83] Raman,[48] UV–vis,[60,82] MS,[44,49,50] melt./dec.,[12b,83] magn. d.,[12b] elec. d.,[45] thermo. d.;[44,47,50,51] complex with THF (**2o**): pink,[22,693] X-ray,[693] IR, MS,[22] UV;[60] with phen: dark red, IR, melt./dec.;[123] with $^{c}C_6H_{11}NC$ (**9o**): NMR, IR, melt./dec.,[130] with $OP(OEt)_3$: pink, IR, NMR, dip.[696]
	Tm	**1p**	yellow green,[14] X-ray,[36,38] powder diffr.,[18] NMR,[38,65] IR,[14,84] Raman,[43] UV–vis,[60,84] MS,[44,49,50,67] melt./dec.,[14] magn. d.,[14] thermo. d.;[44,46,47,50,51,67,69] complex with THF (**2p**): NMR,[38] UV, IR;[84] with 3THF: melt./dec.[25] with (−)-nicotine: NMR;[65] with $^{c}C_6H_{11}NC$ (**9p**): IR, melt./dec.,[130] NMR,[65,130] with $OP(OEt)_3$: green, IR, NMR, dip.[696]
	Yb	**1q**	dark green,[12b,83] X-ray,[39] NMR,[65,72,85] IR,[22,83,87] UV–vis,[60,71,72,86–90] MS,[44,49,50,67,74] melt./dec.,[12b,83,87] magn. d.,[12b] elec. d.,[45] thermo. d.;[44,46,50,51,52d,67,74] complex with THF (**2q**): green,[87,96] X-ray,[108] IR,[87,96] NMR,[85] UV,[73,86,87,90] melt./dec.;[87] with 2THF: melt./dec.;[25] with MeTHF: UV;[73] with $OS(Me)C_6H_4Me$-4 (**4q**): X-ray, UV;[121b] tetrahydrothiophene: UV;[90] with NH_3: green, IR, melt./dec.,[87] UV,[86,87,88] NMR;[96] with NEt_3: UV;[90] with pyrrole: UV;[90] with py (**5q**): green, IR,[23a] UV,[23a,86] NMR;[65,85] with pyrazine (**6q**): green brown, X-ray, NMR, MS, IR, magn. d.;[122] bond angles;[3e] with $^{c}C_6H_{11}PH_2$: green, UV; with $C_6H_5PH_2$: green, UV; with $(^{c}C_6H_{11})_2PH$: UV; with $HPPh_2$: UV;[89] with PEt_3: UV;[90] with PBu_3: synthesis;[72] with $P(^{c}C_6H_{11})_3$: UV;[89] with PPh_3: black, melt./dec.,[96] UV;[86,89] with Me_2PPh: UV; with ClP^{t}Bu$_2$: UV;[89] with NCMe (**7q**): olive green, IR,[23a] UV;[23a,89] with NCEt (**8q**): X-ray;[128] with NCPh: UV; with NCC_6H_4Me-4: UV; with NCC_6H_4Cl-4: UV;[89] with $^{c}C_6H_{11}NC$ (**9q**): green,[96,139] NMR,[65,85,130] IR,[96,130] UV,[60,73,86] melt./dec.,[96,130,139] magn. d.,[96] with $OP(OEt)_3$: green, IR, NMR, dip.[696]

Table 1 (Continued)

compound	Ln		color, characterization, etc.
$(C_5H_5)_3Ln$	Lu	**1r**	colorless,[14] X-ray,[34] NMR,[14,34,87] IR,[14] Raman,[48] MS,[44,49,50,67] melt./dec.,[14] magn. d.,[14] thermo. d.;[34,44,47,50,51,67] complex with THF (**2r**): X-ray,[105] colorless,[106,111] NMR;[106] with ${}^cC_6H_{11}NC$ (**9r**): NMR, IR, melt./dec.;[130] with CH_2PPh_3: colorless, NMR, IR, melt./dec.,[143] with $OP(OEt)_3$: colorless, IR, NMR, dip.[696]
$[Na(THF)_n][Ln(C_5H_5)_4]$	La	**10c**	$n = 1$: beige, NMR, IR[113]
	Ce	**10d**	$n = 1$: red, NMR, IR, magn. d.,[109,113] UV[109]
	Pr	**10e**	$n = 0$: green yellow, NMR, IR, magn. d.[113]
	Nd	**10f**	$n = 1$: light red, IR, magn. d.[113]
$[Na(THF)][(C_5H_5)_3LnI]$	Ce		black brown, magn. d.[109]
$Na[(C_5H_5)_3LnBH_4]$	Pr		NMR[119]
$Na\{[(C_5H_5)_3Ln]_2(BH_4)\}$	Pr		NMR[119]
$Na[(C_5H_5)_3LnO^tBu]$	Pr		NMR[119]
$[Na(phen)_3][(C_5H_5)_3Ln\text{-}Cl](phen)$	La		colorless, NMR, IR[695]
	Pr		yellow, X-ray, IR[695]
	Nd		blue, IR[695]
$[Na(THF)_6]\{[(C_5H_5)_3Ln]_2(\mu\text{-}H)\}$	Lu	**11r**	complex with 2 THF: colorless, X-ray, NMR, IR[149]
$[Bu_4N][(C_5H_5)_3LnNCS]$	Pr		UV[147]
$[Bu_4N]\{[(C_5H_5)_3Ln]_2(\mu\text{-}NCS)\}$	Pr		NMR[119]
$[Bu_4N][(C_5H_5)_3LnBr]$	La		colorless, NMR[146c]
$[Bu_4N][(C_5H_5)_3LnI]$	La		colorless, NMR[146c]
$[Bu_4N][(C_5H_5)_3LnNCBH_3]$	Pr		NMR[119]
$(C_5H_5)_3LnFU(C_5H_5)_3$	Yb		IR[148]
$[Li(THF)_4][(C_5H_5)_3LnMe]$	Pr		NMR[119]
$[Li(THF)_4][(C_5H_5)_3LnAlH_4]$	Pr		NMR[119]
$[Li(DME)_3][(C_5H_5)_3LnPh]$	Nd		X-ray[145,146]
$[Li(DME)_3]\{[(C_5H_5)_3Ln]_2(\mu\text{-}H)\}$	Nd		purple,[151] X-ray[145,152]
$[Li(DME)_3]\{[(C_5H_5)_3Ln]_2(\mu\text{-}N_3)\}$	Sm	**12h**	yellow, X-ray, NMR, IR, melt./dec.[150]
$[Li(DME)_3]\{[(C_5H_5)_3Ln]_2(\mu\text{-}Cl)\}$	Sm		yellow, X-ray, NMR, melt./dec.[153]
$[Li(DME)_3]\{[(C_5H_5)_3Ln]_2(\mu\text{-}Me)\}$	Sm		NMR[154]
	Lu		NMR[154]
$[Li(DME)_3]\{[(C_5H_5)_3Ln]_2(\mu\text{-}GeMe_3)\}$	Sm		yellow, NMR[153]

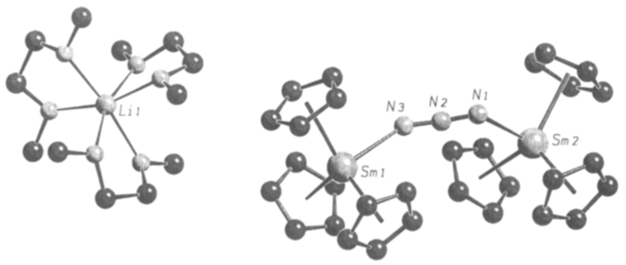


Figure 6. Structure of $[Li(DME)_3][(C_5H_5)_3Sm(\mu\text{-}N_3)Sm(C_5H_5)_3]$ (**12h**) in the crystal.[150]

nolanthanides containing the anions $[(C_5H_5)_3LnX]^-$ (Ln = Pr, X = O^tBu, Me, Bu, AlH_4, BH_4, $NCBH_3$; Ln = Nd, X = $NCBH_3$), on the existence of $[Bu_4N][((C_5H_5)_3Pr)_2(\mu\text{-}X)]$ (X = NCS, $NCBH_3$) and $Na\{[(C_5H_5)_3Pr]_2(\mu\text{-}BH_4)\}$. Two years later, the hydrido

$$\underset{\mathbf{2}}{2(C_5H_5)_3Ln(THF)} + MX \xrightarrow{S} \underset{\mathbf{11,\ 12}}{[M(S)_n][(C_5H_5)_3Ln(\mu\text{-}X)Ln(C_5H_5)_3](THF)_m} \quad (6)$$

Ln = Lu: M = Na; S = THF; $n = 6$; $m = 2$;
X = H, D (**11r**)

Ln = Sm: M = Li; S = DME; $n = 3$; $m = 0$;
X = N_3 (**12h**)

complex $[Na(THF)_6]\{[(C_5H_5)_3Lu]_2(\mu\text{-}H)\}(THF)_2$ (**11r**) was isolated from the reaction between $(C_5H_5)_2LuCl(THF)$ and sodium hydride in THF,[149] and an X-ray structural analysis showed it to be like the corresponding azido species **12h** (Figure 6).[150] Both types of compounds can be obtained from **2** or from the reaction of $(C_5H_5)_2NdCl(LiCl)_2$ and lithium methylnaphthalene. The latter reaction is not very well understood.[145,151,152]

$(C_5H_5)_2Sm(\mu\text{-}Cl)_2Na(DME)$ reacts with $LiGeMe_3$ in DME forming $[Li(DME)_3][(C_5H_5)_3Sm(\eta\text{-}Cl)Sm(C_5H_5)_3]$, which was proven by an X-ray structural analysis. Excess of $LiGeMe_3$ is necessary to make isolation of extremely air-sensitive $[Li(DME)_3][(C_5H_5)_3Sm(\eta\text{-}GeMe_3)Sm(C_5H_5)_3]$ possible.[153] Finally, it should be mentioned that ^1H-NMR studies indicate that the reactions of **1** with MeLi in DME results in the formation of the methyl-bridged derivatives $[Li(DME)_3][(C_5H_5)_3Ln(\mu\text{-}Me)Ln(C_5H_5)_3]$ (Ln = Sm, Lu).[154]

Tris(cyclopentadienyl) rare earth complexes and some of their adducts discussed above are used as starting materials for the synthesis of other organo rare earth compounds,[94,155−163] as reducing agents,[164−168] as reagents to make other organometallic compounds,[169] as catalysts,[170−174] and as precursor for electronic doping materials.[175−177]

A list of references for spectroscopic and other data of solvent-free tris(cyclopentadienyl)lanthanides, their Lewis base adducts, and other tris(cyclopentadienyl) derivatives of the rare earths together with references found after completion of the manuscript is given in Table 1.

2. Derivatives with Substituted Cyclopentadienyl Ligands

While tris(cyclopentadienyl) metal complexes of the rare earths with three C_5H_5 ligands have been studied in great detail the corresponding derivatives with substituted cyclopentadienyl groups $C_5H_nR_{5-n}$ have received much less attention. The synthetic routes to synthesize complexes with three monosubstituted-cyclopentadienyl ligands (Table 2) follow the methods used for Cp_3Ln compounds. New methods are found or have been developed recently to get the

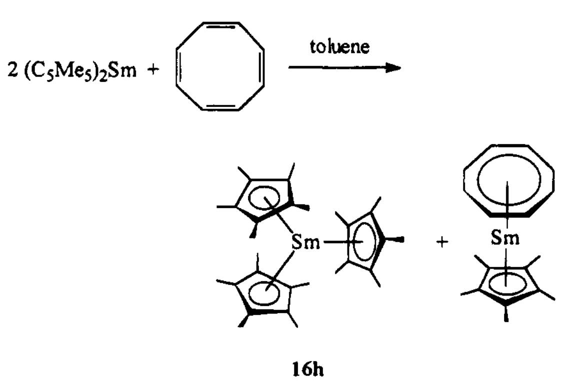
Table 2. Spectroscopic and Other Data of Tris(cyclopentadienyl)lanthanide Compounds Containing Substituted Cyclopentadienyl Ligands

complex	Ln		color, characterization, etc.
$(MeC_5H_4)_3Ln$	Sc	**13a**	orange-red, diff., IR, NMR[697]
	Y	**13b**	complex with THF: NMR[6c,178]
	La	**13c**	colorless,[179] NMR,[52a] cond.,[180] MS,[181] melt./dec.,[179] X-ray;[182] complexes with THF: MeCN, Me_4NF and other donors[52a]
	Ce	**13d**	yellow orange,[40] X-ray,[40] IR,[40] MS,[40] melt./dec.;[40] complexes with THF,[40,183a,184] $[N(CH_2CH_2)_3CH]$,[183a,b] PMe[3,185] $[P(OCH_2)_3CEt]$,[183a,b] NCEt,[40] CNEt,[40] CN*t*Bu,40 $CN^cC_6H_{11}$[85]
	Pr	**13e**	NMR,[119] PE,[186] MS;[180] complex with CN^tBu,[119] $CN^cC_6H_{11}$[85]
	Nd	**13f**	reddish blue,[187] X-ray,[188] MS,[22,180] melt./dec.;[187,188] complex with $CN^cC_6H_{11}$[85]
	Sm	**13h**	orange,[28,92,141] IR,[22] MS;[22] complex with $Co(CO)_4$ and $Fe(CO)_2(C_5H_5)$[140,141]
	Gd	**13k**	yellow,[22] IR,[22] MS[22]
	Tb	**13l**	complex with THF: lumines.[99,104]
	Dy	**13m**	PE[186]
	Ho	**13n**	complex with H_2O: X-ray[93]
	Er	**13o**	use for MOCVD[177]
	Tm	**13p**	green yellow,[84] UV,[84] MS,[180] melt./dec.[84]
	Yb	**13q**	dark green, diff,[697] X-ray,[189] IR,[189,697] NMR,[697] MS,[180] melt./dec.,[189,697] v.p.,[697] reaction;[190] complex with CN^tBu[119]
$(EtC_5H_4)_3Ln$	Sc		MS[44b]
$(PrC_5H_4)_3Ln$	Sc		MS[44b]
$(^iPrC_5H_4)_3Ln$	Sc		MS[44b]
	La		MS,[192,193a] thermo. d.[191]
	Ce		melt./dec.[193b]
	Pr		MS,[192,193a] thermo. d.,[191] catalyst[194a]
	Nd		MS,[192,193a] thermo. d.[191]
	Sm		MS[193a]
	Gd		synthesis, use for MOCVD[194b]
	Ho		catalyst[194a]
	Yb		MS,[193a] melt./dec.[177]
$(^iBuC_5H_4)_3Ln$	Nd		green violet, X-ray, IR, MS; complex with THF[195]
$(^tBuC_5H_4)_3Ln$	La		complex with THF: white yellow, NMR, IR;[196] with $LiCl(THF)_3$: white, X-ray, IR, NMR[703]
	Ce		purple, NMR, IR, MS, melt./dec.,[40] reactions[184,520]
	Nd		green violet, IR, MS, DTG, melt./dec.;[197] complex with $LiCl(THF)_3$: X-ray;[698] with $LiBr(THF)_3$: X-ray, IR,[194c]
	Sm		orange, NMR, IR[196]
	Dy		yellow, IR, MS, DTG, melt./dec.[196]
	Tm		greenish, IR, MS, DTG, melt./dec[197]
$(^tBuCH_2C_5H_4)_3Ln$	Nd		blue, IR, MS, melt./dec.[195]
$(MeOCH_2CH_2C_5H_4)_3Ln$	La		colorless,[198a] X-ray[198b]
	Pr		yellow, X-ray[198a]
	Nd		blue, IR, MS, melt./dec.[195]
	Sm		yellow,[699] X-ray,[198b,699] NMR, MS, melt./dec,[699] UV−vis[704]
	Yb		dark green, MS, melt./dec.[699]
$(Me_2NCH_2CH_2C_5H_4)_3Ln$	La		white, X-ray, IR, NMR, MS, melt./dec.[700]
	Nd		blue violet,[195] X-ray,[700] IR, MS, melt./dec.[195]
$(Me_3SiC_5H_4)_3Ln$	Ce		blue, NMR, IR, MS, melt./dec.; complexes with NCEt, CNEt, CN^tBu[40]
	Pr		NMR; complex with THF[119]
$[(Me_3Si)_2C_5H_3]_3Ln$	Ce	**14d**	blue, X-ray, NMR, IR, MS, melt./dec.; complex with CN^tBu[40]
	Sm	**14h**	X-ray, NMR, IR, magn. d.[199]
$(Et_3SiC_5H_4)_3Ln$	Pr		$OS(Me)C_6H_4Me$-4 adduct: UV and NMR[121b]
$(Me_4C_5H)_3Ln$	La	**15c**	green yellow, X-ray, NMR, MS, melt./dec.[200a,701]
	Nd	**15f**	blueviolet, NMR, MS, melt./dec.[701]
	Sm	**15h**	blood-red, X-ray, NMR, MS, melt./dec.[200a,701]
	Tb	**15l**	orange, X-ray, NMR, MS, melt./dec.[200a,701]
$[C_5H_2Me(CH_2)_5]_3Ln$	Nd		green, X-ray, IR, MS[702]
$(C_5Me_5)_3Ln$	Sm	**16h**	red, X-ray, NMR, IR[201]

more interesting complexes with two or more substituents on the cyclopentadienyl ring, like $[(Me_3Si)_2C_5H_3]_3Sm$ (**14h**), which can be made by metathesis of $SmCl_3$ and $KC_5H_3(SiMe_3)_2$.[199] Although all attempts to get the analogous cerium derivative **14d** by salt elimination methods failed, **14d** was readily formed according to eq 7:[40]

$$Ce[N(SiMe_3)_2]_3 + 3(Me_3Si)_2C_5H_4 \rightarrow \underset{\mathbf{14d}}{[(Me_3Si)_2C_5H_3]_3Ce} + 3(Me_3Si)_2NH \quad (7)$$

Although the pentamethylcyclopentadienyl system is particularly popular in the organometallic chemistry of the rare earths, it was only recently that Evans et al. obtained the first tris(cyclopentadienyl)lanthanide complex containing three bulky pentamethylcyclopentadienyl ligands[201] according to eq 8:



16h

(8)

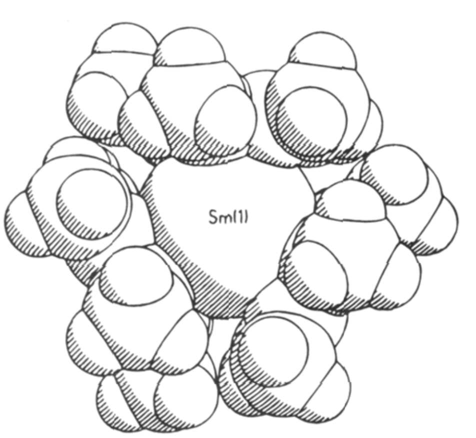


Figure 7. Space-filling model of $(Me_5C_5)_3Sm$ (**16h**).[201] (Reprinted from ref 201. Copyright 1991 American Chemical Society).

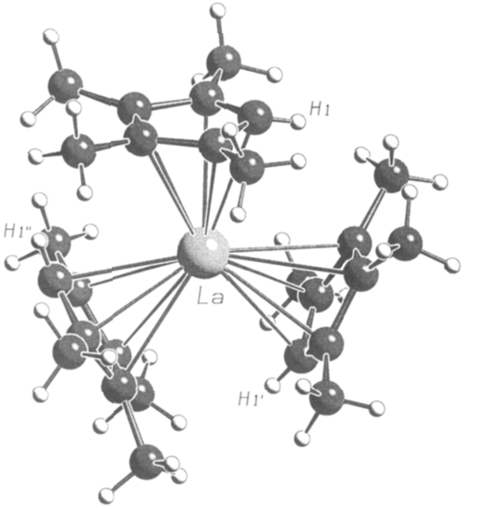


Figure 8. Structure of $(Me_4C_5H)_3La$ (**15c**) in the crystal.[200]

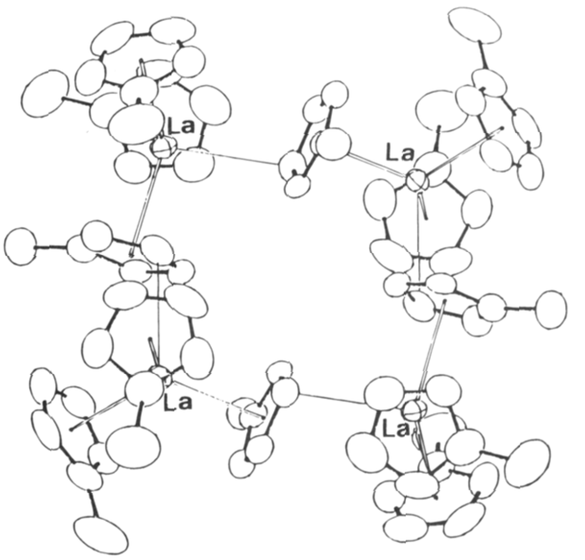


Figure 9. Structure of $[(MeC_5H_4)_3La]_4$ (**13c**) in the crystal.[182] (Reprinted from ref 182. Copyright 1991 Elsevier Sequoia).

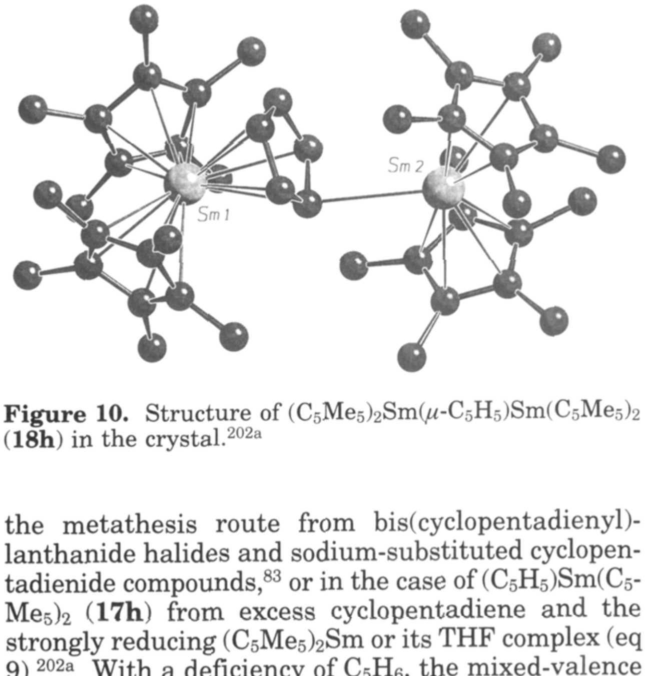


Figure 10. Structure of $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$ (**18h**) in the crystal.[202a]

In the solid state **16h** is a discrete monomer (Figure 7)[201] just as the analogous tetramethylcyclopentadienyl derivatives **15c** (Figure 8), **15h**, and **15l**,[200] the bis(trimethylsilyl)cyclopentadienyl derivatives **14d**[40] and **14h**,[199] or $(MeOCH_2CH_2C_5H_4)_3Pr$[198] as well as tris(methylcyclopentadienyl)ytterbium (**13q**),[189] whereas the derivatives **13c** (Figure 9),[182] **13d**[40] and **13f**[188] crystallize as cyclic tetramers.

The mono- and disubstituted tris(cyclopentadienyl)lanthanides show, in general, chemical behavior similar to that of the unsubstituted tris(cyclopentadienyl) complexes. They form stable, monomeric 1:1 adducts with Lewis bases like THF, $OS(Me)C_6H_4Me\text{-}4$, nitriles, isonitriles, phosphanes, some of which have been studied by X-ray diffraction (see Table 2). Evidence for adducts with transition metal carbonyls and nitrosyls has been derived from infrared spectroscopy, whereas the water adduct, $(MeC_5H_4)_3Ho(OH_2)$, has been characterized by X-ray crystallography.[93]

3. Miscellaneous Derivatives

Heteroleptic tris(cyclopentadienyl)lanthanide complexes containing two different substituted cyclopentadienyl ligands (Table 3) could be prepared using the metathesis route from bis(cyclopentadienyl)lanthanide halides and sodium-substituted cyclopentadienide compounds,[83] or in the case of $(C_5H_5)Sm(C_5Me_5)_2$ (**17h**) from excess cyclopentadiene and the strongly reducing $(C_5Me_5)_2Sm$ or its THF complex (eq 9).[202a] With a deficiency of C_5H_6, the mixed-valence complex $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$ (**18h**) forms. The coordination environment around the Sm(III) ions in **18h** (Figure 10) is similar to that found for the Sm atom in **17h**, which was also observed as one of the products formed in the reaction of $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ and KC_5H_5.[208]

$$(C_5Me_5)_2Sm(THF)_n + C_5H_6 \xrightarrow[-n\mathrm{THF}]{\text{hexane}} \underset{\mathbf{17h}}{(C_5H_5)Sm(C_5Me_5)_2} + {}^1/_2H_2 \quad (9)$$

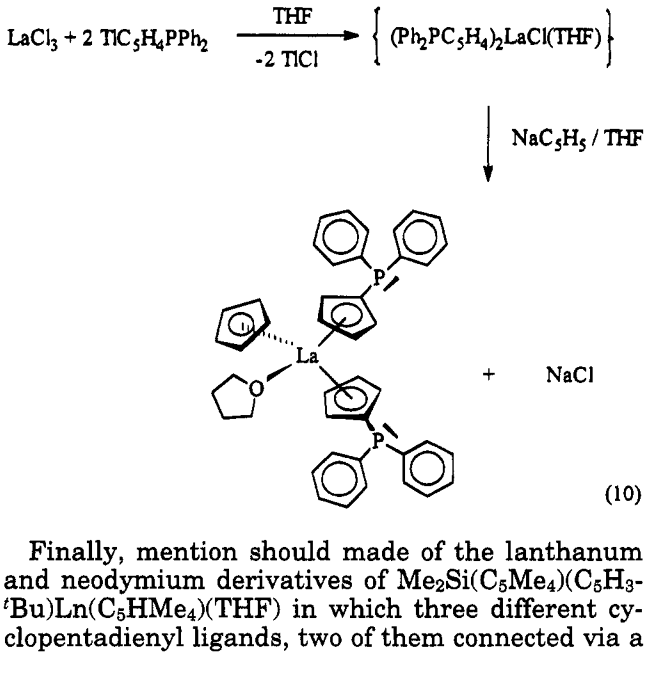
$n = 0, 2$

In addition to a series of heteroleptic tris(cyclopentadienyl)lanthanide complexes containing ring-bridged dicyclopentadienyl ligands with[93,205] and without[204] a coordinating oxygen atom within the bridge, just three other compounds of this type are in the literature, $(C_5H_5)Y(C_5H_4CH_2CH_2OMe)_2$,[174] $(C_5H_5)_2Yb$-

Table 3. Spectroscopic and Other Data of Miscellaneous Tris(cyclopentadienyl)lanthanide Derivatives

complex	Ln		color, characterization, etc.
$(C_5H_5)_2Ln(C_5H_4Me)$	Er		pink, IR, melt./dec.[83]
$(C_5H_5)_2Ln(C_5H_4CH_2CH_2OMe)$	Y		X-ray[198b]
$(C_5H_5)Ln(C_5H_4Me)_2$	Yb		green, IR, melt./dec.[83]
$(C_5H_5)Ln(C_5Me_5)_2$	Sm	**17h**	orange-red, X-ray, NMR, IR, magn. d.[202a]
$(C_5H_5)Ln(C_5H_4CH_2CH_2OMe)_2$	Y		catalyst[174]
$(C_5H_5)_2Ln(C_5H_4PPh_2O)$	Yb		complex with $OPPh_3$: yellow, X-ray, NMR, UV, IR[202b]
$(C_5H_5)Ln(C_5H_4PPh_2)_2$	La		complex with THF: colorless, X-ray, NMR, MS[203]
$(C_5H_5)Ln[C_5H_4(CH_2)_5C_5H_4]$	Y		complex with THF: white, IR, NMR, melt./dec.[204]
$(C_5H_5)Ln[(C_5H_4CH_2CH_2)_2O]$	Y		colorless, NMR, IR, MS, melt./dec.[93,205]
	Nd		blue, IR, MS, melt./dec.[205]
	Gd		pale yellow, IR, MS, melt./dec.[205]
	Ho		pale yellow[93]
	Er		pink, IR, MS, melt./dec.[205]
	Yb		dark green, IR, MS, melt./dec.[205]
	Lu		white, NMR, IR, MS, melt./dec.[205]
$(MeC_5H_4)Ln[(C_5H_4CH_2CH_2)_2O]$	Y		white, NMR, IR, MS, melt./dec.[93,205]
	Ho		yellow[93]
	Yb		dark green, IR, MS, melt./dec.[205]
$[(C_5Me_5)_2Ln]_2(\mu\text{-}C_5H_5)$	Sm	**18h**	brown, X-ray, NMR, IR, magn. d.[202a]
$Me_2Si(C_5H_3Bu^t)_2LnC_5HMe_4$	La		complex with THF: yellowish, X-ray, NMR, MS, melt./dec.[200b]
	Nd		complex with THF: blue, MS, melt./dec.[200b]
$Me_2Si(C_5Me_4)(C_5H_3Bu^t)Ln(C_5MHMe_4)(THF)$	La		colorless, X-ray, NMR, MS, melt./dec.[705]
	Nd		colorless, NMR, MS, melt./dec.[705]
$[Me_2Si(C_5H_4)_2]_3Ln_2$	Yb		green, IR, UV[550]
$[2,6\text{-}(CH_2C_5H_4)_2C_5H_3N]_3Ln_2$	Pr		yellow, NMR[707]
$(C_7H_{11})_3Ln$	Nd	**19f**	green, X-ray, NMR, IR;[206a] reactions[706]
	Sm	**19h**	pink, NMR, reactions[706]
	Gd	**19k**	X-ray [206b]
	Lu	**19r**	orange, X-ray, NMR, melt./dec.[207]

$(C_5H_4PPh_2O)(OPPh_3)$,[202b] and $(C_5H_5)La(C_5H_4PPh_2)_2$.[203] The X-ray structure of the Yb(III) complex indicates that the ytterbium atom is eight coordinate with two η^5-bonded cyclopentadienyl groups and the oxygen atoms of Ph_3PO and the $OPPh_2C_5H_4$ ligands are bound to Yb rather than 10 coordinate with three η^5-bonded cyclopentadienyl groups and one oxygen of Ph_3PO.[202b] The latter bidentate, monomeric lanthanum complex (Figure 11) is obtained by reaction of $LaCl_3$ with the thallium salt, $TlC_5H_4PPh_2$, in THF followed by subsequent treatment with NaC_5H_5 (eq 10):



(10)

Finally, mention should made of the lanthanum and neodymium derivatives of $Me_2Si(C_5Me_4)(C_5H_3\text{-}{}^tBu)Ln(C_5HMe_4)(THF)$ in which three different cyclopentadienyl ligands, two of them connected via a Me2Si bridge, are bonded to a lanthanide metal,[705] to the dinuclear ytterbium complex $[Me_2Si(C_5H_4)_2]_3Yb_2$,[550] the dinuclear praseodymium complex $[2,6\text{-}(CH_2C_5H_4)_2C_5H_3N]_3Pr_2$,[707] and to organolanthanide compounds with three 2,4-diethylenedienyl ligands, often named "open-Cp ligands". Reaction of $NdCl_3$ or $LuCl_3$ with 3 equiv of potassium 2,4-dimethylpentadienide yields $(C_7H_{11})_3Nd$ (**19f**)[206a] or the corresponding lutetium derivative (**19r**),[207] respectively. Variable-temperature NMR spectroscopy shows that **19f** is fluxional in solution, whereas the solid-state structure of $(\eta^3\text{-}C_7H_{11})Lu(\eta^5\text{-}C_7H_{11})_2$ (Figure 12) exhibits two different sets of ligands in contrast to the structure of **19f** which has three identical pentadienyl ligands. **19f** reacts with $NdCl_3$ in THF yielding $(C_7H_{11})NdCl_2$.[209] The X-ray structural analysis of the gadolinium derivative **19k** has also been done.[206b]

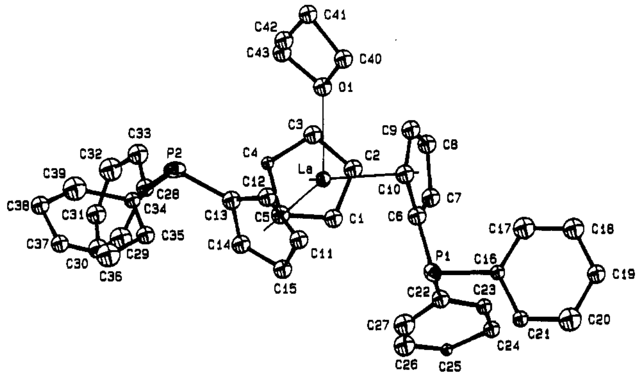


Figure 11. Structure of $(C_5H_5)La(C_5H_4PPh_2)_2(THF)$ in the crystal.[203]

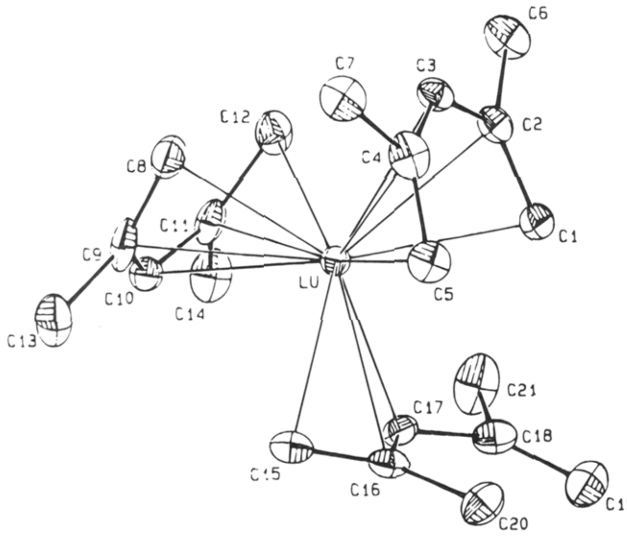


Figure 12. Structure of $(C_7H_{11})_3Lu$ (**19r**) in the crystal.[207]

B. Bis(cyclopentadienyl) Rare Earth Complexes

1. Bis(cyclopentadienyl) Rare Earth Halides and Pseudo Halides

a. Cyclopentadienyl Derivatives. The rapid development of organolanthanide complexes with η^1-bonded ligands was only possible when the bis(cyclopentadienyl)lanthanide halides became available. In 1963 Dubeck et al.[155] reported on the synthesis of a number of thermally stable, but air-sensitive, bis(cyclopentadienyl)lanthanide chlorides. Although a couple of different synthetic approaches[84,155,210] have been proposed since then, the direct synthesis from $LnCl_3$ and NaC_5H_5 (eq 11) or the comproportionation reaction between $LnCl_3$ and $Ln(C_5H_5)_3$ (eq 12) in THF are the most useful.

$$LnCl_3 + 2NaC_5H_5 \xrightarrow{THF} \underset{\mathbf{20}}{(C_5H_5)_2LnCl} + 2NaCl \quad (11)$$

$$LnCl_3 + 2Ln(C_5H_5)_3 \xrightarrow{THF} \underset{\mathbf{20}}{3(C_5H_5)_2LnCl} \quad (12)$$

Although reactions 11 and 12 appear to be quite general, it was already noted that the lanthanides with large ionic radii (La through Nd) failed to give isolable compounds. Due to the fundamental importance of the complexes **20**, single-crystal X-ray structure determinations of $(C_5H_5)_2LnCl$ with Ln = Sc (**20a**),[211,212] Gd (**20k**),[213] Dy (**20m**),[214] Ho (**20n**),[249a] Er (**20o**),[215] Yb (**20q**),[216,217] and Lu (**20r**)[707] have been described. From ebulliometric measurements, it was known that these two ring compounds are dimeric in benzene and monomeric in THF. **20a** was the first complex of this series to be structurally characterized, and it consists of well-separated dimers, in which two $(C_5H_5)_2Sc^+$-units are symmetrically bridged by two chloride ions, as shown in Figure 13.

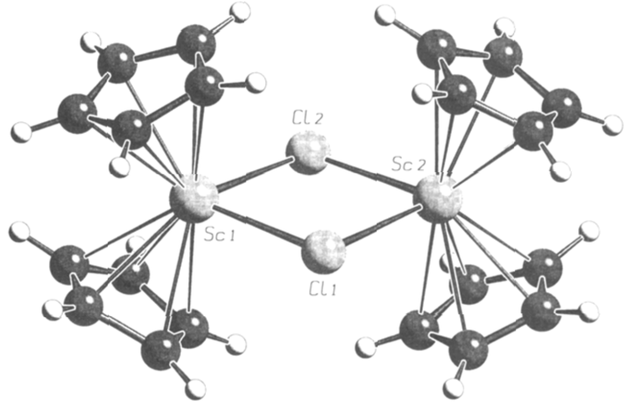


Figure 13. Structure of $[(C_5H_5)_2ScCl]_2$ (**20a**) in the crystal.[211,212]

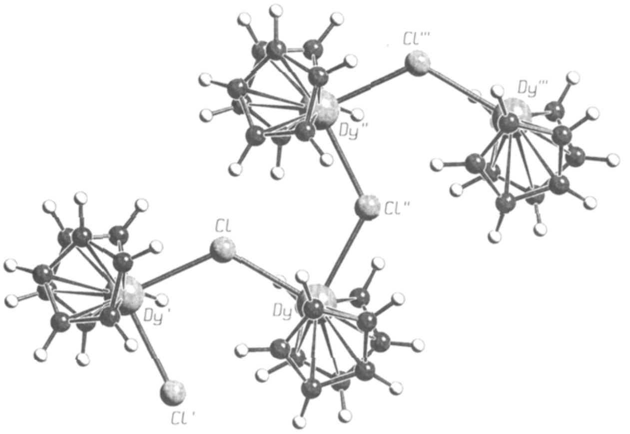


Figure 14. Structure of $[(C_5H_5)_2DyCl]_2$ (**20m**) in the crystal.[214]

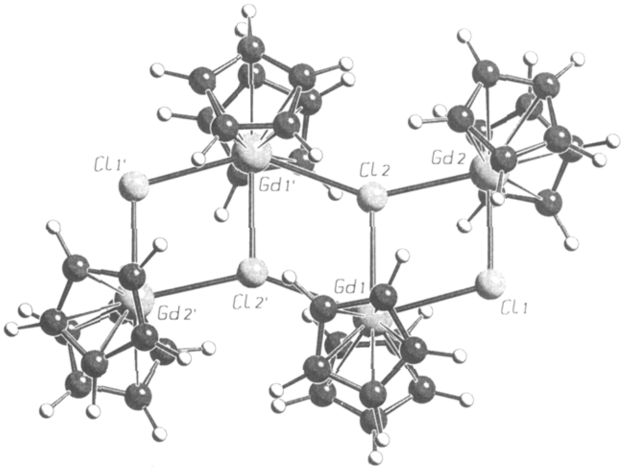


Figure 15. Structure of $[(C_5H_5)_2GdCl]_4$ (**20k**) in the crystal.[213]

Isolated dimers have also been found for the erbium and ytterbium complexes **20o** and **20q.** However, a structural change is observed on going to the lanthanide ions with larger ionic radii. Thus, the dysprosium complex **20m** is made up of infinite double chains (Figure 14), in which each chloride ion bridges two Dy^{3+} ions, whereas the gadolinium complex **20k** consists of tetramers $[(C_5H_5)_2GdCl]_4$ (Figure 15).

While the coordination environment of each Dy^{3+} in **20m** is identical throughout the crystal, two

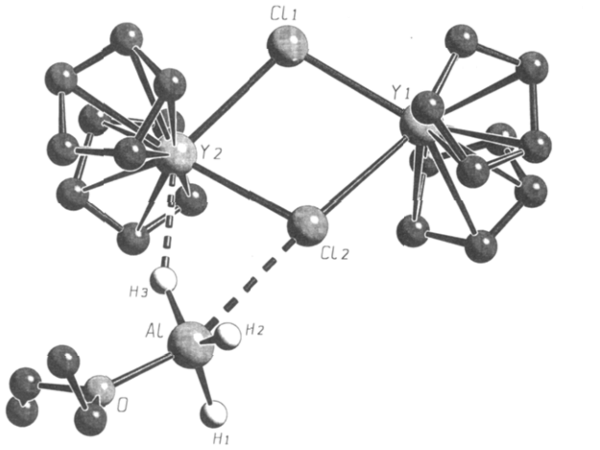


Figure 16. Structure of $[(C_5H_5)_2YCl]_2(AlH_3)(OEt_2)$ in the crystal.[219a]

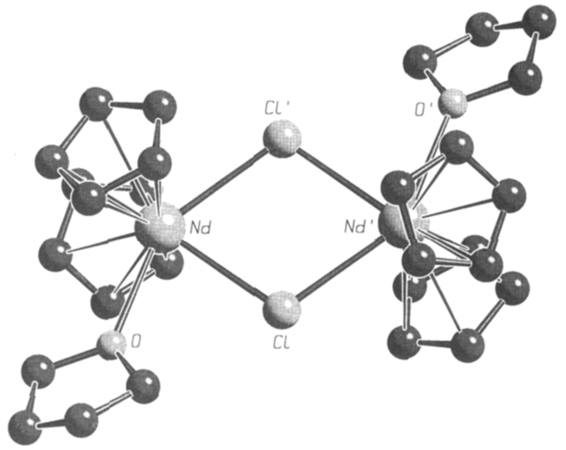


Figure 17. Structure of $[(C_5H_5)_2NdCl(THF)]_2$ (**21f**) in the crystal.[220a]

nonequivalent species of Gd^{3+} exist in **20k** with formal coordination numbers of eight and nine.

Although Lewis bases readily cleave the $[(C_5H_5)_2LnCl]_2$ dimers (*vide infra*) three reports on the reaction of Lewis bases with **20b**[218,219] or **20f**,[151] show that the dimeric structure of **20** is retained. **20b** reacts in Et_2O or benzene with $AlH_3{\cdot}OEt_2$ and $AlH_3{\cdot}NEt_3$ to form $[(C_5H_5)_2YCl]_2{\cdot}AlH_3{\cdot}OEt_2$[218] and $[(C_5H_5)_2YCl]_2{\cdot}2(AlH_3{\cdot}NEt_3)$,[219] respectively. X-ray structure studies revealed, in both cases, unaltered $[(C_5H_5)_2YCl]_2$ dimers in which the Y^{3+} centers bind either one or two additional molecules of $AlH_3{\cdot}OEt_2$ or $AlH_3{\cdot}NEt_3$ presumably via Al−H−Y bonds (Figure 16).

The tendency of the bigger lanthanide ions to adopt higher coordination numbers is reflected in the recently elucidated structures of $[(C_5H_5)_2NdCl(THF)]_2$ (**21f**)[145,151,220a] (Figure 17) and $[(C_5H_5)_2ErCl(THF)]_2$ (**21o**).[220b] Both Ln^{3+} ions reside in the center of a distorted trigonal bipyramid. The stability of **21f** may provide an explanation for the observation that solvent-free bis(cyclopentadienyl)lanthanide chlorides have only been obtained from Sm through Lu.

Although the bis(cyclopentadienyl)lanthanide chlorides greatly outnumber the corresponding fluorides, bromides, and iodides, some complexes of the type $[(C_5H_5)_2LnBr]_2$ with Ln = Sm (**22h**),[80] Gd (**22k**),[221] Dy (**22m**),[222] Er (**22o**),[222] and Yb (**22q**)[216,217,223] have been prepared. The latter compounds have been obtained from stoichiometric reactions similar to eq 11, except that $LnBr_3$ rather than $LnCl_3$ is used. Structural data are available for all compounds mentioned above except for **22h**. It is interesting to note that almost all bis(cyclopentadienyl)lanthanide bromide complexes that have been structurally characterized so far belong to the $[(C_5H_5)_2ScCl]_2$-type structure. However, two solid-state structures have been found for the gadolinium complex **22k**. Sublimation at 130 °C afforded spherical crystals of $[(C_5H_5)_2GdBr]_2$ which belonged to the $[(C_5H_5)_2ScCl]_2$-type structure, but at 150 °C, needle-shaped crystals were obtained. An X-ray diffraction study of these needles revealed a polymeric structure which is reminiscent of the double chains found in **20m**. The existence of two crystalline modifications of **22k** can be explained by the temperature dependence of the gaseous phase equilibrium between dimeric and monomeric molecules as indicated in eq 13. Below 130 °C the concentration of $[(C_5H_5)_2GdBr]_2$ in the gas phase is higher than that of monomeric $(C_5H_5)_2GdBr$, leading to the formation of crystals that are made up of isolated dimers. As the temperature is raised to 150 °C, the concentration of $(C_5H_5)_2GdBr$ increases which in turn favors the formation of infinite chains of $[(C_5H_5)_2GdBr]_x$ upon cooling to room temperature. The latter considerations are based upon qualitative and quantitative results of the fragment ions in the mass spectra, which have been recorded at various ion-source temperatures.[221]

$$[(C_5H_5)_2GdBr]_2 \underset{130\ ^\circ C}{\overset{150\ ^\circ C}{\rightleftharpoons}} 2(C_5H_5)_2GdBr \qquad (13)$$

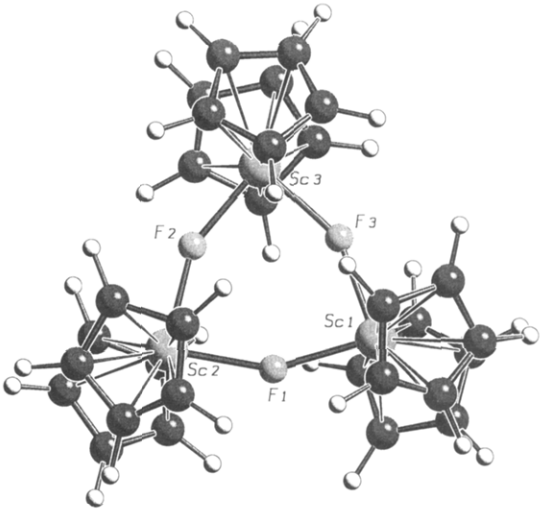


Figure 18. Structure of $[(C_5H_5)_2ScF]_3$ in the crystal.[20]

To date, only one example of a bis(cyclopentadienyl) rare earth fluoride has been reported. $[(C_5H_5)_2ScF]_3$ (Figure 18) was isolated from the reaction of ScF_3 with excess $Na(C_5H_5)$ which was originally designed to produce $Sc(C_5H_5)_3$.[20]

In contrast, the three known solvent-free bis(cyclopentadienyl)lanthanide iodides $[(C_5H_5)_2LnI]_2$ (Ln = Sm (**23h**),[80] Er (**23o**),[155] and Yb (**23q**)[223]) have been reported but they are poorly characterized. There are also only two cyanide complexes in the

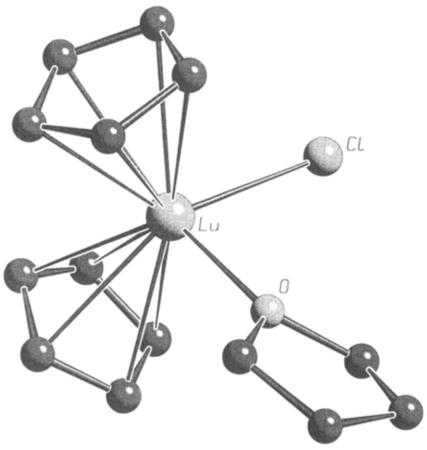


Figure 19. Structure of $(C_5H_5)_2LuCl(THF)$ (**21r**) in the crystal.[230]

literature $(C_5H_5)_2NdCN$ and $(C_5H_5)_2YbCN$ which were synthesized from the corresponding **1** and liquid HCN in benzene.[224]

Monomeric THF adducts of the type $(C_5H_5)_2LnCl(THF)$ (**21**) are best prepared by dissolving **20** in THF followed by subsequent crystallization. However, only $(C_5H_5)_2LnCl(THF)$ with Ln = Sc (**21a**),[225] Y (**21b**),[226] Nd (**21f**),[227] Eu (**21i**),[23c] Gd (**21k**),[228] Yb (**21q**),[229] and Lu (**21r**)[230] have been studied in detail. These compounds are remarkably thermally stable and are reported to sublime under reduced pressure without loosing the coordinated THF. A single-crystal diffraction study of **21r** revealed the expected structure (Figure 19).[230] Both cyclopentadienyl rings are η^5-bound to the Lu^{3+} ion and the centroids of the cyclopentadienyl rings, the Cl^- ion and the oxygen atom of the THF molecule define a polyhedron around lutetium which is often referred to as a pseudo or distorted tetrahedron, a structure type that is common in organolanthanide chemistry and it will be encountered in a variety of complexes with formally eight-coordinate lanthanide ions.

The coordinated THF in the above-mentioned complexes, as well as that of $(C_5H_5)_2LuBr(THF)$,[231] can be readily displaced by a variety of Lewis bases such as MeCN,[124] ${}^cC_6H_{11}NC$,[124] $4\text{-}MeC_6H_4CN$,[124] bipy,[232] or phen.[123] Using DME as a solvent and omitting the sublimation step in the work-up procedure, Schumann et al. obtained alkali chloride-stabilized bis(cyclopentadienyl)lanthanide chlorides of the general formula $(C_5H_5)_2Ln(\mu\text{-}Cl)_2Na(DME)_n$ of nearly all rare earth metals (eq 14).[153,233]

$$LnCl_3 + 2NaC_5H_5 \xrightarrow{DME} (C_5H_5)_2Ln(\mu\text{-}Cl)_2Na(DME)_n + NaCl \quad (14)$$

Ln = Sm, Gd, Dy, Er, Yb, Lu ($n = 1$);
Ho, Lu ($n = 2$)

Finally the bimetallic complex $(C_5H_5)_2Y(\mu\text{-}Cl)_2Al(CH_3)_2$,[234] the zwitterionic compound $(C_5H_5)_2Lu(Cl)(CH_2PPh_3)$,[235] $(C_5H_5)_2LuBr(PhCH_2NH_2)_n$ ($n = 1, 2$),[231] as well as an anionic iodide complex thought to have the composition $[Na(THF)_4][(C_5H_5)_2CeI_2]$,[109] have been described. References for bis(cyclopentadienyl)lanthanide halides and pseudohalides are given in Table 4.

b. Pentamethylcyclopentadienyl Derivatives. It should be pointed out that much of the recent success in the synthesis of highly reactive organolanthanide species can be attributed to the favorable chemical properties of complexes with a bis(pentamethylcyclopentadienyl) ligand environment. These compounds usually have high solubilities in nonpolar solvents, crystallize well, and are stable toward ligand redistribution due to the size of the pentamethylcyclopentadienyl ligand. Within the bis(pentamethylcyclopentadienyl)lanthanide halide series, the majority of complexes are organolanthanide chlorides.

Very recently, however, a number of fluoride complexes have been isolated and most of them structurally characterized. The base-free complexes $(C_5Me_5)_2Yb(\mu\text{-}F)Yb(C_5Me_5)_2$ (**24q**),[262] $(C_5Me_5)_6Yb_4F_4$ (**25q**),[262,263] and $(C_5Me_5)_6Yb_5F_9$ (**26q**)[264] show unexpected and unprecedented structures. Not surprisingly, none of them had been prepared from LnF_3 since the trifluorides of the lanthanides are commonly regarded as being too insoluble, even in polar solvents, and therefore too unreactive toward organo alkali reagents. A very elegant way of forming lanthanide–element bonds has been described for the bivalent lanthanides (notably Sm, Eu, and Yb) which utilizes the reduction potential of organolanthanide(II) complexes. Thus, $(C_5Me_5)_2Yb$ reacts with C_6F_6 in toluene (eq 15) to form two paramagnetic mixed-valence complexes which were identified as **24q** and **25q** by X-ray crystallography.

$$\text{“}(C_5Me_5)_2Yb + C_6F_6\text{”} \xrightarrow{PhMe} \underset{\mathbf{24q}}{[(C_5Me_5)_2Yb]_2(\mu\text{-}F)} + \underset{\mathbf{25q}}{(C_5Me_5)_6Yb_4F_4} \quad (15)$$

The molecular structure of **24q** (Figure 20) shows a crystallographically constrained linear Yb(2)···F–Yb(1) unit in which each Yb atom is surrounded by four η^5-bound (C_5Me_5) rings oriented so as to minimize intramolecular steric repulsion. This geometry (the centroids of the rings define a tetrahedron) is very typical for homobimetallic bis(pentamethylcyclopentadienyl)lanthanide complexes and appears to be independent on the nature of the additional ligands that are attached to the lanthanide ion. The bridging fluoride ion is closer to Yb(2) (208.4(2) pm) than to Yb(1) (231.7(2) pm) which allows the assignment of Yb(2) as Yb^{3+} and Yb(1) as Yb^{2+}. Thus **24q** can be regarded as being composed of two distinct fragments, namely $(C_5Me_5)_2Yb^{III}F$ and $(C_5Me_5)_2Yb^{II}$. This trapped-valence formulation is supported by results from variable-temperature measurements of the magnetic susceptibility which showed no indication of spin coupling.

The paramagnetic compound **25q** can be obtained either by heating **24q** or oxidizing $(C_5Me_5)_2Yb$ with AgF. The crystal structure of **25q** (Figure 21) consists of a regularly arranged cyclic set of two $(C_5Me_5)_2Yb^{III}F$ and two $(C_5Me_5)Yb^{II}F$ fragments which is held together by four fluoride bridges. While the

Table 4. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Halides and Pseudohalides

complex	Ln		color, characterization, etc.
$(C_5H_5)_2LnF$	Sc		orange, X-ray, NMR, IR, MS;[20] complex with $CN^{c}C_6H_{11}$[124]
$(C_5H_5)_2LnCl$	Sc	**20a**	green-yellow,[236] X-ray,[211,212] PE,[237] NMR,[41,236] melt./dec.;[236] complex with THF (**21a**)[225]
	Y	**20b**	colorless,[238] NMR,[204,220d,239,240] PE,[186,241,242,243] MS;[220e] X-ray of complex with AlH_3 and Et_2O,[218,219a] AlH_3 and NEt_3;[219b] complex with THF (**21b**);[226] complex with Me_2AlCl[234]
	La	**20c**	complex with 2phen[123]
	Ce	**20d**	complex with 2phen[123]
	Pr	**20e**	complex with 2phen[123]
	Nd	**20f**	green;[227] complex with THF (**21f**): PE,[220c] X-ray;[145,151,220a,227] complex with phen and 2phen;[123] reactions[244]
	Sm	**20h**	yellow,[153,155,210] UV,[84] MS,[80] lumines.[245] magn. d.,[155] melt./dec.;[55] complex with MeCN;[124] complex with NaCl(DME);[153] reactions[171,246,247,248]
	Eu	**20i**	complex with THF: violet, NMR[23c]
	Gd	**20k**	colorless,[155] X-ray,[213] IR,[83] PE,[81,186] MS,[220e] XPS,[232,241,242] magn. d.,[155,228] complex with THF (**21k**),[228] bipy,[232] NaCl(DME)[153]
	Tb	**20l**	brownish,[153] MS,[220e] reaction;[249a] complex with NaCl(DME)[153]
	Dy	**20m**	yellow,[155] X-ray,[214] MS,[220e] XPS,[232] magn. d.,[155] melt./dec.,[155] reactions;[246] complex with bipy,[232] NaCl(DME)[153]
	Ho	**20n**	yellow,[155] X-ray,[249b] IR,[83] MS,[220e] XPS,[232,241,242] magn. d.,[155,250] melt./dec.,[155] reactions,[171,246] complex with bipy,[232] MeCN,[124] $NaCl(DME)_2$[153]
	Er	**20o**	pink,[155] X-ray,[215,220b] IR,[83,232,250] MS,[220e] XPS,[232,241,242] magn. d.,[155] melt./dec.,[155] reactions,[246] MOCVD;[175] complex with THF (**21o**),[220b] bipy,[232] phen,[123] NaCl(DME)[153]
	Tm	**20p**	yellow,[238] UV,[84] melt./dec.,[238] reactions;[171] complex with NaCl(DME)[153]
	Yb	**20q**	yellow,[210,251] orange,[155,223,113] X-ray,[216,217] IR,[83] UV,[84] NMR,[65,85] XPS,[232,241,242] MS,[67,220e] magn. d.,[155,216,228] melt./dec.,[155] reactions;[173,246,252] complex with THF (**21q**),[111,228,229,253] bipy,[232] $CN^{c}C_6H_{11}$,[124] CNC_6H_4Me-4,[124] NaCl(DME)[153]
	Lu	**20r**	white,[155] X-ray,[708] IR,[155] NMR,[204,220d] MS,[220e] XPS,[232,241] melt./dec.,[155] reactions;[173,252,254–257,481] complex with THF (**21r**)[111,149,175,230,258] (X-ray[230]), bipy,[232] NaCl(DME),[153] NaCl(DME)[2,233] Ph_3PCH_2[235]
$(C_5H_5)_2LnBr$	Sm	**22h**	brown, IR, MS,[80] magn. d.[259]
	Gd	**22k**	X-ray,[221] magn. d.[259,260]
	Dy	**22m**	X-ray,[222] magn. d.[259]
	Er	**22o**	X-ray, magn. d.[223]
	Yb	**22q**	orange red,[223] X-ray,[216,217] magn. d.;[216] complex with THF,[261] $NC^{c}C_6H_{11}$[124]
	Lu	**22r**	complex with THF, $PhCH_2NH_2$, $2PhCH_2NH_2$ (X-ray)[231]
$(C_5H_5)_2LnI$	La	**23c**	complex with THF: NMR[146c]
	Ce	**23d**	complex with $NaI(THF)_4$: brown red, magn. d.[109]
	Sm	**23h**	black, IR, MS[80]
	Er	**23o**	pink, melt./dec.[155]
	Yb	**23q**	synthesis[223]
$(C_5H_5)_2LnCN$	Nd		light blue, IR[224]
	Yb		yellow, IR[224]
$(C_5H_5)_2LnNCS$	Yb		complex with MeCN: IR[550]

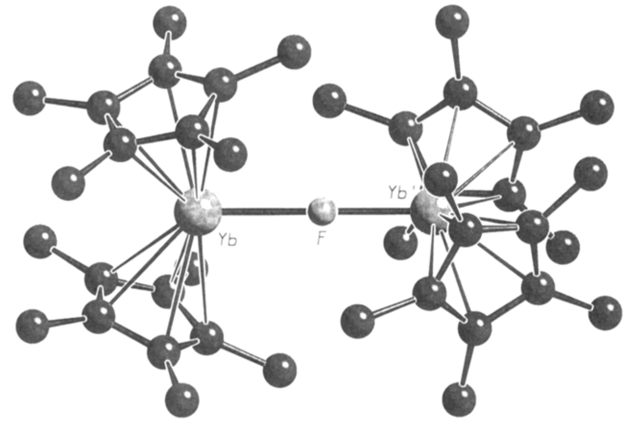


Figure 20. Structure of $(C_5Me_5)_2Yb(\mu\text{-}F)Yb(C_5Me_5)_2$ (**24q**) in the crystal.[262]

coordination geometry of the trivalent ytterbium ions is very common and resembles a distorted tetrahedron, the bivalent ytterbium atoms reside in the center of a trigonal planar ligand array. The exceptional stability of **25q** is reflected both by the fact that **24q** thermally decomposes to form **25q** and the observation that **25q** is formed exclusively, even when a 4-fold excess of AgF is used. Although **24q** and **25q** display nearly linear μ_2-fluoride bridges, much more complex structures with μ_2-, μ_3-, and μ_4-fluoride bridges are known. The cluster complex **26q** was identified as the reaction product of $(C_5Me_5)_2Yb(Et_2O)$ and perfluoro olefins (eq 16):[264]

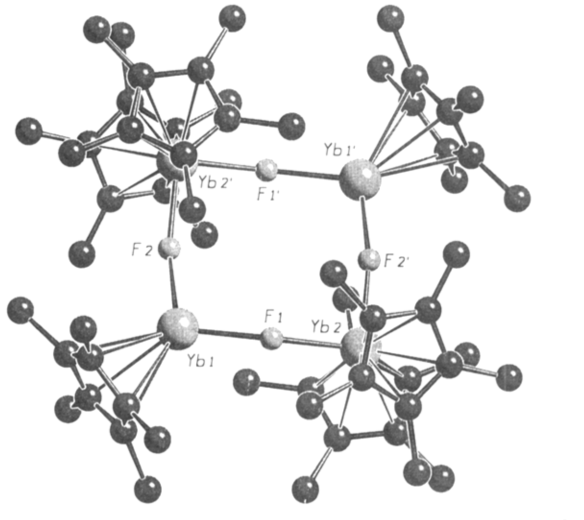


Figure 21. Structure of $(C_5Me_5)_6Yb_4F_4$ (**25q**) in the crystal.[263]

$$\text{“}(C_5Me_5)_2Yb(Et_2O) + C_9F_{18}\text{”} \xrightarrow{PhMe} \underset{\mathbf{26q}}{(C_5Me_5)_6Yb_5F_9} \quad (16)$$

Unlike **24q** and **25q**, the product of eq 16, **26q**, has all of its ytterbium's trivalent.[264] It is evident from

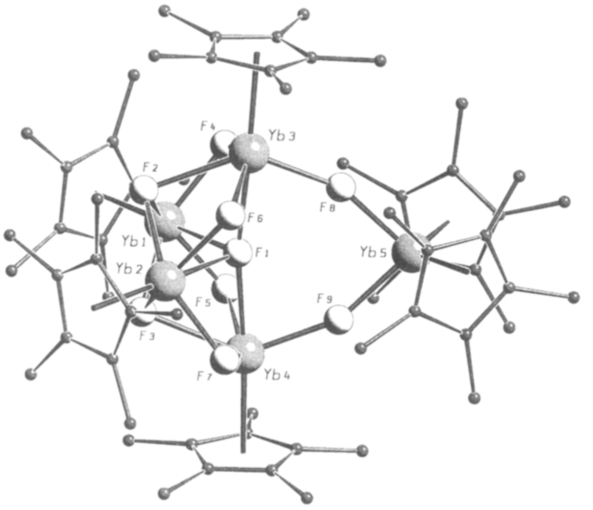


Figure 22. Structure of $(C_5Me_5)_6Yb_5F_9(PhMe)$ (**26q**) in the crystal.[264]

Figure 22, that **26q** is composed of one $(C_5Me_5)_2Yb(\mu\text{-}F)$ and four $(C_5Me_5)Yb(\mu\text{-}F)_2$ units. The former can be regarded as a bis(pentamethylcyclopentadienyl)ytterbium fluoride, having normal bond distances and displaying the common pseudo-tetrahedral geometry.

When the reaction shown in eq 16 is carried out in diethyl ether, solvated organolanthanides are obtained which exhibit much simpler monomeric structures.

$$\text{“}(C_5Me_5)_2Yb(Et_2O) + C_9F_{18}\text{”} \xrightarrow{Et_2O} (C_5Me_5)_2YbF(Et_2O) \quad (17)$$

The X-ray structure analysis of the bent sandwich compounds $(C_5Me_5)_2YbF(Et_2O)$[264] and $(C_5Me_5)_2YbF(THF)$[264] established the first terminal ytterbium–fluoride bond distances of 202.6(2) and 201.5(4) pm, respectively.

In contrast to bis(cyclopentadienyl)lanthanide chlorides, much less effort has been made to prepare solvent-free bis(pentamethylcyclopentadienyl)lanthanide derivatives. However $[(C_5Me_5)_2LnCl]_x$ with Ln = Sc, $x = 1$ (**27a**),[265] Y, $x = 2$ (**27b**),[266] Ce, $x = n$ (**27d**),[267] Pr, $x = n$ (**27e**)[268] and Sm, $x = n$ (**27h**)[269] have been synthesized and characterized (eqs 18 and 19). In general, heating solvated or alkali halide stabilized complexes under reduced pressure affords the desired unsolvated complexes which may be purified by sublimation or by recrystallization from toluene.

$$(C_5Me_5)_2LnCl(THF) \xrightarrow[10^{-4}-10^{-5}\ \text{Torr}]{90-120\ ^\circ\text{C}} \underset{\mathbf{27}}{1/x[(C_5Me_5)_2LnCl]_x} + THF \quad (18)$$

$$(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li{\cdot}(THF)_2 \xrightarrow[4\times10^{-5}\ \text{Torr}]{285\ ^\circ\text{C}} \underset{\mathbf{27}}{1/x[(C_5Me_5)_2LnCl]_x} + LiCl + 2THF \quad (19)$$

The scandium complex **27a** is monomeric by cryoscopy,[265] which is in marked contrast to the dimeric parent compound $[(C_5H_5)_2ScCl]_2$ (**20a**). Likewise, the X-ray structures of **27b** (Figure 23)[266] and **27h** (Figure 24)[269] revealed an unsymmetrically bridged dimer and a nearly symmetrical trimer, respectively. Presumably these intriguing structural changes can be ascribed to the steric demand of two bulky pentamethylcyclopentadienyl ligands and to markedly different ionic radii of eight-coordinate Y^{3+} ($r = 101.9$ pm) and Sm^{3+} ($r = 107.9$ pm). Both of the pentamethylcyclopentadienyl rings in **27b** coordinate to the yttrium ions in an η^5-fashion at normal bond distances, and their relative orientation is apparently governed by the necessity to minimize mutual steric repulsion. Thus, the averaged magnitudes of the torsion angles between the centroids of the cyclopentadienyl rings and the yttrium atoms $\langle|\tau|\rangle$ $\{\tau_{ij}(C_{ni}-Y(1)-Y(2)-C_{nj})$ with $i = 1, 2; j = 3, 4\}$ is close to 90° compared to $\langle|\tau|\rangle = 0°$ in **20a**. As it is evident from Figure 23, Y(2) is only attached to the bridging chlorine ion Cl(1), whereas Y(1) binds to Cl(1) and to Cl(2). Despite large differences in the electronic structure of yttrium and ytterbium, the similarities between **27b** and **24q** are very striking, as far as the relative orientation of the cyclopentadienyl ligands or the asymmetric halide bridge is concerned. Although it might be argued that there is sufficient space for only one bridging atom in **27b**, theoretical molecular orbital studies of $(C_5H_5)_2Ln^+$ ions[270] indicate that additional ligands (such as another hypothetical bridging ligand) can only bind to the lanthanide center within the equatorial girdle that bisects the $C_{n1}-C_{n2}$ vector. An interaction between the seven-coordinate atom Y(2) and Cl(2) seems unlikely.

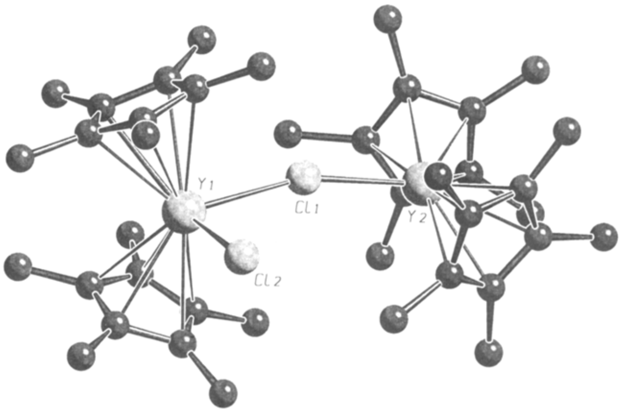


Figure 23. Structure of $(C_5Me_5)_2Y(\mu\text{-}Cl)Y(Cl)(C_5Me_5)_2$ (**27b**) in the crystal.[266]

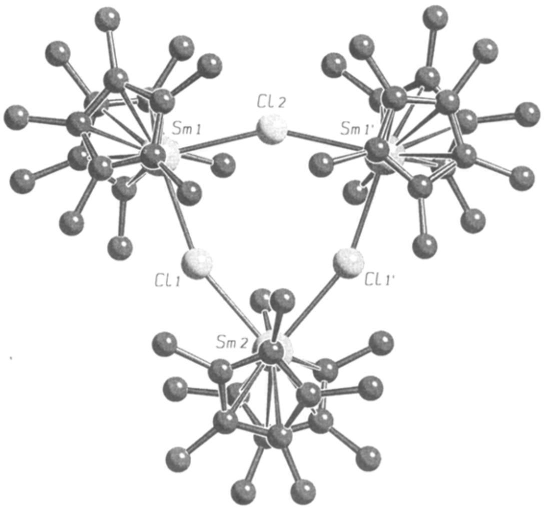


Figure 24. Structure of $[(C_5Me_5)_2SmCl]_3$ (**27h**) in the crystal.[269]

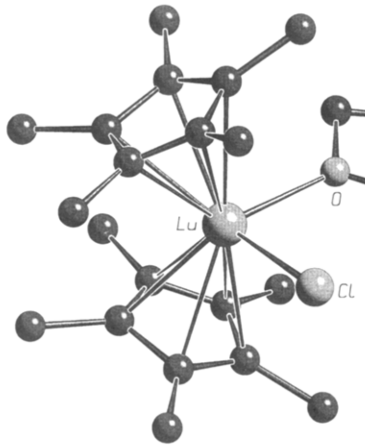


Figure 25. Structure of $(C_5Me_5)_2LuCl(THF)$ (**28r**) in the crystal.[283]

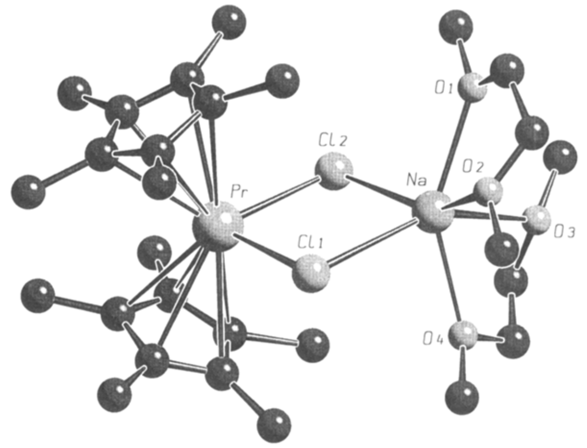


Figure 26. Structure of $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(DME)_2$ in the crystal.[268,294]

The fact that the analogous bis(pentamethylcyclopentadienyl)samarium chloride (**27h**) (Figure 24) forms a regular trimer with three slightly bent Cl bridges and eight-coordinate samarium ions as opposed to dimeric **27b** can be rationalized by considering electronic and steric factors. On the one hand, the cyclic arrangement provides for a maximum number of anionic ligands around each samarium ion which is desirable for electrostatic reasons. On the other hand, the elongated Sm–(μ-Cl) bond distances (av 288(2) pm compared to 276(1) pm in the related anion $[(C_5Me_5)_2(Cl)Sm(\mu\text{-}Cl)Sm(Cl)(C_5Me_5)_2]^-$)[269] strongly suggest that steric repulsion play an important role. The question, however, as to why **27h** adopts a trimeric rather than dimeric structure (for instance that of the $[(C_5H_5)_2ScCl]_2$ type) is unknown.

Comparable bromides and iodides, i.e. $(C_5Me_5)_2SmBr$,[271] $(C_5Me_5)_2LnI$, Ln = Sc,[265,272] Ce,[273] and Sm[271] have been prepared but no structural information is available. In the case of $(C_5Me_5)_2SmI$, the absolute bond disruption enthalpy of the Sm–I bond has been measured.[271]

Despite steric crowding in bis(pentamethylcyclopentadienyl)lanthanide derivatives, the lanthanide ion is still capable of binding a variety of Lewis bases. Monomeric THF adducts of the general formula $(C_5Me_5)_2LnCl(THF)$ with Ln = Sc (**28a**),[272] Y (**28b**),[274–278] Ce (**28d**),[279] Nd (**28f**),[280] Sm (**28h**),[276] Ho (**28n**),[281] Yb (**28q**),[280,282] and Lu (**28r**)[283] have been prepared and most of them have been structurally characterized. They are all similar to the lutetium complex **28r** (Figure 25), in which the lutetium atom is tetrahedral.

The existence of a dynamic equilibrium between free and coordinated THF with a barrier to exchange of 54 kJ/mol at 0 °C has been shown by variable temperature NMR spectroscopy[283] and THF can be readily replaced by other Lewis bases. In particular, bis(pentamethylcyclopentadienyl)lanthanide halides and pseudo halides react with THF, Et_2O,[264,285,286,287] acetone,[277] $Me(OCH_2CH_2)_4OMe$,[269] pyridine,[277,280] MeCN,[289] ^tBuNC,[284,291] $Me_2PCH_2PMe_2$,[288] and 1,5-pentamethylenetetrazol [290] yielding 1:1 complexes.

In 1980, Wayda and Evans[292] showed that two pentamethylcyclopentadienyl ligands were able to stabilize lanthanide ions which were as large as Nd^{3+} (r = 110.9 pm). The reaction of $NdCl_3$ and two equivalents of LiC_5Me_5 in THF afforded a blue, pentane soluble complex of proposed formula $(C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(THF)_2$. In ensuing years alkali halide-stabilized bis(pentamethylcyclopentadienyl)lanthanide halides of virtually all of the rare earth elements have been prepared (eq 20):

$$2MC_5Me_5 + LnCl_3 \xrightarrow{\text{solvent}} (C_5Me_5)_2Ln(\mu\text{-}Cl)_2M(S)_x + MCl \quad (20)$$

$M = Li, Na, K; S = THF, Et_2O, DME, tmed;$
$x = 1 \text{ or } 2$

Single-crystal X-ray structures show the yellow $(C_5Me_5)_2Ce(\mu\text{-}Cl)_2Li(OEt_2)_2$,[293] the green $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(DME)_2$,[268,294] (Figure 26) and the dark purple $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ [288] have structures in which the two halogens bridge between the lanthanide and the alkali metal. Similar complexes with M = Mg[295] or Al,[277,282] as well as some iodides,[282,289] have also been prepared and characterized. In general, the majority of bis(pentamethylcyclopentadienyl)lanthanide halides form anionic complexes with coordination of 1 equiv of alkali halide. The reason for their formation, in competition with neutral solvent adducts like e.g. **28** under virtually the same reaction conditions, is not fully understood but demonstrates the ability of the lanthanide ions to tolerate different types of ligands in the coordination sphere. Thus, even subtle change in the reaction conditions and in the work-up procedure can result in isolation of different reaction products.

Only two bis(pentamethylcyclopentadienyl)lanthanide cyanides have been reported. According to eq 21 they are formed by reductive cleavage of a CN–R bond by $(C_5Me_5)_2Sm(THF)_2$, generating trimers with bridging cyanide.[291]

$$(C_5Me_5)_2Sm(THF)_2 + \text{excess CNR} \xrightarrow{\text{PhMe}} {}^1/_3[(C_5Me_5)_2Sm(\mu\text{-}CN)(CNR)]_3 \quad (21)$$

$R = {}^cC_6H_{11}, {}^tBu$

A single-crystal X-ray diffraction study of the cyclohexylcyanide complex (Figure 27) establishes the existence of three $(C_5Me_5)_2Sm^{III}(CN^cC_6H_{11})$ fragments connected via $[\mu\text{-}\eta^2\text{-}(CN)]$-bridges; it also shows inclusion of three molecules of toluene per lanthanide fragment in the lattice. In contrast, the *tert*-butyl

Table 5. Spectroscopic and Other Data of Bis(pentamethylcyclopentadienyl)lanthanide Halides and Pseudohalides

complex	*Ln*		*color, characterization, etc.*
$(C_5Me_5)_2LnF$	Eu		complex with Et_2O: orange-red, NMR, IR, UV[264]
	Sm		complex with Et_2O: yellow, NMR, IR, UV,[264] with $BF_3(THF)$: X-ray[296]
	Yb		complex with Et_2O: red-orange,[264,287] X-ray, NMR, IR, UV;[264] with THF: red-orange, X-ray, NMR;[264] with $PF_5(DME)$: purple[297]
$[(C_5Me_5)_2Ln]_2(\mu\text{-}F)$	Yb	**24q**	brown, X-ray, NMR, magn. d.[262]
$(C_5Me_5)_6Ln_4F_4$	Yb	**25q**	orange-red,[262,263] X-ray, melt./dec.[263]
$(C_5Me_5)_6Ln_5F_9$	Yb	**26q**	(+ PhMe): red, X-ray[264]
$(C_5Me_5)_2LnCl$	Sc	**27a**	yellow,[272] NMR, IR,[265] lumines.;[298a,b] complex with THF (**28a**);[265,272] with $(C_5H_5)_2WCO$: NMR[299]
	Y	**27b**	white,[277,278] yellow,[266] X-ray,[266] NMR, IR;[266,277,278] complex with THF (**28b**): white,[275,277,278] yellow,[266,277] X-ray,[276] NMR,[266,274–277] IR;[275,277] with acetone: yellow, NMR, IR;[277] with py: white, NMR, IR;[277] with $MgBr_2(THF)_2$: colorless, IR;[295] with Et_2AlCl: colorless, NMR, IR[277]
	Ce	**27d**	orange, IR,[284] NMR, IR;[145,267] dimer: yellow;[293] complex with THF (**28d**): yellow-orange,[279,284] X-ray,[279] NMR, IR,[279,284] magn. d.,[279] lumines.;[289] with $2CN^tBu$: yellow, NMR, IR[284]
	Pr	**27e**	green, melt./dec.[268]
	Nd	**27f**	complex with THF (**28f**): green,[280,300] IR, melt./dec.[280]
	Sm	**27h**	orange-red, X-ray,[269] NMR, IR;[269,271] complex with Et_2O: orange, NMR, UV;[285] with THF (**28h**): orange, X-ray, NMR[276]
	Ho	**27n**	complex with THF (**28n**): brown, X-ray, MS, melt./dec.[268,281]
	Yb	**27q**	complex with Et_2O: purple, NMR, UV;[286,287] with THF (**28q**): purple,[280,282] X-ray,[301] NMR, IR, UV,[282] lumines.,[302] melt./dec.;[280,282] with py: purple, IR, melt./dec.;[280] with $(Me_2PCH_2PMe_2)$: purple, X-ray, IR, magn. d., melt./dec.;[288] with $AlCl_3$: blue, X-ray, NMR, IR, UV, melt./dec.[282]
	Lu	**27r**	complex with THF (**28r**): X-ray, NMR;[283] with $AlCl_3$: white, NMR[282]
$(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li(LB)$	Y		LB = $2Et_2O$: colorless, NMR, IR;[277] DME: white, NMR, IR;[277] 2THF: X-ray;[303] 3THF: X-ray;[303] tmed: colorless, NMR, IR[272]
	La		LB = $2Et_2O$: white,[304,305] pale yellow,[293] NMR[293,304]
	Ce		LB = $2Et_2O$: yellow,[293,306] X-ray,[293] NMR, IR,[306] lumines.;[61,289,293] 2THF;[273] 2.5THF: yellow, NMR, IR;[284] DME: yellow, NMR, IR;[284] py;[145] tmed: yellow, NMR, IR[284]
	Pr		LB = $2Et_2O$: pale green,[293]
	Nd		LB = $2Et_2O$: blue, IR, melt./dec,[280] catalyst;[307] 2THF: blue, NMR, IR, UV, magn. d.;[292] tmed: blue, IR, melt./dec.[280]
	Sm		LB = $2Et_2O$;[304,308] 2THF: orange, NMR, IR, magn. d.;[276] tmed: yellow, melt./dec.[280]
	Gd		LB = 2THF,[145] IR, melt./dec.[309]
	Yb		green, IR;[282] LB = $2Et_2O$: purple,[280,282,297] X-ray, NMR, IR, UV,[282,297] melt./dec.;[280] tmed: violet, mel./dec.[280]
	Lu		LB = $2Et_2O$: white, NMR, IR, melt./dec.[268,280,310]
$(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Na(LB)$	Y		LB = $2Et_2O$: colorless, NMR, IR;[277] tmed: pale yellow, NMR, IR[277]
	Pr		LB = $2Et_2O$: greenish, NMR, melt./dec.,[268,294] lumines.;[293] 2DME: green, X-ray, NMR, melt./dec.[268,294,310]
	Nd		LB = $2Et_2O$: blue, IR, melt./dec.[280]
	Sm		LB = Et_2O: orange, melt./dec.;[280] tmed: yellow, melt./dec.[280]
	Gd		colorless;[268] LB = $2Et_2O$: colorless, melt./dec.;[268] 2DME: colorless, MS, melt./dec.[268]
	Tb		LB = $2Et_2O$: colorless, melt./dec.;[268] 2DME: colorless, MS, melt./dec.[268]
	Dy		LB = $2Et_2O$: colorless, MS, melt./dec.;[268] 2DME: colorless, MS, melt./dec.[268]
	Ho		LB = 2DME: brown, MS, melt./dec.[268]
	Er		LB = $2Et_2O$: pink, melt./dec.;[268] 2DME: pink, MS, melt./dec.[268]
	Tm		LB = $2Et_2O$: green, melt./dec.;[268] 2DME: green-yellow, MS, melt./dec.[268]
	Yb		LB = $2Et_2O$: purple,[268,280] NMR,[268,310] IR,[280] melt./dec.;[268,280] tmed: violet, melt./dec.[280]
	Lu		LB = 2THF: reaction[146c]
$(C_5Me_5)_2Ln(\mu\text{-}Cl)_2K(LB)$	Y		LB = THF;[266] 2THF: white, NMR[178,266]
	La		LB = $2Et_2O$: colorless, NMR;[294] 2DME: colorless, NMR, melt./dec,[268,294] reactions[446]
	Ce		LB = THF: yellow, X-ray, NMR, magn. d.[279] lumines.,[289] reactions;[440] 2DME: yellow, MS, melt./dec.[268]
	Nd		LB = THF: reactions.[440]
	Sm		LB = THF: reactions.[440,501]
$(C_5Me_5)_{10}Ln_5Cl_5$(tetraglyme)	Sm		orange, X-ray[269]
$(C_5Me_5)_2LnBr$	Sm		reddish rust, NMR, IR[271]
	Yb		complex with THF: NMR[287]
$(C_5Me_5)_2LnI$	Sc		NMR,[265,272] lumines.[298b]
	La		complex with 2NCMe: colorless, NMR[289]
	Ce		polymer,[273] lumines.;[289] complex with THF: orange, NMR, IR,[284] lumines.;[289] with 2NCMe: yellow, X-ray, NMR, IR, lumines.,[289] reactions;[311] with $(C_5H_5)(CO)_3WK(THF)_2$: yellow, NMR, IR, lumines.[289]
	Sm		polymer, purple, NMR, IR;[271] complex with THF: X-ray, NMR, IR, magn. d.,[276] reactions;[271,290] with $C_6H_{10}N_4$: X-ray, NMR, IR[290]
	Yb		complex with THF[287]
$(C_5Me_5)_2Ln(\mu\text{-}I)_2Li(LB)$	Yb		LB = $2Et_2O$: purple, X-ray, NMR, IR, UV[282,297]
	La		LB = 2THF: colorless, NMR[289]
	Ce		LB = 2THF: orange, NMR, lumines.[289]
$[(C_5Me_5)_2Ln]_3(\mu\text{-}CN)_3(LB)_3$	Sm		LB = CN^tBu (+2THF): yellow, X-ray, NMR, IR;[291] $CN^cC_6H_{11}$ (+3toluene): yellow, X-ray, NMR, IR[291]

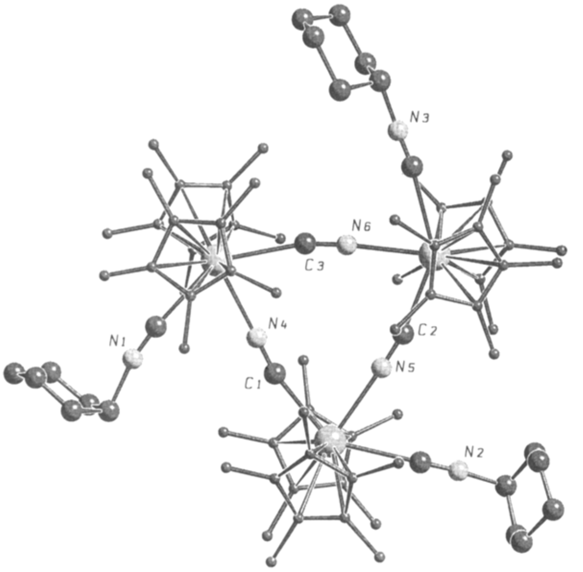


Figure 27. Structure of $[(C_5Me_5)_2Sm(\mu\text{-}CN)(CN^cC_6H_{11})]_3$ in the crystal.[291]

complex crystallizes with two molecules of tetrahydrofuran.[291]

References to the known bis(pentamethylcyclopentadienyl)lanthanide halides and pseudohalides are given in Table 5.

c. Derivatives with Other Substituted Cyclopentadienyl Rings. The use of cyclopentadienyl derivatives as π-ligands is a well-known strategy to introduce either subtle or major changes into the chemical or physical properties of metal complexes, depending on the number and nature of the substituents. However, despite the immense diversity of available or imaginable cyclopentadiene derivatives, the most important complexes with respect to completeness of the rare earth series, are derived from cyclopentadienes of the type RC_5H_5 with R = Me, ^{t}Bu, Me_3Si, Me_2PhSi, and $MeOCH_2CH_2$ or 1,3-$R_2C_5H_4$ with R = ^{t}Bu and Me_3Si (Table 6). The synthesis of e.g. bis(methylcyclopentadienyl)lanthanide chlorides dates back to 1963, and the synthetic route is identical to that used for the preparation of the unsubstituted parent compounds **1**.[155] As expected, these complexes exhibit similar properties and structures as **1**, except that they have a better solubility. In addition, the cyclopentadienyl rings show reduced librational motion around the pseudo-5-fold rotation axis in the solid state structure of bis(methylcyclopentadienyl)ytterbium chloride.[312]

Significant changes are observed in complexes containing coordinating side chains bonded to the cyclopentadienyl ligands. $[(MeOCH_2CH_2C_5H_4)_2LnCl]_2$ are dimers, as expected, but the dimers show intramolecular coordination of both oxygen atoms of the methoxyethyl ligands to the lanthanide ions. This conclusion was deduced first from XPS spectra[242,325] and then later proved by an X-ray structural analysis of the lanthanum derivative (Figure 28). The structure shows that the lanthanum ion is coordinated by two oxygen atoms at nearly equal distances.[326] In contrast, $(Me_2NCH_2CH_2C_5H_4)_2NdCl$ is a monomer with two nitrogen atoms coordinated to the neodymium (Figure 29).[195]

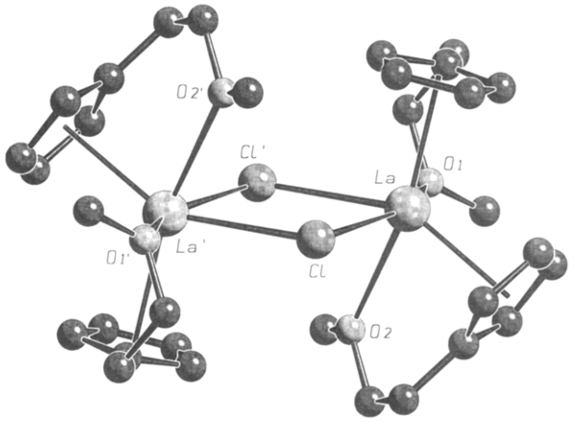


Figure 28. Structure of $[(MeOCH_2CH_2C_5H_4)_2LaCl]_2$ in the crystal.[326]

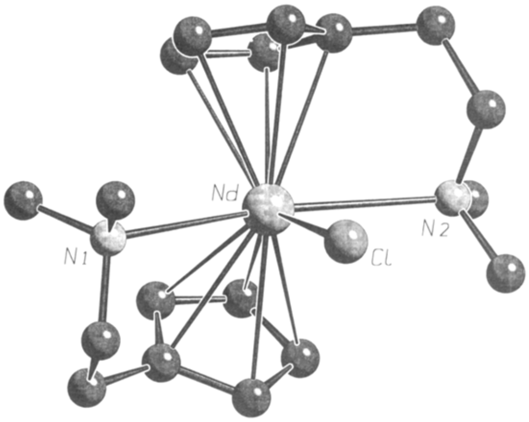


Figure 29. Structure of $(Me_2NCH_2CH_2C_5H_4)_2NdCl$ in the crystal.[195]

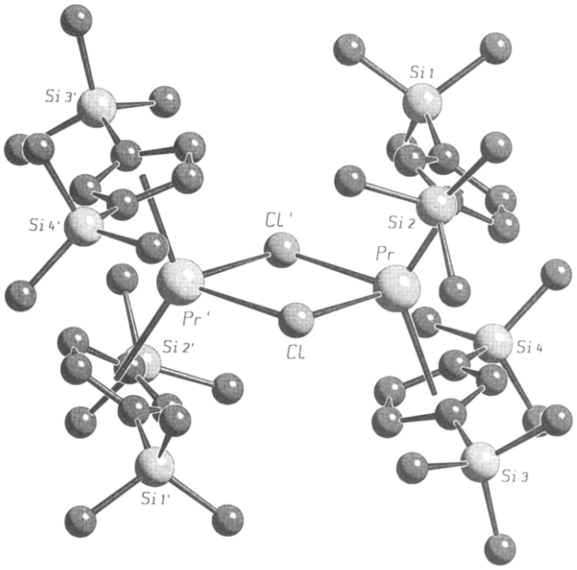


Figure 30. Structure of $\{[(Me_3Si)_2C_5H_3]_2PrCl\}_2$ (**29e**) in the crystal.[339]

A different approach to complexes of high thermal stability, volatility, and high solubility in hydrocarbon solvents has been made by Lappert et al.[338,339,342] They demonstrated that bis(trimethylsilyl)cyclopentadienyl ligands are capable of imparting favorable chemical properties, such as solubility in hydrocarbons, to rare earth metal complexes. The series $\{[(Me_3Si)_2C_5H_3]_2LnCl\}_2$ (**29**) has been extended to all rare earth elements except for the radioactive promethium. Single-crystal X-ray structure determinations of **29a**,[339] **29e** (Figure 30),[339] **29q**,[339] and **29r**[146c] revealed that these are isomorphous.

Table 6. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Halides Containing Other Substituted Cyclopentadienyl Ligands

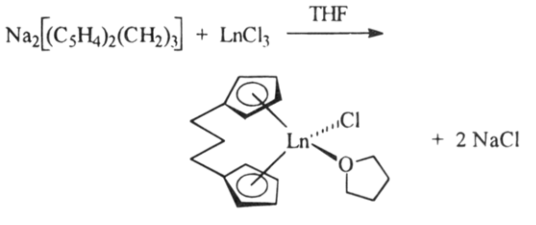
complex	Ln		color, characterization, etc.
$(MeC_5H_4)_2LnF$	Yb		complex with THF: orange, NMR, IR[264]
$[(Me_3Si)_2C_5H_3]_2LnF$	La		complex with BF_3, Et_2O, 2NCMe: NMR[313]
	Ce		complex with BF_3,[311] Et_2O, 2NCMe: NMR, IR[313]
$(MeC_5H_4)_2LnCl$	Y		NMR,[6c,178,314,220d] MS;[220e] complex with THF: NMR[6c,178]
	Sm		complex with THF: orange, NMR, IR,[315a] X-ray[315b]
	Gd		colorless, melt./dec.,[155] IR[83]
	Tb		white, IR, lumines.;[104] complex with THF: lumines.[104]
	Dy		synthesis[141]
	Ho		synthesis[141]
	Er		pink, melt./dec.,[155] MS,[220e] IR[83]
	Yb		red, melt./dec.,[155] X-ray,[312] MNDO[316]
	Lu		NMR,[314,220d] MS[220d]
$(^tBuC_5H_4)_2LnCl$	Pr		green, X-ray, IR,[318a] complex with 2THF: green, X-ray, IR[317,318b]
	Nd		complex with 2THF: purple, IR[317,318b]
	Sm		yellow,[196,708] X-ray,[708] NMR, IR,[196] reactions;[247] complex with DME: IR[317,319]
	Gd		pale yellow, X-ray, NMR, IR,[318a] complex with THF: white, IR[317,318b]
	Er		pink, IR[318a]
	Yb		complex with THF:[320] orange,[318b] X-ray,[318b,321] IR[317,318b,321]
	Lu		cream white,[196] X-ray,[708] NMR, IR,[196] MS[197]
$(Me_3SiC_5H_4)_2LnCl$	Y		synthesis,[322] X-ray, NMR, IR[226]
	Yb		red, melt./dec.,[323] MS[324]
$(MeOCH_2CH_2C_5H_4)_2LnCl$	Y		white, NMR,[545] IR,[242,325,545] XPS,[242,325] catalyst[167,174]
	La		X-ray, NMR,[326] IR,[242,325,326] XPS[242]
	Pr		IR[325,326]
	Nd		IR,[242,325,326] XPS[242]
	Sm		synthesis[325]
	Gd		IR, XPS[242,325]
	Dy		X-ray[189b]
	Ho		IR, XPS[242,325]
	Er		IR, XPS[242,325]
	Tm		synthesis[325]
	Yb		X-ray,[198b] IR, XPS[242,325]
$(Me_2NCH_2CH_2C_5H_4)_2LnCl$	Nd		blue, X-ray, IR, MS, melt./dec.[195]
	Lu		melt./dec., MS, IR[700]
$[(CH_2)_5C_5H_2Me]_2LnCl$	Nd		dimer: blue, MS[702]
$[(CH_2)_6C_5H_2Me]_2LnCl$	Nd		dimer: blue, MS[702]
$(Ph_2PC_5H_4)_2LnCl$	Yb		dimer: orange, X-ray, NMR, UV, MS[709]
$[(CO)_3MnC_5H_4]_2LnCl$	Yb		formation[327]
$(Me_2C_5H_3)_2LnCl$	Y		NMR, IR, THF complex[328]
$(^tBu_2C_5H_3)_2LnCl$	Ce		X-ray,[329] reactions[248,329−331]
	Nd		blue, X-ray, NMR, IR, MS[332]
	Sm		reactions[248]
	Lu		X-ray, NMR,[333] reactions[334−337]
$[(Me_3Si)_2C_5H_3]_2LnCl$	Sc	**29a**	white,[338] X-ray,[339] melt./dec.[338]
	Y	**29b**	white, melt./dec.[338,339]
	La	**29c**	white, melt./dec.,[338,339,146c] NMR[146c]
	Ce	**29d**	yellow, melt./dec.[338,339]
	Pr	**29e**	yellow,[338] X-ray,[339] melt./dec.[338]
	Nd	**29f**	green-blue, melt./dec.[338,339]
	Sm	**29h**	yellow, melt./dec.[338,339]
	Eu	**29i**	brown-violet, melt./dec.[338,339]
	Gd	**29k**	white, melt./dec.[338,339]
	Tb	**29l**	white, melt./dec.[338,339]
	Dy	**29m**	white, melt./dec.[338,339]
	Ho	**29n**	pink ?, melt./dec.[338,339]
	Er	**29o**	pink, melt./dec.[338,339]
	Tm	**29p**	yellow, melt./dec.[338,339]
	Yb	**29q**	maroon,[338] X-ray,[339] melt./dec.,[338] reactions[199]
	Lu	**29r**	colorless,[146c] white,[338,339] melt./dec.,[338,339,146c] NMR, X-ray[146c]
$(C_5HMe_4)_2LnCl$	Ho		THF complex: yellow, melt./dec., NMR[701]
	Tm		THF complex: yellow, melt./dec., NMR[701]
	Lu		THF complex: colorless, melt./dec., NMR[701]
$(PrC_5Me_4)_2LnCl$	Nd		IR, melt./dec.[309]
$(C_5Ph_5)_2LnCl$	Lu		yellow, NMR, IR, UV, MS, melt./dec.[340]
$(^tBuC_5H_4)_2LnI$	Sm		complex with THF; with 2MeCN: X-ray[341]
$(Me_3SiC_5H_4)_2LnI$	Yb		red-brown, melt./dec.[323]
$(MeOCH_2CH_2C_5H_4)_2LnI$	Y		white,[710] X-ray,[198b,710] NMR, MS, IR[710]
	La		white,[710] X-ray,[198b,710] NMR, MS, IR[710]
	Sm		X-ray,[198b] reactions[711]
	Yb		red,[699] X-ray,[198b] melt./dec., MS[699]
$(PhCH_2OCHMeCH_2C_5H_4)_2LnI$	Sm		yellow, NMR, MS, IR[712]
$[(Me_3Si)_2C_5H_3]_2LnI$	La		complex with 2MeCN: NMR[313]
	Ce		complex with 2MeCN: NMR, IR[313]

Table 6 (Continued)

complex	Ln	color, characterization, etc.
$(MeOCH_2CH_2C_5H_4)_2Ln][Co(CO)_4]$	Sm	complex with THF: yellow, melt./dec.; NMR, IR[711]
	Yb	complex with THF: red, X-ray, melt./dec., NMR, IR[711]
$(Me_3SiC_5H_4)_2Ln(\mu\text{-}Cl)_2Li(LB)$	Y	LB = 2THF: colorless; tmed: colorless[322]
$(MePh_2SiC_5H_4)_2Ln(\mu\text{-}Cl)_2Li(LB)$	Yb	LB = $2Et_2O$: orange, X-ray[282]
	Lu	without LB: white, NMR[282]
$(Ph_2PC_5H_4)_2Ln(\mu\text{-}Cl)_2Na(LB)$	Yb	LB = DME: orange, X-ray, NMR, IR[713]
$({}^tBu_2C_5H_3)_2Ln(\mu\text{-}Cl)_2Li(LB)$	Ce	LB = tmed: X-ray[330,331]
	Sm	LB = tmed: yellow-green, X-ray[714]
	Lu	LB = $2Et_2O$ colorless;[337] 2THF: colorless, X-ray;[714] tmed: colorless, X-ray[335,337]
$[(Me_3Si)_2C_5H_3]_2Ln(\mu\text{-}Cl)_2Li(LB)$	Sc	LB = 2THF: colorless[338,339,342]
	Y	LB = 2THF: colorless;[338,339,342] DME;[342] tmed[342]
	La	LB = 2THF: colorless;[338,339,342] tmed;[342] 4THF[343]
	Ce	LB = 2THF: yellow;[338,339,342] $2Et_2O$: lumines.[289]
	Pr	LB = 2THF: pale green[338,339,342]
	Nd	LB = 2THF: blue-green,[338,339,342] X-ray, DME[342]
	Yb	LB = 2THF: orange-red, melt./dec.[338,339,342]
$(EtC_5Me_4)_2Ln(\mu\text{-}Cl)_2Li(LB)$	Y	without LB[322]
	Nd	LB = 2THF: melt./dec.[145,309]
	Sm	LB = 2THF: orange, NMR, IR, magn. d.[276]
	Gd	LB = 2THF: IR, melt./dec.[145,309]
	Yb	LB = 2THF: IR, melt./dec.[309]
$(PrC_5Me_4)_2Ln(\mu\text{-}Cl)_2Li(LB)$	Nd	LB = 2THF: IR, melt./dec.[309]
	Gd	LB = 2THF: IR, melt./dec.[309]
	Yb	LB = 2THF: IR, melt./dec.[309]
$(PrC_5Me_4)_2Ln(\mu\text{-}Cl)_2K(LB)$	Nd	LB = 2THF: IR, melt./dec.[145]
	Yb	LB = 2THF: IR, melt./dec.[309]
$[K(THF)_x][\{(Me_3Si)_2C_5H_3\}_2LnI_2]$	Ce	yellow-green, NMR, IR[313]
$[Cation][\{(Me_3Si)_2C_5H_3\}_2LnCl_2]$	Y	cation = $N(PPh_3)_3$[343]
	Pr	cation = PPh_4[343]
	Nd	cation = PPh_2CH_2Ph; $AsPh_4$: X-ray[343]
	Dy	cation = PPh_2CH_2P[343]
	Tm	cation = PPh_4[343]

In summary, progressive substitution of the cyclopentadienyl ligand with alkyl or trimethylsilyl groups resulted in complexes displaying properties that are intermediate between bis(cyclopentadienyl)- and bis(pentamethylcyclopentadienyl)lanthanide complexes. Not surprisingly, the complexes under discussion form neutral dimers like e.g. $[(Me_3SiC_5H_4)_2YCl]_2$,[226] in which the bridge can be cleaved by Lewis bases (in general solvent molecules) to form monomeric adducts like e.g. $({}^tBuC_5H_4)_2SmI(MeCN)_2$.[341] Furthermore, addition products with alkali halides are formed, which contain bridging halides like e.g. $[({}^tBu_2C_5H_3)_2Ce(\mu\text{-}Cl)_2Li(tmed)]$,[330] or terminal halogens in ionic species like e.g. in $[Li(Et_2O)_2][(MePh_2SiC_5H_4)_2YbCl_2]$.[282]

d. Ring-Bridged Bis(cyclopentadienyl) Rare Earth Halides. Prior to the early 1980s, no thermally stable bis(cyclopentadienyl)lanthanide alkyl complex of the large lanthanide metals (La, Ce, Pr, and Nd) had been prepared, due to the absence of appropriate starting materials, such as the corresponding bis(cyclopentadienyl)lanthanide chlorides. Then, simultaneously with the introduction of pentamethylcyclopentadiene as an ancillary ligand in lanthanide chemistry,[292] Tsutsui et al.[344] demonstrated that isolable lanthanum and cerium complexes may also be obtained by using ligands that were essentially as small as cyclopentadiene, but the cyclopentadienyl groups were linked by a 1,3-propanediyl chain. Verifying these early results, Qian et al.[164,345] obtained a series of complexes by reacting $Na_2[(C_5H_4)_2(CH_2)_3]$ with a number of representative lanthanide chlorides according to eq 22:



(22)

30

Ln = Y (**30b**), La (**30c**), Pr (**30e**), Nd (**30f**), Gd (**30k**), Dy (**30m**), Ho (**30n**), Er (**30o**), Yb (**30q**), Lu (**30r**)

In the past decade a variety of complexes with two to six carbon atoms bridging the two cyclopentadienyl rings have been prepared (Table 7).[204,243,345–347] Al-

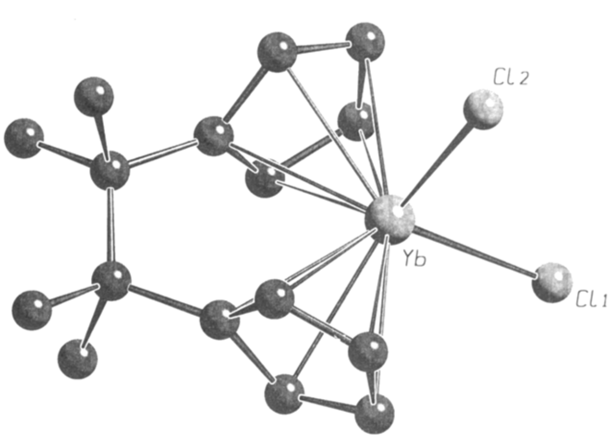


Figure 31. Structure of the anion of $[Mg_2Cl_3(THF)_6][(C_5H_4CMe_2CMe_2C_5H_4)YbCl_2]$ in the crystal.[346]

Table 7. Spectroscopic and Other Data of Ring-Bridged Bis(cyclopentadienyl)lanthanide Halides

complex	Ln		color, characterization, etc.
$(CMe_2C_5H_4)_2LnCl$	Sm		complex with THF: yellow,[347a] X-ray,[715] NMR, IR, MS,[347a,715] melt./dec;[347a] with MgCl2/3THF: yellow, X-ray[718]
	Yb		orange, IR, NMR, MS, melt./dec.;[347b] complex with $2[MgCl_2(THF)_3]$: X-ray[346]
$[(CH_2)_3(C_5H_4)_2]LnCl$	Y	**30b**	complex with THF[164]
	La	**30c**	pale yellow,[57] NMR,[57,241,344a] PE;[57] complex with THF[164]
	Ce	**30d**	brown, NMR,[57] magn. d.[57,344a]
	Pr	**30e**	complex with THF: pale yellow, IR, melt./dec., magn. d.;[344b,c,345] with bipy: yellow, melt./dec., magn. d.[345]
	Nd	**30f**	complex with THF: blue-green, IR, melt./dec., magn. d.;[344b,c,345] with bipy: pale yellow, melt./dec., magn. d.[345]
	Gd	**30k**	complex with THF: pale yellow, IR, melt./dec.,magn. d.[344b,c,345]
	Dy	**30m**	complex with THF: orange-yellow, IR, melt./dec., magn. d.;[344b,c,345] with bipy: yellow, melt./dec., magn. d.[345]
	Ho	**30n**	complex with THF: yellow, IR, melt./dec., magn. d.;[344b,c,345] with bipy: yellow, melt./dec., magn. d.[345]
	Er	**30o**	complex with THF: orange-red, IR, melt./dec., magn.d.,[344b,c,345] solubility;[241] with bipy: orange-yellow, melt./dec., magn. d.[345]
	Yb	**30q**	complex with THF: red, IR, melt./dec., magn. d.;[344b,c,345] reaction;[348] with bipy: orange-yellow, melt./dec., magn. d.[345]
	Lu	**30r**	complex with THF: pale yellow,[344c,345] NMR,[241,345] melt./dec.,[345] reaction;[164] with bipy: pale-yellow, IR, melt./dec.[345]
$[(CH_2)_5(C_5H_4)_2]LnCl$	Y		complex with THF: pale yellow, IR, melt./dec.,[204] NMR,[204,220d,241]
	Sm		complex with THF: yellow, IR, melt./dec.[204]
	Gd		complex with THF: white, IR, melt./dec.[204]
	Dy		complex with THF: yellow, IR, melt./dec.[204]
	Er		complex with THF: orange, IR, melt./dec.[204]
	Lu		complex with THF: pale yellow, IR, melt./dec.[204] NMR[204,220d,241]
$[C_6H_4\text{-}m\text{-}(CH_2C_5H_4)_2]LnCl$	Y		complex with THF: pale yellow, NMR, IR, MS, melt./dec.[243]
	La		complex with THF: white, NMR, IR, MS, melt./dec.[243]
	Nd		complex with THF: purple, IR, MS, melt./dec.[243]
	Dy		complex with THF: pale yellow, IR, MS, melt./dec.[243]
	Er		complex with THF: orange-red, IR, MS, melt./dec.[243]
	Yb		complex with THF: orange-yellow, IR, MS, melt./dec.[243]
$[C_6H_4\text{-}p\text{-}(CH_2C_5H_4)_2]LnCl$	La		complex with THF: white, NMR, IR, MS, melt./dec.[243]
	Pr		complex with THF: pale yellow, IR, MS, melt./dec.[243]
	Nd		complex with THF: purple-blue, IR, MS, melt./dec.[243]
$[C_4H_2O(CH_2C_5H_4)_2\text{-}2,5]LnCl$	Y		dimer: yellow, NMR, MS, IR, melt./dec.[716]
	Nd		dimer: purple, MS, IR, melt./dec.[716]
	Sm		dimer: orange, MS, IR, melt./dec.[716]
	Yb		dimer: red, MS, IR, melt./dec.[716]
$[C_5H_3N(CH_2C_5H_4)_2\text{-}2,6]LnCl$	Y		dimer: yellow, NMR, MS, IR, XPS[707]
	Pr		dimer: yellow-green, NMR, MS[707]
	Nd		dimer: light blue, NMR, MS[707]
	Sm		dimer: yellow lemon, NMR, MS[707]
	Dy		dimer: yellow-orange, MS, XPS[707]
	Er		dimer: pink, MS, XPS[707]
	Yb		dimer: orange, NMR, MS[707]
	Lu		dimer: yellow-orange, NMR, MS, XPS[707]
$[O(CH_2CH_2C_5H_4)_2]LnCl$	Y		green,[241] NMR,[205,220d,241] MS,[220e,241] IR, XPS, melt./dec.[241]
	Nd		green, IR, XPS, MS, melt./dec.[220e,241]
	Gd		white, IR, XPS, MS, melt./dec.[220e,241]
	Ho		pale yellow, IR, MS, XPS, melt./dec.[220e,241]
	Er		orange, IR, XPS, MS, melt./dec.[220e,241]
	Yb		red, IR, XPS, MS, melt./dec.[220e,241]
	Lu		white,[241] NMR,[205,220d,241] MS,[220e] IR, XPS, melt./dec.[241]
$[MeN(CH_2CH_2C_5H_4)_2]LnCl$	Y		reactivity,[174] white, melt./dec., IR, MS, NMR[357b]
	Nd		purple, melt./dec., IR, MS[357b]
	Sm		orange, melt./dec., IR, MS[357b]
	Yb		red, melt./dec., IR, MS[357b]
$Me_2Si(C_5H_4)_2LnCl$	Y	**31b**	MS,[324] reactions[550]
	Yb	**31q**	red,[349,550] melt./dec., X-ray,[349] MS,[324,349] complex with MeCN: reactions[550]
$Me_2Si(C_5H_4)_2LnBr$	Yb	**32q**	X-ray[217]
$Me_2Si(C_5H_4)_2Ln(NCS)(NCMe)$	Yb		pink, NMR[550]
$Me_2Si(C_5H_3{}^tBu)_2Ln(\mu\text{-}Cl)_2Li(THF)_3$	Nd		blue, X-ray[350]
$Me_2Si(C_5H_3{}^tBu)_2LnCl$	Sc		synthesis, reactions[351,352]
$Me_2Si\{C_5H_2(SiMe_3){}^tBu\}_2Ln(\mu\text{-}Cl)_2Li(THF)_2$	Y		X-ray[353,686]
$Me_2Si(C_5H_4)(C_5Me_4)Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$	Lu		colorless, NMR, IR[354]
$Et_2Si(C_5H_4)(C_5Me_4)Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$	Y		colorless, NMR, IR[354]
	Lu		colorless, NMR, IR[354]
$Me_2Si(C_5Me_4)_2Ln(\mu\text{-}Cl)_2Li(LB)$	Sc		LB = 2THF[352]
	Nd		LB = 2 Et_2O: pale green, NMR, IR[362a]
	Sm		LB = 2 Et_2O[362a]
	Lu		LB = 2 Et_2O: colorless, NMR, IR[362a]

Table 7 (Continued)

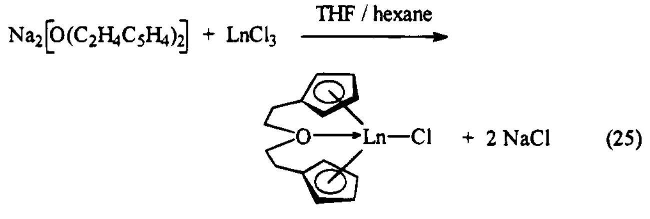
complex	Ln	color, characterization, etc.
$Me_2Si(C_5Me_4)(C_5H_3{}^tBu)Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$	La	yellow, NMR, MS, melt./dec.[705]
	Lu	green, MS, melt./dec.[705]
$[Me_2Si(C_5Me_4)_2Ln]_2(\mu\text{-}Cl)_3Li(THF)_2$	Nd	X-ray[362a]
$Me_2Si(C_5Me_4)(C_5H_3C_{10}H_{18})Ln(\mu\text{-}Cl)_2$	Sm	complex with 2 Et_2O[355]
(*R*)-$Me_2Si(C_5Me_5)[(-)\text{-menthyl}C_5H_3]Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$	Y	colorless, NMR, UV, CD[726]
	Sm	orange, NMR, UV, CD[726]
	Lu	colorless, NMR, UV, CD[726]
(*S*)-$Me_2Si(C_5Me_5)[(-)\text{-menthyl}C_5H_3]Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$	Sm	orange, NMR[726]
(*S*)-$Me_2Si(C_5Me_5)[(-)\text{-menthyl}C_5H_3]Ln(\mu\text{-}Cl)_2Li(DME)$	Sm	yellow, NMR, UV, CD[726]
	Lu	colorless, NMR, UV, CD[726]
(*R*)-$Me_2Si(C_5Me_5)[(+)\text{-neomenthyl}C_5H_3]Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$	Y	colorless, NMR, UV, CD[726]
	La	colorless, NMR[726]
	Nd	pale blue, NMR[726]
	Sm	orange, NMR, UV, CD[726]
	Lu	colorless, X-ray, NMR, UV, CD[726]
(*S*)-$Me_2Si(C_5Me_5)[(+)\text{-neomenthyl}C_5H_3]Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$	Sm	orange, NMR, UV, CD[726]
(*R*)-$Me_2Si(C_5Me_5)[(+)\text{-neomenthyl}C_5H_3]Ln(\mu\text{-}Cl)_2Li(DME)$	Sm	yellow, NMR[726]
(*R*)-$Me_2Si(C_5Me_5)[(-)\text{-phenylmenthyl}C_5H_3]Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$	Y	NMR[726]
(*S*)-$Me_2Si(C_5Me_5)[(-)\text{-phenylmenthyl}C_5H_3]Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$	Y	colorless, NMR, UV, CD[726]
$Me_2Ge(C_5Me_4)_2Ln(\mu\text{-}Cl)_2Li(THF)_2$	Nd	blue, NMR[356]
	Sm	yellow, X-ray, NMR[356]
	Eu	blue, X-ray, NMR, melt./dec.[350]
	Ho	yellow, NMR[356]
	Tm	green-yellow, NMR, melt./dec.[350]
	Yb	brown, NMR, melt./dec.[350]
	Lu	colorless, X-ray, NMR[356]
$[O(SiMe_2C_5H_4)_2LnCl$	Pr	complex with THF: yellow, UV, NMR, melt./dec.[717]
	Yb	dimer: orange, X-ray, NMR, MS[717]

though most of them have been characterized by various spectroscopic methods, only one of them has been subjected to an X-ray structure determination (Figure 31).[346]

In many respects, complexes containing heteroatoms in the bridge, notably silicon or oxygen, have attracted much attention. It has been shown that stereorigidity of the ligand array and coordinative saturation of the lanthanide ion can be achieved by utilizing a 1,5-(3-oxapentamethylene) bridge (eqs 23–25):[241]

$$2NaC_5H_5 + O(C_2H_4Cl)_2 \xrightarrow{-10\ ^\circ C} O(C_2H_4C_5H_5)_2 + 2NaCl \quad (23)$$

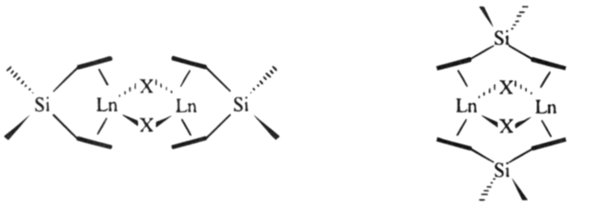
$$O(C_2H_4C_5H_5)_2 + 2Na \xrightarrow{THF} Na_2[O(C_2H_4C_5H_4)_2] + H_2 \quad (24)$$



Due to the flexibility of the chain, which allows the central oxygen atom to approach the lanthanide ion, monomeric and solvent-free complexes were isolated.[241] The oxygen atom coordinates the lanthanide ion intramolecularly as shown by X-ray crystallography of $[O(C_2H_4C_5H_4)_2Y]_2(\mu\text{-}OH)(\mu\text{-}N_2C_3HMe_2)$.[357a] Initial systematic investigations on nitrogen containing ring-linked bis(cyclopentadienyl)lanthanide chlorides indicate that intramolecular stabilization via nitrogen coordination occurs in chloride-bridged dimers.[357b]

While the introduction of the above ring-bridged bis(cyclopentadienyl) ligands originated in the desire to get access to kinetically stable complexes of the larger lanthanide ions Nd^{3+}, Pr^{3+}, Ce^{3+}, and La^{3+}, the necessity to reduce steric congestion of the central ion in bis(pentamethylcyclopentadienyl)lanthanide alkyl and hydride complexes sparked the development of singly heteroatom bridged, and in most cases peralkylated ancillary π-ligand systems. The interest in constrained systems emerged in the early 1980s when bis(pentamethylcyclopentadienyl)lanthanide methyl and hydride compounds were found to activate C–H bonds[358,359,360] and to catalyze hydrogenation and polymerization of olefins with high reaction rates.[358,361] However, these complexes have been suggested to suffer from steric congestion about the metal center, which severely limited their application in the polymerization of olefins other than ethene. The methodology of using "tied"-back ligands in order to reduce steric crowding, while preserving the beneficial properties of a bis(permethylcyclopentadienyl) ligand environment, is well established in transition metal and actinoid chemistry, also has been adapted to lanthanide chemistry.[362a,352,354]

Sterically less encumbered organolanthanide halides, which may serve as starting materials for the synthesis of exceptionally reactive organolanthanide hydrides, have been prepared with ligands of the type $Me_2Si(C_5H_3R)_2{}^{2-}$ (R = H,[217,324,349] ${}^tBu$[350–352]), $R'_2Si(C_5H_4)(C_5Me_4)^{2-}$ (R′ = Me, Et),[354] $Me_2Si(C_5Me_4)_2{}^{2-}$,[362a] and $Me_2Ge(C_5Me_4)_2{}^{2-}$.[350,356] These anionic ligands can be prepared in metathetical reactions from $M[C_5H_4R]$ or $M[C_5Me_4H]$ (M = alkali metal) with Me_2SiCl_2, Et_2SiCl_2 and Me_2GeCl_2, respectively, followed by deprotonation with Na, ${}^nBuLi$, or MeLi. Moreover, a stepwise procedure allows the preparation of mixed π-ligands; $Me_2SiCl(C_5HMe_4)$ and Me_2



chelating ligand metal-bridging ligand

Figure 32. Two possible arrangements for ligands $Me_2Si(C_5H_4)_2^{2-}$ to act as chelating or metal-bridging ligand.

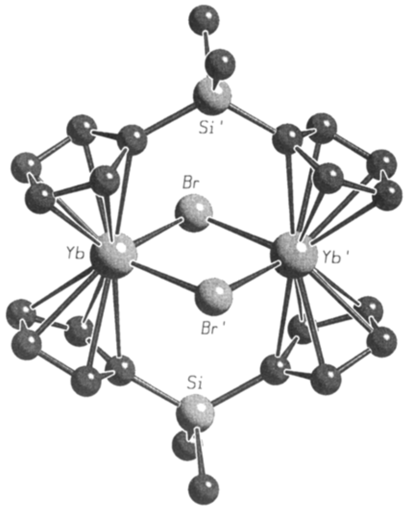
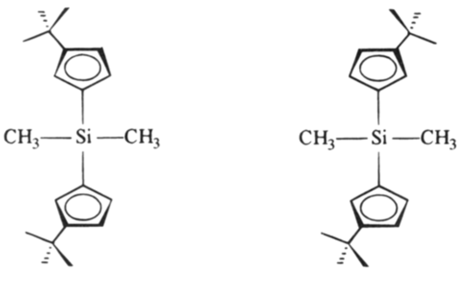


Figure 33. Structure of $[Me_2Si(C_5H_4)_2YbBr]_2$ (**32q**) in the crystal.[217]



meso isomer rac isomer

Figure 34. The relative orientation of the *tert*-butyl groups in $Me_2Si(C_5H_3{}^tBu)_2^{2-}$ ligands.

$GeCl(C_5HMe_4)$ are stable and can be isolated in high yields as colorless liquids from stoichiometric reactions of LiC_5HMe_4 with Me_2SiCl_2[354] and Me_2GeCl_2,[350] respectively.

Interestingly, the coordination chemistry of the above ligands has shown remarkable differences with respect to the ligand-to-metal bonding modes. Figure 32 shows the two possible isomers which may result when two $Me_2Si(C_5H_4)_2^{2-}$ ligands are combined with a rectangular planar $[Ln(\mu\text{-}X)]_2^{4+}$ unit.

Structure determinations of $[Me_2Si(C_5H_4)_2YbX]_2$ (X = Cl (**31q**),[349] Br (**32q**) (Figure 33)[217]) showed the metal-bridging mode to be preferred. Simple model calculations are in accord with these results.[217] In the case of mixed π-ligands such as $Et_2Si(C_5H_4)(C_5Me_4)^{2-}$ a high degree of flexibility which included intermolecular ligand exchange under very mild conditions was observed.[354]

Unsymmetrically substituted bis(cyclopentadienyl) ligands (such as $Me_2Si(C_5H_3{}^tBu)_2^{2-}$) are potentially useful in the synthesis of chiral organolanthanide complexes. Figure 34 demonstrates the relative orientation of the *tert*-butyl groups which determines the nature of the ligand.

It was however shown that $Me_2Si(C_5H_3{}^tBu)_2Li_2$ reacts with $ScCl_3$ or $NdCl_3$ to produce exclusively the achiral isomer $\{meso\text{-}Me_2Si(C_5H_3{}^tBu)_2LnCl{\cdot}B\}_x$ (Ln = Sc, base free, $x = 1$; and Ln = Nd, B = $ClLi(THF)_3$, $x = 2$). In the case of the Sc compound, the NMR spectrum clearly showed two resonances for the methyl groups attached to silicon, a result that is in accordance with the *meso* isomer. The NMR spectrum of the paramagnetic Nd complex could not be readily interpreted, but a single-crystal structure determination proved it to belong to the *meso* type (Figure 35).[350]

Due to the great number of methyl groups, complexes of these ligands exhibit high solubility in nonpolar solvents such as pentane and toluene. Bridged compounds are somewhat less soluble in hydrocarbons due to the increase in their dipole moment. The X-ray crystal structure of $[Me_2Si(C_5Me_4)_2Nd]_2(\mu\text{-}Cl)_3Li(THF)_2$ (Figure 36) shows $Me_2Si(C_5Me_4)_2^{2-}$ acting as a chelating rather than a metal-bridging ligand. Consequently, each of the crystal

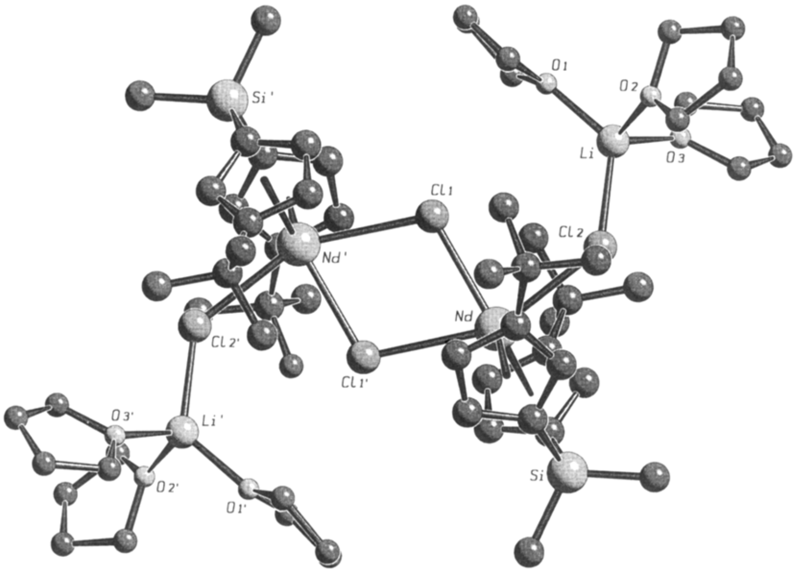


Figure 35. Structure of $[Me_2Si(C_5H_3{}^tBu)_2Nd(\mu\text{-}Cl)_2Li(THF)_3]_2$ in the crystal.[350]

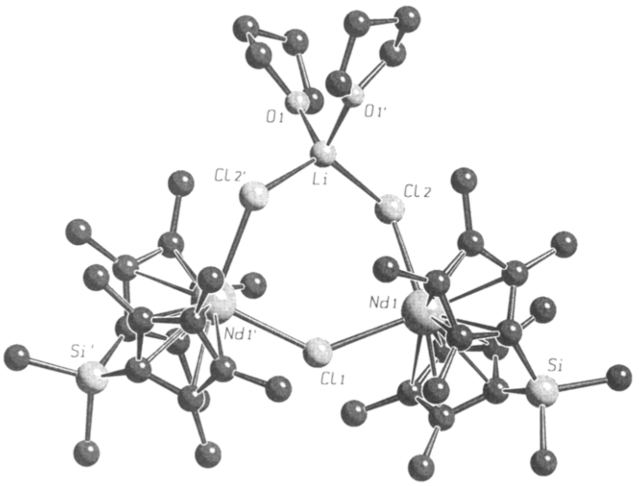


Figure 36. Structure of $[Me_2Si(C_5Me_4)_2Nd]_2(\mu\text{-}Cl)_3Li(THF)_2$ in the crystal.[362a]

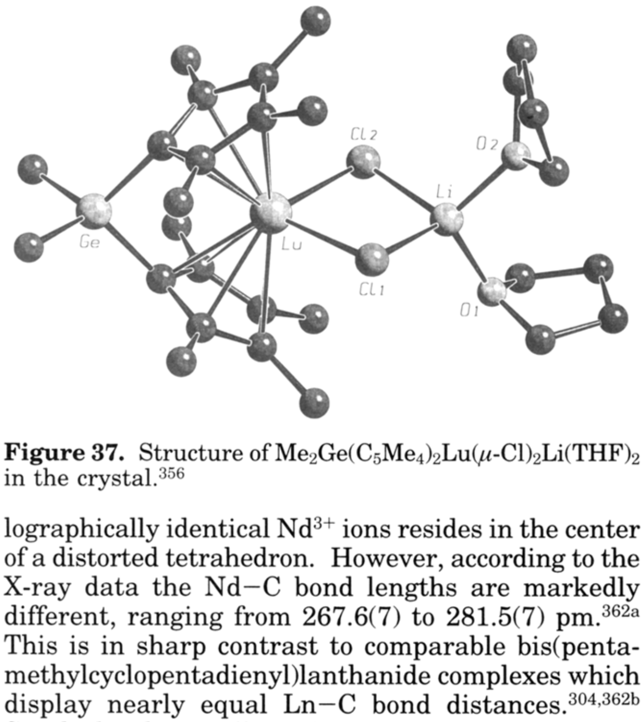
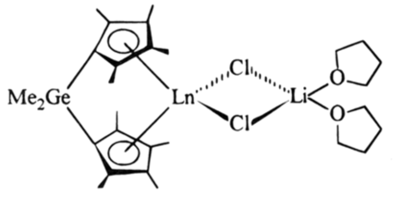


Figure 37. Structure of $Me_2Ge(C_5Me_4)_2Lu(\mu\text{-}Cl)_2Li(THF)_2$ in the crystal.[356]

lographically identical Nd^{3+} ions resides in the center of a distorted tetrahedron. However, according to the X-ray data the Nd−C bond lengths are markedly different, ranging from 267.6(7) to 281.5(7) pm.[362a] This is in sharp contrast to comparable bis(pentamethylcyclopentadienyl)lanthanide complexes which display nearly equal Ln−C bond distances.[304,362b] Similarly, the small Me_2Si bridge results in closing of the Cp_g−Nd−Cp_g angle and the corresponding opening of the coordination sphere around Nd^{3+} ($Cp_g-Nd-Cp_g = 134.4°$ in $(C_5Me_5)_2NdCH(SiMe_3)_2$[304] and 121.3° in $[Me_2Si(C_5Me_4)_2Nd]_2(\mu\text{-}Cl)_3Li(THF)_2$).[362a]

Similar results have been obtained by using a Me_2Ge bridge. Several lanthanide trichlorides react with $Li_2[Me_2Ge(C_5Me_4)_2]$ in boiling THF according to eq 26 yielding the corresponding dimethylgermyl-bridged complexes:[350,356]

$$Li_2\left[Me_2Ge(C_5Me_4)_2\right] + LnCl_3 \xrightarrow[-LiCl]{THF}$$



(26)

Ln = Nd, Sm, Eu, Ho, Tm, Yb, Lu

The Sm, Eu, and Lu derivatives have been characterized by X-ray structural analyses. Not surprisingly, they are all isomorphous. The structure of the lutetium derivative is shown in Figure 37.[350,356]

More recently several other ligands containing two connected cyclopentadienyls like $(C_5H_4CMe_2CMe_2C_5H_4)$,[715] 2,5-$(C_5H_4CH_2)_2C_4H_2O$,[716] 2,6-$(C_5H_4CH_2)_2C_5H_3N$,[707] and the disiloxane $(C_5H_4SiMe_2)_2O$[717] have been used to prepare new bis(cyclopentadienyl) rare earth halides.

e. Other Bis(cyclopentadienyl) Rare Earth Halides. Table 8 contains some bis(cyclopentadienyl) rare earth chlorides, which were not included in the previous chapters. They contain either two different cyclopentadienyl ligands, or two different rare earth elements, or "special" cyclopentadienyl ligands.

Several scandocene chloride complexes **33a**−**37a** containing two different substituted cyclopentadienyl ligands have been made and characterized by ^1H and ^{13}C NMR studies. They were used to synthesize the corresponding bis(cyclopentadienyl)scandium alkyl complexes, such as $Cp^*Cp^{**}ScR$, which were used in connection with the determination of relative bond dissociation energies of early transition metal compounds.[363] $(C_5H_5)YbCl_2(THF)_3$ reacts in toluene at −10 °C with $Na_2[C_5H_4CMe_2CMe_2C_5H_4]$ or $Na_2[(C_5H_4)_2SiMe_2]$ to give the red complexes $[\text{-}CMe_2(C_5H_4)(C_5H_5)YbCl]_2$ or $Me_2Si[(C_5H_4)(C_5H_5)YbCl]_2$ which were characterized only by elemental analyses.[364]

The first complex containing two different rare earth metals, $Me_2Si(C_5H_4)_2Y\text{-}(\mu\text{-}Cl)_2Yb(C_5H_4)_2SiMe_2$, was not isolated but its existence was deduced by its fragmentation pattern in the mass spectrum of the reaction mixture, isolated after stirring a mixture of the symmetrical complexes $[Me_2Si(C_5H_4)_2Y(\mu\text{-}Cl)]_2$ and $[Me_2Si(C_5H_4)_2Yb(\mu\text{-}Cl)]_2$ in THF at room temperature.[324]

Finally it should be mentioned that two tetraphenylborate complexes with organolanthanide cations containg the "open-Cp ligands" 2,4-dimethylpentadienylcyclopentadienyl[706] as well as the first rare earth complexes with π-bonded heteroaromatic ligands have been prepared. Neodymium trichloride reacts with Na(pyr) (pyr = $NC_4H_2{}^tBu_2$-2,5) to give $[(pyr)_2Nd(\mu\text{-}Cl)_2\{Na(THF)\}_2(\mu\text{-}Cl)_2Nd(pyr)_2]$, which could be characterized by an X-ray structural analysis.[758] $Li[C_4Me_4P]$ reacts with YCl_3 and $LuCl_3$ to give $(C_4Me_4P)_2Y(\mu\text{-}Cl)_2Li(DME)_n$ ($n = 1, 2$) and $(C_4Me_4P)_2Lu(\mu\text{-}Cl)_2Li(Et_2O)_2$, respectively. No crystal structure was reported, but high $^1J(YP)$ coupling constants of about 45 Hz and small $^1J(PC)$ coupling constants of 6.4 Hz are suggestive of π-interaction between the rare earth ions and the tetramethylphospholyl ions.[365] A second example is the first carborane analogue of an yttrocene derivative, the sandwich complex $[Li(THF)_4][Li(THF)\{(Me_3Si)_2C_2B_4H_4\}_2YCl(THF)]$, which was isolated from the reaction of YCl_3 with $Li_2[2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4]$ in benzene. It was characterized by ^1H-, ^{11}B-, and ^{13}C-NMR and an X-ray structural analysis (Figure 38).[366]

2. Bis(cyclopentadienyl) Rare Earth Chalcogenides

According to the concept of hard and soft acids and bases (HSAB),[367] the rare earth metals are hard

Table 8. Spectroscopic and Other Data of Other Bis(cyclopentadienyl)lanthanide Halides

complex	Ln		color, characterization, etc.
$(C_5Me_5)(C_5Me_4Pr)LnCl$	Sc	**33a**	amber, NMR[363]
$(C_5Me_5)(C_5Me_4CH_2Ph)LnCl$	Sc	**34a**	amber, NMR[363]
$(C_5Me_4CH_2Ph)(C_5Me_4CH_2C_6H_4Me\text{-}3)LnCl$	Sc	**35a**	amber, NMR[363]
$(C_5Me_4CH_2C_6H_4Me\text{-}3)(C_5Me_4CH_2C_6H_4CF_3\text{-}3)LnCl$	Sc	**36a**	off-white, NMR[363]
$(C_5Me_4CH_2C_6H_4Me\text{-}3)(C_5Me_4CH_2C_6H_4NMe_2)LnCl$	Sc	**37a**	off-white, NMR[363]
$[-CMe_2(C_5H_4)(C_5H_5)LnCl]_2$	Yb		red[364]
$Me_2Si[C_5H_4)(C_5H_5)LnCl]_2$	Yb		red[364]
$Me_2Si(C_5H_4)_2Y(\mu\text{-}Cl)_2Yb(C_5H_4)_2SiMe_2$	Y, Yb		MS[324]
$[(C_7H_{11})_2Ln][BPh_4]$	Nd		greenish-yellow, NMR[706]
	Sm		violet[706]
$({}^tBu_2C_4H_2N)_2Ln(\mu\text{-}Cl)_2[Na(THF)_2](\mu\text{-}Cl)_2Ln(NC_4H_2{}^tBu_2)_2$	Nd		blue, X-ray, MS, melt./dec.[758]
$(C_4Me_4P)_2Ln(\mu\text{-}Cl)_2Li(DME)_n$	Y		$n = 1, 2$: NMR[365]
$(C_4Me_4P)_2Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$	Lu		NMR[365]
$[Li(THF)_4][Li(THF)\{(Me_3Si)_2C_2B_4H_4\}_2LnCl(THF)]$	Y		colorless, X-ray, NMR, IR, melt./dec.[366]

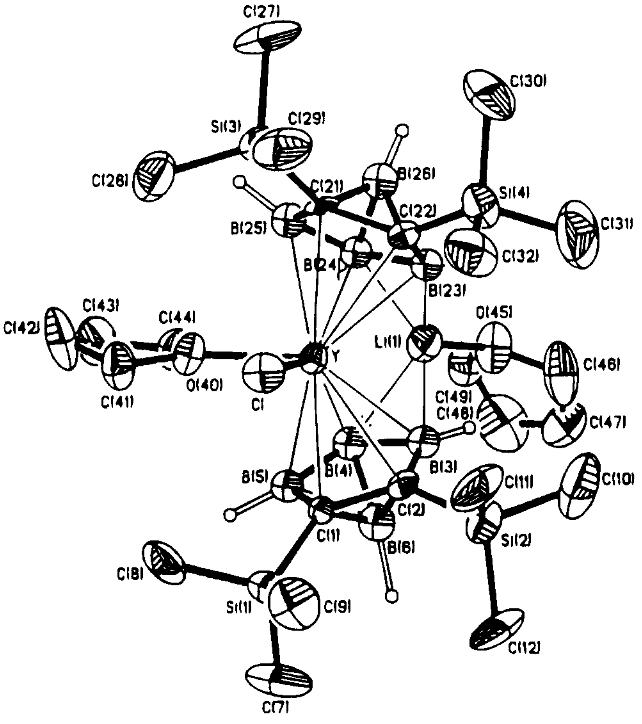


Figure 38. Structure of $[Li(THF)\{(Me_3Si)_2C_2B_4H_4\}_2YCl(THF)]^-$ in the crystal.[366] (Reprinted from ref 366. Copyright 1991 American Chemical Society.)

Lewis acids and form thermodynamically stable bonds with ligands containing hard donor atoms like oxygen. The stability of the lanthanide−chalcogen bond decreases significantly as the "softness" of the higher homologues of oxygen increases. Therefore the first bis(cyclopentadienyl)lanthanide−oxygen compounds were discovered very early,[155] while first preparations of bis(cyclopentadienyl)lanthanide sulfur,[368] selenium,[369,370] and tellurium[370] species, respectively, were described during the last decade.

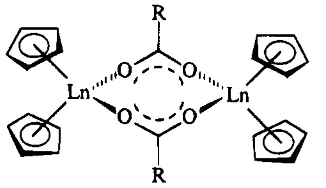
a. Compounds with Rare Earth to Oxygen Bonds. *i. Cyclopentadienyl Derivatives.* Following the successful isolation of the first bis(cyclopentadienyl)lanthanide chlorides, bis(cyclopentadienyl)lanthanide alkoxides and carboxylates have been prepared by reacting the corresponding chlorides with sodium alkoxides or carboxylates, respectively.[155] Since the original discoveries, many analogous complexes have been made and characterized (Table 9) as shown in eqs 27−29.

$$\underset{\textbf{21}}{(C_5H_5)_2LnCl(THF)} + MOR \xrightarrow{THF} (C_5H_5)_2LnOR + MCl \quad (27)$$

M = Na: R = Me, Ln = Dy, Er, Yb;[155]
R = ^{t}Bu, Ln = Sm;[375] R = Ph, Ln = Yb[155]

M = K: R = Me, Ln = Y[373,226]

$$\underset{\textbf{21}}{2\,(C_5H_5)_2LnCl(THF)} + 2\,NaO_2CR \xrightarrow[-2\,NaCl]{THF}$$



(28)

R = H: Ln = Er[155]

R = Me: Ln = Sc,[236] Sm,[80] Er, Yb[155]

R = Ph: Ln = Yb[155]

$$(C_5H_5)_2LnCl(phen)_n + NaO_2CCF_3 \xrightarrow[-NaCl]{THF} (C_5H_5)_2Ln(\eta^2\text{-}O_2CCF_3)(phen)_n \quad (29)$$

n = 1, Ln = Pr, Nd; n = 2, Ln = La, Ce, Pr, Nd[123]

The apparent dimeric structure of these carboxylate complexes has been deduced from molecular weight determinations in benzene[155,236] and from mass spectra.[80] Due to the presence of coordinated phen the trifluoroacetate derivatives are expected to exist in the unidentate form.[123] In 1986, Evans et al.[379] showed the bis(cyclopentadienyl)lanthanide derivatives $[(C_5H_5)_2Ln(\mu\text{-}OCH{=}CH_2)]_2$ to be dimers. They found that these enolate complexes are formed by anion metathesis from $[(C_5H_5)_2LnCl]_2$ and $LiOCH{=}CH_2$, as well as by thermal decomposition of $(C_5H_5)_2Y(CH_2SiMe_3)(THF)$ or $[(C_5H_5)_2YbMe]_2$ in the presence of LiCl and THF, showing that ring opening of THF was the source of the enolate. Recently, the X-ray structural analyses of $[(C_5H_5)_2YbOCH_2CH{=}CHMe]_2$,[320] the chiral compound $[(C_5H_5)_2PrOCH(Me)CO_2{}^iBu]_2$,[121b] and $[(C_5H_5)_2YbO^iPr]_2$[374] proved the

Table 9. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Oxygen Compounds

compound	Ln		color, characterization, etc.
$(C_5H_5)_2LnOH$	Y		complex with THF: NMR, IR;[159] complex with PhC$\equiv$CPh: X-ray[159]
$[(C_5H_5)_2Ln]_2O$	Yb		intermediate[371]
	Lu		complex with 2THF: X-ray, NMR, melt./dec.[372]
$(C_5H_5)_2LnOMe$	Y		NMR,[373,226] IR;[226] ionic complexes $\{[Na(THF)_3]_2(C_5H_5)\}\{[(C_5H_5)_2Y]_3(OMe)_2O\}$: X-ray, $[K(THF)_4]\{[(C_5H_5)_2Y]_3(OMe)_2O\}$: NMR, IR[226]
	La		use as a dopand[176a]
	Dy		yellow, melt./dec.[155]
	Er		pink, melt./dec.[155]
	Yb		orange, melt./dec.[155]
$(C_5H_5)_2LnOPr$	Dy		yellow, MS, IR, melt./dec.[374]
	Ho		yellow, MS, IR, melt./dec.[374]
	Yb		yellow, X-ray, MS, IR, melt./dec.[374]
$(C_5H_5)_2LnO^iBu$	Dy		pale yellow, MS, IR[719]
	Yb		yellow,[719,720] NMR, UV,[121b] MS,[719,720] IR, melt./dec.[720]
$(C_5H_5)_2LnO^tBu$	Sm		colorless, IR, melt./dec.[375]
	Lu		complex with THF: colorless, NMR, melt./dec.[369]
$(C_5H_5)_2LnOC_5H_{11}$	Sm		yellow, MS, rections.[690]
$(C_5H_5)_2LnOCH_2Ph$	Lu		complex with THF: colorless, NMR[376]
$(C_5H_5)_2LnO(CH_2)_4PPh_2$	Lu	**38q**	colorless, X-ray, MS, melt./dec.[372]
$(C_5H_5)_2LnOCH_2(C_4H_3O)$	Nd		blue, IR, MS, XPS, melt./dec.[377]
	Yb		yellow, IR, MS, XPS, melt./dec.[377]
$(C_5H_5)_2LnO(C_6H_{12}N)$	Pr		NMR, UV[121b]
$(C_5H_5)_2Ln(menth)$	Pr		NMR, UV[121b]
$(C_5H_5)_2LnOCMeCHCOOEt$	Yb		therm. d.[52d]
$(C_5H_5)_2LnOCH(Me)COO^iBu$	Pr		X-ray, UV, NMR[121b]
	Sm		NMR, UV[121b]
	Yb		yellow, X-ray, NMR, UV, IR, melt./dec.[720]
	Lu		NMR[121b]
$(C_5H_5)_2LnOC_{10}H_7$	Yb		orange, MS, IR, melt./dec.; complex with THF: X-ray, MS, IR[163]
$(C_5H_5)_2LnOCH_2C_5H_4Fe(C_5H_5)$	Sm		yellow, MS, melt./dec.[378]
$(C_5H_5)_2LnOCH{=}CH_2$	Y		white, NMR, IR, melt./dec.[379]
	Yb		orange, IR, melt./dec.[379]
	Lu		straw, NMR, IR, melt./dec.[379]
$(C_5H_5)_2LnOCH_2CH{=}CHMe$	Yb		yellow-green, X-ray[380]
$(C_5H_5)_2Ln(OC(Me){=}CHMe$	Dy		dimer, pale yellow, X-ray[719]
	Yb		dimer, orange, X-ray[719]
$(C_5H_5)_2LnOC(iPr){=}CMe_2$	Lu		complex with THF: colorless, NMR[146c]
$(C_5H_5)_2LnOPh$	Yb		red, melt./dec.[155]
$(C_5H_5)_2LnOC_6H_4NH_2$-2	Nd		blue-gray, NMR, IR, MS, XPS, melt./dec.[161]
	Yb		yellow, NMR, IR, MS, XPS, melt./dec.[161]
$(C_5H_5)_2LnOC_6H_4CHO$-2	Nd		yellow, IR, MS, XPS, melt./dec.[377]
	Yb		yellow, IR, MS, XPS, melt./dec.[377]
$(C_5H_5)_2LnOC_6H_3Ph_2$-2,6	Nd		complex with 2THF: X-ray, IR, MS[162]
$(C_5H_5)_2LnO(C_9H_6N)$	Nd		green, NMR, IR, MS, XPS, melt./dec.[161]
	Yb		yellow, NMR, IR, MS, XPS, melt./dec.[161]
$(C_5H_5)_2Ln[\eta^2\text{-}O_2C_2(X)(Y)]$	Sc		$X = Si(SiMe_3)_3$, Y = MeTHF, PMe_2Ph; orange, NMR; $X = Ge(SiMe_3)_3$, Y = THF[381]
$(C_5H_5)_2LnOC(X){=}C(X)OLn(C_5H_5)_2$	Sc		$X = C(O)SiPh_2{}^tBu$, $C(O)Si(SiMe_3)_3$: green, $X = C(O)Ge(SiMe_3)_3$: blue; NMR, IR, melt./dec.[381]
$(C_5H_5)_2Ln(acac)$	Sc	**39a**	pale yellow, NMR, melt./dec.[236]
	Nd	**39f**	purple, IR, MS, melt./dec.[160]
	Sm	**39h**	yellow, IR, MS, melt./dec.[160]
	Gd	**39k**	pale yellow, IR, MS, melt./dec.[160]
	Dy	**39m**	yellow, IR, MS, melt./dec.[160]
	Er	**39o**	pink, IR, MS, melt./dec.[160]
	Yb	**39q**	orange,[223,382,383] X-ray,[384] UV,[382] MS,[383,385] melt./dec.[382,383] thermo. d.[52d]
$(C_5H_5)_2LnOC(^tBu){=}CHC(O)^tBu$	Yb		yellow,[383] NMR,[382] MS,[382,383,385] melt./dec.[382,383]
$(C_5H_5)_2LnOC(Me){=}CHC(O)Ph$	Yb		yellow, melt./dec.,[383] MS[383,385]
$(C_5H_5)_2LnOC(Me){=}CHC(O)CF_3$	Yb		orange,[383,721] X-ray,[721] MS,[383,385] melt./dec.,[383] thermo. d.[52d]
$(C_5H_5)_2LnOC(CF_3){=}CHC(O)(C_4H_3S)$	Yb		yellow, IR, melt./dec.,[383] MS[383,385]
$(C_5H_5)_2LnOC(Ph){=}CHC(O)Ph$	Yb		intermediate[223]
$(C_5H_5)_2LnOC(Me){=}CHC(NPh)Me$	Yb		yellow, UV, MS, melt./dec.[382]
$(C_5H_5)_2LnOC(Ph){=}C(C_4H_8N_2O)$	Yb		yellow, IR, melt./dec.,[383] MS[383,385]
$(C_5H_5)_2LnO_2CH$	Er		pink, melt./dec.[155]
	Yb		orange[155]
$(C_5H_5)_2LnO_2CMe$	Sc		yellow, NMR, melt./dec.[236]
	Sm		yellow, IR, MS,melt./dec.,[80] thermo. d.[52d]
	Gd		thermo. d.[52d]
	Tb		thermo. d.[52d]
	Er		pink, melt./dec.[155]
	Yb		orange[155,223,385] IR, UV, MS,[386] melt./dec.[155]
	Lu		thermo. d.[52d]
$(C_5H_5)_2LnO_2CCF_3$	La		complex with 2phen: brown, NMR, IR, melt./dec.[123]
	Ce		complex with 2phen: red brown, IR, melt./dec.[123]
	Pr		complex with phen: yellow, IR, melt./dec.; with 2phen: brown, IR, melt./dec.[123]
	Nd		complex with phen: brown, IR, melt./dec.; with 2phen: brown, IR, melt./dec.[123]
	Yb		orange, UV, IR, MS[386]

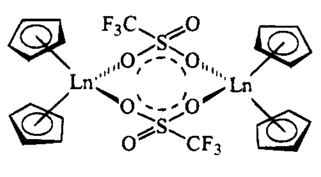
Table 9 (Continued)

compound	Ln		color, characterization, etc.
$(C_5H_5)_2LnO_2CBu$	Yb		yellow,[387] NMR[72]
$(C_5H_5)_2LnO_2CPh$	Yb		orange,[155,386] IR,[386,388] UV, MS,[386] melt./dec.[155]
$(C_5H_5)_2LnO_2CC_6H_4Cl$-2	Yb		IR, MS, XPS, melt./dec.[388]
$(C_5H_5)_2LnO_2CC_6H_4Br$-2	Yb		IR, MS, XPS, melt./dec.[388]
$(C_5H_5)_2LnO_2CC_6H_4I$-2	Yb		IR, MS, XPS, melt./dec.[388]
$(C_5H_5)_2LnO_2CC_6H_4OEt$-2	Yb		IR, MS, XPS, melt./dec.[388]
$(C_5H_5)_2LnO_2CC_6H_4OPr$-2	Yb		IR, MS, XPS, melt./dec.[388]
$(C_5H_5)_2LnO_2CC_6H_4NHPh$-2	Yb		IR, MS, XPS, melt./dec.[388]
$(C_5H_5)_2LnO_2CC_6H_2Me_3$	Yb		yellow, IR, MS, UV[386]
$(C_5H_5)_2LnO_2CC_6F_5$	Yb		yellow,[223,386] X-ray,[233] IR, UV, MS[386]
$(C_5H_5)_2LnO_2CC_6Br_5$	Yb		yellow, IR, UV, MS[386]
$(C_5H_5)_2LnO_2CC_6F_4CO_2Me$-2	Yb		orange, IR, UV, MS[386]
$(C_5H_5)_2LnO_2CC_5H_4N$-2	Yb		yellow, IR, MS[223,386]
$(C_5H_5)_2LnO_2C(C_9H_6N)$	Yb		complex with py: purple, IR, UV, MS[386]
$(C_5H_5)_2LnO_2C(CH_2)_3NMe_2$	Y		yellow, X-ray[389]
$(C_5H_5)_2LnO_2CSi(SiMe_3)_3$	Sc		yellow, X-ray, NMR, melt./dec.[390]
$(C_5H_5)_2LnO_2CSiPh_2{}^tBu$	Sc		NMR, IR, melt./dec.[390]
$(C_5H_5)_2LnOOC_5H_5$	Sm		lumines.[78]
	Eu		lumines.[78]
$(C_5H_5)_2LnONCMe_2$	Gd		dimer, X-ray, MS, IR[722]
$(C_5H_5)_2LnONO$	Yb		dimer, orange, MS, IR; complex with THF: X-ray, MS, IR[723]
$(C_5H_5)_2LnONO_2$	Ce		complex with $NaNO_3(THF)_2$: tan, NMR, IR, melt./dec.[112]
$(C_5H_5)_2LnO_2S(O)CF_3$	Sc	**40a**	colorless, NMR, MS[389]
	Yb	**40q**	orange, X-ray, IR; melt./dec.[391]
	Lu	**40r**	colorless, NMR, MS;[389,392] complex with THF: colorless[392]
$(C_5H_5)_2LnOSi(SiMe_3)_3$	Sc		NMR[390]
$(C_5H_5)_2LnOC{}^tBu$	Lu		pale yellow, NMR, IR[393]
$[(C_5H_5)_2LnOC({}^tBu){=}C{=}O]_2$	Lu		purple, X-ray, NMR, IR[393]
$(C_5H_5)_2LnOCMo(CO)_2(C_5H_5)$	Er		IR[141b]
$(C_5H_5)_2LnOCW(CO)_2(C_5H_5)$	Dy		IR[141b]
	Er		IR[141b]
	Yb		IR[141b]
$(C_5H_5)_2LnOCRe(CO)_4$	Lu		complex with THF: orange, NMR, IR, melt./dec.,[376] catalyst[173]
$[(C_5H_5)_2Ln]_2[Fe_3(CO)_{11}]$	Yb		synthesis[394]
$(C_5H_5)_2LnOCCo(CO)_3$	Sm	**41h**	complex with 2THF: yellow, NMR, IR, melt./dec.[395]
	Ho	**41n**	complex with THF: NMR, IR, melt./dec.[395]
	Yb	**41q**	catalyst;[173] complex with THF: orange-yellow,[252] NMR,[395] IR,[252,395,396] UV,[396] melt./dec.,[252,395] catalyst,[111,397] complex with 2THF: IR, UV[252,396]
	Lu	**41r**	complex with THF: yellow, IR, melt./dec.;[252,397] complex with 2THF: catalyst[173,252]
$[(C_5H_5)_2Ln]_2[Rh_4(CO)_8]$	Yb		complex with DME: IR[394]

dimeric nature of these derivatives. The latter alkoxide, as well as its Dy and Ho analogues, were prepared by stoichiometric reaction of **1** with propanol.[374] Another alternative procedure leading to dimeric metallorganic lanthanide–oxygen derivatives $[(C_5H_5)_2Yb(\mu,\eta^2\text{-}O_2CR)]$ (R = H,[155] ^{n}Bu[72,387]) is the treatment of **1q** with carboxylic acids or their sodium salts.

In the context of carboxylate complexes it should be mentioned that metathetical reactions of lanthanide triflates with 2 equiv of NaC_5H_5 and subsequent removal of coordinated solvent molecules yield solvent-free bis(cyclopentadienyl)lanthanide trifluoromethanesulphonates **40** (eq 30).[389,392] The dimeric

$$2\ Ln(OSO_2CF_3)_3 + 4\ NaC_5H_5 \xrightarrow[-4\ Na(SO_3CF_3)]{THF}$$



(30)

40

Ln = Sc (**40a**), Lu (**40r**),[389,392] Yb (**40q**)[391]

structure of the Yb derivative **40q** was shown by an X-ray structural analysis (Figure 39).[391]

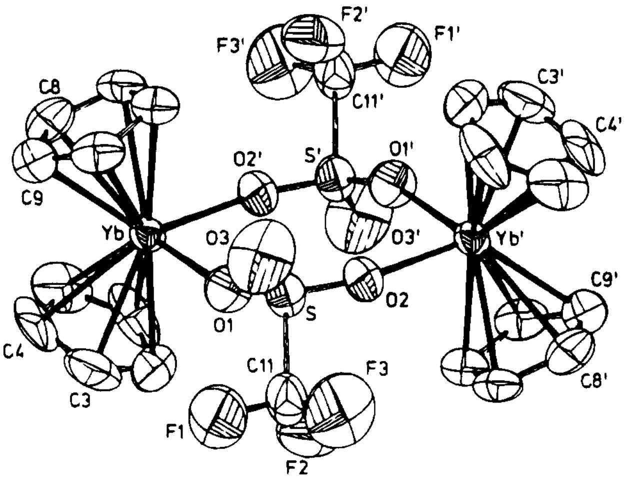
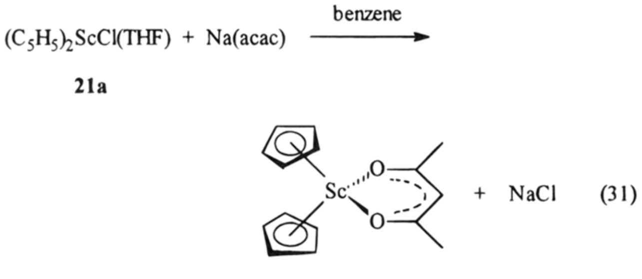


Figure 39. Structure of $[(C_5H_5)_2YbOSO_2CF_3]_2$ (**40q**) in the crystal.[391] (Reprinted from ref 391. Copyright 1992 Elsevier Sequoia).

On the other hand, **21a** reacts with the sodium acetylacetonato ligand in boiling benzene to form the monomeric complex **39a** (eq 31).[236] A similar metathesis is possible with bulky aryloxide ligands as shown by the X-ray structural analyses of $(C_5H_5)_2YbOC_{10}H_7(THF)$[163] or $(C_5H_5)_2NdOC_6H_3Ph_2$-2,6$(THF)_2$.[162]

Reactions of several β-diketones, β-ketoimines,[72,160,382-385] and similarly chelating ligands,



21a

39a

(31)

such as salicylaldehyde, furfuryl alcohol,[377] 8-hydroxyquinoline, or *o*-aminophenol,[161] with tris(cyclopentadienyl)lanthanides (eq 32) afford monomeric,

1 **39**

(32)

Ln = Nd (**39f**), Sm (**39h**), Gd (**39k**), Dy (**39m**), Er (**39o**),[160] Yb (**39q**)[384]

intramolecularly stabilized bis(cyclopentadienyl) lanthanide oxygen complexes with liberation of cyclopentadiene. The X-ray structural analysis of $(C_5H_5)_2$-Yb(acac) (**39q**) (Figure 40) indicates the monomeric nature of these derivatives.[384]

Bis(cyclopentadienyl)lanthanide alkoxides can also be obtained from tris(cyclopentadienyl)lanthanides and equimolar amounts of nonchelating alcohols containing acidic hydrogens, as demonstrated by the reaction of $Nd(C_5H_5)_3$ with 2,6-diphenylphenol in THF yielding $(C_5H_5)_2NdOC_6H_3Ph_2$-2,6$(THF)_2$. Despite the presence of the bulky phenoxide ligand the neodymium ion attains a formal coordination number of nine and the geometry is a distorted trigonal bipyramid.[162] Organolanthanide peroxides of the type $(C_5H_5)_2Ln$-OOC_5H_5 have been described for Ln = Sm and Eu.[78]

A completely different way for preparation of organolanthanide carboxylates and dionates was found by Deacon et al. Oxidizing $(C_5H_5)_2Yb(DME)$ with thallous, mercuric, argentic, or cuprous carboxylates,[223,386] or β-diketonates,[223] gave the corresponding compounds shown in eqs 33 and 34:

$$mn(C_5H_5)_2Yb(DME) + mM(O_2CR)_n \xrightarrow{\text{THF or DME}} n[(C_5H_5)_2YbO_2CR]_m + mM \quad (33)$$

$$mn(C_5H_5)_2Yb(DME) + mM[R'C(O)CHC(O)R'] \xrightarrow{\text{THF or DME}} n\{(C_5H_5)_2Yb[OC(R')CHC(O)R']\}_m + mM \quad (34)$$

$M = Tl, Ag$ ($n = 1$) or $M = Hg, Cu$ ($n = 2$)

$m = 1$: $R = C_6H_2(2,4,6\text{-}Me_3)$, pyridine-2-yl, (quinoline-2-yl)·(py); $R' = Ph$

$m = 2$: $R = Me, CF_3, Ph, C_6F_5$; $R' = Me$ (**39q**)

$m = ?$ (1 or 2): $R = C_6(3,4,5,6\text{-}F_4)CO_2Me, C_6Br_5$

The mass spectrum of $(C_5H_5)_2Yb[OC(Me)CHC(O)$-$Me]$ (**39q**), prepared by transmetalation, showed dimer ions,[223] a result in sharp contrast of the result of the single-crystal X-ray structure analysis which showed a monomeric constitution.[384] The nonvolatility of $(C_5H_5)_2YbO_2CC_6F_4CO_2Me$ and $(C_5H_5)_2YbO_2$-CC_6Br_5 prevents the observation of Yb-containing ions, but mass spectrometric investigations of other derivatives $(C_5H_5)_2YbO_2CR$ however, indicate the existence of monomers, with η^2-chelating ligands (R = 2,4,6-$C_6H_2Me_3$, C_5H_4N-2, C_9H_5NOH-2, and R′ = Ph), or of dimers, with μ-η^2-ligand bridges (R = Me, Ph, CF_3, C_6F_5). The dimeric structure of the perfluorophenyl derivative is shown by an X-ray crystallographic determination (Figure 41).

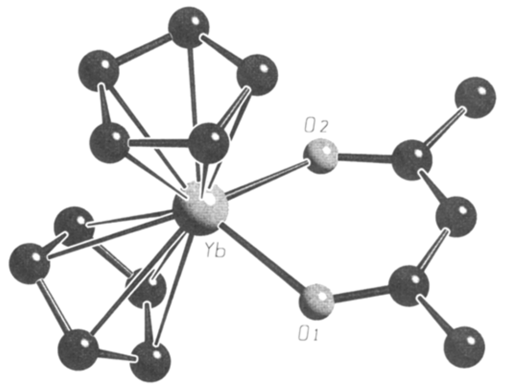


Figure 40. Structure of $(C_5H_5)_2Yb(acac)$ (**39q**) in the crystal.[384]

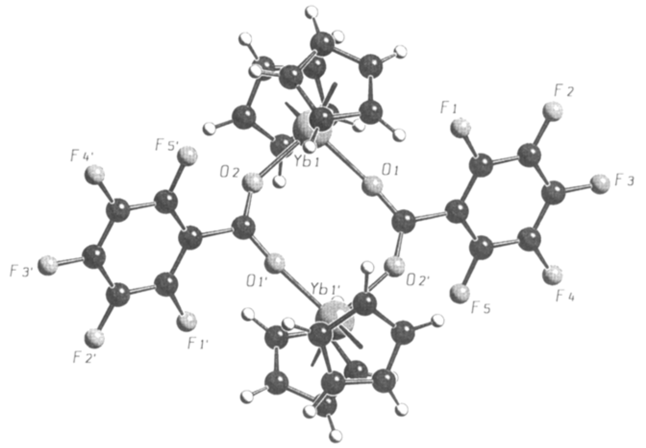
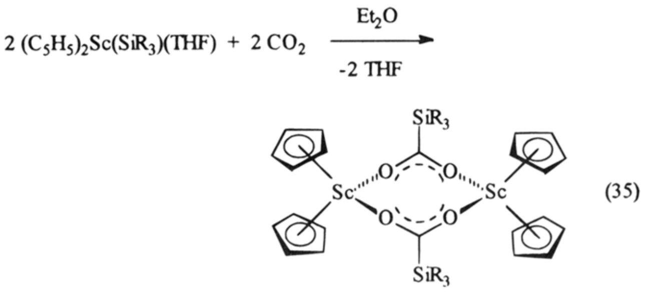


Figure 41. Structure of $[(C_5H_5)_2YbO_2CC_6F_5]_2$ in the crystal.[223]

During the study of the reactivity of d^0 transition metal to silicon bonds relative to unsaturated inorganic and organic reagents, Tilley[390] discovered an uncommon method for the preparation of dimeric bis(cyclopentadienyl) rare earth complexes with bulky carboxylates since the insertion of carbon dioxide into the Sc−Si bond of bis(cyclopentadienyl)(trialkylsilyl)-scandium derivatives yields the dimeric products (eq 35). NMR investigations showed that $(C_5H_5)_2ScO_2$-



(35)

$R_3 = (SiMe_3)_3$, $Ph_2{}^tBu$

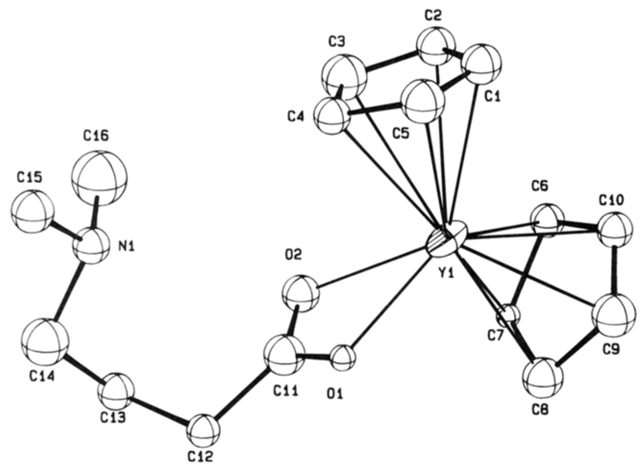


Figure 42. Structure of $(C_5H_5)_2Y[\eta^2\text{-}O_2C(CH_2)_3NMe_2]$ in the crystal.[389]

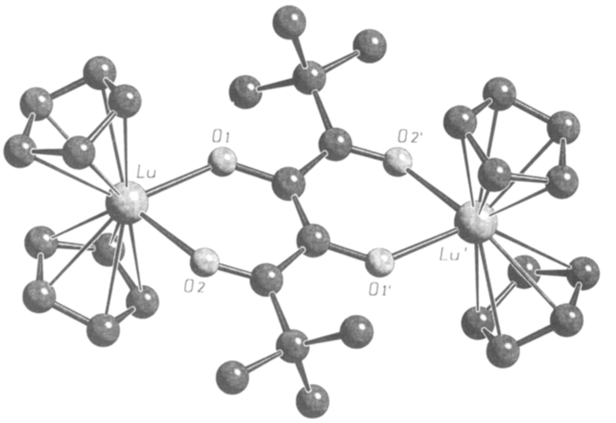


Figure 43. Structure of $[(C_5H_5)_2LuOC(^tBu){=}C{=}O]_2$ in the crystal.[393]

$CSi(SiMe_3)_3$ decomposes in solution with elimination of CO generating polymeric $[(C_5H_5)_2ScOSi(SiMe_3)_3]_x$.[390]

The activation of carbon dioxide was also observed by bis(cyclopentadienyl)[3-(dimethylamino)propyl]yttrium, resulting in the formation of $(C_5H_5)_2Y[\eta^2\text{-}O_2C(CH_2)_3NMe_2]$. The single-crystal X-ray structure determination shows a bidentate chelating carboxylate system but no transannular Y–N interactions (Figure 42).[389]

In the early 1980s, Evans et al.[393] were successful in the activation of carbon monoxide with the alkylbis(cyclopentadienyl)lutetium complex $(C_5H_5)_2Lu(^tBu)(THF)$. The reaction proceeds via the single insertion product $(C_5H_5)_2Lu[\eta^2\text{-}C(O)^tBu]$, which reacts with additional CO to give the binuclear complex $[(C_5H_5)_2Lu(CO)(^tBu)CO]_2$ (Figure 43), in which the two $(C_5H_5)_2Lu$ units are bridged by an enedione diolate ligand. Ketene–carbene intermediates are discussed as likely intermediates during the formation of the two six-membered metallacyclic rings.

Scandocene silyl and germyl complexes $(C_5H_5)_2Sc(ER_3)(THF)$ ($ER_3 = Si(SiMe_3)_3$, $SiPh_2{}^tBu$, $Ge(SiMe_3)_3$) react with carbon monoxide via scandoxy ketene derivatives, which are trapped as the adducts $(C_5H_5)_2Sc[OC(ER_3)C(L)O]$ (L = THF, MeTHF, PMe_2Ph) (e.g. eq 36) or as enedione diolates $[(C_5H_5)_2Sc[OC(ER_3)CO]_2$.[381]

It has also been reported that the monomeric alkoxide $(C_5H_5)_2Lu(OCH_2Ph)(THF)$ is formed quantitatively from the dimeric lutetium hydride $[(C_5H_5)_2Lu(\mu\text{-}H)(THF)]_2$ and the double molar amount of benzaldehyde as result of a nucleophilic addition of lutetium hydride to the carbonyl group.[376]

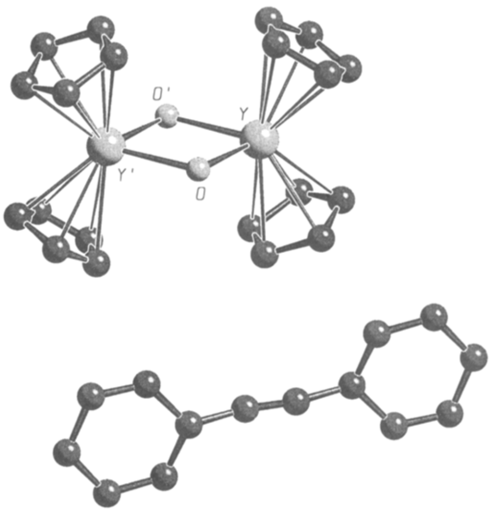
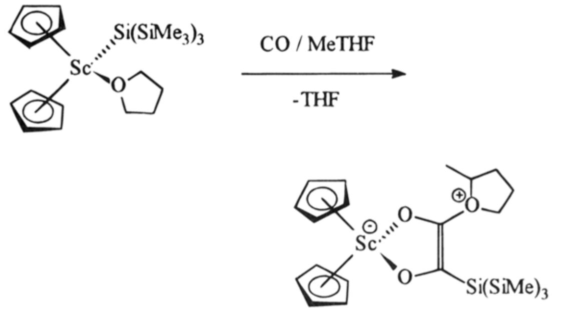


Figure 44. Structure of $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(PhCCPh)$ in the crystal.[159]



(36)

Complexes of uncommon constitution were obtained by reaction of the organoyttrium derivative $[Li(THF)_4]\{[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}$ with different amounts of methanol in THF at low temperatures. The stepwise substitution of the μ-bridging hydride atoms by methoxo groups leads eventually, under liberation of molecular hydrogen, to $[Li(THF)_4]\{[(C_5H_5)_2Y(\mu\text{-}H)]_x[(C_5H_5)_2Y(\mu\text{-}OMe)]_{3-x}(\mu_3\text{-}H)\}$ ($x = 2$, 1) and finally to the ionic species with $x = 0$. The latter compound crystallizes from THF as $[Li(THF)_3]_2\{[(C_5H_5)_2Y(\mu\text{-}OMe)]_3(\mu_3\text{-}H)\}_2$. (See also section II.B.5.a, bis(cyclopentadienyl) rare earth hydrides.[398])

Hydrolysis of metallorganic compounds of the rare earths is a common decomposition procedure, which implies that hydroxo complexes are formed at some time during the net reaction. However, metallorganic lanthanide hydroxides were not prepared and unambiguously characterized before 1988. The partial hydrolysis of (*tert*-butyl)bis(cyclopentadienyl)yttrium yields in the presence of diphenylethyne the organoyttrium hydroxide $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(PhCCPh)$ (Figure 44).[159]

The cleavage of THF is postulated to occur in the formation of $\{(C_5H_5)_2Lu[\mu\text{-}O(CH_2)_4PPh_2]\}_2$ (**38r**) since it crystallizes from THF solutions of $(C_5H_5)_2LuPPh_2(THF)$. It was suggested that the THF ring in $(C_5H_5)_2LuPPh_2(THF)$ opens. Then subsequent migration of the diphenylphosphine groups to the opened ends of the C_4H_8 chain results in the formation of the four-membered ring with alternating Lu–O bonds in **38r** (Figure 45).[372]

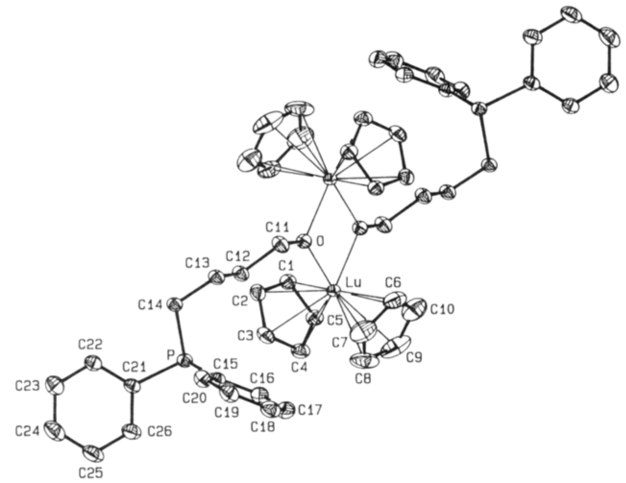


Figure 45. Structure of $\{(C_5H_5)_2Lu[\mu\text{-}O(CH_2)_4PPh_2]\}_2$ (**38r**) in the crystal.[372]

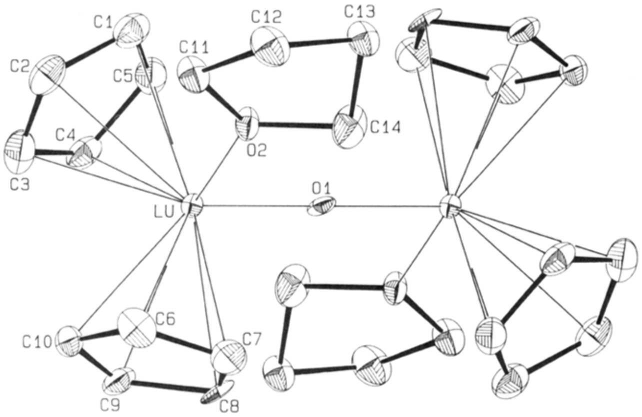


Figure 46. Structure of $[(C_5H_5)_2Lu(THF)]_2(\mu\text{-}O)$ in the crystal.[372]

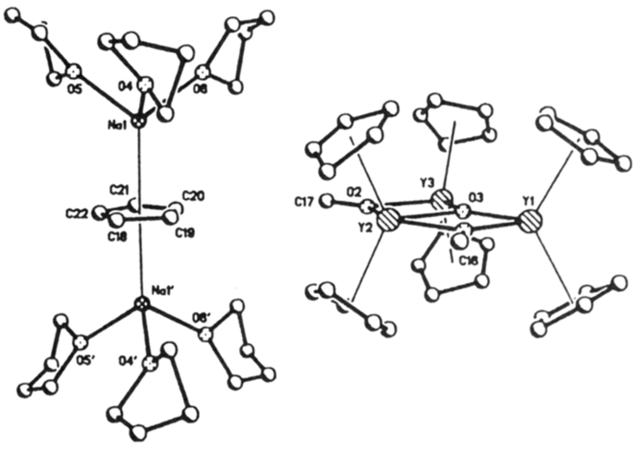


Figure 47. Structure of $\{[Na(THF)_3]_2(\mu\text{-}C_5H_5)\}\{[(C_5H_5)_2Y]_3(\mu\text{-}OMe)_2(\mu_3\text{-}O)\}$ in the crystal.[226] (Reprinted from ref 226. Copyright 1992 American Chemical Society.)

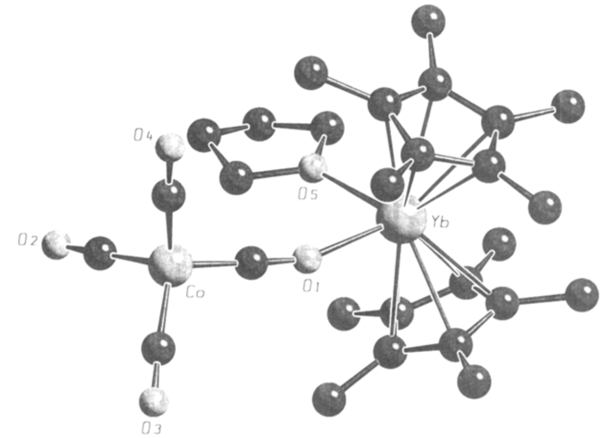


Figure 48. Structure of $(THF)(C_5Me_5)_2Yb(\mu\text{-}OC)Co(CO)_3$ in the crystal.[399]

The tendency of the rare earth elements to incorporate oxygen into their coordination sphere is also reflected in the isolation of the oxo-bridged dimer $[(C_5H_5)_2Lu(THF)]_2(\mu\text{-}O)$ which was obtained by hydrolysis of the diphenylarsino derivative $(C_5H_5)_2LuAsPh_2(THF)$. A single-crystal X-ray structure analysis reveals the presence of a strictly linear Lu−O−Lu unit (Figure 46).[372] It is noteworthy that the product of the oxidation of $(C_5H_5)_2Yb(DME)$ by trimethylamine oxide or triphenylarsine oxide, respectively, has been identified as the tetrahydrofuran-free Yb analogue, $[(C_5H_5)_2Yb]_2O$,[371] although nothing is known about its molecular structure.

Recently, simple metathetical reactions of bis(cyclopentadienyl)yttrium chlorides with alkali metal alkoxides have been found to yield also trimetallic alkoxide oxide complexes which contain the anion $\{[(C_5H_5)_2Y]_3(\mu\text{-}OMe)_2(\mu_3\text{-}O)\}^-$. Structural data are available for the complex that crystallizes with the countercation $\{[Na(THF)_3]_2(\mu\text{-}C_5H_5)\}^+$ (Figure 47).[226]

Starting from water-free ammonium cerium nitrate and NaC_5H_5, Gradeff et al.[112] reported that it is possible to produce the bis(cyclopentadienyl)dinitratocerium species, $(C_5H_5)_2Ce(NO_3)_2Na(THF)_2$, which decomposes explosively upon heating. The proposed structural formula is related to the well-established class of bis(pentamethylcyclopentadienyl)lanthanide halides of the type $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Na(Et_2O)_2$,[286] with the nitrate replacing chloride. Furthermore, the bis(cyclopentadienyl)lutetium alkyl complexes $(C_5H_5)_2Lu(\mu\text{-}CH_3)_2Li(THF)_2$ and $(C_5H_5)_2Lu(^tBu)(THF)$ react with *tert*-butyl alcohol with formation of the bis(cyclopentadienyl) *tert*-butoxide species $(C_5H_5)_2Lu(O^tBu)(THF)$.[369]

Many complexes are known in which the strongly Lewis acidic rare earth elements are linked together by isocarbonyl (Ln = Dy, M = W; Ln = Er, M = W, Mo; Yb, M = Mn, W;[141] Ln = Sm, Ho, Yb, Lu, M = Co;[111,173,395,396] Ln = Yb, M = Rh[394]) or isonitrosyl[141] (Ln = Yb, M = Cr) bonds with transition metal fragments. A typical example is the isocarbonyl complex $(THF)(C_5H_5)_2Yb(\mu\text{-}OC)Co(CO)_3$ (**41q**), in which the isocarbonyl group acts as a bridge between the two metal centers. This complex is accessible either via a photo-induced electron transfer process by exposing divalent $[(C_5H_5)_2Yb(THF)_2][Co(CO)_4]$ to ultraviolet radiation or, by redox reaction of divalent ytterbocene and $Co_2(CO)_8$, or from $[(C_5H_5)_2Yb(THF)_2][Co(CO)_4]$ by removal of one molecule THF in vacuum.[396] However, in the bimetallic cluster, $(THF)(C_5H_5)_2LuRu(CO)_2(C_5H_5)$, there is a direct metal−metal bond and the carbonyl groups are terminal.[256]

ii. Pentamethylcyclopentadienyl Derivatives. First reports on bis(pentamethylcyclopentadienyl) compounds with lanthanide−oxygen bonds came from Tilley and Andersen in 1981.[399] After cleavage of the Co−Co bond of $Co_2(CO)_8$ by the one-electron reducing agent $(C_5Me_5)_2Yb(Et_2O)$ (molar ratio 1:1 or 1:2) in toluene and subsequent recrystallization from a

Table 10. Spectroscopic and Other Data of Bis(pentamethylcyclopentadienyl)lanthanide Oxygen Compounds

compound	Ln		color, characterization, etc.
$[(C_5Me_5)_2Ln]_2O$	Sm	**50h**	orange, X-ray, IR,[400] NMR,[400,724] MS,[401] sublimation byproduct;[402] complex with 2THF: brownish-yellow; with 2 phthalan: brownish-yellow, NMR;[724] with 2CN^{t}Bu: orange,[724] X-ray,[290] NMR,[290,724] IR[290]
	Yb	**50q**	orange, NMR, MS, IR, melt./dec., magn. d.[401]
$(C_5Me_5)_2LnOMe$	Y		complex with Et_2O: colorless, NMR, IR[278]
$(C_5Me_5)_2LnOEt$	Y	**43b**	complex with Et_2O: colorless, NMR, IR[278]
	Sm	**43h**	complex with Et_2O: yellow, NMR, IR, magn. d.;[403] with THF: NMR[404]
	Lu	**43r**	synthesis;[358] NMR[360]
$(C_5Me_5)_2LnO^iPr$	Y		complex with Et_2O: yellow, NMR, IR[278]
$(C_5Me_5)_2LnO^nBu$	Sm	**44h**	complex with THF: yellow, NMR, IR, magn. d.[403]
$(C_5Me_5)_2LnO^tBu$	Sm		orange, NMR, IR[271]
	Yb		complex with NH_3: orange, NMR, IR, melt./dec.[370]
	Lu		complex with THF: colorless, NMR, melt./dec.[369,405]
$(C_5Me_5)_2LnOCH^tBu_2$	La		complex with OC^tBu_2: yellow, NMR, IR[406]
	Sm		yellow, NMR, IR[271]
$(C_5Me_5)_2LnO(CH_2)_4C_5Me_5$	La	**46c**	complex with THF: colorless, NMR, melt./dec.[200b]
	Nd	**46f**	complex with THF: blue, X-ray, melt./dec.[200b]
	Sm	**46h**	complex with THF: orange, X-ray, NMR, IR[208]
	Tm	**46p**	complex with THF: yellow, melt./dec.[200b]
	Lu	**46r**	complex with THF: colorless, X-ray, NMR, melt./dec.[200b]
$(C_5Me_5)_2LnOC_6H_3{}^tBu_2$	La		white, NMR, IR[407]
	Ce		red, NMR, IR[408]
$(C_5Me_5)_2LnOC_6H_2$-4-Me-2,6-$^tBu_2$	La		NMR[409]
	Ce		NMR[409]
$(C_5Me_5)_2LnOC_6H$-2,3,5,6-Me_4	Sm		orange, X-ray, NMR, IR[410]
$(C_5Me_5)_2Ln(acac)$	Y		yellow, NMR, IR[278]
$(C_5Me_5)_2LnOCMe_2CH_2COMe$	La		yellow, NMR, IR[406]
	Ce		red, X-ray, NMR, IR[406]
$(C_5Me_5)_2LnOCEt{=}CHMe$	La		complex with Et_2CO: yellow, NMR, IR[406]
	Ce		complex with Et_2CO: red, NMR, IR[406]
$(C_5Me_5)_2LnO_2C^tBu$	Yb	**47q**	red, NMR, IR, melt./dec., magn. d.[368]
$(C_5Me_5)_2LnO_2CCF_3$	Yb	**48q**	violet, MS, IR, melt./dec.[368]
$(C_5Me_5)_2LnO_2CCH_2C_6H_3Me_2$	Y		colorless, NMR, IR[411]
$(C_5Me_5)_2LnO_2CCH(SiMe_3)_2$	Y		colorless, NMR, IR[411]
$(C_5Me_5)_2LnO_2CC_6H_4Me$-4	Sc		pale yellow, X-ray;[412] synthesis[352]
$(C_5Me_5)_2LnOSiMe_3$	Yb		complex with NH_3: orange, NMR, IR, melt./dec.[370]
$[(C_5Me_5)_2Ln(THF)]_2(OSiMe_2OSiMe_2O)$	Sm	**45h**	yellow, X-ray, NMR, IR, magn. d.[403]
$[(C_5Me_5)_2Ln]_2[OC(CH\text{-}2\text{-}py)-]_2$	Sm		(+2toluene): yellow-orange, X-ray, NMR, IR[413]
$[(C_5Me_5)_2Ln]_2[OCN(Ph)]_2$	Sm		(+2toluene): green, X-ray, NMR, IR;[108,414] UV[108]
$[(C_5Me_5)_2LnO]_2(C_{16}H_8)$	Sm	**49h**	yellow-orange, X-ray, NMR, IR;[415] complex with 2THF: X-ray, NMR, IR[290]
$[(C_5Me_5)_2Ln]_2\{[(3\text{-}MeC_6H_4N)OC-]_2\}$	Sm		dark green, NMR[108]
$[(C_5Me_5)_2Ln]_2[(C_6H_5N)OCCO(NC_6H_4NMe_2\text{-}4]$	Sm		dark brown, NMR[108]
$[(C_5Me_5)_4Ln_2(O_2CCCO)(THF)]_2$	Sm		dark brown, X-ray, IR[416]
$[(C_5Me_5)_2(Ph_3PO)Ln]_2(OCH{=}CHO)$	Sm		orange, X-ray, NMR, IR[417]
$(C_5Me_5)_2Ln(CO)_2CH(SiMe_3)_2$	Nd		dark red, NMR, IR[304]
$(C_5Me_5)_2Ln[\eta^2\text{-}C(O)C_6H_5]$	Sc		synthesis[352]
$(C_5Me_5)_2LnOCH{=}W(C_5H_5)_2$	Sc		NMR, IR[299]
$(C_5Me_5)_2LnOCH{=}Co(CO)(C_5H_5)$	Sc		yellow-orange, NMR, IR[299]
$(C_5Me_5)_2LnOCH{=}Rh(CO)(C_5H_5)$	Sc		NMR[299]
$(C_5Me_5)_2LnOC(Me){=}Mo(C_5H_5)_2$	Sc		NMR, IR[299]
$(C_5Me_5)_2LnOC(Me){=}W(C_5H_5)_2$	Sc		brown, NMR, IR[299]
$(C_5Me_5)_2LnOC(Me){=}Co(CO)(C_5H_5)$	Sc	**42a**	orange, X-ray, NMR, IR[299]
$(C_5Me_5)_2LnOC(Me){=}Rh(CO)(C_5H_5)$	Sc		NMR, IR[299]
$(C_5Me_5)_2LnOC(CH_2CH_2Ph){=}Co(CO)(C_5H_5)$	Sc		red-orange, NMR, IR[299]
$(C_5Me_5)_2LnOC(NMe_2){=}Co(CO)(C_5H_5)$	Sc		NMR, IR[299]
$(C_5Me_5)_2LnOCMn(CO)_4$	Yb		complex with $^1/_4$toluene: dark blue, X-ray, NMR, IR, melt./dec.[418]
$(C_5Me_5)_2LnRe(CO)_5$	Yb		complex with $^1/_4$toluene: dark red, NMR, IR, melt./dec.[418]
$[(C_5Me_5)_2Ln]_2(OC)_4[Fe_3(CO)_7]$	Yb		violet, X-ray, NMR, IR , melt./dec., magn. d.[419]
$(C_5Me_5)_2Ln(OC)_2Fe(C_5Me_5)$	Sm		dark red, X-ray, NMR, MS, IR, melt./dec.[420]
$(C_5Me_5)_4Ln_2(\mu\text{-}OCO)(\mu\text{-}OC)_2Fe_2(CO)(C_5H_5)_2$	Dy		complex with 2toluene: X-ray, NMR, IR[421]
$(C_5Me_5)_2LnCo(CO)_4$	Sm		complex with THF: orange, NMR, IR, magn. d.[422]
$(C_5Me_5)_2Ln(OC)Co(CO)_3$	Yb		complex with THF: blue, X-ray, NMR, magn. d.;[399] IR[418]
$[(C_5Me_5)_2Ln]_2[Co_3(C_5H_5)_2(CO)_4]$	Yb		blue, NMR, melt./dec.[423]
$[(C_5Me_5)_2Ln]_2[Co_3(C_5H_4Me)_2(CO)_4]$	Yb		complex with toluene: purple, NMR, IR, melt./dec.[423]
$[(C_5Me_5)_2Ln]_2(OC)_4[Co_3(C_5H_4SiMe_3)_2]$	Yb		X-ray, NMR, IR, ESR[423]

THF$-$Et$_2$O$-$pentane mixture blue prisms of $(THF)(C_5Me_5)_2Yb(\mu\text{-}OC)Co(CO)_3$ (Figure 48), the pentamethylcyclopentadienyl analogue of **41q**, were obtained. A summary of known bis(pentamethylcyclopentadienyl) species with lanthanide oxygen bonds is given in Table 10.

In the suceeding years the utility of divalent decamethylmetallocenes as electron transfer reagents toward transition metal carbonyl derivates has been shown clearly by the synthesis of a considerable number of bis(pentamethylcyclopentadienyl)lanthanide transition metal complexes with Ln$-$OC$-$M interac-

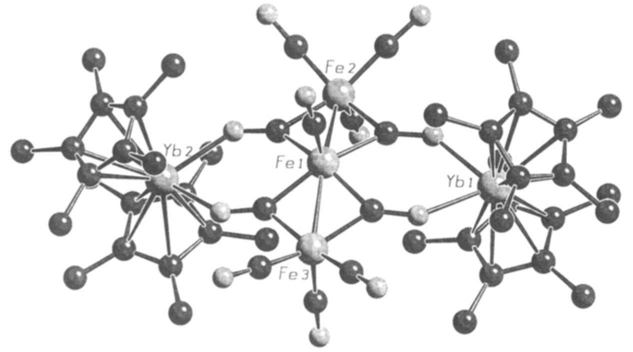


Figure 49. Structure of $[(C_5Me_5)_2Yb]_2(\mu_3\text{-}OC)_4[Fe_3(CO)_7]$ in the crystal.[419]

tions. Because of the better crystallization properties of pentamethylcyclopentadienyl species, compared to cyclopentadienyl compounds, the crystal structures of several new complexes could be elucidated completely by single-crystal X-ray studies. The reactions of samarium or ytterbium decamethylmetallocenes with $[(C_5Me_5)Fe(CO)_2]_2$, $Mn_2(CO)_{10}$, $Fe_3(CO)_{12}/Fe_2(CO)_9$, or $(C_5H_5)Co(CO)_2$ yield $[(C_5Me_5)_2Sm(\mu\text{-}OC)_2Fe(C_5Me_5)]_2$,[420] $\{[(C_5Me_5)_2Yb(\mu\text{-}OC)_xMn(CO)_{5-x}]\cdot{}^1/_4(PhMe)\}_y$ ($x = 2$, $y = 2$; $x = 3$, $y = \infty$),[418] $[(C_5Me_5)_2Yb]_2(\mu_3\text{-}OC)_4[Fe_3(CO)_7]$ (Figure 49),[419] and $[(C_5Me_5)_2Yb]_2(\mu_3\text{-}OC)_4[Co_3(C_5H_4SiMe_3)_2]$,[423] respectively. No X-ray structures are available for "$(THF)(C_5Me_5)_2SmCo(CO)_4$",[422] "$(C_5Me_5)_2YbRe(CO)_5\cdot{}^1/_4(PhMe)$",[418] and "$[(C_5Me_5)_2Yb]_2[Co_3(C_5H_4R)_2(CO)_4]$" (R = H, Me).[423]

Bis(pentamethylcyclopentadienyl)lanthanide halides[289,421] and alkyls[299] react with some metal carbonyl derivatives to give the oligomeric species $[(C_5Me_5)_4Dy_2(\mu\text{-}OCO)(\mu\text{-}OC)_2Fe_2(CO)(C_5H_5)_2]_2\cdot(PhCH_3)_2$,[421] and the ionic cerium complex $[K(THF)_2][(C_5Me_5)_2(I)Ce(\mu\text{-}OC)W(CO)_2(C_5H_5)]$.[289] The following scandoxycarbenes (eqs 37 and 38) are known:[299]

$$(C_5Me_5)_2ScR + (C_5H_5)M(CO)_2 \xrightarrow{\text{toluene}} (C_5Me_5)_2ScOC(R){=}M(CO)(C_5H_5) \quad (37)$$

M = Co: R = H, Me (**42a**), NMe_2, CH_2CH_2Ph

M = Rh: R = Me

$$(C_5Me_5)_2ScR + (C_5H_5)_2MCO \xrightarrow{\text{toluene}} (C_5Me_5)_2ScOC(R){=}M(C_5H_5)_2 \quad (38)$$

M = Mo: R = Me

M = W: R = H, Me

The above transformations are attributed to the strongly Lewis acidic character of the scandium ion, which activates the carbonyl group toward an intramolecular migration of the organic group R to form the acyl. A single-crystal X-ray structure determination of **42a** reveals a μ_2-η^2-carbonyl ligand in addition to the scandoxycarbene moiety bridging both metal fragments (Figure 50).[299]

Three synthetic routes have been used to prepare simple monomeric bis(pentamethylcyclopentadienyl)alkoxolanthanide derivatives. Firstly, it is possible to use lanthanoid alkyls as starting materials. Alcoholysis of bis(pentamethylcyclopentadienyl)alkyllanthanide complexes affords the desired alkoxo products (eqs 39 and 40):[369,405]

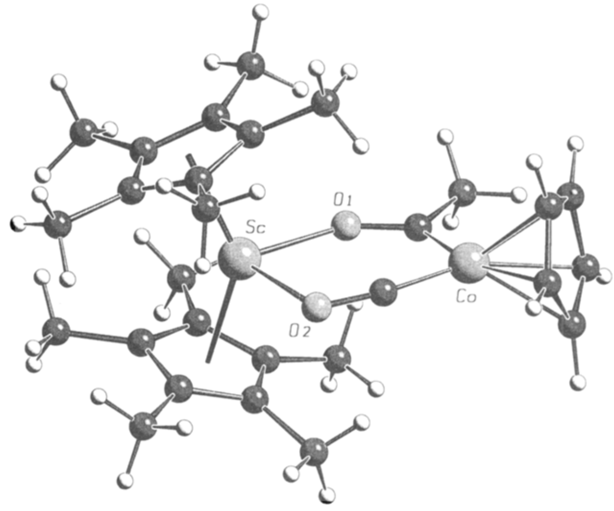


Figure 50. Structure of $[(C_5Me_5)_2ScOC(Me){=}](\mu\text{-}OC)Co(C_5H_5)$ (**42a**) in the crystal.[299]

$$(C_5Me_5)_2LnCH(SiMe_3)_2 + ROH \xrightarrow[-H_2C(SiMe_3)_2]{S'} (C_5Me_5)_2Ln(OR)(Et_2O)_n \quad (39)$$

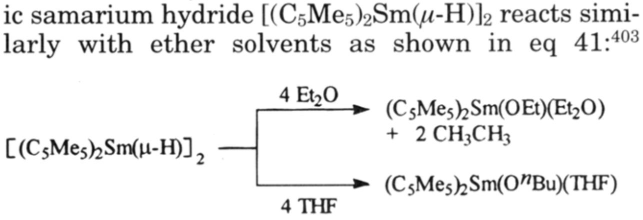
Ln = Y: R = Me, Et (**43b**), ^{i}Pr; $n = 1$;
S′ = Et_2O[278]

Ln = La, Ce: R = $C_6H_3(2,6\text{-}{}^tBu_2)$; $n = 0$;
S′ = pentane[407,408]

$$(C_5Me_5)_2Lu(\mu\text{-}Me)_2Li(THF)_2 + 2{}^tBuOH \xrightarrow[-2CH_4]{Et_2O} (C_5Me_5)_2Lu(O^tBu)(THF) + LiO^tBu \quad (40)$$

Even diethyl ether reacts with $(C_5Me_5)_2Sm(Me)(THF)$ to form the ethoxide−THF adduct $(C_5Me_5)_2Sm(OEt)(THF)$.[404] It is worth mentioning that the exchange reaction of the aryloxide tris(2,6-di-*tert*-butylphenoxo)lanthanum yields with an excess of LiC_5Me_5 traces of $(C_5Me_5)_2La[OC_6H_3(2,6\text{-}{}^tBu)_2]$.[407] Detailed data on the disproportionation of $(C_5Me_5)La[OC_6H_3(2,6\text{-}{}^tBu)_2]_2$ to $(C_5Me_5)_2La[OC_6H_3(2,6\text{-}{}^tBu)_2]$ and $La[OC_6H_3(2,6\text{-}{}^tBu)_2]_3$ are given in the same article.

The second convenient synthetic strategy is derived from reaction of the lanthanide hydride compounds. Watson obtained $(C_5Me_5)_2LuOEt$, by activation of the sp^3 C−H bonds of diethyl ether, from in situ generated lutetium hydride $(C_5Me_5)_2LuH$.[358,360] The dimeric samarium hydride $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ reacts similarly with ether solvents as shown in eq 41:[403]



(41)

$[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ is said to form a fleetingly stable complex in THF, most resonably of composition $(C_5Me_5)_2SmH(THF)$, which then converts to **44h** im-

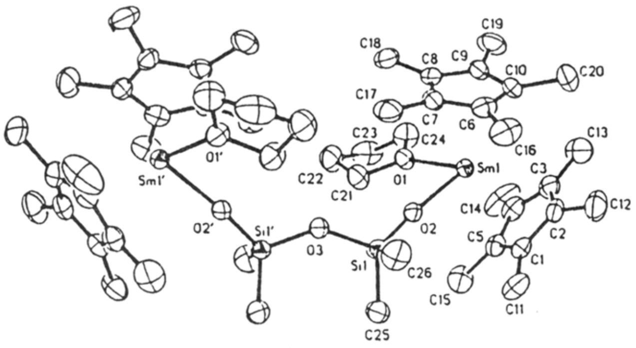
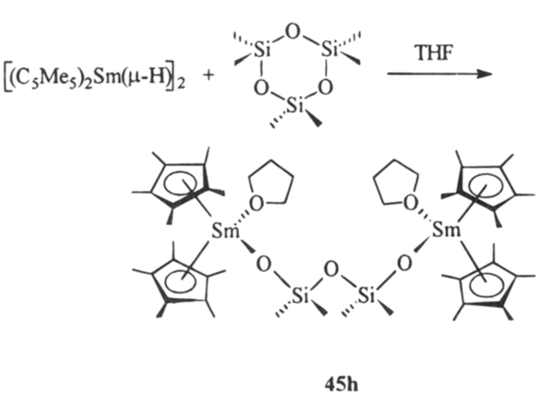


Figure 51. Structure of $[(C_5Me_5)_2Sm(THF)]_2[\mu\text{-}\eta^2\text{-}(OSiMe_2OSiMe_2O)]$ (**45h**) in the crystal.[403] (Reprinted from ref 403. Copyright 1991 American Chemical Society.)

mediately. The identity of the oily samarium butoxide complex **44h** has been established independently by its metathetical synthesis from $(C_5Me_5)_2SmCl(THF)$ and NaOBu in a 5:1 hexane−THF solvent mixture. Marks et al.[271] described, in connection with investigations of bond disruption enthalpies, several bis(pentamethylcyclopentadienyl)samarium derivatives such as dimeric $[(C_5Me_5)_2Sm(\mu\text{-}O^tBu)]_2$ and monomeric $(C_5Me_5)_2SmOCH^tBu_2$ by treatment of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ with toluene solutions of *tert*-butyl alcohol or $HOCH^tBu_2$, respectively. The corresponding lanthanum hydride $[(C_5Me_5)_2La(\mu\text{-}H)]_2$ reacts with excess di-*tert*-butyl ketone giving the alkoxy adduct $(C_5Me_5)_2La(OCH^tBu_2)(OC^tBu_2)$.[406] The reactive nature of the samarium hydride is shown by dissolving $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ in THF, which had been distilled from glassware lubricated with high-vacuum silicone grease, which generated the bridged samarium siloxide compound $[(C_5Me_5)_2Sm(THF)]_2[\mu\text{-}\eta^2\text{-}(OSiMe_2OSiMe_2O)]$ (**45h**) (Figure 51) in high yield. **45h** can also be obtained by reaction of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ with hexamethylcyclotrisiloxane according to eq 42.[403]



(42)

45h

Thirdly, the electron transfer capacity of divalent permethylated metallocenes of ytterbium and samarium can be used in the synthesis of bis(pentamethylcyclopentadienyl)lanthanoid alkoxides. For example, the preparation of $(C_5Me_5)_2SmOC_6H(2,3,5,6\text{-}Me_4)$ has been accomplished by reaction of $(C_5Me_5)_2Sm(THF)_2$ with 2,3,5,6-tetramethylphenol in toluene.[410] However, addition of KC_5Me_5 to a toluene solution of $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$, which is accessible from $(C_5Me_5)_2Sm(THF)_2$ and $AgBPh_4$, results in the formation of $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ (**46h**) (eq 43).[208]

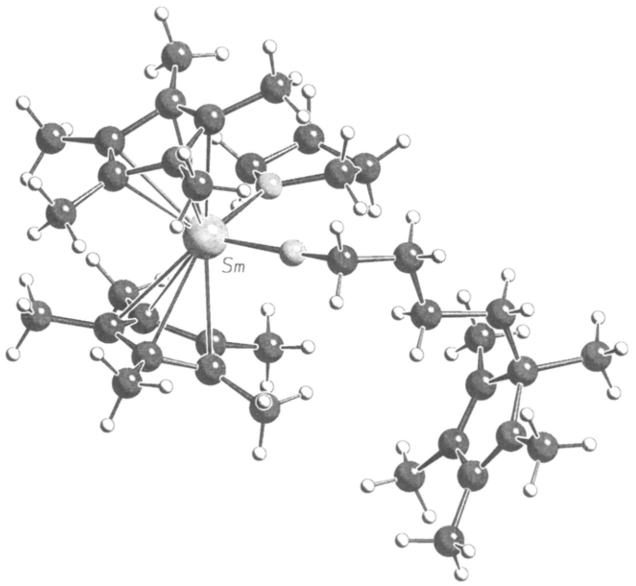
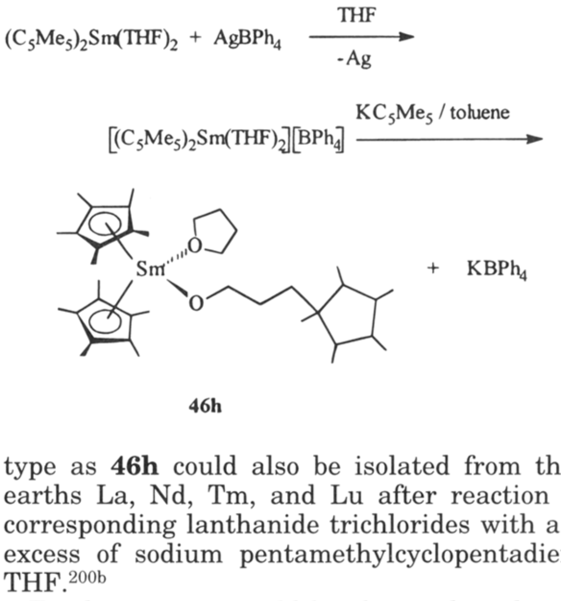


Figure 52. Structure of $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$ (**46h**) in the crystal.[208]

The structure of **46h** (Figure 52) illustrates, once again, the oxophilic nature of the rare earths. The Lewis acidic Sm^{3+} ion of $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ is assumed to form an oxonium ion that is coordinated to THF, which is opened by a nucleophilic attack of the anion $C_5Me_5^-$.[208] Complexes of a similar type as **46h** could also be isolated from the rare earths La, Nd, Tm, and Lu after reaction of the corresponding lanthanide trichlorides with a 3-fold excess of sodium pentamethylcyclopentadienyl in THF.[200b]



(43)

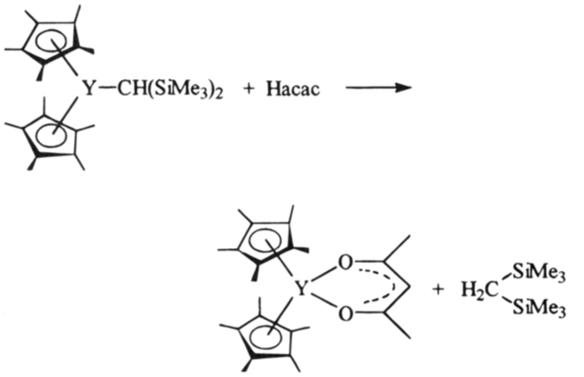
46h

Furthermore, it could be shown that cleavage of diorganoperoxides by the divalent bis(pentamethylcyclopentadienyl)ytterbium ammonia adduct leads to trivalent alkoxides or siloxides as shown in eq 44.[370]

$$2(C_5Me_5)_2Yb(NH_3)_2 + ROOR \xrightarrow{\text{toluene}} (C_5Me_5)_2Yb(OR)(NH_3) + 2NH_3 \quad (44)$$

$$R = {}^tBu,\ SiMe_3$$

Acetylacetonato complexes of bis(pentamethylcyclopentadienyl)lanthanoid species are also known. Stoichiometric reaction between the yttrium derivative $(C_5Me_5)_2YCH(SiMe_3)_2$ and 2,4-pentadione gives the permethylated analogue of **39**[278] (eq 45):



(45)

Additional early lanthanide aldolates have been prepared recently by reaction of bis(pentamethylcyclopentadienyl)lanthanide carbyls with acetone. However, addition of higher ketones, e.g., 3-pentanone, did not result in C−C coupling but gave enolate−ketone adducts.[406]

Metathetical exchange processes of bis(pentamethylcyclopentadienyl)lanthanoid chlorides with sodium carboxylates, which were published 1982 by Tilley et al.,[368] provide a facile synthesis of bis(pentamethylcyclopentadienyl)carboxylato derivatives.

$$(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Na(Et_2O)_2 + NaO_2CR \rightarrow (C_5Me_5)_2Yb(\eta^2\text{-}O_2CR) + 2NaCl \quad (46)$$

$R = {}^tBu$ (**47q**), CF_3 (**48q**)

Mass spectrometric studies of **47q** show, besides the monomeric molecular ion, higher peaks due to oligomers, whereas the mass spectrum of **48q** shows exclusively monomeric molecular ions. The monomeric character of the exceptionally air stable scandium carboxylate $(C_5Me_5)_2Sc[\eta^2\text{-}O_2CC_6H_4(4\text{-}Me)]$, which is accessible by insertion of carbon dioxide into the scandium−aryl bond of the *p*-tolyl species $(C_5Me_5)_2ScC_6H_4(4\text{-}Me)$, has been verified by a single-crystal X-ray structure determination (Figure 53).[412] Related CO_2 insertion reactions are reported for the yttrium analogues giving $(C_5Me_5)_2Y[\eta^2\text{-}O_2CCH(SiMe_3)_2]$ and $(C_5Me_5)_2Y[\eta\text{-}O_2CCH_2C_6H_3(3,5\text{-}Me_2)]$.[411] Exposure of $(C_5Me_5)_2NdCH(SiMe_3)_2$ to carbon monoxide leads to the dimer $[(C_5Me_5)_2Nd(CO)_2CH(SiMe_3)_2]_2$ which is assumed to be a dione diolate species,[304] while $(C_5Me_5)_2ScPh$ reacts with CO to give the monomeric acyl $(C_5Me_5)_2Sc[\eta^2\text{-}C(O)Ph]$.[352]

Reaction of the low-valent, strongly reducing samarium complex $(C_5Me_5)_2Sm(THF)_2$ with carbon monoxide at 90 psi for prolonged periods gives the dimetal-substituted ketenecarboxylate of the general formula $[(C_5Me_5)_4Sm_2(O_2CCCO)(THF)]_2$ (Figure 54) in low yield. The mechanism of this unusual reaction is not known.[416] The reduction of CO and the induction of C=C double bond formation is observed when arene solutions of the samarium hydride $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ are exposed to carbon monoxide. Addition of Ph_3PO to the liquor yields crystals of the enediolate-bridged compound *cis*-$[(C_5Me_5)_2(Ph_3PO)Sm]_2\text{-}[\mu\text{-}\eta^2\text{-}(OCH{=}CHO)]$, which isomerizes at room temperature in solution to the corresponding *trans* species.[417]

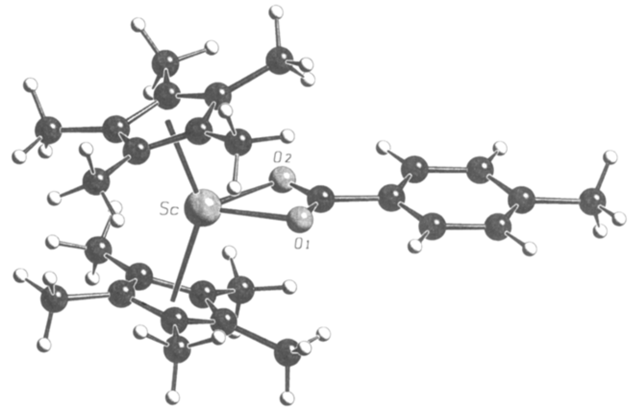


Figure 53. Structure of $(C_5Me_5)_2Sc(\eta^2\text{-}O_2CC_6H_4Me\text{-}4)$ in the crystal.[412]

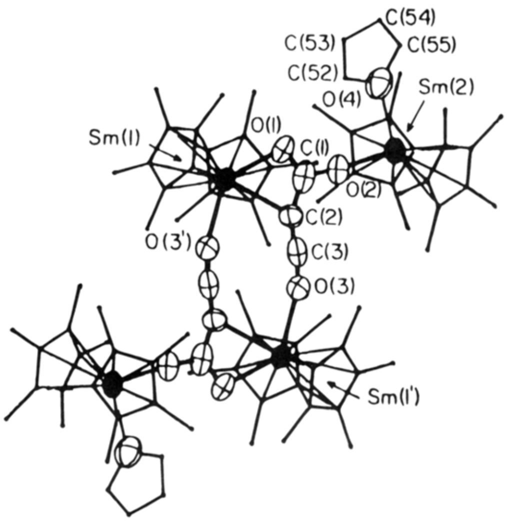


Figure 54. Structure of $[(C_5Me_5)_4Sm_2(O_2CCCO)(THF)]_2$ in the crystal.[416] (Reprinted from ref 416. Copyright 1985 American Chemical Society.)

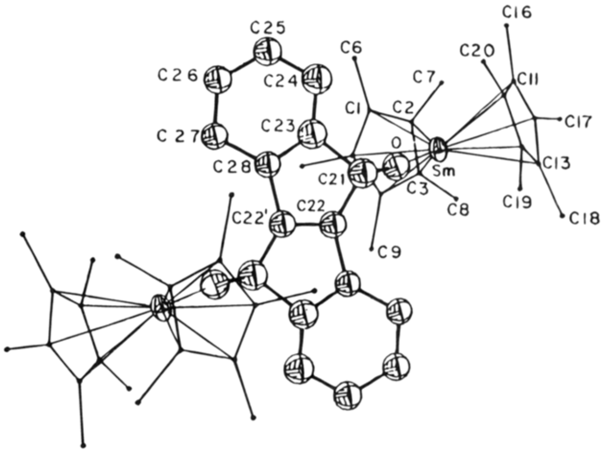
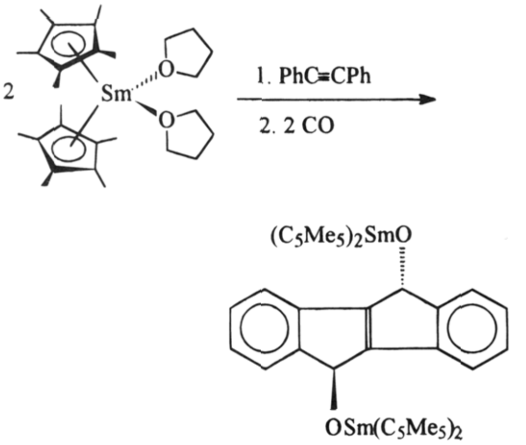


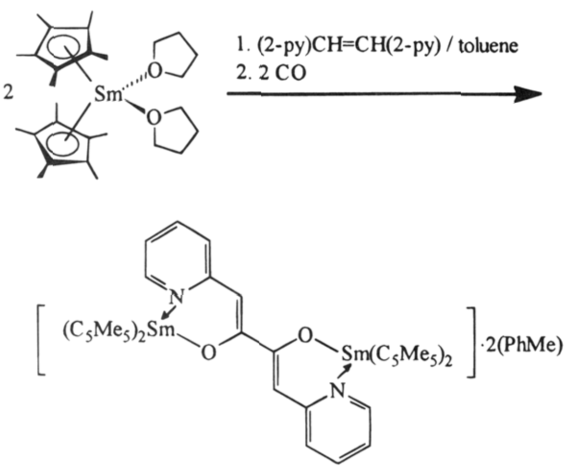
Figure 55. Structure of $[(C_5Me_5)_2Sm(THF)]_2[\mu\text{-}\eta^2\text{-}(O_2C_{16}H_{10})]$ in the crystal.[290] (Reprinted from ref 290. Copyright 1988 Pergamon.)

Other carbon monoxide activation reactions of divalent permethylated samarocene derivatives have been described by Evans et al. They functionalize unsaturated hydrocarbon substrates, such as stilbene (eq 47),[415] 1,2-di-2-pyridylethene (eq 48),[413] azobenzene (eq 49), 3,3′-azatoluene, or the mixed species $PhN{=}N[C_6H_4(4\text{-}NMe_2)]$[108] as shown by X-ray crystallographic characterization of the resulting trivalent samarium dimers:

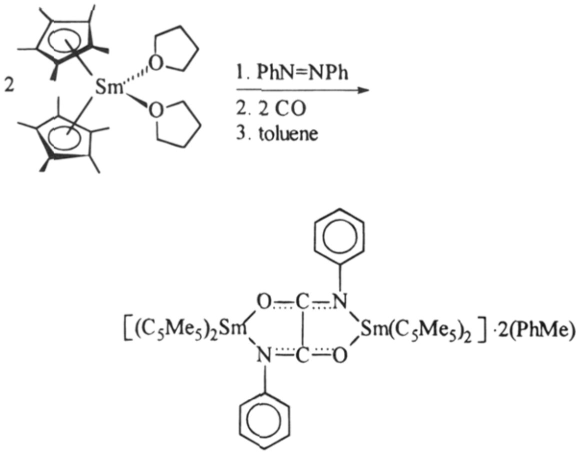


(47)

49h



(48)



(49)

Reactions of $(C_5Me_5)_2Ln(THF)_2$[400] or their base-free derivatives,[401] with oxygen-containing substrates such as NO, N_2O, pyridine *N*-oxide, or 1,2-epoxybutane, allow the isolation of the rigorously linear oxo-bridged bimetallic species $[(C_5Me_5)_2Ln]_2(\mu\text{-}O)$ (Ln = Sm (**50h**),[402] Yb (**50q**)), in acceptable yields; the N_2O reactions work best.[401] Atwood et al.[290] obtained the tetracyclic dihydroindenoindene diolate derivative **49h** when the oxo species **50h** was crystallized from THF and toluene in presence of CN^tBu. Single-crystal X-ray structures of both products, $[(C_5Me_5)_2Sm(THF)]_2[\mu\text{-}\eta^2\text{-}(O_2C_{16}H_{10})]$ (Figure 55) and $[(C_5Me_5)_2Sm(CN^tBu)]_2(\mu\text{-}O)$ were reported.

iii. Derivatives with Other Substituted Cyclopentadienyl Rings. The number of compounds in this class is small (see Table 11). Besides the two dimeric methylcyclopentadienyl acetate complexes $[(MeC_5H_4)_2Ln(\mu\text{-}\eta^2\text{-}O_2CMe)]_2$ (Ln = Gd, Er), which have been prepared from $(MeC_5H_4)_2LnCl$ and sodium acetate,[155] the yttrium enolate $[(MeC_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ is known[379] as is the methoxide $[(Me_3SiC_5H_4)_2Y(\mu\text{-}OMe)]_2$,[226] and some chiral bis(alkylcyclopentadienyl)lanthanide alkoxides.[121b,380] For instance, the synthesis and structure of the chiral dimer, $[(MeC_5H_4)_2Yb(\mu\text{-}O\overline{CH(CH_2)_3O})]_2$ (**51q**) (Figure 56) have been published recently.[380]

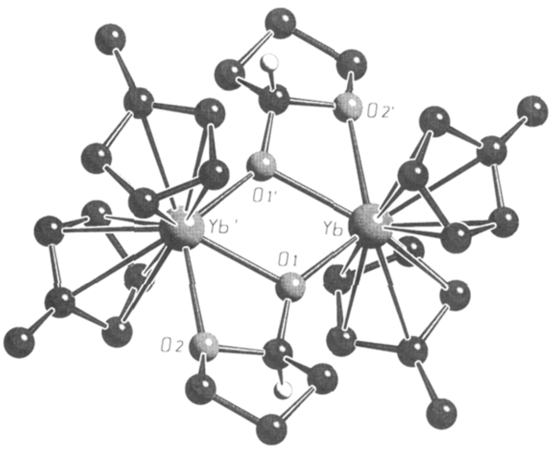


Figure 56. Structure of $\{(MeC_5H_4)_2Yb[\mu\text{-}O(C_4H_7O)]\}_2$ (**51q**) in the crystal.[380]

The synthesis of two bis(*tert*-butylcyclopentadienyl)cerium alkoxides, **52d** and **53d** (eq 50), has been

$$2(^tBuC_5H_4)_3Ce + 2ROH \xrightarrow{\text{hexane}} [(^tBuC_5H_4)_2Ce(\mu\text{-}OR)]_2 + 2\,^tBuC_5H_6 \quad (50)$$

R = ^{i}Pr (**52d**), Ph (**53d**)

accomplished by equimolar reactions of trivalent cerium metallocene with 2-propanol or phenol, liberating *tert*-butylcyclopentadiene.[184] Suitable crystals of **52d** have been investigated by a X-ray structure analysis, which establishes the existence of dimeric units with pseudo-tetrahedral cerium ions and bridging isopropoxide groups.

Using trimethylsilyl-substituted cyclopentadienyl ligands, Hitchcock et al.[425] succeeded in preparing the first pure trivalent organolanthanide hydroxides by accurate hydrolysis of the appropriate divalent samarocene and ytterbocene derivatives, $[(Me_3Si)_2C_5H_3]_2Sm(THF)$ and $(Me_3SiC_5H_4)_2Yb(Et_2O)$. Single crystals of $\{[(Me_3Si)_2C_5H_3]_2Sm(\mu\text{-}OH)\}_2$ (**54h**) (Figure 57) as well as of $[(Me_3SiC_5H_4)_2Yb(\mu\text{-}OH)]_2$ were grown from toluene and diethyl ether solutions, respectively, and their identities were established by X-ray diffraction studies.[425] Recently, the solid-state structure of the lutetium homologue **54r**[146c] was described as were the related dimers $[(RC_5H_4)_2Ln(\mu\text{-}OH)]_2$ (R = ^{t}Bu, Ln = Dy, Nd; [197] R = CH_2CH_2OMe, Ln = Er[424]), and $\{[O(CH_2CH_2C_5H_4)_2]Y(\mu\text{-}OH)\}_2$[93] (Figure 58).

The accidental isolation of the oxo-bridged ytterbium organyl $[(MeC_5H_4)_2Yb(THF)](\mu\text{-}O)$ from THF solutions of $(MeC_5H_4)_3Yb$ (**13q**) in the presence of glyoxal bis(*tert*-butylimine) emphasizes that small amounts of water leads to hydroxide species.[190]

Table 11. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Oxygen Compounds Containing Other Substituted Cyclopentadienyl Ligands

compound	Ln		color, characterization, etc.
$[(MeC_5H_4)_2Ln]_2O$	Yb		complex with 2THF: light green, X-ray[190]
$(MeC_5H_4)_2Ln(menth)$	Pr		NMR, UV[121b]
	Yb		orange, melt./dec.;[380] UV[121b]
$(MeC_5H_4)_2LnO(C_4H_7O)$	Yb	**51q**	dimer, yellow orange, X-ray, melt./dec.[380]
$(MeC_5H_4)_2LnOCH(Et)CO_2Et$	Pr		NMR, UV[121b]
$(MeC_5H_4)_2Ln(OCH{=}CH_2)$	Y		dimer, straw, X-ray, NMR, IR, melt./dec.[379]
$(MeC_5H_4)_2LnO_2CMe$	Gd		white, melt./dec.[155]
	Er		pink, melt./dec.[155]
$(MeC_5H_4)_2LnW(C_5H_5)(CO)_3$	Dy		IR[141b]
	Ho		IR[141b]
$(EtC_5H_4)_2LnOCH(Me)Et$	Yb		UV[121b]
$(^tBuC_5H_4)_2LnOH$	Nd		dimer, X-ray, MS, IR[197]
	Dy		dimer, X-ray[197]
$(^tBuC_5H_4)_2LnO^iPr$	Ce	**52d**	dimer, yellow, X-ray, NMR, MS, IR, melt./dec.[184]
$(^tBuC_5H_4)_2LnOPh$	Ce	**53d**	dimer, yellow, NMR, MS, IR, melt./dec.[184]
$(MeOCH_2CH_2C_5H_4)_2LnOH$	Ho		dimer, yellow, X-ray[725]
	Er		dimer, X-ray[424]
$(Me_3SiC_5H_4)_2LnOH$	Yb		dimer, yellow, X-ray[425]
$(Me_3SiC_5H_4)_2LnOMe$	Y		dimer, X-ray, NMR, IR[226]
$(Me_3SiC_5H_4)_2Ln(\mu\text{-}O^tBu)_2Li(THF)_2$	Y		X-ray, NMR[581]
$[(Me_3Si)_2C_5H_3]_2LnOH$	Sm	**54h**	dimer, yellow, X-ray[425]
	Lu	**54r**	dimer, X-ray, NMR, melt./dec.[146c]
$[(Me_3Si)_2C_5H_3]_2Ln(\mu\text{-}OC)W(CO)(C_5H_5)(\mu\text{-}CO)$	Ce	**55d**	dimer, yellow, NMR, IR;[313] X-ray, lumines.;[311] with NCMe: $[(Me_3Si)_2C_5H_3]_2Ln(NCMe)_x]^+[(C_5H_5)W(CO)_3]^-$ [311]
$[C_5H_4(CH_2)_3C_5H_4]LnO_2CCF_3$	La		complex with THF: reaction[164]
$[O(CH_2CH_2C_5H_4)_2]LnOH$	Y		dimer, colorless, X-ray, NMR, IR[93]

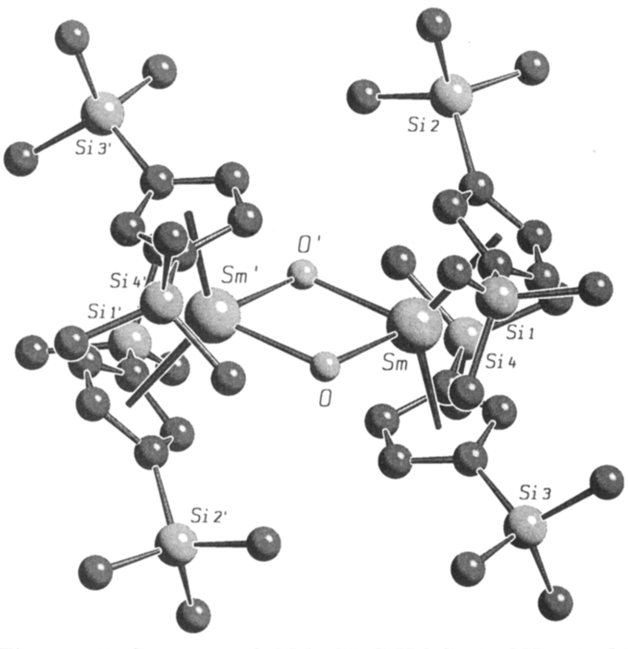


Figure 57. Structure of $\{[(Me_3Si)_2C_5H_3]_2Sm(\mu\text{-}OH)\}_2$ (**54h**) in the crystal.[425]

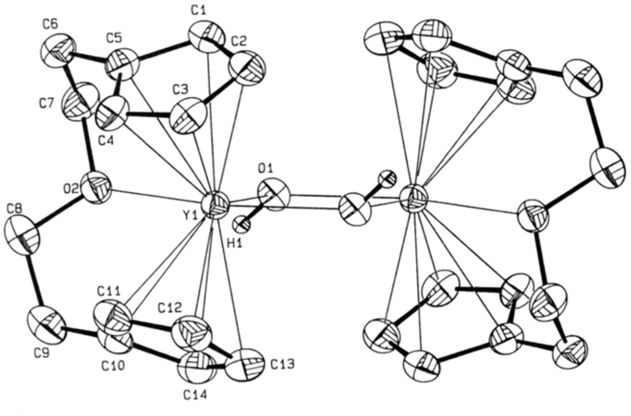


Figure 58. Structure of$\{[O(CH_2CH_2C_5H_4)_2]Y(\mu\text{-}OH)\}_2$ in the crystal.[93]

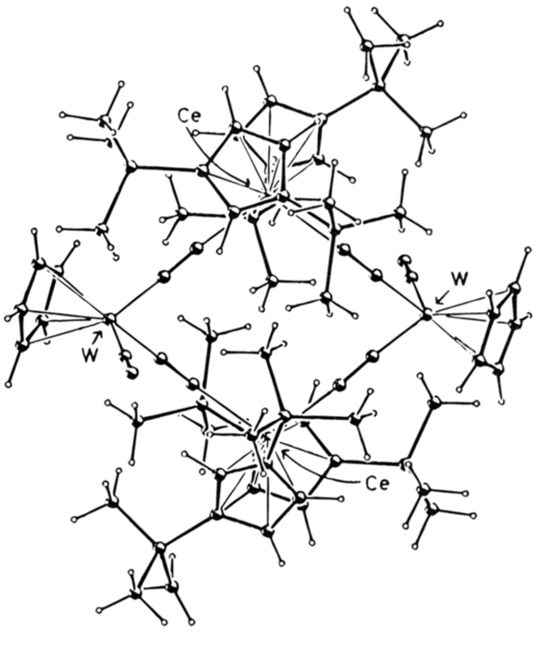
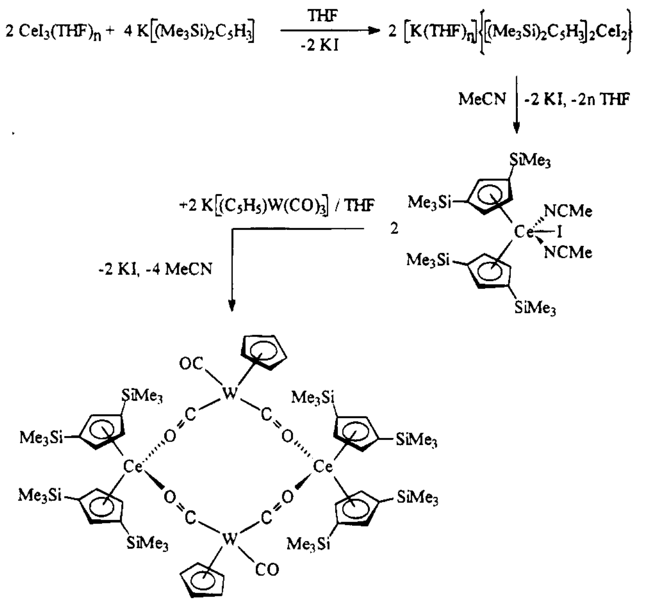


Figure 59. Structure of $\{[(Me_3Si)_2C_5H_3]_2Ce(\mu\text{-}OC)W(CO)(C_5H_5)(\mu\text{-}CO)\}_2$ (**55d**) in the crystal.[311] (Reprinted from ref 311. Copyright 1988 Chemical Society of London.)

Some heterobimetallic isocarbonyl (Ln = Dy, Ho, M = W) and isonitrosyl (Ln = Yb, M = Cr) derivatives of organolanthanides with two monomethyl-substituted cyclopentadienyl ligands have been mentioned in literature.[141] The single-crystal X-ray structure determination of the cerium−tungsten metallacycle $\{[(Me_3Si)_2C_5H_3]_2Ce(\mu\text{-}OC)W(CO)(C_5H_5)(\mu\text{-}CO)\}_2$ (**55d**) reveals a 12-membered ring in which two cerium and two tungsten atoms are linked alternately by four η^2-bridging carbonyl groups (Figure 59).[311] The nonluminescent character of the Ce^{3+} centers is assumed to be due to a close cerium−tungsten contact that results in excited-state energy transfer. Sequential treatment of cerium triiodide (eq 51) with potassium bis(trimethylsilyl)cyclopentadienyl, acetonitrile, and K[C_5H_5)W(CO)$_3$] yields **55d**:[313]



55d (51)

b. Compounds with Rare Earth to Sulfur, Selenium, and Tellurium Bonds. The lesser stability of bonds between "hard" rare earth elements and the heavier chalcogenides, which are "soft" donors according to Pearsons concept,[367] has already been mentioned. Perhaps it is not surprising that organolanthanides with lanthanide to sulfur bonds are more rare than the analogous species with oxygen. The synthesis of complexes with lanthanide–selenium or even lanthanide–tellurium linkages was accomplished in only a few cases. At this time, the pool of known compounds containing Ln–E (E = S, Se, Te) units is restricted to five different structural types: $Cp_2Ln(\mu\text{-}E_2R)$ [$Cp_2 = (C_5Me_5)_2, (CMe_2C_5H_4)_2$], $Cp_2Lu(\mu\text{-}ER)_2Li(THF)_2$ [$Cp_2 = (C_5H_5)_2, (C_5Me_5)_2$], $Cp_2Ln(ER)(S')$ [$Cp_2 = (C_5Me_5)_2, (CMe_2C_5H_4)_2$; S′ = solvent], $[(C_5Me_5)_2Ln]_2(\mu\text{-}E)$ and $[Cp_2Ln(\mu\text{-}ER)]_2$ [$Cp_2 = ({}^tBuC_5H_4)_2, (C_5Me_5)_2$]. Important data of these chalcogenides are summarized in Table 12 (sulfur derivatives) and Table 13 (selenium and tellurium derivatives).

Dithiocarbamates, the first metallorganic species with rare earth to sulfur bonds were synthesized as long ago as 1982 by metathesis of bis(pentamethylcyclopentadienyl)lanthanide chlorides with sodium diethyldithiocarbamate in diethyl ether (eq 52, Figure 60).[368] Later, Teuben et al.[411] described the formation

$$(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Na(Et_2O)_2 + NaS_2CNEt_2 \xrightarrow[-2NaCl]{Et_2O} \underset{\textbf{56}}{(C_5Me_5)_2Ln(\eta^2\text{-}S_2CNEt_2)} \quad (52)$$

Ln = Nd (**56f**), Yb (**56q**)

of $(C_5Me_5)_2Y(\eta^2\text{-}S_2CH_2C_6H_3Me_2\text{-}3,5)$ from the insertion of carbon disulfide into the Yb–C bond in $(C_5Me_5)_2YCH_2C_6H_3Me_2\text{-}3,5$.

Table 12. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Chalcogenides Containing Lanthanide to Sulfur Bonds

compound	Ln		color, characterization, etc.
$(C_5H_5)_2LnSC_4H_9$	Dy		dimer, MS, reaction[690]
$(C_5H_5)_2Ln(\mu\text{-}S^tBu)_2Li(THF)_2$	Lu		white, NMR, melt./dec.[369]
$[(C_5Me_5)_2Ln]_2S$	Sm		complex with 2 THF: yellow, X-ray, NMR[727]
	Yb		red, NMR, IR, MS, melt./dec., magn. d.[401]
$[(C_5Me_5)_2Ln]_2S_3$	Sm		complex with THF: orange, NMR, IR[727]
$(C_5Me_5)_2LnSMe$	Yb		complex with NH_3: NMR, IR, melt./dec.[370]
$(C_5Me_5)_2LnS^nPr$	Sm		orange, NMR, IR[271]
$(C_5Me_5)_2LnS^tBu$	Sc		complex with 4-(dimethylamino)pyridine: NMR[728]
$(C_5Me_5)_2Ln(\mu\text{-}S^tBu)_2Li(THF)_2$	Lu	**58r**	colorless, X-ray, NMR, melt./dec.[369,405]
$(C_5Me_5)_2LnSCH_2Ph$	Yb		complex with Et_2O: purple, NMR, IR, melt./dec.; with NH_3: NMR, IR, melt./dec.[370]
$(C_5Me_5)_2LnSPh$	Yb		complex with Et_2O: purple, NMR, IR;[370] with NH_3: red, NMR, IR, melt./dec.;[370] X-ray[426]
$(C_5Me_5)_2LnSC_6H_4Me\text{-}3$	Yb		complex with Et_2O: purple, NMR, IR, melt./dec.; with NH_3: NMR, IR, melt./dec.[370]
$(C_5Me_5)_2LnSC_6H_4Me\text{-}4$	Yb		complex with Et_2O: purple, NMR, IR, melt./dec.; with NH_3: NMR, IR, melt./dec.[370]
$(C_5Me_5)_2LnSC_6H_2Me_3\text{-}2,4,6$	Sm		complex with THF: orange, NMR, IR, MS, melt./dec.[427]
	Yb		purple, NMR, IR, melt./dec.[370]
$(C_5Me_5)_2LnS_2CCH_2C_6H_3Me_2\text{-}3,5$	Y		white, NMR, IR[411]
$(C_5Me_5)_2LnS_2CNMe_2$	Nd		green, NMR, MS, IR, melt./dec.[300]
	Sm		orange, X-ray, NMR, MS, IR, melt./dec.[427]
$(C_5Me_5)_2LnS_2CNEt_2$	Nd	**56f**	green, NMR, MS, IR, melt./dec., magn. d.[368]
	Yb	**56q**	purple, melt./dec.,[368,370] X-ray, NMR, IR, MS, magn. d.[368]
$(C_5Me_5)_2LnS_2PMe_2$	Yb		violet, NMR, IR, melt./dec.[370]
$(C_5Me_5)_2LnS_2PEt_2$	Yb		NMR, IR, melt./dec.[370]
$(MeC_5H_4)_2LnS^tBu$	Ce		purple, NMR, IR, melt./dec.[184]
$({}^tBuC_5H_4)_2LnS^nBu$	Y		ref 428
$({}^tBuC_5H_4)_2LnS^tBu$	Y		ref 428
$({}^tBuC_5H_4)_2LnSCH_2Ph$	Y		ref 428
	Lu		ref 428
$({}^tBuC_5H_4)_2LnSPh$	Y		colorless, NMR, melt./dec.[428]
	Ce		pink, NMR, MS, IR, melt./dec.[184]
	Lu		colorless, NMR, melt./dec.[428]
$({}^tBuC_5H_4)_2LnS^iPr$	Ce		magenta, X-ray, NMR, MS, IR, melt./dec,[184] reactions[520]
$(CMe_2C_5H_4)_2LnS_2CNMe_2$	Sm		yellow, NMR, MS, IR, melt./dec.[347b]
	Yb		orange red, NMR, MS, IR, melt./dec.[347b]
$(CMe_2C_5H_4)_2LnS_2P(OMe)_2$	Sm		yellow, NMR, MS, IR, melt./dec.[347b]
	Yb		red, NMR, MS, IR, melt./dec.[347b]

Table 13. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Chalcogenides Containing Lanthanide to Selenium and Tellurium Bonds, Respectively

compound	Ln		color, characterization, etc.
$(C_5H_5)_2Ln(\mu\text{-}SePh)_2Li(THF)_2$	Lu	**57r**	colorless, X-ray, NMR, melt./dec.[369]
$[(C_5Me_5)_2Ln]_2Se$	Sc		yellow, X-ray, NMR, UV[728]
	Sm		complex with 2 THF: orange, X-ray, NMR, IR[727]
	Yb	**59q**	purple, X-ray, NMR, IR, MS, melt./dec., magn. d.[401]
$[(C_5Me_5)_2Ln]_2Se_3$	Sm		complex with THF: dark red, X-ray, NMR, IR,[727] reactions[730]
$(C_5Me_5)_2LnSeCH_2SiMe_3$	Sc		yellow, NMR, UV[728]
$(C_5Me_5)_2LnSePh$	Yb		complex with Et_2O: purple, NMR, IR, melt./dec.; with NH_3: NMR, IR, melt./dec.[370]
$(C_5Me_5)_2LnSeC_6H_2Me_3$-2,4,6	Nd		complex with THF: olive green, NMR, IR, melt./dec.[300]
	Sm		complex with THF: orange, NMR, IR, MS, melt./dec.[427]
$(C_5Me_5)_2LnSeC_6H_2(CF_3)_3$-2,4,6	Sm		complex with THF: orange, X-ray, NMR, MS, IR, melt./dec.[427]
$(^tBuC_5H_4)_2LnSePh$	Y		complex with C_6H_6: colorless, X-ray, NMR, melt./dec.[428]
	Lu		colorless, NMR, melt./dec.[428]
$(CMe_2C_5H_4)_2LnSeC_6H_2Me_3$-2,4,6	Sm		yellow, NMR, MS, IR; melt./dec.[347b]
$[(C_5Me_5)_2Ln]_2Te$	Sc		orange,[728,731] X-ray, NMR, UV, reactions,[728]
	Sm		complex with 2THF: dark red, X-ray, NMR, IR[727]
	Yb	**60q**	X-ray,[429] green, NMR, MS, melt./dec., magn. d.[401]
$[(C_5Me_5)_2Ln]_2Te_2$	Sm		brown, X-ray, NMR[727]
$[(C_5Me_5)_2Ln]_2Te_3$	Sm		black, NMR, IR[727]
$[(C_5Me_5)_2Ln]_2(Se_2Te)$	Sm		complex with THF: orange, X-ray, NMR[727]
$(C_5Me_5)_2LnTeH$	Sc		complex with 4-(dimethylamino)pyridine: NMR[728]
$(C_5Me_5)_2LnCHDCHD^tBu$	Sc		yellow, NMR[728,731]
$(C_5Me_5)_2Ln(CH_2)_4CH{=}CMe_2$	Sc		NMR[728]
$(C_5Me_5)_2Ln(CH_2)_4CH{=}CH_2$	Sc		NMR[728]
$(C_5Me_5)_2LnCH_2C_5H_9$-*c*	Sc		NMR[728]
$(C_5Me_5)_2LnTeCH_2Ph$	Sc		yellow, X-ray, NMR[728]
$(C_5Me_5)_2LnTeCH_2SiMe_3$	Sc		orange, NMR, UV[728]
$(C_5Me_5)_2LnTePh$	Sc		yellow, NMR, UV[728]
	Yb		complex with Et_2O: olive-green, NMR, IR, melt./dec.; with NH_3: X-ray, NMR, IR, melt./dec.[370]
$(C_5Me_5)_2LnTeC_6H_2Me_3$-2,4,6	Sm		complex with THF: orange, X-ray, NMR, MS, IR, melt./dec.[427]
$[(C_5Me_5)_2LnTeCH_2SiMe_3]_2Te$	Sc		NMR[728]
$(^tBuC_5H_4)_2LnTeMe$	Y		colorless, NMR[430]
$[Me_2Si(C_5H_3{}^tBu)_2Ln]_2Te$	Sc		purple, NMR, reactions; complex with $2PMe_3$: red-purple, X-ray, NMR[732]
$Me_2Si(C_5H_3{}^tBu)_2LnTeCH_2SiMe_3$	Sc		orange, NMR, reactions[732]

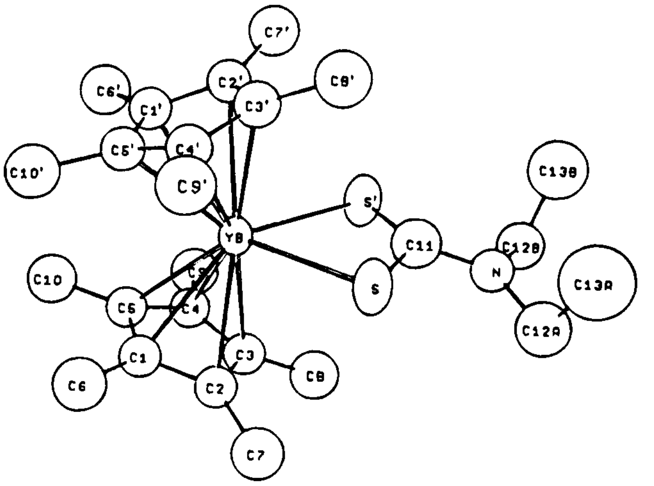


Figure 60. Structure of $(C_5Me_5)_2Yb(\eta^2\text{-}S_2CNEt_2)$ (**56q**) in the crystal.[368] (Reprinted from ref 368. Copyright 1982 American Chemical Society.)

Andersen et al.[370] showed that it is also possible to isolate **56q** after S−S bond cleavage of tetraethylthiuram disulfide $[Et_2NC(S)S-]_2$ with divalent permethylated ytterbocene. In addition, $(C_5Me_5)_2Yb(Et_2O)$ reacts with dithiophosphinates with formation of trivalent dialkyldithiophosphinatoytterbium derivatives and in addition to two other phosphorous-containing species, according to eq 53.[370]

$$4(C_5Me_5)_2Yb(Et_2O) + 5R_2P(S)P(S)R_2 \xrightarrow{\text{toluene}/-4Et_2O} 4(C_5Me_5)_2Yb(\eta^2\text{-}S_2PR_2) + R_2PPR_2 + 2R_2P(S)PR_2 \quad (53)$$

R = Me, Et

Recently, Edelmann et al. reported the synthesis of the dithiocarbamates $(C_5Me_5)_2Ln(\eta^2\text{-}S_2CNMe_2)$ (Ln = Nd, Sm) from $[K(THF)_n][(C_5Me_5)_2NdCl_2]$[300] or $(C_5Me_5)_2Sm(THF)_2$[427] with tetramethylthiuram disulfide $[Me_2NC(S)S-]_2$ as well as the synthesis of $(CMe_2C_5H_4)_2Ln(\eta^2\text{-}S_2CNMe_2)$ (Ln = Sm, Yb) via reductive cleavage of the S−S bond with corresponding divalent lanthanidocenes.[347b] The latter reaction works analogously with bis(dimethoxythiophosphoryl) disulfide $[(MeO)_2P(S)S-]_2$ yielding the complexes $(CMe_2C_5H_4)_2Ln[\eta^2\text{-}S_2P(OMe)_2]$ (Ln = Sm, Yb).[347b]

Much later the synthesis and X-ray crystallography verification of the first organolanthanide-selenium compound was reported: Schumann et al. published in 1988 a series of methane-liberating reactions of bis(cyclopentadienyl)lutetium alkyls with acidic reagents such as benzeneselenol and 2-methylpropane-2-thiol (eq 54).[405,369]

$$Cp_2Lu(\mu\text{-}Me)_2Li(THF)_2 + 2HER \xrightarrow{Et_2O} Cp_2Lu(\mu\text{-}ER)_2Li(THF)_2 + 2CH_4 \quad (54)$$

E = Se: R = Ph; Cp = (C_5H_5) (**57r**)

E = S: R = ^{t}Bu; Cp = (C_5H_5), (C_5Me_5) (**58r**)

The single-crystal X-ray structure analyses of **57r** (Figure 61) and **58r** showed that both of the metal atoms Lu and Li were arranged in puckered four-atom units, containing two bridging seleno or thio groups, respectively.

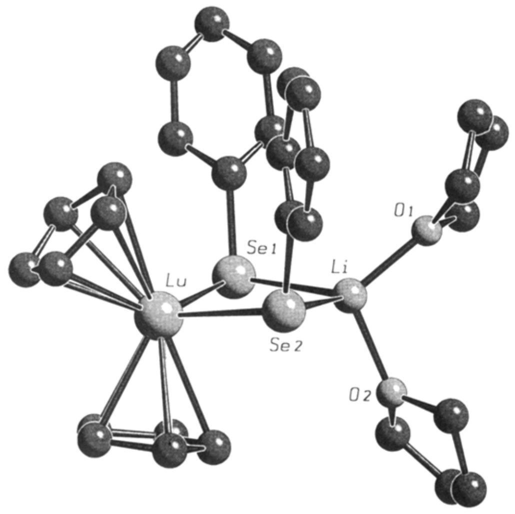


Figure 61. Structure of $(C_5H_5)_2Lu(\mu\text{-}SePh)_2Li(THF)_2$ (**57r**) in the crystal.[369]

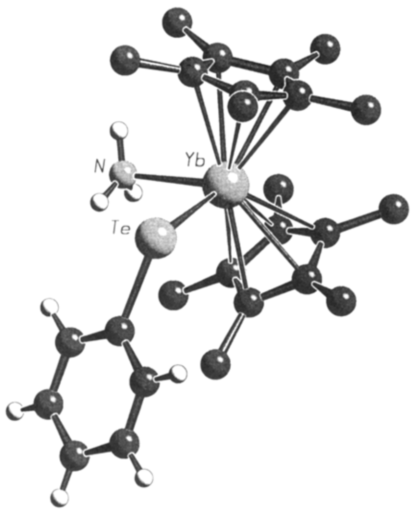


Figure 62. Structure of $(C_5Me_5)_2Yb(TePh)(NH_3)$ in the crystal.[370]

Reductive cleavage of S−S, Se−Se, or Te−Te bonds by divalent permethylated ytterbocenes provided access for the first time to monomeric organolanthanides with a rare earth linkage to the higher homologues of oxygen (Figure 62). The diethyl ether and ammonia complexes have been described, as shown in eqs 55 and 56.[370]

$$2(C_5Me_5)_2Yb(Et_2O) + REER \xrightarrow{Et_2O} 2(C_5Me_5)_2Yb(ER)(Et_2O) \quad (55)$$

$E = S$: $R = Ph, CH_2, Ph, C_6H_4Me\text{-}3, C_6H_4Me\text{-}4$
$E = Se$: $R = Ph$
$E = Te$: $R = Ph$

$$2(C_5Me_5)_2Yb(NH_3)_2 + REER \xrightarrow{toluene} 2(C_5Me_5)_2Yb(ER)(NH_3) + NH_3 \quad (56)$$

$E = S$: $R = Me, Ph, CH_2Ph, C_6H_4Me\text{-}3, C_6H_4Me\text{-}4$
$E = Se$: $R = Ph$
$E = Te$: $R = Ph$

Similar bis(pentamethylcyclopentadienyl)neodymium and -samarium monomers with a terminal chalcogenide ligand have been obtained as THF adducts by reactions of $[K(THF)_n][(C_5Me_5)_2NdCl_2]$[300] or $(C_5Me_5)_2Sm(THF)_2$,[427] with disulfides, diselenides, or ditellurides: $(C_5Me_5)_2Ln(EC_6H_2Me_3\text{-}2,4,6)(THF)$ (Ln = Nd, E = Se; Ln = Sm, E = S, Se, Te) and $(C_5Me_5)_2Sm[SeC_6H_2(CF_3)_3\text{-}2,4,6](THF)$. However, the the use of the sterically less demanding bridged bis(cyclopentadienyl) dianion $[(CMe_2C_5H_4)_2]^{2-}$ allows isolation of the solvent-free mesityl species $(CMe_2C_5H_4)_2SmSeC_6H_2Me_3\text{-}2,4,6$.[347b]

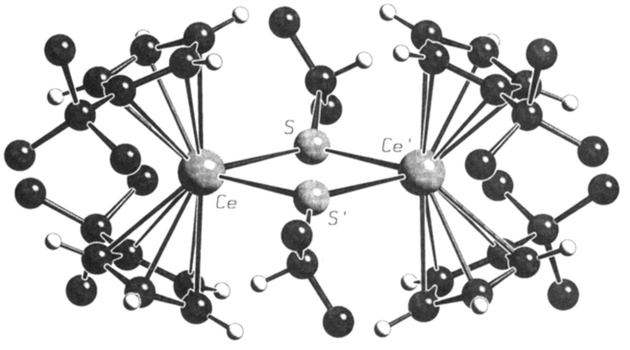


Figure 63. Structure of $[(^tBuC_5H_4)_2Ce(\mu\text{-}S^iPr)]_2$ in the crystal.[184]

In analogy to electron transfer processes affording the oxo-bridged compound $[(C_5Me_5)_2Ln]_2(\mu\text{-}O)$ (**50**), Andersen et al.[401] described the synthesis of the bridging chalcogenides $[(C_5Me_5)_2Yb]_2(\mu\text{-}E)$ [E = S, Se (**59q**), Te (**60q**)] from $(C_5Me_5)_2Yb(Et_2O)$ and the appropriate trialkylphosphine species R_3PE (R = ^{n}Bu, Ph). While the sulfur derivative could be synthesized from $(C_5Me_5)_2Yb(Et_2O)$ with either COS or As_2S_3, but not from elemental sulfur, $(C_5Me_5)_2Yb(Et_2O)$ was shown to react with elemental selenium and tellurium to give the complexes **59q** and **60q**, respectively. X-ray crystallographic data for the selenium dimer **59q** show that the Yb−Se−Yb angle is 171°. The reason for the change in geometry between the selenium and oxygen analogous is not known.

The dimeric complexes $[Cp_2Ln(\mu\text{-}ER)]_2$ (Cp_2 = $(^tBuC_5H_4)_2$, $(C_5Me_5)_2$) are also known. Preparative routes are based on reactions of thiols with trivalent lanthanide hydrides (eq 57)[271] or homoleptic alkylcyclopentadienyllanthanides (eq 58).[184]

$$[(C_5Me_5)_2Sm(\mu\text{-}H)]_2 + 2HS^nPr \rightarrow [(C_5Me_5)_2Sm(\mu\text{-}S^nPr)]_2 + 2H_2 \quad (57)$$

$$2(RC_5H_4)_3Ce + 2HSR' \rightarrow [(RC_5H_4)_2Ce(\mu\text{-}SR')]_2 + 2RC_5H_5 \quad (58)$$

$R = Me$: $R' = {}^tBu$
$R = {}^tBu$: $R' = {}^iPr, Ph$

While the dimeric character of the Sm derivative is supported by cryoscopy, the structure of the cerium thiolate, $[(^tBuC_5H_4)_2Ce(\mu\text{-}S^iPr)]_2$ (Figure 63), has been determined by X-ray crystallography.

Recently, many dimeric chalcogen derivatives of organolanthanides $[(^tBuC_5H_4)_2Ln(\mu\text{-}ER)]_2$ (Ln = Y, ER = SPh, S^{n}Bu, S^{t}Bu, SCH$_2$Ph, SePh; Ln = Lu, ER = SPh, SCH$_2$Ph, SePh;[428] Ln = Y, R = TeMe[430]) have been reported. While the sulfur and selenium compounds were synthesized from the cleavage of Ln−

Me σ-bonds in $[(^tBuC_5H_4)_2Ln(\mu\text{-}Me)]_2$ by dichalcogenides R−E−E−R, the tellurium complex was prepared by insertion of metallic tellurium into the Ln−Me σ-bond of $[(^tBuC_5H_4)_2Ln(\mu\text{-}Me)]_2$.

3. Bis(cyclopentadienyl) Rare Earth Pnicogenides

Similar to rare earth chalcogenide compounds, a close relationship exists between the stability of lanthanide−pnicogen bonds and the degree of hardness or softness[367] of the group-15 element. Consequently, many compounds exist with nitrogen to lanthanide bonds, whereas only one is known with a lanthanide−bismuth bond.

a. Compounds with Rare Earth to Nitrogen Bonds. *i. Cyclopentadienyl Derivatives.* The synthesis of the first organometallic lanthanide−nitrogen complex was published in 1963 (eq 59):[155]

$$(C_5H_5)_2ErCl + NaNH_2 \xrightarrow{THF} \underset{\textbf{61o}}{(C_5H_5)_2ErNH_2} + NaCl \quad (59)$$

Three years later, in 1966, Fischer et al.[96] showed (eq 60) that the ammonia adduct of tris(cyclopentadienyl)ytterbium decomposes upon heating above 200 °C to give cyclopentadiene and the ytterbium amide **61q**:

$$(C_5H_5)_3Yb(NH_3) \xrightarrow{200-250\ °C} \underset{\textbf{61q}}{(C_5H_5)_2YbNH_2} + C_5H_6 \quad (60)$$

In succeeding publications **61q** has been described as the dimer $[(C_5H_5)_2Yb(\mu\text{-}NH_2)]_2$.[65,67,72,431] The dimerization by way of bridging NH_2 groups for **61q** is supported by mass spectroscopic studies[67,431] and by the crystal structure of the methylcyclopentadienyl analogue.[432]

Evans et al.[433,434] reported in 1983 the synthesis of *N*-alkylformimidoyl rare earth complexes (**62** and **63**) from the organoyttrium hydride $[(C_5H_5)_2Y(\mu\text{-}H)(THF)]_2$ or its deuterated derivative with 2-methylpropane-2-butylisonitrile as outlined in eq 61. The

$$[(C_5H_5)_2Ln(\mu\text{-}X)(THF)]_2 + 2\,^tBuN{\equiv}C \xrightarrow{THF} \underset{\textbf{62, 63}}{\{(C_5H_5)_2Ln[\mu\text{-}\eta^2\text{-}(XC{=}N^tBu)]\}_2} \quad (61)$$

Ln = Y: X = H (**62b**), D (**63b**)

Ln = Er: X = H (**62o**)

dimeric formimidoyl geometry of **62b** (Figure 64) (and later on of **62o**[434]), suggested by spectroscopical data, was proved by a X-ray diffraction study.

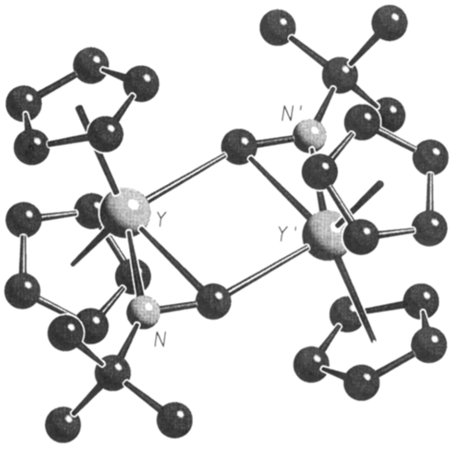


Figure 64. Structure of $\{(C_5H_5)_2Y[\mu\text{-}\eta^2\text{-}(HC{=}N^tBu)]\}_2$ (**62b**) in the crystal.[433,434]

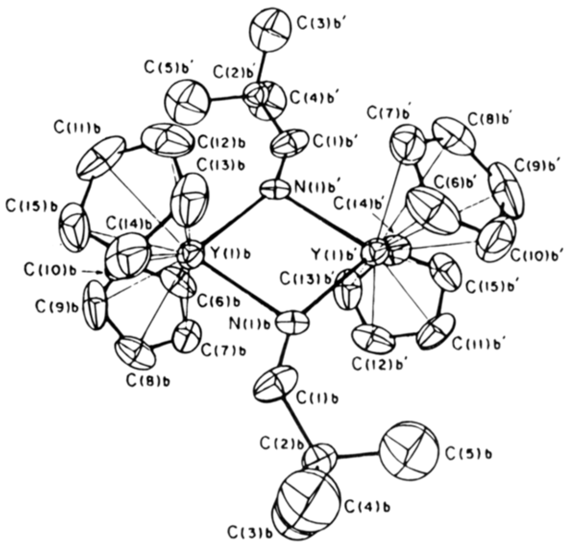


Figure 65. Structure of $\{(C_5H_5)_2Y[\mu\text{-}N{=}CH^tBu]\}_2$ in the crystal.[435] (Reprinted from ref 435. Copyright 1984 American Chemical Society.)

A series of dimeric alkylideneamidoyttrium species could be prepared (eq 62) from reaction of the yttrium

$$[(C_5H_5)_2Y(\mu\text{-}X)(THF)]_2 + 2RC{\equiv}N \xrightarrow{THF} \{(C_5H_5)_2Y[\mu\text{-}N{=}C(X)(R)]\}_2 \quad (62)$$

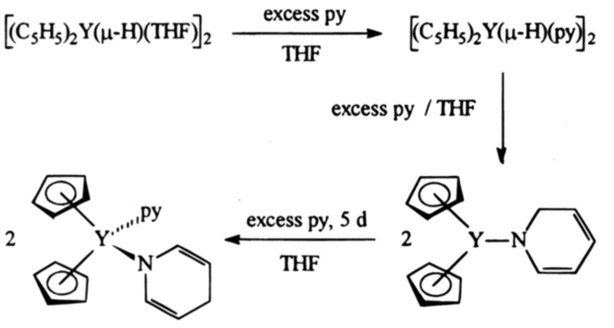
X = H: R = Me, ^{t}Bu

X = D: R = Me, ^{t}Bu

hydride and organonitriles. The X-ray structure analysis of $\{(C_5H_5)_2Y[\mu\text{-}N{=}CH^tBu]\}_2$ (Figure 65) shows two bis(cyclopentadienyl)yttrium units connected by two asymmetric Y−N bridge bonds.[435]

Another dimeric tetrakis(cyclopentadienyl)dilanthanide derivative is accessible by ligand exchange between $(C_5H_5)_2YbC_6F_5$ and succinimide. The proposed bimetallic composition of $\{(C_5H_5)_2Yb[\mu\text{-}\eta^2\text{-}(\overline{NC(O)CH_2CH_2C}(O))]\}_2{\cdot}(THF)$, with bridging Yb: :N: :C: :O: :Yb interactions and only one molecule of tetrahydrofuran, has been deduced mainly from infrared spectra and mass spectrometrical measurements.[229]

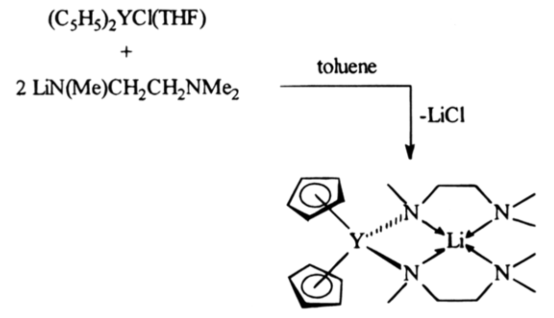
Pyridine reacts with $[(C_5H_5)_2Y(\mu\text{-}H)(THF)]_2$ in nonpolar solvents (such as pentane) to give the pyridine adduct, but in polar solvents (such as THF) Y−H adds to the pyridine ring. As shown in eq 63, a 10-fold excess of pyridine generates a pyridine adduct, which then rapidly rearranges to the 1,2-addition product, which then isomerizes to the 1,4-addition species. At least this is proposed to occur over the 5-day reaction period:[435]



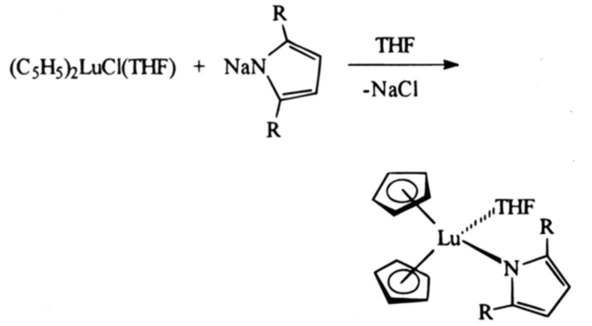
(63)

A related benzylamide, $(C_5H_5)_2LuNHCH_2Ph$, and its corresponding deuterated isotopomer $(C_5H_5)_2LuNDCH_2Ph$ were prepared by Beletskaya et al.[436] from the amine and $(C_5H_5)_2LuPh(THF)$ in THF at low temperatures.

About the same time, Schumann et al. used lithium *N,N,N'*-trimethylethylenediamide[437] and sodium pyrrolyle derivatives[438] to introduce these new ligands into the cyclopentadienyl chemistry of the rare earth elements (eqs 64 and 65). The pyrrole ligand is isoelectronic with the cyclopentadienyl group, and it is known to coordinate to d-transition metals either by way of the lone pair on nitrogen as a monohapto ligand or by way of its π-electrons as a pentahapto ligand (Figure 66). The X-ray structure diffraction study showed that the monomer was bonded to two pentahapto cyclopentadienyl groups, one monohapto 2,5-dimethylpyrrole ligand and one monohapto tetrahydrofuran molecule.[438]



(64)



(65)

R = H, Me

Finally, some anionic bis(cyclopentadienyl)lanthanide amides have been isolated from reactions of the methyl-bridged organolanthanide alkyls $(C_5H_5)_2Ln(\mu\text{-}Me)_2Li(tmed)$ with the protonic acid, diphenylamine.[439] Steric reasons are supposed to be responsible for the instability of the bridged intermediates $(C_5H_5)_2Ln(\mu\text{-}NPh_2)_2Li(tmed)$, since these hypothetical species rearrange in benzene solutions to precipitate the insoluble cation−anion complex $[Li(tmed)_2][(C_5H_5)_2Ln(NPh_2)_2]$ (Ln = Sm, Lu) with two terminal diphenylamido ligands. Recrystallization from a 3:1 mixture of THF/diethylether affords $[Li(THF)_4][(C_5H_5)_2Lu(NPh_2)_2]\cdot(Et_2O)$ (Figure 67).

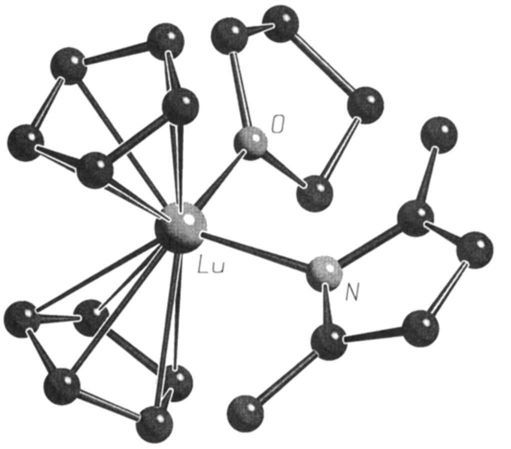


Figure 66. Structure of $(C_5H_5)_2Lu(NC_4H_2Me_2)(THF)$ in the crystal.[438]

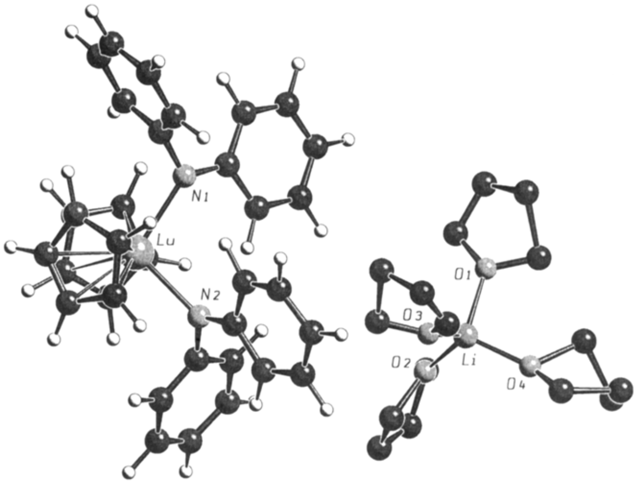


Figure 67. Structure of $[Li(THF)_4][(C_5H_5)_2Lu(NPh_2)_2]\cdot(Et_2O)$ in the crystal.[439]

Very recently, Campion et al. reported the synthesis of blue $(C_5H_5)_2ScN(C_6H_3Me_2\text{-}2,6){-}C(SiMe_3){=}C\text{-}\{NC_8H_9[Si(SiMe_3)_2]\}$ from reaction of $(C_5H_5)_2ScSi(SiMe_3)_3(THF)$ with 2 equiv of $CNC_6H_3Me_2\text{-}2,6$ in benzene.[381]

A survey of known bis(cyclopentadienyl) derivatives with rare earth to nitrogen bonds is given in Table 14.

ii. Pentamethylcyclopentadienyl Derivates. Development of bis(pentamethylcyclopentadienyl) complexes of the rare earths containing Ln−N bonds started comparatively late, 1981, with the preparation of the amides $(C_5Me_5)_2LnN(SiMe_3)_2$ (Ln = Nd (**64f**), Yb (**64q**)) from sodium bis(trimethylsilyl)amide and the chlorides $[Li(Et_2O)_2][(C_5Me_5)_2NdCl_2]$ and $(C_5Me_5)_2YbCl(py)$, respectively (eq 66).[280] The first

$$(C_5Me_5)_2YCl(THF) + NaN(SiMe_3)_2 \xrightarrow[-THF]{toluene} \underset{\textbf{64b}}{(C_5Me_5)_2YN(SiMe_3)_2} + NaCl \quad (66)$$

Table 14. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Pnicogenides Containing Lanthanide to Nitrogen Bonds

compound	Ln		color, characterization, etc.
$(C_5H_5)_2LnNH_2$	Er	**61o**	pink, melt./dec.[155]
	Yb	**61q**	yellow, IR, melt./dec.,[96] NMR,[65,72,85] MS[67,431]
$(C_5H_5)_2LnN(D)CH_2Ph$	Lu		yellow, NMR, melt./dec.[436]
$(C_5H_5)_2Ln(\mu\text{-}NPh_2)_2Li(tmed)$	Lu		NMR[439]
$(C_5H_5)_2Ln(\mu\text{-}NPh_2)(\mu\text{-}Me)Li(tmed)$	Lu		NMR[439]
$[Li(THF)_4][(C_5H_5)_2Ln(NPh_2)_2]$	Lu		($+Et_2O$): colorless, X-ray, NMR, melt./dec.[439]
$[Li(tmed)_2][(C_5H_5)_2Ln(NPh_2)_2]$	Sm		yellow, NMR, melt./dec.[439]
$(C_5H_5)_2Ln(NC_4H_4)$	Lu		complex with THF: yellow, NMR, melt./dec.[438]
$(C_5H_5)_2Ln(NC_4Me_2H_2)$	Lu		complex with THF: yellowish, X-ray, NMR, melt./dec.[438]
$(C_5H_5)_2Ln(NC_5H_6)$	Y		complex with py: orange, NMR[435]
$(C_5H_5)_2Ln(NC_4H_4O_2)$	Yb		(+THF): IR, MS[229]
$(C_5H_5)_2LnN{=}CHMe$	Y		white, IR, NMR[435]
$(C_5H_5)_2LnN{=}C(D)Me$	Y		IR[435]
$(C_5H_5)_2LnN{=}CH^tBu$	Y		colorless, X-ray, NMR, IR[435]
$(C_5H_5)_2LnN{=}C(D)^tBu$	Y		IR[435]
$(C_5H_5)_2Ln[N(Me)CH_2CH_2NMe_2]_2Li$	Y		colorless, NMR[437]
$(C_5H_5)_2LnN(C_6H_3Me_2\text{-}2,6)C(SiMe_3){=}C\{NC_8H_9[Si(SiMe_3)_2]\}$	Sc		blue, NMR, IR, melt./dec.[381]
$\{(C_5H_5)_2Ln[\mu,\eta^2\text{-}(HC{=}N^tBu)]\}_2$	Y	**62b**	colorless, X-ray, NMR, IR[433,434]
	Er	**62o**	pink, X-ray, IR[434]
$\{(C_5H_5)_2Ln[\mu,\eta^2\text{-}((D)C{=}N^tBu)]\}_2$	Y	**63b**	IR, NMR[434]

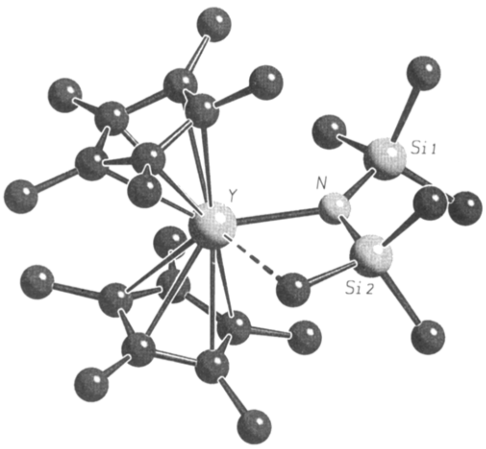


Figure 68. Structure of $(C_5Me_5)_2YN(SiMe_3)_2$ (**64b**) in the crystal.[275]

crystal structure was solved for the yttrium analogue **64b** (Figure 68).[275]

The coordinative unsaturation at the yttrium atom (formal coordination number of seven) results in weak γ-agostic Y–methyl contacts and the somewhat short Y–N distance. This short Y–N distance is proposed to result by donation of the nitrogen lone pair to the electron-deficient yttrium center.[275]

Analogous results were obtained in reactions of the early lanthanide complexes, $(C_5Me_5)_2LnCl_2K(THF)$ (Ln = Ce, Nd, Sm), with $KN(SiMe_3)_2$ yielding the amides **64d**, **64f**, and **64h**.[440] The permethylated yttrocene, lanthanocene, and cerocene bis(trimethylsilyl)amides, **64b**, **64c**, and **64d**, were prepared by either addition of pentamethylcyclopentadiene to THF-d_8 solutions of $Ln[N(SiMe_3)_2]_3$ (Ln = La, Ce or Y)[441] or by metathetical exchange reactions of the corresponding halides $[(C_5Me_5)_2LnCl]_n$ (Ln = La,[441] Ce[284]) with $NaN(SiMe_3)_2$. Metathesis of $(C_5Me_5)_2YCl(THF)$ with sodium pyrrole proceeds similarly, yielding the permethylyttrocene complex $(C_5Me_5)_2Y(NC_4H_4)(THF)$.[438]

Much research has also focused on the reactivity of coordinatively unsaturated 14-electron species, like bis(pentamethylcyclopentadienyl)lanthanide alkyls or hydrides, with various nitriles, isonitriles, or amines. For example, the scandium azomethine insertion complexes, $(C_5Me_5)_2ScN{=}CRR'$, are formed on reactions of the scandium alkyls (or hydrides) with nitriles, R′CN, via intermediate bis(pentamethylcyclopentadienyl)alkylscandium nitrile adducts according to eq 67:[442]

$$(C_5Me_5)_2ScR + R'C{\equiv}N \rightarrow (C_5Me_5)_2Sc(R)(N{\equiv}CR') \rightarrow (C_5Me_5)_2ScN{=}C(R)(R') \quad (67)$$

R = Me: R′ = Me, ^tBu, $CH{=}CH_2$

R = C_6H_4Me-4: R′ = C_6H_4Me-4

R = H: R′ = ^tBu (**65a**), C_6H_4OMe-4 (**66a**)

The outcome of the reaction of $(C_5Me_5)_2ScMe$ with nitriles strongly depends on using a 1:1 stoichiometry, since with excess *p*-anisonitrile at 80 °C, the double insertion product $(C_5Me_5)_2ScNHC(C_6H_4OMe\text{-}4)CHC(C_6H_4OMe\text{-}4)NH$ is obtained. Incidentally, **65a** was shown to undergo a nitrile exchange with *p*-anisonitrile yielding **66a** and 2-methylpropane-2-nitrile. Furthermore, hydrogenation of the species **65a** and **66a** occurs by way of a reversible four-center mechanism to give the bis(pentamethylcyclopentadienyl)scandium amide compounds, $(C_5Me_5)_2ScNHCH_2R'$ (R′ = ^tBu, C_6H_4OMe-4). The ^tBu derivative can be hydrogenated catalytically to $^tBuCH_2NH_2$ (4 atm dihydrogen), but unfortunately the competing irreversible insertion of 2-methylpropane-2-nitrile into the Sc–N bond also occurs, forming $(C_5Me_5)_2ScN{=}C^tBu(NHCH_2{}^tBu)$.[442] The amide, $(C_5Me_5)_2ScNHCH_2{}^tBu$, as well as a series of other bis(pentamethylcyclopentadienyl)amidoscandium complexes have been obtained using the following exchange reactions (eqs 68 and 69):

$$(C_5Me_5)_2LnR + R'NH_2 \rightarrow (C_5Me_5)_2Sc(NHR')(R'NH_2)_n + RH \quad (68)$$

$Ln = Sc$:[442] $R = Me, H; R' = H, Me, Ph, CH_2{}^tBu; n = 0$

$Ln = Sc$:[442] $R = Me, H; R' = CH_2C_6H_4OMe\text{-}4; n = 1$

$Ln = Ce$:[284] $R = CH(SiMe_3)_2; R' = {}^tBu; n = 1$

$$(C_5Me_5)_2LnR + HNR'_2 \rightarrow (C_5Me_5)_2LnNR'_2 + RH \quad (69)$$

$Ln = Sc$:[442] $R = R' = Me$

$Ln = Ce$:[284] $R = CH(SiMe_3)_2, R' = SiMe_3$

$Ln = Nd, Sm$:[271] $R = H, R' = Me$

Due to the electron deficiency at the formal 14-electron lanthanide center, the permethylated lanthanocene azomethines and amides might have some π-donation of the nitrogen lone pair to the rare earth metal.

Other versatile preparative reagents for the synthesis of bis(pentamethylcyclopentadienyl)lanthanide imides and iminoacyls are represented by the permethylyttrocene alkyls $(C_5Me_5)_2YCH(SiMe_3)_2$ and $(C_5Me_5)_2YCH_2C_6H_3Me_2$-3,5 as shown in eqs 70 and 71:[411]

$$(C_5Me_5)_2YR + 2{}^tBuC{\equiv}N \rightarrow (C_5Me_5)_2Y[N{=}C({}^tBu)(R)](NC{}^tBu) \quad (70)$$

$R = CH(SiMe_3)_2, CH_2C_6H_3Me_2\text{-}3,5$

$$(C_5Me_5)_2YCH_2C_6H_3Me_2\text{-}3,5 + 2C{\equiv}NR \xrightarrow{Et_2O} (C_5Me_5)_2Y\{\eta^2\text{-}[C(CH_2C_6H_3Me_2\text{-}3,5){=}NR]\}(CNR)_n \quad (71)$$

$R = {}^tBu$ ($n = 1$) (**67b**), $C_6H_3Me_2$-2,6 ($n = 0$) (**68b**)

The insertion derivatives $(C_5Me_5)_2Y[N{=}C({}^tBu)(R)](NC{}^tBu)$ retain a 2-methylpropane-2-nitrile ligand and thereby the yttrium center acquires a 16-electron configuration. The permethylyttrocene iminoacyl **67b** also coordinates one isonitrile molecule to give an 18-electron complex, while bulky 2,6-xylyleneisonitrile only gives a 16-electron species **68b**. The comparatively small Lewis base THF-d_8 has been shown to reduce the coordinative unsaturation of **68b** by generating the 18-electron THF-d_8 adduct $(C_5Me_5)_2Y\{\eta^2\text{-}[C(CH_2C_6H_3Me_2\text{-}3,5){=}NC_6H_3Me_2\text{-}2,6]\}$(THF-$d_8$). The single-crystal X-ray structure determination of the latter complex (Figure 69) reveals a pseudotetrahedral environment for the yttrium atom and confirms the dihapto bonding of the iminoacyl ligand to the metal center.[411]

Watson reported 1983 the first successful metalation of pyridine at the α-position with liberation of dihydrogen or methane from bis(pentamethylcyclopentadienyl)lutetium hydrides or alkyls respectively.[360] Two years later, permethylated yttrocence alkyls were shown to react in an analogous manner (eq 72).[278]

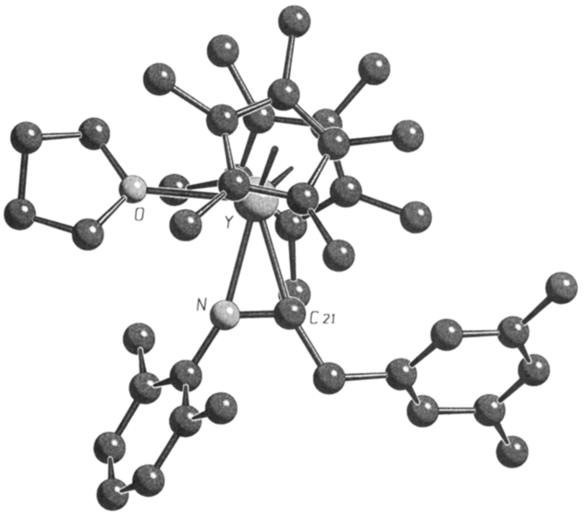
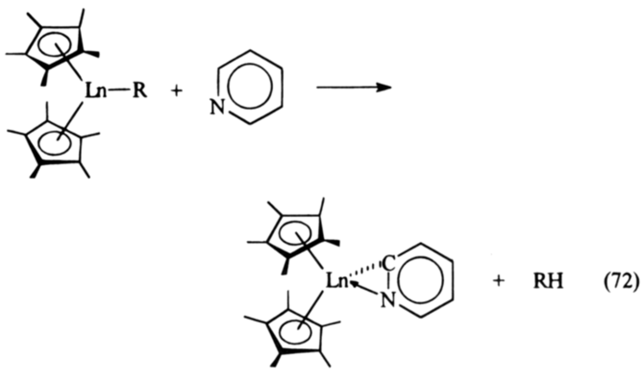


Figure 69. Structure of $(C_5Me_5)_2Y\{\eta^2\text{-}[C(CH_2C_6H_3Me_2\text{-}3,5){=}NC_6H_3{}^tBu_2\text{-}2,6]\}$(THF-$d_8$) in the crystal.[411]



Ln = Sc:[265,272] R = Me
Ln = Lu:[360] R = H, Me
Ln = Y:[278] R = $CH(SiMe_3)_2$

The tetrahydrofuran-containing complex $(C_5Me_5)_2Y[\eta^2\text{-}(NC_5H_4)]$(THF) is accessible from the THF adduct of $(C_5Me_5)_2LnMe$ and equimolar amounts of pyridine in a solution of deuterated benzene. $(C_5Me_5)_2LnMe$ gives the orthometalation product of α-picoline in THF, $(C_5Me_5)_2Y[\eta^2\text{-}(NC_5H_3Me\text{-}6)]$(THF).[278]

Solvent-free bis(pentamethylcyclopentadienyl)scandium methyl is a convenient starting material for the preparation of permethylscandocene hydrazide species such as with the anhydrous hydrazine derivatives (eq 73):[443]

$$(C_5Me_5)_2ScMe + H_2NNR_2 \xrightarrow{\text{petroleum ether}} (C_5Me_5)_2ScNHNR_2 + CH_4 \quad (73)$$

$R = H, Me$

Since all attempts to obtain suitable crystals of the hydrazido compounds failed, the spectral data are not reliable for distinguishing between monohapto, dihapto, or other fluxional structures with N−H agostic interactions; the exact structure is still unknown. However, the authors favor an η^2-[$NHNR_2$] structure. Addition of acetonitrile to $(C_5Me_5)_2ScNHNR_2$ (R = H, Me) leads to the heterometallacycles $(C_5Me_5)_2$-

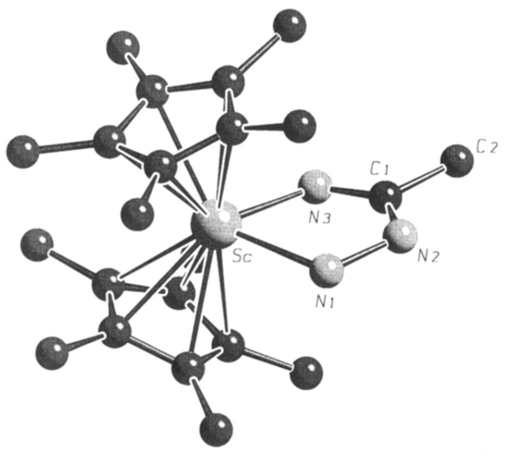


Figure 70. Structure of $(C_5Me_5)_2ScNHCMeNNH_2$ in the crystal.[443]

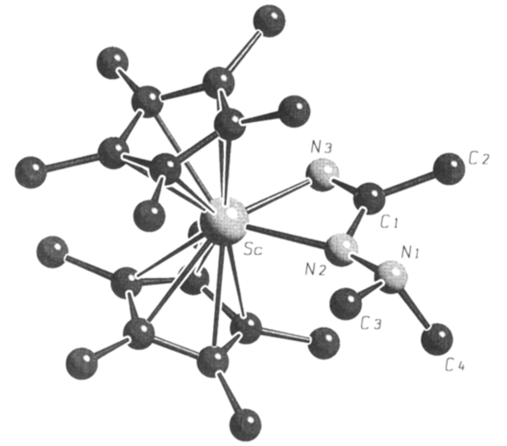


Figure 71. Structure of $(C_5Me_5)_2ScNHCMeNNMe_2$ in the crystal.[443]

$ScNHCMeNNH_2$ and $(C_5Me_5)_2ScNHCMeNNMe_2$. X-ray crystallographic studies showed the five-membered (Figure 70) and the four-membered ring (Figure 71) metallacycle, respectively. The possible reaction mechanisms have been discussed in detail.[443]

Divalent $(C_5Me_5)_2Sm(THF)_2$, which reacts as a single electron reductant toward several organic and inorganic compounds, behaves similarly toward heterocyclic nitrogen bases. In the middle 1980s, it was reported that a toluene solution of $(C_5Me_5)_2Sm(THF)_2$ reduces azobenzene to form the dimer $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{-}N_2Ph_2)$ in which there is a short *o*-phenyl hydrogen distance (Figure 72).[108,444a] The stoichiometry is important, since equimolar amounts of $(C_5Me_5)_2Sm(THF)_2$: azobenzene in THF give the monomeric THF adduct $(C_5Me_5)_2Sm(\eta^2\text{-}N_2Ph_2)(THF)\cdot 0.5(THF)$. The closely related complexes $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2\text{-}N_2(C_6H_4Me\text{-}3)_2]$ (**69h**) and $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2\text{-}N_2(C_6H_4NMe_2\text{-}4)Ph]$ (**70h**) have been obtained in analogous reactions of 2 equiv of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of 3,3′-azatoluene $PhN{=}NC_6H_4NMe_2\text{-}4$, respectively.[108]

The insertion product of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{-}N_2Ph_2)$ and carbon monoxide, $[(C_5Me_5)_2Sm]_2\{\mu\text{-}\eta^4\text{-}[(PhN)OCCO(NPh)]\}\cdot 2(PhMe)$ has been mentioned in the section on lanthanide–oxygen bonds containing bis(pentamethylcyclopentadienyl) species. In a pressurized CO atmosphere **69h** and **70h** behave analogously, giving the dimeric molecules with two $(C_5Me_5)_2Sm$ fragments bridged by the doubly deprotonated *N*,*N*′-diphenyloxamide.[108]

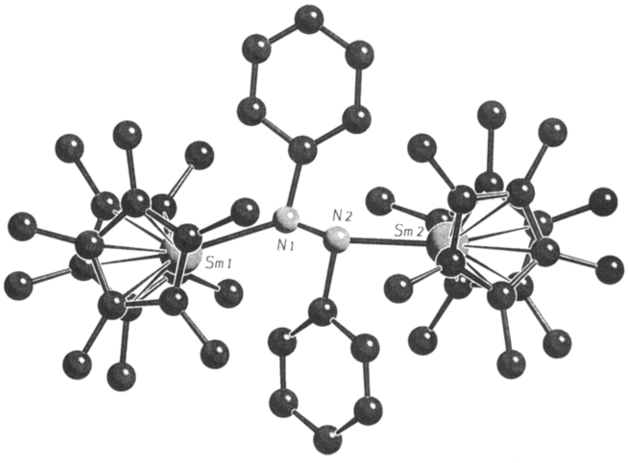
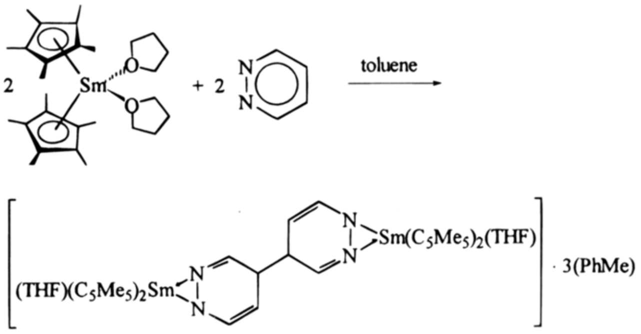


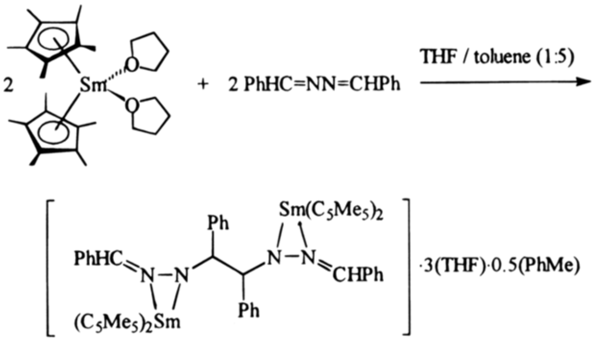
Figure 72. Structure of $[(C_5Me_5)_2Sm]_2(\mu,\eta^2\text{-}N_2Ph_2)$ in the crystal.[108,444a]

The trimetallic samarium species $\{(C_5Me_5)_2Sm(CNR)[\mu\text{-}\eta^2\text{-}(CN)]\}_3$ (R = ${}^cC_6H_{11}$, ${}^tBu$) are accessible by reductive cleavage of the corresponding isonitriles, when added in excess to toluene solutions of $(C_5Me_5)_2Sm(THF)_2$ (see eq 21 and Figure 27; bis(pentamethylcyclopentadienyl)lanthanide pseudo halides).[291]

Additional reductive coupling reactions of pyridazine (eq 74) and benzaldehyde azine (eq 75), respectively, could be observed in the presence of equimolar amounts of $(C_5Me_5)_2Sm(THF)_2$, affording the two bimetallic products, characterized by X-ray crystallography:[444b]



(74)



(75)

Bipyridine reacts with $(C_5Me_5)_2Sm(THF)_2$ to give the 1:1 adduct $(C_5Me_5)_2Sm(\eta^2\text{-}N_2C_{10}H_8)$ (Figure 73), which is formulated as trivalent permethylsamarocene and a η^2-bonded bipyridyl radical.[444b]

Recently, synthesis and structure of a mononuclear η^2-hydrazine complex has been reported:[445] Protonation of the structurally characterized organosama-

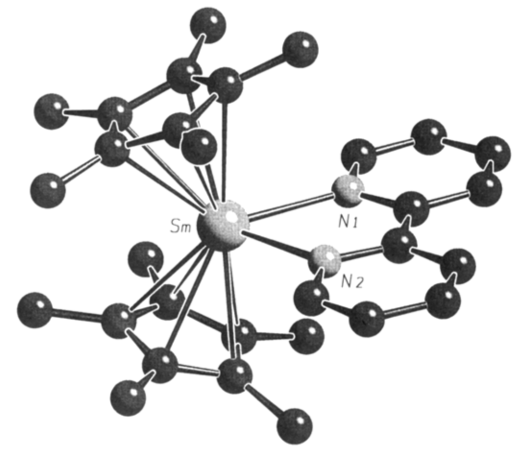


Figure 73. Structure of $(C_5Me_5)_2Sm(\eta^2\text{-}N_2C_{10}H_8)$ in the crystal.[444b]

rium $(N_2H_2)^{2-}$ species $[(C_5Me_5)_2(THF)Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2H_2)$ with 2 equiv of $(Et_3NH)BPh_4$ in THF results in formation of $[(C_5Me_5)_2Sm(\eta^2\text{-}N_2H_4)(THF)][BPh_4]$ with side-on coordination of the hydrazine ligand.

It should be also pointed out that even antiaromatic systems like *N*-heterocyclic dianions of quinoxaline and phenazine are stabilized on coordination between two $(C_5Me_5)_2La$ units. Close La−N bonds as well as La−C contacts characterize this new type of organolanthanides[446] (Figure 74).

To conclude, a few bis(pentamethylcyclopentadienyl)aminosamarium derivatives have been briefly mentioned in connection with studies of organolanthanide-centered hydroamination/cyclization reactions of aminoolefins,[447,517] with studies of reactions of decamethylsamarocene with 1,4-diazadienes,[625] and polycyclic nitrogen heterocycles,[733] and an unexpected CO insertion product, $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}OC(NC_5H_4)_2)$ was reported.[734]

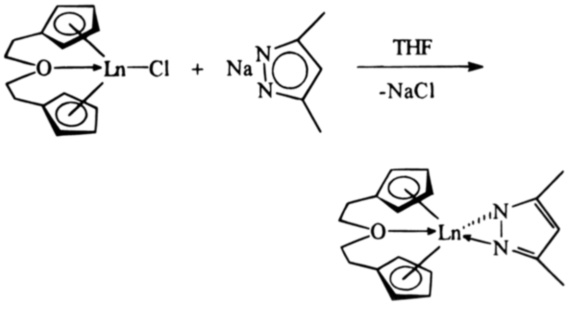
Important data of bis(pentamethylcyclopentadienyl) species with rare earth to nitrogen bonds are summarized in Table 15.

iii. Derivatives with Other Substituted Cyclopentadienyl Rings. The compounds of this class, known up to day are listed in Table 16. In 1990, Weidlein et al. prepared $[(MeC_5H_4)_2Yb(\mu\text{-}NH_2)]_2$,[432,448] the methylcyclopentadienyl congener of **61q**. The single-crystal X-ray study proves its dimeric character and shows the two bridging amido fragments (Figure 75).

The yttriumorganyl $\{(MeC_5H_4)_2Y[\mu\text{-}N{=}CHMe]\}_2$ can be obtained in a manner analogous to that of the unsubstituted cyclopentadienyl species, that is from $[(MeC_5H_4)_2Y(\mu\text{-}H)(THF)]_2$ and acetonitrile. The ^1H NMR spectrum of the hydride with excess pyridine in polar solvents gives evidence for the 1,2-addition product $(MeC_5H_4)_2Y(NC_5H_6)$.[435] Also known is $\{(MeC_5H_4)_2Y[\mu\text{-}\eta^2\text{-}(HC{=}N^tBu)]\}_2$, the bis(methylcyclopentadienyl)yttrium analogue of **62b**, as is the structurally characterized (*N*-alkylformimidoyl)erbium complex **62o**, prepared similarly.[433,434]

The chiral organolanthanides $[Me_2Si(Me_4C_5)(C_5H_3R^*)]LnN(SiMe_3)_2$ (Ln = Y, La, Sm, Lu; R* = (+)-neomenthyl; Sm: R* = (−)-menthyl, (+)-neomenthyl, (−)-phenylmenthyl) are of considerable interest since they can be used as precatalysts for enantioselective or diastereoselective hydroamination/cyclization processes for the conversion of aminoolefins to chiral pyrrolidines and piperidines.[449,726,736]

The use of lanthanide chlorides, in which two aromatic cyclopentadienyl units $\eta^5\text{-}C_5H_4$ are connected by an 3-oxapentamethylene fragment, are interesting, since the oxygen lone pairs coordinate to the lanthanide metal in the pyrazolate (eq 76) complexes.[357a]



(76)

71

Ln = Y (**71b**), Lu (**71r**)

Partial hydrolysis of the lanthanide 1,3-dimethylpyrazolates **71** has enabled the isolation of dinuclear complexes with both rare earth metals coordinated by the 1,1′-(3-oxapentamethylene)bis(cyclopentadienyl) system which are bridged by the 1,3-dimethylpyrazolate nitrogens as well as by a hydroxyl group. X-ray structure analysis of $\{[C_5H_4(CH_2)_2O(CH_2)_2C_5H_4]Ln\}_2(\mu\text{-}\eta^2\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$

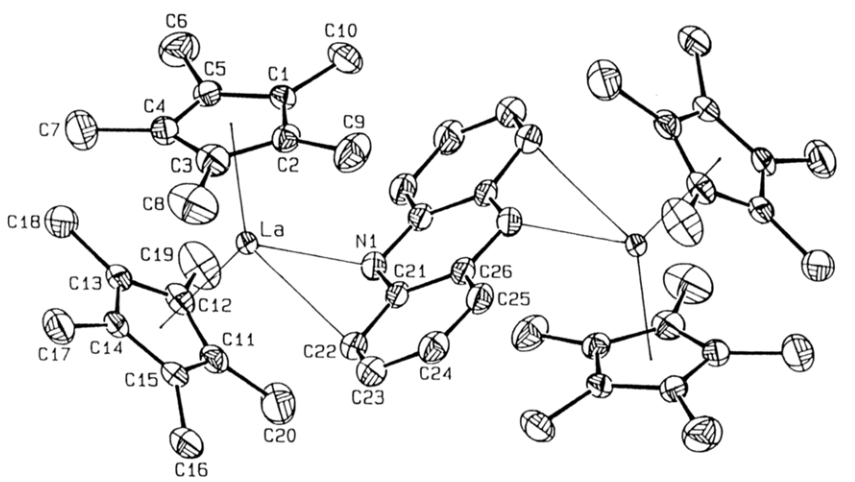


Figure 74. Structure of $[(C_5Me_5)_2La]_2(C_{12}H_8N_2)$ in the crystal.[446]

Table 15. Spectroscopic and Other Data of Bis(pentamethylcyclopentadienyl)lanthanide Pnicogenides Containing Lanthanide to Nitrogen Bonds

compound	Ln		color, characterization, etc.
$(C_5Me_5)_2LnNH_2$	Sc		white, NMR, IR[442]
$(C_5Me_5)_2LnNHMe$	Sc		NMR, IR[442]
	La		complex with $MeNH_2$: colorless, X-ray, NMR, IR, reactions[517]
$(C_5Me_5)_2LnNHEt$	La		complex with $EtNH_2$: colorless, NMR, IR, reactions[517]
	Nd		complex with $EtNH_2$: blue, NMR, reactions[517]
$(C_5Me_5)_2LnNHC_3H_7$	Sm		complex with $H_2NC_3H_7$: NMR[447]
$(C_5Me_5)_2LnNH^tBu$	Ce		complex with $NH_2{}^tBu$: gold brown, NMR, IR[284]
$(C_5Me_5)_2LnNHCH_2{}^tBu$	Sc		NMR, IR[442]
$(C_5Me_5)_2LnNHCH_2C_6H_4OMe\text{-}4$	Sc		NMR; complex with $NH_2CH_2C_6H_4OMe\text{-}4$: IR[442]
$(C_5Me_5)_2LnNHPh$	Sc		NMR, IR[442]
$(C_5Me_5)_2LnNH(CH_2)_3CH{=}CH_2$	Sm		complex with $NH_2(CH_2)_3CH{=}CH_2$: NMR[447]
$(C_5Me_5)_2LnNHCH_2CMe_2CH_2CH{=}CH_2$	La		complex with $H_2NCH_2CMe_2CH_2CH{=}CH_2$: NMR[517]
	Sm		complex with $H_2NCH_2CMe_2CH_2CH{=}CH_2$: NMR[447]
$(C_5Me_5)_2LnNHCH_2CH{=}CHCH_2CH_2NMe_2$	Sm		NMR[447]
$(C_5Me_5)_2LnNMe_2$	Sc		NMR, IR[442]
	Sm		orange, NMR, IR[271]
$(C_5Me_5)_2Ln(NC_4H_4)$	Y		complex with THF: colorless, NMR, MS, melt./dec.[438]
$(C_5Me_5)_2Ln(NC_5H_6)$	Y		NMR[734]
$(C_5Me_5)_2LnN(CH_2)_3CHMe$	La		complex with $HN(CH_2)_3CHMe$: white, NMR, IR, reactions[517]
$(C_5Me_5)_2LnNCH_2CMe_2CH_2CHMe$	La		complex with $HN(C_5H_{10})CHMe$: pale yellow, NMR, IR, reactions[517]
$(C_5Me_5)_2LnN(SiMe_3)_2$	Y	**64b**	colorless, X-ray, NMR, IR,[275] NMR[441]
	La	**64c**	white, NMR, IR,[441] reactions[517]
	Ce	**64d**	red,[284,440] NMR,[284,440,441] IR[284]
	Nd	**64f**	blue,[280,440] IR, melt./dec.,[280] NMR,[440] reactions[517]
	Sm	**64h**	orange, X-ray, NMR[440]
	Yb	**64q**	purple, IR, melt./dec.[280]
$(C_5Me_5)_2Ln[N(R){=}CHCH{=}NR]$	Sm		R = ^iPr: dark blue, NMR, IR, MS, melt./dec.[625]
	Sm		R = ^tBu: dark blue, X-ray, NMR, IR, MS, melt./dec.[625]
	Sm		R = $^cC_6H_{11}$: brown, NMR, IR, MS, melt./dec.[625]
	Sm		R = $C_6H_4Me\text{-}4$: dark green, NMR, IR, MS, melt./dec.[625]
$(C_5Me_5)_2LnNHCR{=}CHCR{=}NH$	Sc		R = $C_6H_4OMe\text{-}4$: yellow, IR, NMR[442]
$(C_5Me_5)_2LnNHNH_2$	Sc		white, NMR, MS, IR[443]
$(C_5Me_5)_2LnNHNMe_2$	Sc		yellow, NMR, IR[443]
$(C_5Me_5)_2Ln[NHCMeNNH_2]$	Sc		white, X-ray, NMR, IR[443]
$(C_5Me_5)_2Ln[NHCMeNNMe_2]$	Sc		tan, X-ray, NMR, IR[443]
$(C_5Me_5)_2Ln(\eta^2\text{-}N_2Ph_2)$	Sm		complex with THF (+0.5THF): green, X-ray, NMR, IR, magn. d.[108]
$[(C_5Me_5)_2Ln]_2[(\mu,\eta^2\text{-}N_2Ph_2)$	Sm		dark blue,[108,414,444a] X-ray, NMR, magn.d., IR,[108,444a] UV[444a]
$[(C_5Me_5)_2Ln]_2[\mu,\eta^2\text{-}N_2(C_6H_4NMe_2\text{-}4)Ph]$	Sm	**70h**	dark green, NMR[108]
$[(C_5Me_5)_2Ln]_2[\mu,\eta^2\text{-}N_2(C_6H_4Me\text{-}3)_2]$	Sm	**69h**	dark blue, NMR[108]
$[(C_5Me_5)_2Ln]_2(N_2C_4H_4C_4H_4N_2)$	Sm		complex with 2THF: orange, X-ray, NMR, IR[444b]
$[(C_5Me_5)_2Ln]_2[N(N{=}CHPh)CH(Ph){-}]_2$	Sm		orange, X-ray, NMR, IR[444b]
$(C_5Me_5)_2Ln(\eta^2\text{-}N_2C_{10}H_8)$	Sm		dark brown, X-ray, NMR, IR, UV−vis, magn. d.[444b]
$[(C_5Me_5)_2Ln]_2[\mu\text{-}(C_8H_4N_2\text{-}2,3\text{-}Me_2)]$	La		dark green, X-ray, NMR[446]
$[(C_5Me_5)_2Ln]_2[\mu\text{-}(C_{12}H_8N_2)]$	La		orange, X-ray, NMR[446]
$[(C_5Me_5)_2Ln]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{13}H_9N)_2]$	Sm		orange, X-ray, NMR, IR[733]
$[(C_5Me_5)_2Ln]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{12}H_8N_2)]$	Sm		dark brown, X-ray, NMR, IR[733]
$[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2H_2)$	Sm		complex with 2 THF: X-ray, NMR[445]
$[(C_5Me_5)_2Ln(\eta^2\text{-}N_2H_4)][BPh_4]$	Sm		complex with THF: X-ray, NMR[445]
$(C_5Me_5)_2LnN{=}CH^tBu$	Sc	**65a**	pale yellow, NMR, IR[442]
$(C_5Me_5)_2LnN{=}CH(C_6H_4OMe\text{-}4)$	Sc	**66a**	yellow, NMR, IR[442]
$(C_5Me_5)_2LnN{=}CMe_2$	Sc		NMR, IR[442]
$(C_5Me_5)_2LnN{=}C(C_6H_4Me\text{-}4)_2$	Sc		orange, NMR, IR[442]
$(C_5Me_5)_2LnN{=}CMe(^tBu)$	Sc		NMR, IR[442]
$(C_5Me_5)_2LnN{=}CMe(CH{=}CH_2)$	Sc		yellow, NMR, IR[442]
$(C_5Me_5)_2LnN{=}C^tBu(CH_2C_6H_3Me_2\text{-}3,5)$	Y		complex with NC^tBu: colorless, NMR, IR[411]
$(C_5Me_5)_2LnN{=}C^tBu[CH(SiMe_3)_2]$	Y		complex with NC^tBu: colorless, NMR, IR[411]
$(C_5Me_5)_2LnN{=}C^tBu(NHCH_2{}^tBu)$	Sc		white, NMR, IR[442]
$[(C_5Me_5)_2Ln]_2(\mu\text{-}C_{12}H_{10}N_4)$	Sm		green, melt./dec.[625]
$(C_5Me_5)_2Ln\{\eta^2\text{-}[C(CH_2C_6H_3Me_2\text{-}3,5){=}N^tBu]\}$	Y	**67b**	complex with CN^tBu: white, IR, NMR[411]
$(C_5Me_5)_2Ln\{\eta^2\text{-}[C(CH_2C_6H_3Me_2\text{-}3,5){=}NC_6H_3Me_2\text{-}2,6]\}$	Y	**68b**	pale yellow, NMR, IR; complex with THF-d_8: pale yellow, X-ray, IR[411]
$(C_5Me_5)_2Ln\text{-}\eta^2\text{-}(NC_5H_4)$	Sc		X-ray,[265,272] NMR, IR, reactions[265]
	Y		red,[278] yellow,[734,746] NMR, IR;[278,734] complex with THF: NMR;[278,734] complex with py: NMR, reactions[734]
	Lu		NMR[360]
$(C_5Me_5)_2Ln(\eta^2\text{-}NC_5H_3Me\text{-}6)$	Y		complex with THF: NMR[278,734]
$[(C_5Me_5)_2Ln]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}OC(NC_5H_4)_2]$	Y		purple, X-ray, NMR, IR[734]

Table 16. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Pnicogenides Containing Other Substituted Cyclopentadienyl Ligands and Lanthanide to Nitrogen Bonds

compound	Ln		color, characterization, etc.
$(MeC_5H_4)_2LnNH_2$	Yb		yellow-green,[412] X-ray, IR[432]
$(MeC_5H_4)_2LnNC_5H_6$	Y		NMR[435]
$(MeC_5H_4)_2LnN{=}CHMe$	Y		NMR[435]
$(MeC_5H_4)_2Ln[\mu,\eta^2\text{-}(HC{=}N^tBu)]$	Y		dimer: colorless, NMR, IR[433,434]
$[Me_2Si(Me_4C_5)(C_5H_3\text{-menthyl})]LnN(SiMe_3)_2$	Y		colorless, X-ray,NMR, CD;[726] reactions[736]
	Sm		orange, X-ray, NMR, CD;[449,726] reactions[736]
	Lu		colorless, NMR, CD;[726] reactions[736]
$[Me_2Si(Me_4C_5)(C_5H_3\text{-neomenthyl})]LnN(SiMe_3)_2$	Y		pale yellow, NMR, CD;[726] reactions[736]
	La		colorless, NMR, CD;[726] reactions[449,736]
	Sm		orange, X-ray, NMR, CD;[726] reactions[449,736]
	Lu		colorless, NMR, CD;[726] reactions[736]
$[Me_2Si(Me_4C_5)(C_5H_3\text{-phenylmenthyl})]LnNHPr$	Y		complex with NH_2Pr: NMR[726]
$[Me_2Si(Me_4C_5)(C_5H_3\text{-phenylmenthyl})]LnN(SiMe_3)_2$	Y		pale yellow, NMR;[726] reactions[736]
$[C_5H_4(CH_2)_2O(CH_2)_2C_5H_4]Ln(\eta^2\text{-}N_2C_3HMe_2)$	Y	**71b**	white, IR, melt./dec.[357a]
	Lu	**71r**	white, IR, melt./dec.[357a]
$\{[C_5H_4(CH_2)_2O(CH_2)_2C_5H_4]Ln\}_2(\mu,\eta^2\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$	Y		X-ray, IR[357a]
	Lu		X-ray[357a]

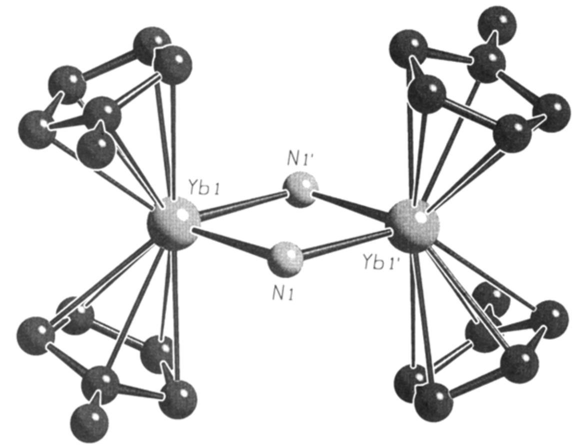


Figure 75. Structure of $[(MeC_5H_4)_2Yb(\mu\text{-}NH_2)]_2$ in the crystal.[432]

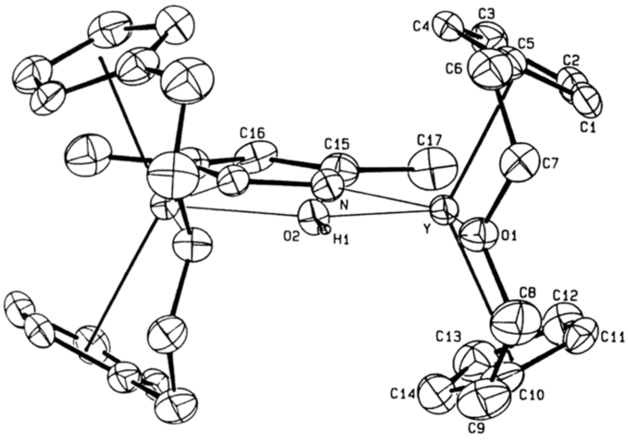


Figure 76. Structure of $\{[C_5H_4(CH_2)_2O(CH_2)_2C_5H_4]Y\}_2(\mu\text{-}\eta^2\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$ in the crystal.[357a]

Ln = Y (Figure 76), Lu) confirms the unusual existence of a closed five-membered, two lanthanide atoms involving chain, which connects two (3-oxapentamethylene)dicyclopentadienyl ligand systems.[357a]

b. Compounds with Rare Earth to Phosphorus, Arsenic, Antimony, and Bismuth Bonds. The first reports on trivalent bis(cyclopentadienyl)lanthanide compounds with bonds to phosphorus originate from Schumann et al. They synthesized according to eq 77 phosphino complexes of the heavier rare earths from the bis(cyclopentadienyl) rare earth chlorides and lithium phosphides.[249a,450]

$$(C_5H_5)_2LnCl(THF) + LiP(^tBu)R \xrightarrow{\text{THF/pentane}} (C_5H_5)_2LnP(^tBu)R + LiCl \quad (77)$$

$$R = {}^tBu\text{: } Ln = Tb, Ho, Er, Tm, Yb, Lu$$

$$R = Ph\text{: } Ln = Tb, Ho, Er, Yb, Lu$$

Cryoscopical molecular weight studies in benzene gave values higher than expected for monomers, and these organolanthanide phosphides are assumed to be oligomers.[450]

The synthesis[89] of $(C_5H_5)_2YbP(C_6H_{11})_2$ proceeds via metathesis of $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$ and $LiP(^cC_6H_{11})_2$ similar to the route shown in eq 77. The preparation of the (di-*tert*-butylphosphino)erbium derivative could also be done by solvent-free reaction of bis(cyclopentadienyl)erbium chloride with the corresponding dialkyl(trimethylsilyl)phosphane under reduced pressure (eq 78):[249a]

$$(C_5H_5)_2ErCl + Me_3SiP^tBu_2 \xrightarrow{\text{6 days}} (C_5H_5)_2ErP^tBu_2 + Me_3SiCl \quad (78)$$

Alkane elimination reactions have been developed especially with samarium, making halide-free products possible. These synthesis methods are outlined in eq 79. The permethylated samarium derivative,

$$[Cp_2Sm(\mu\text{-}R)]_2 + 2HPR'_2 \xrightarrow{\text{toluene}} 2Cp_2SmPR'_2 + 2HR \quad (79)$$

$$Cp = (MeC_5H_4)\text{: } R = C{\equiv}C^tBu;\ R' = Ph^{315a}$$

$$Cp = (C_5Me_5)\text{: } R = H;\ R' = Et^{271}$$

$(C_5Me_5)_2SmPEt_2$, is thought to be a monomer analogous to the monomethylated species $(MeC_5H_4)_2SmPPh_2$, which isopiestic molecular weight determination indicates to be a monomer in toluene. The (trimethylsilyl)methyllutetium compound $(C_5H_5)_2Lu(CH_2SiMe_3)(THF)$ reacts with diphenylphosphane and diphenylarsane with evolution of tetramethyl-

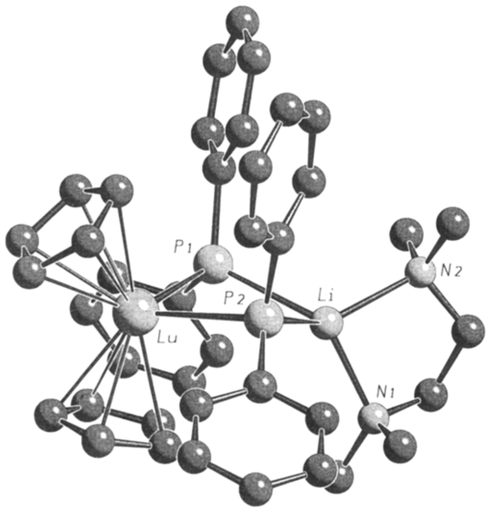


Figure 77. Structure of $(C_5H_5)_2Lu(\mu\text{-}PPh_2)_2Li(tmed)$ in the crystal.[451]

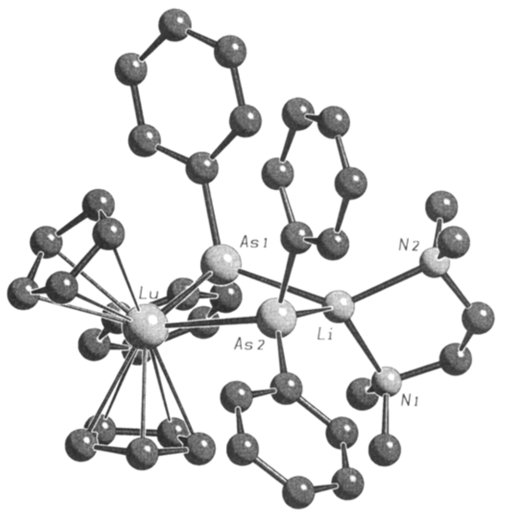


Figure 78. Structure of $(C_5H_5)_2Lu(\mu\text{-}AsPh_2)_2Li(tmed)$ in the crystal.[452]

silane affording bis(cyclopentadienyl)phosphano- and bis(cyclopentadienyl)arsanolutetium THF-adducts (eq 80).[372]

$$(C_5H_5)_2Lu(CH_2SiMe_3)(THF) \xrightarrow[-SiMe_4]{+HEPh_2} (C_5H_5)_2Lu(EPh_2)(THF) + SiMe_4 \quad (80)$$

E = P, As

The methane elimination reaction shown in eq 81 was developed for the synthesis of diphenylphosphido[451] and -arsenido[452] anions. NMR monitoring of the reaction showed that the reaction proceeds stepwise, giving the monomethyl compounds as an intermediate.

$$(C_5H_5)_2Lu(\mu\text{-}Me)_2Li(S')_n \xrightarrow[-CH_4]{+HEPh_2} (C_5H_5)_2Lu(\mu\text{-}Me)(\mu\text{-}EPh_2)Li(S')_n \xrightarrow[-CH_4]{+HEPh_2} (C_5H_5)_2Lu(\mu\text{-}EPh_2)_2Li(S')_n \quad (81)$$

E = P: S′ = tmed ($n = 1$), THF ($n = 2$)

E = As: S′ = tmed ($n = 1$)

The first X-ray crystallographically examined organolanthanide−phosphorus complex, $(C_5H_5)_2Lu(\mu\text{-}PPh_2)_2Li(tmed)$ (Figure 77), crystallizes with one disordered toluene for two Lu fragments,[451] whereas the first and sole X-ray crystallographically characterized bis(cyclopentadienyl)lanthanide arsenic compound, $(C_5H_5)_2Lu(\mu\text{-}AsPh_2)_2Li(tmed)$ (Figure 78), contains one molecule of benzene per asymmetric unit.[452]

Only two bis(cyclopentadienyl) derivatives of the rare earth elements have been published, which show bonds to antimony and bismuth. The samarium bismuth complex $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Bi_2)$ (**72h**) the first dibismuth complex of an f element, was prepared according to eq 82. The structure possesses a planar $Ln_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Bi_2)$ unit in which the Bi_2 moiety coordinates two lanthanides in a side-on bonding mode (Figure 79).[453]

$$4(C_5Me_5)_2Sm + 2BiPh_3 \rightarrow \underset{\textbf{72h}}{[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Bi_2)} + 2PhPh + 2(C_5Me_5)_2SmPh \quad (82)$$

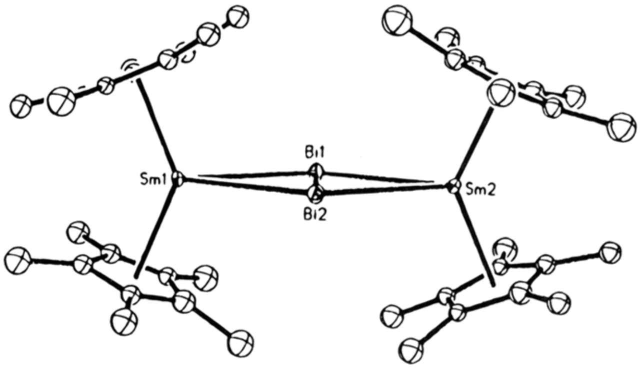


Figure 79. Structure of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Bi_2)$ (**72h**) in the crystal.[453] (Reprinted from ref 453. Copyright 1991 American Chemical Society.)

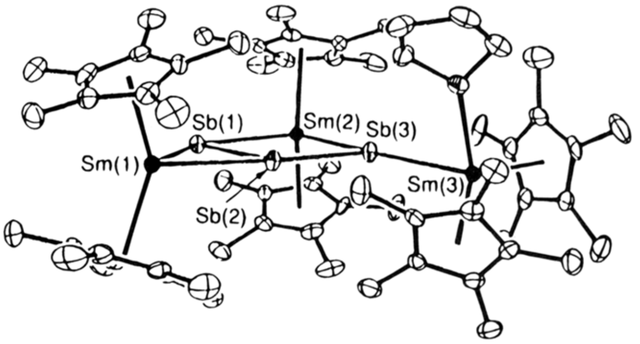


Figure 80. Structure of $[(C_5Me_5)_2Sm]_3(\mu\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-}Sb_3)$(THF) in the crystal.[454] (Reprinted from ref 454. Copyright 1992 Chemical Society of London.)

Recent studies of the reactivity of the divalent metallocene $(C_5Me_5)_2Sm$ allowed the isolation of the bent triatomic Zintl ion $(Sb_3)^{3-}$ in form of the trivalent organolanthanide THF adduct $[(C_5Me_5)_2Sm]_3(\mu\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-}Sb_3)$(THF) (Figure 80) after treatment of $(C_5Me_5)_2Sm$ with Sb^nBu_3 in toluene.[454]

A summary of important data of bis(cyclopentadienyl) compounds with rare earth to phosphorus, arsenic, antimony and bismuth bonds is given in Table 17.

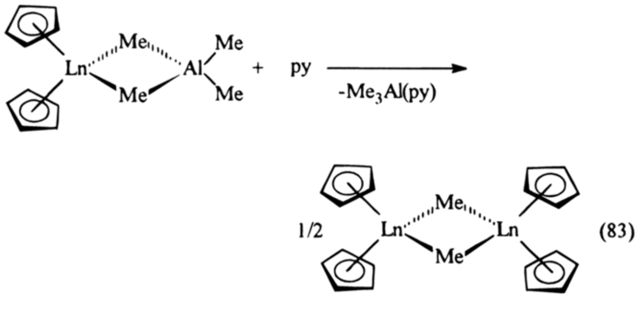
Table 17. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Pnicogenides Containing Lanthanide to Phosphorus, Arsenic, Antimony, and Bismuth Bonds, Respectively

compound	Ln	color, characterization, etc.
$(C_5H_5)_2LnP(^tBu)_2$	Tb	yellowish, NMR, IR, melt./dec.^{249a,450}
	Ho	yellow, NMR, IR, melt./dec.^{249a,450}
	Er	pink, NMR, IR, melt./dec.^{249a,450}
	Tm	yellow, melt./dec.^{450}
	Yb	white, melt./dec.^{450}
	Lu	white, melt./dec.^{450}
$(C_5H_5)_2LnP(^cC_6H_{11})_2$	Yb	orange, MS^{89}
$(C_5H_5)_2LnP(^tBu)Ph$	Tb	yellow, melt./dec.^{450}
	Ho	yellow, melt./dec.^{450}
	Er	pink, melt./dec.^{450}
	Yb	yellow, melt./dec.^{450}
	Lu	white, melt./dec.^{450}
$(C_5H_5)_2LnPPh_2$	Lu	complex with THF: NMR^{372}
$(C_5H_5)_2Ln(\mu\text{-}PPh_2)_2Li(THF)_2$	Lu	colorless, NMR, melt./dec.^{451}
$(C_5H_5)_2Ln(\mu\text{-}PPh_2)_2Li(tmed)$	Lu	colorless, X-ray, NMR, melt./dec.^{451}
$(C_5H_5)_2Ln(\mu\text{-}PPh_2)(\mu\text{-}Me)Li(tmed)$	Lu	NMR^{451}
$(C_5H_5)_2Ln(\mu\text{-}PPh_2)(\mu\text{-}Me)Li(THF)_2$	Lu	NMR^{451}
$(C_5Me_5)_2LnPEt_2$	Sm	NMR, IR^{271}
$(MeC_5H_4)_2LnPPh_2$	Sm	orange, NMR, magn. d.^{315a}
$(C_5H_5)_2LnAsPh_2$	Lu	complex with THF: NMR^{372}
$(C_5H_5)_2Ln(\mu\text{-}AsPh_2)_2Li(tmed)$	Lu	yellow, X-ray, NMR, melt./dec.^{452}
$(C_5H_5)_2Ln(\mu\text{-}AsPh_2)(\mu\text{-}Me)Li(tmed)$	Lu	NMR^{452}
$[(C_5Me_5)_2Ln]_3Sb_3$	Sm	complex with THF: red brown, X-ray, NMR^{454}
$[(C_5Me_5)_2Ln]_2Bi_2$	Sm **72h**	X-ray, NMR, IR^{453}

4. Bis(cyclopentadienyl) Rare Earth Complexes with Rare Earth to Element Group 14 Bonds

a. Compounds with Rare Earth to Carbon Bonds. *i. Cyclopentadienyl Derivatives.* References to known bis(cyclopentadienyl)lanthanides with lanthanide to carbon bonds are given in Table 18.

Bis(cyclopentadienyl)lanthanide alkyls and aryls may be prepared in metathetical reactions from $[(C_5H_5)_2LnCl]_2$ (**20**) or $(C_5H_5)_2LnCl(THF)$ (**21**) in THF with the appropriate Grignard or organolithium reagents. Although solvent-free methyl complexes had been prepared from **20** and MeLi,[250] the majority of the known species were produced by cleaving methyl−aluminum bonds of $(C_5H_5)_2Ln(\mu\text{-}Me)_2AlMe_2$ with Lewis bases (such as pyridine)[234,455] as outlined in eq 83.



73

Ln = Y (**73b**), Dy (**73m**), Ho (**73n**), Er (**73o**), Tm (**73p**), Yb (**73q**)

The complexes **73** are reported to be soluble in CH_2Cl_2, hot benzene, and toluene, but insoluble in saturated hydrocarbon solvents. Solution NMR studies carried out on **73b**[455] as well as solid-state single-crystal structure analyses of **73b** (Figure 81)[234] and **73q**[234,455] proved these complexes to be dimeric in nature which contrasts with the initial formulation of **73** as monomers.[250]

The two $(C_5H_5)_2Ln$ moieties are related to each other by a center of symmetry and the lanthanide ions are symmetrically bridged by two methyl groups. The hydrogen atoms could be located from the X-ray data for **73b** so the ambiguity which had existed concerning their positions could be resolved. As shown in Figure 81 none of the hydrogen atoms are located between the Y−C(methyl) vector, and the bonding can be described as an electron deficient Y−C−Y three-center, two-electron bond analogous to that in $(AlMe_3)_2$.[486]

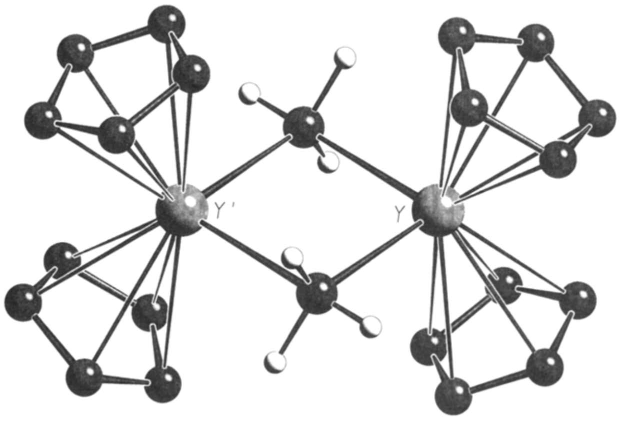


Figure 81. Structure of $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$ (**73b**) in the crystal.[234]

It has been shown that the course of the reaction symbolized by eq 83 depends on the relative Lewis acidity of the rare earth ion and Al^{3+}, since a given base can coordinate to either of the metal ions. Indeed, in the case of Ln = Sc, bases such as THF or pyridine, bind to the Lewis acid Sc^{3+} yielding $(C_5H_5)_2ScMe(THF)$ or $(C_5H_5)_2ScMe(py)$, respectively, and the concomitantly formed $(AlMe_3)_2$ can easily be removed in vacuo (eq 84):

$$(C_5H_5)_2Sc(\mu\text{-}Me)_2AlMe_2 + LB \xrightarrow[-20\ °C]{toluene} (C_5H_5)_2ScMe(LB) + {}^1/_2(AlMe_3)_2 \quad (84)$$

$$LB = THF,^{234}\ py^{455}$$

Table 18. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Complexes Containing Lanthanide to Carbon Bonds

compound	Ln		color, characterization, etc.
$(C_5H_5)_2LnMe$	Sc	**73a**	ND calculations;[736] complex with THF: cream, NMR, IR;[234] with py:[455] cream, NMR, IR[234]
	Y	**73b**	colorless, melt./dec.,[234,455] white,[435] X-ray,[234] NMR,[234,240,435,455,456] IR, MS,[455] bond angles;[3e] complex with THF: reaction[457]
	Gd	**73k**	elec. d.[81]
	Dy	**73m**	pale yellow, melt./dec.,[234,455] IR, MS,[455] magn. d.[234]
	Ho	**73n**	straw, melt./dec.,[234,455] IR, MS,[455] magn. d.[234]
	Er	**73o**	pink,[234,250,455,458] UV,[250,458] IR,[250,455] MS,[455] melt./dec.,[234,455] magn. d.[234,250,455,458]
	Tm	**73p**	pale green, melt./dec., magn. d.[234]
	Yb	**73q**	orange,[250,458,459] orange red, X-ray,[238,455] IR,[250,455,459] MS,[455] melt./dec.,[238,250,455] magn. d.,[238,250] bond angles;[3e] complex with THF: auburn orange, X-ray,[459] melt./dec.[379]
	Lu	**73r**	reaction;[459] complex with THF: colorless, melt./dec.,[375] NMR[375,460]
$(C_5H_5)_2Ln(\mu\text{-}Me)_2Li(LB)_n$	Sm		LB = tmed (n =1): yellow, NMR, melt./dec.[461]
	Er		LB = THF ($n = 2$): pink,[462,463] melt./dec.;[463] LB = tmed ($n = 1$): pink,[462,463] X-ray, melt./dec.[462]
	Lu		LB = THF ($n = 2$): colorless, NMR,[462,463] melt./dec.;[462] LB = tmed ($n = 1$): colorless,[462,463] X-ray,[464] NMR,[462,463,465] melt./dec.[462]
$(C_5H_5)_2Ln(\mu\text{-}Me)_2AlMe_2$	Sc		pale yellow, NMR, melt./dec.,[238,466] MS[238]
	Y		colorless, melt./dec.,[238] X-ray,[466,467] NMR,[238,468] MS[238]
	Gd		colorless,[466] white,[238] melt./dec.,[238,466] MS[238]
	Dy		pale yellow, melt./dec.,[238,466] MS[238]
	Ho		straw, melt./dec.,[238,466] MS[238]
	Er		pink, melt./dec.,[238,466] MS[238]
	Tm		pale green, melt./dec.,[238,466] MS[238]
	Yb		orange red, X-ray, melt./dec.,[238,466] MS,[238] bond angles[3e]
$(C_5H_5)_2Ln(Me)Sn[N(SiMe_3)_2]_2$	Sc		pale yellow, NMR, IR, melt./dec.[469]
$(C_5H_5)_2LnEt$	Lu		complex with THF: colorless, melt./dec.;[375] NMR[375,460]
$(C_5H_5)_2Ln(\mu\text{-}Et)_2AlEt_2$	Sc		pale yellow, NMR[238,466] IR,[238] melt./dec.[466]
	Y		colorless, NMR,[238,466] IR,[238] melt./dec.[466]
	Ho		straw[238]
$(C_5H_5)_2Ln^iPr$	Lu		complex with THF: colorless, NMR, melt./dec.[375]
$(C_5H_5)_2Ln^nBu$	Lu		complex with THF: colorless, melt./dec.;[375] NMR[375,460]
$(C_5H_5)_2Ln^sBu$	Nd		complex with THF: green[157]
	Lu		complex with THF: colorless[157]
$(C_5H_5)_2Ln^tBu$	Y	**74b**	complex with THF: light yellow, NMR, IR[314]
	La	**74c**	complex with 2phen: purple red, NMR, IR, melt./dec.[244]
	Nd	**74f**	complex with THF: green, NMR, IR, melt./dec.;[106,157] with phen: purple red, IR, melt./dec.[244]
	Er	**74o**	complex with THF: pink,[470] orange pink, IR[314,375] melt./dec.[375]
	Yb	**74q**	complex with THF: orange, NMR, IR, melt./dec.[375]
	Lu	**74r**	complex with THF: white, X-ray,[470] colorless,[106,375] IR,[314,375] NMR,[106,314,375,460,470] melt./dec.,[375,460] bond angles[3e]
$(C_5H_5)_2Ln(^tBu)[CH(SiMe_3)(PMe_3)]$	Lu		colorless, NMR, IR, melt./dec.[471]
$(C_5H_5)_2Ln(^tBu)(CH_2PPh_3)$	Lu		NMR, IR, melt./dec.[471]
$(C_5H_5)_2LnCH_2{}^tBu$	Lu		complex with THF: colorless, IR,[375] NMR, melt./dec.[375,460]
$(C_5H_5)_2LnCH_2Ph$	Sm		synthesis[472]
	Lu		colorless, IR,[375] NMR, melt./dec.[375,460]
$(C_5H_5)_2LnCH_2C_6H_4{}^tBu\text{-}4$	Sm		synthesis[472]
$(C_5H_5)_2LnCH_2C_6H_3Me_2\text{-}3,5$	Sm		synthesis[472]
$(C_5H_5)_2LnCPh_3$	Lu		red yellow[375]
$(C_5H_5)_2Ln(CH_2)_3NMe_2$	Lu		colorless, X-ray, NMR, MS, melt./dec.[389]
$(C_5H_5)_2LnCH_2PMe_2$	Lu		colorless, NMR, melt./dec.[473]
$(C_5H_5)_2Ln(\mu\text{-}CH_2)_2P^tBu_2$	Lu		NMR, IR, melt./dec.[474]
$(C_5H_5)_2Ln(\mu\text{-}CH_2)_2PPh_2$	Sc		pale yellow, NMR[475]
$(C_5H_5)_2Ln[(\mu\text{-}CH_2)(\mu,\eta^2\text{-}C_6H_4)PPh_2]$	Lu		colorless, melt./dec.[143,473]
$(C_5H_5)_2Ln(CH_2SiMe_3)(CH_2PPh_3)$	Lu		colorless, NMR, IR, melt./dec.[471]
$(C_5H_5)_2LnCH_2SiMe_3$	Y	**75b**	complex with THF: colorless, X-ray, NMR, IR[459]
	Sm	**75h**	colorless, IR, melt./dec.[375]
	Er	**75o**	complex with THF: light brown, IR, melt./dec.[375]
	Yb	**75q**	complex with THF: red brown, NMR, IR, melt./dec.[375]
	Lu	**75r**	complex with THF: colorless, IR,[375] X-ray, NMR, melt./dec.,[375,460] bond angles[3e]
$[Li_2(DME)_2(\mu\text{-dioxane})][(C_5H_5)_2Ln\text{-}(CH_2SiMe_3)_2]_2$	Y		colorless, X-ray, NMR, IR;[476] NMR[477]
$(C_5H_5)_2LnCH(SiMe_3)_2$	Sm		complex with THF: orange, NMR, IR[106]
	Lu		complex with THF: colorless, NMR, IR[106]
$(C_5H_5)_2LnPh$	Gd		lavender, magn. d.[250,458]
	Er		pink, IR, UV, melt./dec.,[250] magn. d.[458]
	Yb		orange, magn. d.,[250] IR[458]
	Lu		complex with THF: colorless,[436] NMR, melt./dec.[376,436]
$(C_5H_5)_2LnC_6H_4Me\text{-}4$	Gd		pale yellow, melt./dec.; complex with THF: orange yellow, IR, melt./dec.[83]
	Er		light pink, melt./dec., magn. d.; complex with THF: light pink, IR, melt./dec.[83]

Table 18 (Continued)

compound	Ln	color, characterization, etc.
$(C_5H_5)_2LnC_6H_4Me\text{-}4$	Yb	orange red, melt./dec., magn. d.; complex with THF: red, IR melt./dec.[83]
	Lu	complex with THF: colorless, X-ray, IR,[375] NMR, melt./dec.[375,460] bond angles[3e]
$(C_5H_5)_2LnC_6H_4Cl\text{-}4$	Er	pink, melt./dec., magn. d.; complex with THF: orange red, IR, melt./dec.[83]
$(C_5H_5)_2LnC_6H_4\text{-}2\text{-}CH_2NMe_2$	Sc	white, NMR, melt./dec.[478]
	Y	white, X-ray, melt./dec.[239]
$(C_5H_5)_2LnC_6F_5$	Yb	complex with THF: MS, IR, UV[229]
$(C_5H_5)_2LnC_6Cl_5$	Yb	MS, IR, UV[229]
$(C_5H_5)_2LnCH_2CH{=}CH_2$	Sc	orange, NMR, IR, melt./dec.[236]
	Y	complex with THF: colorless, NMR, IR[435]
	Nd	IR[479]
	Sm	yellow, UV;[480] intermediate[737]
	Ho	orange, UV[480]
	Er	pink, UV[480]
$(C_5H_5)_2LnCH_2CH{=}CHCH_3$	Sm	intermediate[737]
$(C_5H_5)_2LnC(Et){=}CHEt$	Y	complex with THF: colorless, NMR, IR[435]
$(C_5H_5)_2SmCH_2CH{=}CHPh$	Sm	intermediate[737]
$(C_5H_5)_2LnC(Ph){=}CHPh$	Y	complex with THF: pink orange, NMR, IR[435]
$[Na(LB)_n][(C_5H_5)_2Ln(C_{14}H_{10})]$	Lu	LB = THF ($n = 1$): orange, NMR,[481] UV;[257] LB = diglyme ($n = 2$): orange, X-ray, NMR[481]
$(C_5H_5)_2LnC[Si(SiMe_3)_3]{=}NC_6H_3Me_2\text{-}2,6$	Sc	yellow green, NMR, IR, melt./dec.[381]
$(C_5H_5)_2Ln[C_5H_3(CH_2NMe_2)]Fe(C_5H_5)$	Sm	complex with THF: red brown, NMR, IR, UV, melt./dec., magn. d.[482]
	Er	NMR, IR, UV, melt./dec., magn. d.[482]
$(C_5H_5)_2LnC{\equiv}C^nBu$	Nd	pink[387]
	Yb	orange red, NMR, IR, melt./dec.[387]
$(C_5H_5)_2LnC{\equiv}C^tBu$	Er	pink, X-ray,[483] IR,[483,484] bond angles[3e]
$(C_5H_5)_2LnC{\equiv}CC_6H_{13}$	Nd	pink[387]
	Yb	yellow, NMR, IR, melt./dec.[387]
$(C_5H_5)_2LnC{\equiv}C^cC_6H_{11}$	Yb	orange red, NMR, IR, melt./dec.[387]
$(C_5H_5)_2LnC{\equiv}CPh$	Sc	yellow, NMR, IR, melt./dec.[236]
	La	complex with 2phen: brown, NMR, IR, melt./dec.[244]
	Nd	complex with phen: brown, IR, melt./dec.[244]
	Gd	yellow, IR, magn. d.,[250,485] melt./dec.,[250] elec. d.[81]
	Ho	sand, UV, magn. d.[250]
	Er	pink, magn. d.,[250,485] IR,[485] UV[250]
	Yb	orange,[250,387,485] NMR, melt./dec.,[387] IR,[229,387,485] UV, MS,[229] magn. d.[250,485]
$(C_5H_5)_2Ln(C{\equiv}CC_5H_4)Fe(C_5H_5)$	Nd	orange[387]
	Yb	orange, NMR, IR, melt./dec.[387]
$(C_5H_5)_2Ln(\eta^5\text{-}C_6H_5)$	Sm	complex with THF: yellow, X-ray, IR[738]

The different reaction paths symbolized by eqs 83 and 84 establish the following relative order of Lewis acidity: $Sc^{3+} > Al^{3+} > Y^{3+} \approx La^{3+} \cdots Lu^{3+}$. Monomeric THF adducts are also known for Y,[457] Yb,[379,459] and Lu[375,460] which were prepared either by dissolving **73** in THF or by reacting $(C_5H_5)_2LnCl(THF)$ (**21**) with MeLi.[460] The ability of the above methyl compounds to react with protonic acids has led to applications in the synthesis of novel hetero bimetallic complexes.[457] Likewise, more strongly basic species of the type $(C_5H_5)_2Ln(\mu\text{-}Me)_2Li(tmed)$[461–465] and $(C_5H_5)_2Ln(\mu\text{-}Me)_2Li(THF)_2$[461–463] have successfully been employed in generating lanthanide to element bonds which would be difficult to prepare otherwise (e.g. refs 451, 452).

Tetraalkylaluminate complexes have already been mentioned because of their usefulness in the preparation of **73**. They are best prepared from **20** and 2 equiv of $LiAlMe_4$ in toluene as outlined in eq 85.[234,238,455,466,468]

$$\underset{\mathbf{20}}{{}^1/_2[(C_5H_5)_2LnCl]_2} + 2LiAlMe_4 \xrightarrow[-2LiCl]{\text{toluene}} (C_5H_5)_2Ln(\mu\text{-}Me)_2AlMe_2 \quad (85)$$

Ln = Sc, Y, Gd, Dy, Ho, Er, Tm, Yb

These complexes are soluble in toluene, benzene, and partly soluble in methylene chloride. The yttrium derivative was shown to be fluxional at 40 °C with regard to site exchange between terminal and bridging methyl groups. Variable-temperature NMR studies established an activation energy of 15.9 kcal mol^{-1} ($T = 392$ K), whereas the analogous scandium compound is nonfluxional. The solid state structure[238,466] of $(C_5H_5)_2Yb(\mu\text{-}Me)_2AlMe_2$, depicted in Figure 82, shows that the $[AlMe_4]^-$ anion coordinates to the ytterbium center with two symmetrical Yb–Me–Al interactions; two methyls on aluminum are terminal.

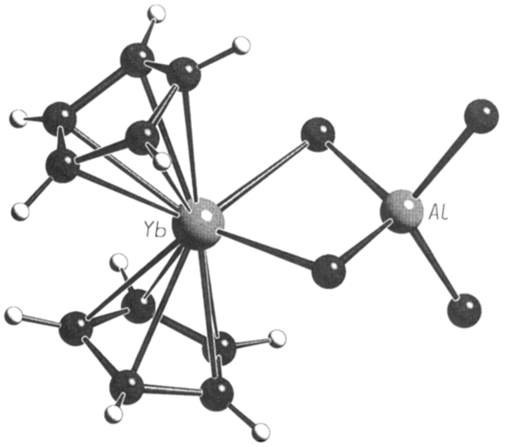


Figure 82. Structure of $(C_5H_5)_2Yb(\mu\text{-}Me)_2AlMe_2$ in the crystal.[238,466]

The methyl complexes discussed so far are kinetically stable which is probably due to the lack of low energetic decomposition pathways. In view of the accumulated data for all alkyl and aryl derivatives of the lanthanides it becomes apparent that the concepts developed for preparation of stable transition metal−η^1-carbyl complexes, that is, the use of alkyls without β-H atoms, sterically demanding as well as chelating alkyl or aryl ligands, can be applied to lanthanide chemistry as well. Owing to the possibility of β-H extrusion, it is not surprising that ethyl,[238,375,460,466] isopropyl,[375] *n*-butyl,[375,460] and *sec*-butyl[157] complexes are less stable and less well-defined relative to the simple methyl compounds. Presumably the steric bulk of the *tert*-butyl group allows isolation of complexes of the type $(C_5H_5)_2Ln{}^tBu(THF)$ (**74**) as outlined in eqs 86,[470] 87,[314,375] and 88.[106,157]

$$\underset{\textbf{20}}{[(C_5H_5)_2LuCl]_2} + {}^tBuLi \xrightarrow{THF} \underset{\textbf{74r}}{(C_5H_5)_2Lu{}^tBu(THF)} + LiCl \quad (86)$$

$$\underset{\textbf{21}}{(C_5H_5)_2LnCl(THF)} + {}^tBuLi \xrightarrow{THF} \underset{\textbf{74}}{(C_5H_5)_2Ln{}^tBu(THF)} + LiCl \quad (87)$$

Ln = Y (**74b**), Er (**74o**), Yb (**74q**), Lu (**74r**)

$$\underset{\textbf{1}}{(C_5H_5)_3Ln} + {}^tBuLi \xrightarrow{THF} \underset{\textbf{74}}{(C_5H_5)_2Ln{}^tBu(THF)} + LiC_5H_5 \quad (88)$$

Ln = Nd (**74f**), Lu (**74r**)

These complexes are thermally stable at most up to 80 °C, but there is evidence that β-H elimination takes place when **74r** is heated to 200 °C.[258] A likely course for the decomposition is given in eq 89:

$$(C_5H_5)_2Lu{}^tBu(THF) \xrightarrow[-THF]{80\ ^\circ C} [(C_5H_5)_2Lu{}^tBu]_n \xrightarrow[-Me_2C{=}CH_2]{200\ ^\circ C} \underset{\textbf{74r}}{[(C_5H_5)_2LuH]_n} \quad (89)$$

In order to prevent decomposition by β-H atom transfer, neopentyl,[375,460] benzyl,[375,460,472] (trimethylsilyl)methyl (**75**),[375,459,460,471,466,477] and bis(trimethylsilyl)methyl[106] complexes have been prepared and characterized. In addition to spectroscopic investigations by proton and carbon NMR, **75r**[375,460] and $[Li_2(DME)_2(\mu\text{-dioxane})][(C_5H_5)_2Ln(CH_2SiMe_3)_2]_2$[476] have been subjected to single-crystal structure analyses. Figure 83 shows that the $Me_3SiCH_2^-$ unit in **75r** is η^1-bonded to the eight-coordinate lutetium ion at a normal bond distance ($d_{Lu-C} = 237.6(17)$ pm). However the Lu−C$_1$−Si angle of 130.7(8)° is substantially greater than expected for a tetrahedrally coordinated sp^3 hybridized carbon atom. (Similar values have been determined for $[Li_2(DME)_2(\mu\text{-dioxane})][(C_5H_5)_2Ln(CH_2SiMe_3)_2]_2$; Y−C−Si = 134.3° and 130.1°.)[476] This phenomenon has been studied theoretically by Tatsumi and Nakamura[487] on ethyl complexes of the actinoids. They concluded that a large bond angle allows the atom orbitals of the α-H atom to overlap with vacant metal orbitals giving rise to α-agostic metal−hydrogen bonds which, in turn, would reduce the negative charge of the σ-bonded carbon atom. This argument may also apply to **75r** and $[Li_2(DME)_2(\mu\text{-dioxane})][(C_5H_5)_2Ln(CH_2SiMe_3)_2]_2$ because Lu^{3+} and Y^{3+} are known to be highly acidic. Further examples of agostic lanthanide to hydrogen and carbon bonds follow in the following section.

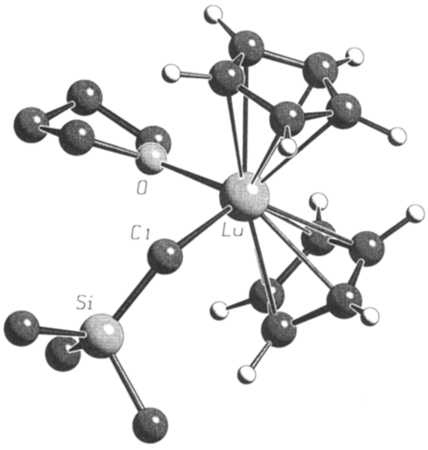


Figure 83. Structure of $(C_5H_5)_2Lu(CH_2SiMe_3)(THF)$ in the crystal.[375,460]

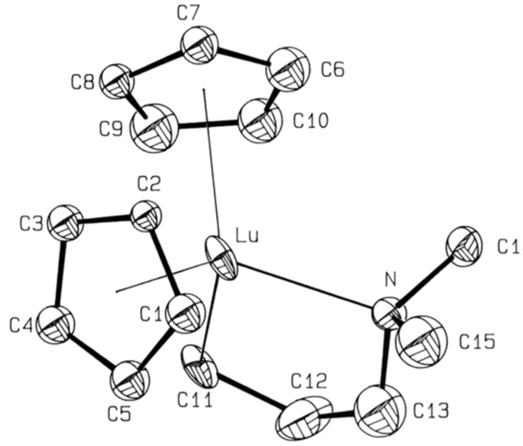
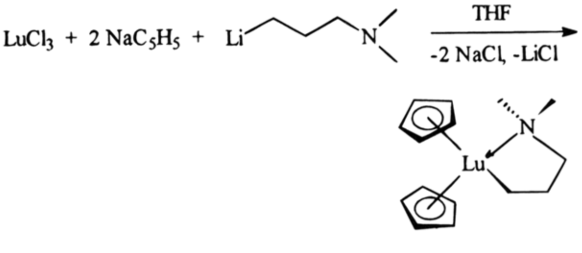


Figure 84. Structure of $(C_5H_5)_2Lu(CH_2)_3NMe_2$ in the crystal.[389]

Bidentate ligands are also effective in stabilizing lanthanide to alkyl linkages even when a β-hydrogen atom is present, since chelating ligands block additional coordination sites that must be vacant for β-hydrogen elimination to occur. For example, use of $Li(CH_2)_3NMe_2$ as bidentate ligand results in the base-free bis(cyclopentadienyl)lanthanide organyl (Figure 84). The originally free coordination site at the rare earth metal is filled by lone pair coordination of the nitrogen atom (eq 90):[389]



(90)

The addition of lithium ylides to equimolar amounts of **21** gives rise to organolanthanide ylides (eq 91):

$$\underset{\mathbf{21}}{(C_5H_5)_2LuCl(THF)} + Li[(CH_2)_2PR_2] \rightarrow (C_5H_5)_2Lu(\mu\text{-}CH_2)_2PR_2 + LiCl \quad (91)$$

$R = {}^tBu,^{474}\ Ph^{475}$

Kinetically stable complexes with bonds to sp^2-hybridized carbon atoms have also been obtained from ligands containing one further donor group.[143,473] Hence, $Li[C_6H_4\text{-}2\text{-}CH_2NMe_2]$[239,478] (see Figure 85) and $Li[(C_5H_5)FeC_5H_3\text{-}2\text{-}CH_2NMe_2]$[482] react in ether with **20** to form monomeric, intramolecularly stabilized complexes according to eq 92.

$$\underset{\mathbf{20}}{{}^1/_2[(C_5H_5)_2LnCl]_2} + LiR \xrightarrow{\text{ether or THF}} (C_5H_5)_2LnR + LiCl \quad (92)$$

$R = C_6H_4\text{-}2\text{-}CH_2NMe_2$: Ln = Sc, Y

$R = (C_5H_5)FeC_5H_3\text{-}2\text{-}CH_2NMe_2$:
Ln = Sm (THF adduct), Er

In addition to chelating aryl ligand, complexes of simple monodentate phenyl derivatives also are known. Some of them were known when the first report on bis(cyclopentadienyl)lanthanide methyl complexes appeared in 1975.[250] For example, aryllithium reagents readily react with **21** in THF, yielding the corresponding aryl complexes according to eq 93. Similar ytterbium compounds were generated by reducing mercury organyls with $(C_5H_5)_2Yb(THF)_2$ as outlined in eq 94.[229]

$$\underset{\mathbf{21}}{(C_5H_5)_2LnCl(THF)} + LiR \rightarrow (C_5H_5)_2LnR(THF) + LiCl \quad (93)$$

$R = C_6H_4CH_3\text{-}4$: Ln = Gd, Er, Yb,[83] Lu[375,460]

$R = C_6H_4Cl\text{-}4$: Ln = Er[83]

$$(C_5H_5)_2Yb(THF)_2 \xrightarrow{HgR_2} (C_5H_5)_2Yb(C_6F_5)(THF) \quad (94)$$

These complexes have been characterized by standard spectroscopic methods and the structure of $(C_5H_5)_2Lu(C_6H_4CH_3\text{-}4)(THF)$ has been elucidated by X-ray crystallography.[375] Coordinated THF can be removed by treatment with e.g. hexane, benzene, or toluene giving rise to the seemingly monomeric, solvent-free complexes. Although both mass spectra and molecular weight determinations of solvent-free "$(C_5H_5)_2Er(C_6H_4Me\text{-}4)$" apparently support the initially monomeric formulation, no solid-state crystal structure has as yet been reported. In view of the enormous amount of structural and chemical knowledge accumulated in the past few years, the existence of monomeric, base-free bis(cyclopentadienyl)lanthanide aryl compounds without bulky substituents in the ortho position seems to be unlikely.

Finally a number of σ-bonded ethynyl complexes have been prepared by a variety of methods which included acid–base reactions,[435,483,484] transmetalation,[236,244,250,435,485] and ligand displacements.[387] The resulting complexes of the type $[(C_5H_5)_2Ln(\eta^1\text{-}C{\equiv}CR)]_x$ (R = ^{n}Bu, ^{t}Bu, Ph, C_6H_{13}, $^cC_6H_{11}$, $C_5H_4FeC_5H_5$) are at least dimeric when unsolvated, as shown by the X-ray structure analysis of $[(C_5H_5)_2Er(\mu\text{-}C{\equiv}C^tBu)]_2$[483] (Figure 86). Apparently the terminal sp^2-hybridized carbon atom of the alkynyl group is capable of bridging two electron-deficient metal ions by way of three-center, two-electron bonds.

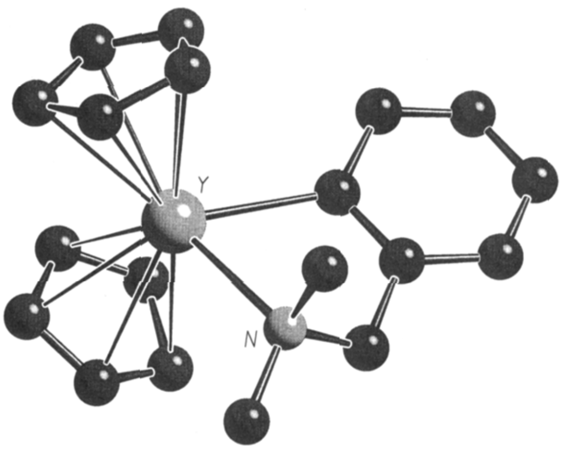


Figure 85. Structure of $(C_5H_5)_2YC_6H_4\text{-}2\text{-}CH_2NMe_2$ in the crystal.[239]

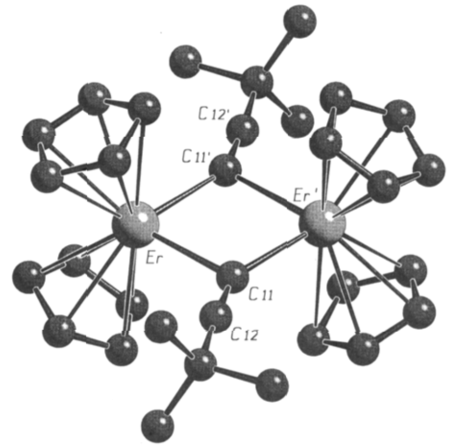


Figure 86. Structure of $[(C_5H_5)_2Er(\mu\text{-}C{\equiv}C^tBu)]_2$ in the crystal.[483]

The synthesis of *N*-alkylformimidoyl rare earth complexes $\{(C_5H_5)_2Ln[\mu\text{-}\eta^2\text{-}(XC{=}N^tBu)]\}_2$ (X = H (**62**), D (**63**))[433,434] have already been discussed within the chapter of bis(cyclopentadienyl) rare earth pnicogenides (see eq 61 and Figure 64). In this context the η^2-iminosilaacyl complex $(C_5H_5)_2ScC[Si(SiMe_3)_3]{=}NC_6H_3Me_2\text{-}2,6$ has to be mentioned,[381] as well as the two known alkenyl species, $(C_5H_5)_2YC(R){=}CH(R)$ (R = Et, Ph).[435] The latter compounds are product of the reaction of bis(cyclopentadienyl)yttrium hydride with internal alkynes (addition of Y–H across the multiple alkyne bond).

The use of bulky anthracene dianion as a ligand in organolanthanide chemistry results in formation of the ionic complex $[Na(diglyme)_2][(C_5H_5)_2Ln(C_{14}H_{10})]$, which the structure of has become available recently (Figure 87).[481]

ii. Pentamethylcyclopentadienyl Derivatives. The chemistry of these species has opened a new chapter in lanthanoid catalysis and C–H activation. Most of the compounds discussed in this chapter (see Table 19) were either prepared to probe reaction paths in

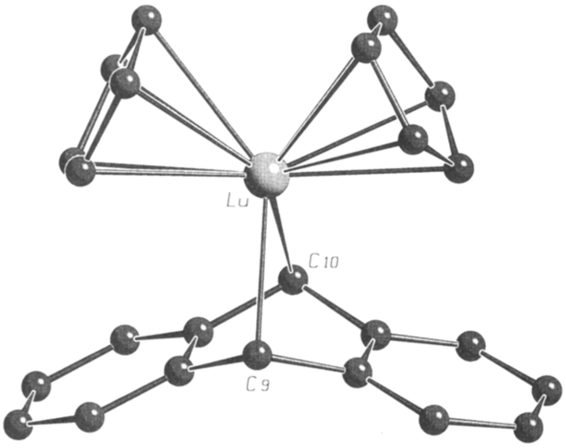


Figure 87. Structure of the anion of $[Na(diglyme)_2][(C_5H_5)_2Lu(C_{14}H_{10})]$ in the crystal.[481]

homogeneous catalytic reactions and C−H activation or to establish structural knowledge of those organolanthanide−carbyl species that serve as starting materials and potential reaction products. To give a detailed account of the latest development in this fast-growing field is beyond the scope of this review, however, the interested reader is referred to the literature covering these topics (e.g. refs 265, 351, 354, 355, 488a, 512, and 515−517).

This fascinating new avenue of organolanthanide chemistry began in 1982 with the discovery of the Ziegler−Natta-type catalyst $(C_5Me_5)_2LuMe(Et_2O)$ by Watson.[358,359] Prior to Watsons studies, the number of investigations in this field remained small due to the short lifetime of these catalysts derived from C_5H_5 ligands, their low solubility in noncoordinating solvents and their rapid and complex decomposition which involved metalation of the C_5H_5 ring. Then, after the unsubstituted cyclopentadienyl ligand was replaced by its permethyl analogue, (C_5Me_5), the above-mentioned problems could be satisfactorily solved and investigations of catalytic processes as well as C−H and C−C bond activations could be studied.

Naturally, the most intriguing transformations have been obtained by using solvent-free and thus extremely electrophilic lanthanide alkyl species in nonpolar solvents, since Lewis bases would occupy a coordination site that must be vacated in order to bind the substrate. But, the preparation of solvent-free bis(pentamethylcyclopentadienyl) rare earth methyl complexes is not easy. The lanthanide ion is determined to keep further donor ligands (i.e. anions or THF/Et_2O) within its coordination sphere. Thus, $(C_5Me_5)_2ScMe$ (**76a**) can only be prepared from $(C_5Me_5)_2ScCl$ (**20a**) and MeLi in the absence of THF as shown in eq 95.

$$\underset{\mathbf{20a}}{(C_5Me_5)_2ScCl} + MeLi \xrightarrow{\text{ether/hexane}} \underset{\mathbf{76a}}{(C_5Me_5)_2ScMe} + LiCl \quad (95)$$

In the presence of THF the sole product obtained was $(C_5Me_5)_2ScCl(THF)$ (**21a**), indicating that the THF complex is inert toward metathetical substitution. **76a** is a yellow, air-sensitive and, as shown by X-ray crystallography, monomeric complex.[265,272] Figure 88 shows that **76a** has the typical structure of a bent metallocene with a terminal methyl group.

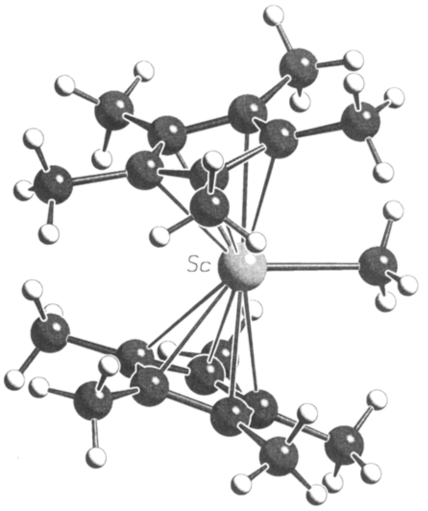


Figure 88. Structure of $(C_5Me_5)_2ScMe$ (**76a**) in the crystal.[265,272]

Compound **76a** rapidly polymerizes ethylene[488a] and mechanistic studies of this and related processes indicate that agostic Sc−H−C interactions may promote the reaction and may also influence the selectivity.[247,518] Although the ^1H chemical shift difference between $(C_5Me_5)_2ScMe$ (**76a**) and $(C_5Me_5)_2ScCH_2D$ of 0.057 ppm indicated the presence of an agostic structure in solution. The solid-state crystal structure determination showed no such interaction, but the resolution of the structure determination was not high enough for the hydrogen atoms to be located. However, it was argued that the position of the methyl group in the plane defined by the centroids of the cyclopentadienyl rings and scandium precludes the formation of an agostic bond, because this interaction would distort the methyl group to one side of the plane.

In an inert solvent such as cyclohexane, **76a** undergoes a variety of reactions with aliphatic and aromatic substrates by a process which is called σ-bond metathesis. Some of the most prominent reactions are outlined in eqs 96−100:[265,272,488a]

$$\underset{\mathbf{76a}}{(C_5Me_5)_2ScMe} + H_2 \rightarrow (C_5Me_5)_2ScH + CH_4 \quad (96)$$

$$\underset{\mathbf{76a}}{(C_5Me_5)_2ScMe} + C_6D_6 \rightarrow (C_5Me_5)_2ScC_6D_5 + CH_3D \quad (97)$$

$$\underset{\mathbf{76a}}{(C_5Me_5)_2ScMe} + CH_2{=}CHMe \rightarrow (C_5Me_5)_2ScCH_2CHMe_2 \xrightarrow[-MeCHMe_2]{CH_2=CHMe} (C_5Me_5)_2ScCH{=}CHMe \quad (98)$$

$$\underset{\mathbf{76a}}{(C_5Me_5)_2ScMe} + CH_2{=}CMe_2 \rightarrow (C_5Me_5)_2ScCH{=}CMe_2 + CH_4 \quad (99)$$

$$\underset{\mathbf{76a}}{(C_5Me_5)_2ScMe} + HC{\equiv}CR \rightarrow (C_5Me_5)_2ScC{\equiv}CR + CH_4 \quad (100)$$

Table 19. Spectroscopic and Other Data of Bis(pentamethylcyclopentadienyl)lanthanide Complexes Containing Lanthanide to Carbon Bonds

compound	Ln		color, characterization, etc.
$(C_5Me_5)_2LnMe$	Sc	**76a**	pale yellow,[265] IR,[265,272] X-ray,[265,272] NMR,[265,272,488a] lumines.;[298b] complex with THF: NMR,[265] synthesis[272]
	Y	**76b**	NMR;[456,488b] complex with Et_2O: NMR;[456] with THF: colorless, IR,[295,489] X-ray,[489] NMR,[295,456,489] reactions[739,740]
	Sm	**76h**	complex with THF: yellow, X-ray, NMR, IR, magn. d.,[404] synthesis[208]
	Yb	**76q**	synthesis;[490] with Et_2O: red, UV,[287] NMR;[287,358] complex with THF: orange[297]
	Lu	**76r**	NMR,[359,456,488b] X-ray;[490] complex with Et_2O: synthesis,[358] NMR;[456] with THF: NMR;[456] with NEt_3: synthesis;[359] with py: synthesis[358]
$(C_5Me_5)_2LnCH_2D$	Y		complex with THF: NMR[491]
$(C_5Me_5)_2Ln(\mu\text{-}Me)_2Li(LB)_n$	Y		LB = Et_2O (n = 1): colorless, NMR, IR[295]
	La		LB = tmed (n = 1):colorless, melt./dec.,[268] NMR[268,294,465]
	Ce		LB = tmed (n = 1): lumines.[61]
	Pr		LB = tmed (n = 1): greenish, NMR,[268,463] melt./dec.[268]
	Yb		(n = 0): synthesis;[358] LB = Et_2O (n = 2): yellow;[297] LB = THF (n = 3): synthesis[358]
	Lu		(n = 0): synthesis;[358] LB = THF (n = 2): colorless, NMR,[268,463] melt./dec.;[268] LB = THF: (n = 3): NMR;[358] LB = tmed (n = 1): colorless,[268,463] melt./dec.,[268] NMR[268,294,463,465]
$(C_5Me_5)_2Ln(Me)_2AlMe_2$	Y	**77b**	colorless, IR,[295] NMR,[295,456] X-ray, thermo. d.[456]
	Sm	**77h**	orange, X-ray, NMR, IR, magn. d.[404]
	Yb	**77q**	synthesis[358]
	Lu	**77r**	synthesis,[358] NMR, thermo. d.[456]
$(C_5Me_5)_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2Ln(C_5Me_5)_2$	Y, Lu		NMR[465]
$(C_5Me_5)_2Ln(Me_4Al)(GaMe_4)Ln(C_5Me_5)_2$	Y		NMR[456]
$(C_5Me_5)_2Ln(Me)_2GaMe_2$	Y		NMR, thermo. d.[456]
	Lu		NMR[456]
$(C_5Me_5)_2Ln(\mu\text{-}Me)(\mu\text{-}Cl)Li(Et_2O)_2$	Y		colorless, NMR, IR[295]
	Yb		brown[297]
$(C_5Me_5)_2LnMe(MgCl_2)(THF)_2$	Y		colorless, NMR, IR[295]
$(C_5Me_5)_2LnEt$	Sc		yellow, X-ray, IR,[265] NMR[265,488a]
$(C_5Me_5)_2Ln(\mu\text{-}Et)_2AlEt_2$	Sm		red, X-ray, NMR, IR, magn. d.[492]
$(C_5Me_5)_2Ln{}^nPr$	Sc		NMR,[265,488a] IR,[265] synthesis[352]
	Sm		synthesis[446]
$(C_5Me_5)_2Ln{}^nBu$	Sc		pale yellow,[488a] NMR[265,488a]
$(C_5Me_5)_2Ln{}^sBu$	Sc		NMR[265]
	Lu		NMR[358,359]
$(C_5Me_5)_2Ln(CH_2)_4Me$	Sc		synthesis,[352] NMR[488a]
$(C_5Me_5)_2Ln(CH_2)_5Me$	Sc		NMR[488a]
$(C_5Me_5)_2LnCH_2CH(Me)CH_2CH_2Me$	Lu		catalysis[359]
$(C_5Me_5)_2LnCHDCHD{}^tBu$	Sc		NMR, reactions[728,731]
$(C_5Me_5)_2LnCH_2CH(Me)CH_2CHMe_2$	Lu		catalysis[359]
$(C_5Me_5)_2LnCH_2{}^cC_5H_9$	Sc		synthesis[728]
$(C_5Me_5)_2LnCH_2Ph$	Sc		yellow, NMR, IR,[265] synthesis[272]
	Y		NMR[493]
	La		NMR[494]
	Ce		X-ray, NMR, IR[494]
	Sm		red orange, NMR; complex with THF: red orange, X-ray, IR, magn. d.,[403] NMR[403,404]
$(C_5Me_5)_2LnCH_2Ph(MgCl_2)(THF)_2$	Y		colorless, NMR, IR[295]
$(C_5Me_5)_2LnCH_2C_6H_3Me_2\text{-}3,5$	Y		yellow, NMR, IR; complex with THF: colorless, NMR, IR[278]
$(C_5Me_5)_2LnCH_2CH_2Ph$	Sc		yellow, NMR[299,488a]
$(C_5Me_5)_2LnCH_2CHDPh$	Sc		yellow[488a]
$(C_5Me_5)_2LnCH_2CH_2C_6H_4Me\text{-}4$	Sc		yellow, NMR[488a]
$(C_5Me_5)_2LnCH_2CH_2C_6H_4CF_3\text{-}4$	Sc		NMR[488a]
$(C_5Me_5)_2LnCH_2CH_2C_6H_4NMe_2\text{-}4$	Sc		yellow, NMR[488a]
$(C_5Me_5)_2LnCH_2CN$	La		white, X-ray, NMR, IR[495]
	Ce		pink, NMR, IR[495]
$(C_5Me_5)_2Ln(\mu\text{-}CH_2)_2PMe_2$	Sm		complex with 2 LiCl: yellow, NMR, IR, melt./dec.[308]
	Lu		colorless, X-ray, NMR, IR, melt./dec.[496]
$(C_5Me_5)_2Ln(\mu\text{-}CH_2)_2P{}^tBu_2$	Sm		complex with 2 LiCl: yellow, NMR, IR, melt./dec.[308]
$(C_5Me_5)_2Ln(\mu\text{-}CH_2)_2PMePh$	Nd		complex with 2 LiCl: blue, NMR, IR, melt./dec.[308]
	Sm		complex with 2 LiCl: yellow, NMR, IR, melt./dec.[308]
$(C_5Me_5)_2Ln(\mu\text{-}CH_2)_2PPh_2$	Nd		complex with 2 LiCl: blue, NMR, IR, melt./dec.[308]
	Sm		complex with 2 LiCl: yellow, NMR, IR, melt./dec.[308]
$(C_5Me_5)_2Ln[(\mu\text{-}CH_2)(\mu,\eta^2\text{-}C_6H_4)PPh_2]$	Y		colorless, X-ray, NMR, IR[493]
	Lu		NMR[360]
$(C_5Me_5)_2LnCH_2SiMe_3$	Sc		white, NMR,[729] reactions[363,511,729]
	Lu		NMR[360]
$[Li(DME)_n][(C_5Me_5)_2Ln(CH_2SiMe_3)_2]$	Pr		n = 3: green, NMR, melt./dec.[268]
	Lu		n = 2: NMR;[465] n = 3: colorless, melt./dec.,[268] NMR[268,294]
$(C_5Me_5)_2LnCH(SiMe_3)_2$	Sc		yellow, NMR[299]

Table 19 (Continued)

compound	Ln		color, characterization, etc.
$(C_5Me_5)_2LnCH(SiMe_3)_2$	Y		colorless, X-ray, IR,[275] NMR,[274,275,497,598] melt./dec.,[274,275] reactions;[741,742] complex with CN^tBu: white, NMR, IR[411]
	La		pale yellow,[304,305,743] IR,[304] NMR[304,441,498]
	Ce		red, IR,[273,284] X-ray,[284] NMR;[273,284,441] complex with NC^tBu: gold, NMR, IR;[284] with $LiCl(Et_2O)_2$: synthesis;[273] with $LiCl(tmed)_2$: synthesis[273]
	Nd		blue green, X-ray, NMR, IR,[304,362b] reactions[742,744]
	Sm		red brown, NMR, IR,[304] reactions[742,744,745]
	Lu		colorless, IR,[304] NMR[304,498]
$(C_5Me_5)_2LnC(=N_2)SiMe_3$	Y		complex with THF: yellow, NMR, IR[499]
	Yb		complex with THF: dark red, IR[499]
	Lu		complex with THF: yellow, NMR, IR[499]
$(C_5Me_5)_2Ln[(^tBu)CPPC(^tBu)]Ln(C_5Me_5)_2$	Sm		orange red, X-ray, NMR, IR, melt./dec.[500]
$(C_5Me_5)_2Ln(C_6H_{11}CNC_6H_{11})$	Sm		red, IR[291]
$(C_5Me_5)_2Ln[C_5H_3(CH_2NMe_2)]Fe(C_5H_5)$	Sm		light brown, NMR, MS, IR, UV, melt./dec., magn. d.[501]
$(C_5Me_5)_2LnC_5H_4(\mu\text{-}H)_2WC_5H_5$	Y		yellow, NMR, IR;[742,746] complex with py: NMR[746]
	Sm		red, X-ray, NMR[742,746]
$(C_5Me_5)_2LnPh$	Sc	**78a**	NMR[265]
	Y	**78b**	NMR[493]
	Sm	**78h**	orange, NMR, IR, magn. d.; complex with THF: orange, X-ray, NMR, magn. d.[502]
	Lu	**78r**	NMR[360]
$(C_5Me_5)_2LnC_6H_4Me\text{-}2$	Sc		off-white, NMR, IR[265]
$(C_5Me_5)_2LnC_6H_4Me\text{-}3$	Sc		NMR[265]
$(C_5Me_5)_2LnC_6H_4Me\text{-}4$	Sc		NMR;[265] complex with $NCC_6H_4Me\text{-}4$: yellow, NMR, IR[442]
$(C_5Me_5)_2LnC_6H_4\text{-}2\text{-}CH_2NMe_2$	Y		white, NMR[493]
$(C_5Me_5)_2LnC_6H_4NMe_2\text{-}2$	Y		red, NMR, IR[493]
$(C_5Me_5)_2LnC_6H_4PMe_2\text{-}2$	Y		NMR, IR[493]
$(C_5Me_5)_2LnC_6H_4OMe\text{-}2$	Y		orange, NMR, IR[493]
$(C_5Me_5)_2LnC_6H_4SMe\text{-}2$	Y		white, NMR, IR[493]
$[(C_5Me_5)_2Ln]_2C_6H_4$	Lu		NMR[360]
$(C_5Me_5)_2LnC_6F_5$	Yb		purple, NMR, melt./dec.[262]
$(C_5Me_5)_2LnCH_2CH=CH_2$	Sc		NMR, IR[265]
	La		NMR[304]
	Nd		NMR, IR[304]
	Sm		orange,[271] red, X-ray, magn. d.,[503] NMR, IR[271,503]
	Lu		synthesis[359]
$(C_5Me_5)_2LnCH_2CH=CHMe$	La		NMR[304]
	Sm		red, X-ray, NMR, IR, magn. d.[503]
$(C_5Me_5)_2LnCH_2CH=CH^nPr$	La		NMR[304]
	Nd		NMR[304]
	Sm		synthesis[503]
$(C_5Me_5)_2Ln(CH_2)_4CH=CMe_2$	Sc		synthesis, reactions[728]
$[(C_5Me_5)_2LnCH_2CH=CH-]_2$	Sm		purple, X-ray, NMR, IR, magn. d.[503]
$[(C_5Me_5)_2LnCH_2CH=CHCH_2-]_2$	Sm		red orange, X-ray, NMR, IR, magn. d.[503]
$(C_5Me_5)_2LnCH_2CH=CHPh$	Sm		red, X-ray, NMR, IR, magn. d.[503]
$(C_5Me_5)_2LnCH_2CMe=CH_2$	Y		with $MgCl_2(THF)_2$: colorless, NMR, IR[295]
	Lu		synthesis[359]
$(C_5Me_5)_2LnCH=CHMe$	Sc		NMR, IR[265]
$(C_5Me_5)_2LnCH=CMe_2$	Sc		NMR, IR[265]
$(C_5Me_5)_2LnCH=CHC_6H_4Me\text{-}4$	Sc		pale yellow, IR[265]
$(C_5Me_5)_2LnCH=CHC_6H_4CF_3\text{-}4$	Sc		NMR[265]
$(C_5Me_5)_2LnCH=CHC_6H_4OMe\text{-}4$	Sc		NMR[265]
$(C_5Me_5)_2LnCMe=CHMe$	Sc		orange,[488a] synthesis[299,352]
$(C_5Me_5)_2LnCHMeC_5H_4N\text{-}2$	Y		NMR[734]
$(C_5Me_5)_2LnCH_2CH_2C_5H_4N\text{-}2$	Y		yellow, NMR, reactions[734]
$(C_5Me_5)_2LnCH_2CHMeC_5H_4N\text{-}2$	Y		brown, NMR, IR[734]
$(C_5Me_5)_2LnCMe=CEtC_5H_4N\text{-}2$	Y		NMR[734]
$(C_5Me_5)_2LnCEt=CMeC_5H_4N\text{-}2$	Y		NMR[734]
$(C_5Me_5)_2Ln^cC_6H_9$	La		NMR[304]
	Nd		NMR[304]
$[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^1,\eta^3\text{-}C_4H_6)$	La		complex with THF: red, X-ray, NMR, melt./dec.[504]
$(C_5Me_5)_2Ln[^tBuCH=CC(^tBu)=CH_2]$	Sm		orange, X-ray[440]
$[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeC_4Me)$	La		deep red, NMR, IR[409]
	Ce		red brown, X-ray, NMR, IR[409]
$[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}{}^tBuC_4{}^tBu)$	Ce		red brown, X-ray, IR[409]
$[(C_5Me_5)_2Ln]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}Me_2CH(CH_2)_2C_4(CH_2)_2CHMe_2]$	Sm		dark red (yellow green), X-ray, NMR[440]
$[(C_5Me_5)_2Ln]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}Ph(CH_2)_2C_4(CH_2)_2Ph]$	Sm		dark red (yellow green), X-ray, NMR[440]
$[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_4Ph)$	Ce		dark green red, NMR, IR[440]
	Nd		dark red, X-ray, NMR, IR[440]
	Sm		red, magn. d., IR,[505] X-ray,[505,506] NMR[3k,505,506]
$[(C_5Me_5)_2Ln]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}1,2,3,4\text{-}(py_4)C_4H_4]$	Sm		red, X-ray, NMR, IR[507]
$[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}pyCHCHpy)$	Sm		red, X-ray, NMR, IR[507]
$[(C_5Me_5)_2Ln]_2(PhC=CPh)$	Sm		black, NMR, IR[508]
$[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$	Sm		X-ray,[503,509] maroon, NMR, IR, magn. d.[509]

Table 19 (Continued)

compound	Ln	color, characterization, etc.
$[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}PhCHCHPh)$	Sm	X-ray,[503,509] red brown, NMR, IR, magn. d.[509]
$[(C_5Me_5)_2Ln]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{14}H_{10})]$	Sm	black, X-ray, NMR, IR[733]
$[(C_5Me_5)_2Ln]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{16}H_{10})]$	Sm	black, X-ray, NMR, IR[733]
$[(C_5Me_5)_2Ln]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{18}H_{12})]$	Sm	green, X-ray, NMR, IR[733]
$[(C_5Me_5)_2Ln]_2[(C_{15}H_{12})]$	Sm	wine red, NMR, IR[733]
$[(C_5Me_5)_2Ln]_2[(C_{12}H_8)]$	Sm	dark blue, NMR, IR[733]
$(C_5Me_5)_2LnCH_2C\equiv CMe$	Y	NMR,[510,734] IR;[510] complex with py: brown-yellow, NMR, IR[734]
	La	NMR[510]
	Ce	NMR[510]
$(C_5Me_5)_2LnCH_2C\equiv C^tBu$	Ce	NMR[510]
$(C_5Me_5)_2LnCH_2C\equiv CSiMe_3$	Ce	NMR[510]
$(C_5Me_5)_2LnC\equiv CH$	Sc	NMR, IR[511]
	Y	complex with py: yellow, NMR, IR[734]
$(C_5H_5)_2LnC\equiv CMe$	Sc	white, NMR, IR[265]
	Y	NMR; complex with Et_2O: colorless, NMR, IR; with THF: NMR, IR[278]
	La	white, NMR, IR[409]
	Ce	purple, IR,[409,512] NMR[512]
$(C_5Me_5)_2LnC\equiv C^tBu$	Ce	purple, NMR, IR;[409,512] complex with THF: orange, NMR, IR[512]
	Sm	yellow, X-ray;[440] complex with THF: NMR, IR[208]
$(C_5Me_5)_2Ln(\mu\text{-}C\equiv C^tBu)_2Li(THF)$	Y	X-ray, NMR, IR[513]
$(C_5Me_5)_2LnC\equiv CCHMe_2$	Sm	complex with THF: NMR[440]
$(C_5Me_5)_2LnC\equiv C(CH_2)_2CHMe_2$	Sm	complex with THF: NMR, IR[440]
$(C_5Me_5)_2LnC\equiv C(CH_2)_2Ph$	Sm	complex with THF: NMR, IR[440]
$(C_5Me_5)_2LnC\equiv CCH_2NEt_2$	Sm	complex with THF: NMR, IR[440]
$(C_5Me_5)_2LnC\equiv CPh$	Y	NMR;[512] complex with Et_2O: white, NMR, IR[278]
	Ce	complex with THF: red, NMR, IR[440]
	Nd	complex with THF: blue, NMR, IR[440]
	Sm	NMR, IR;[271] complex with THF: orange, X-ray, NMR, IR[208]
$K[(C_5Me_5)_2Ln(C\equiv CPh)_2]$	Ce	blue, X-ray, NMR, IR[440]
	Nd	green, NMR, IR[440]
	Sm	orange, X-ray, NMR, IR[440]
$(C_5Me_5)_2LnC\equiv CSiMe_3$	Y	NMR;[512] complex with Et_2O: colorless, NMR, IR[278]
	Ce	NMR[512]
$(C_5Me_5)_2LnC\equiv CLn(C_5Me_5)_2$	Sc	white, X-ray, NMR, IR[511]
$\{(C_5Me_5)_3[\mu^3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Ln_2\}_2$	La	IR[494]
	Ce	X-ray, IR[494]
$(C_5Me_5)_2Ln\text{-}\eta^2\text{-}(NC_5H_4)$	Sc	X-ray,[265,272] NMR, IR, reactions[265]
	Y	red,[278] yellow,[734,746] NMR, IR;[278,734] complex with THF: NMR;[278,734] complex with py: NMR, reactions[734]
	Lu	NMR[360]
$(C_5Me_5)_2Ln(\eta^2\text{-}NC_5H_3Me\text{-}6)$	Y	complex with THF: NMR[278,734]

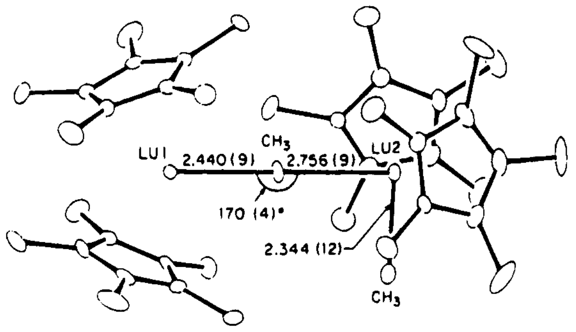
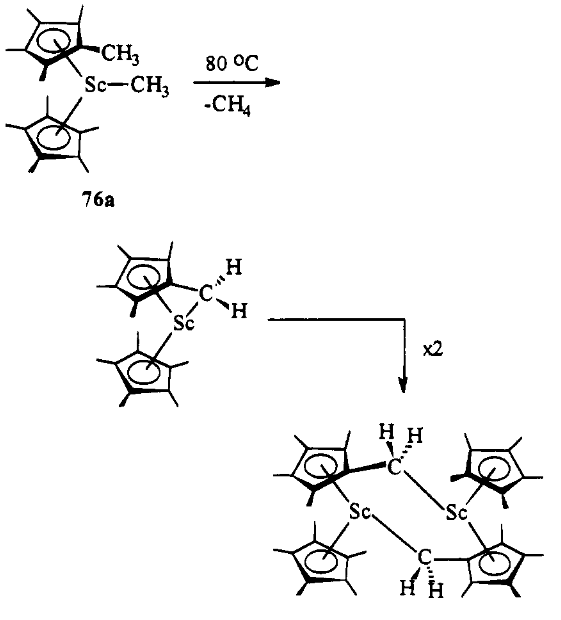


Figure 89. Structure of $[(C_5Me_5)_2LuMe]_2$ (**76r**) in the crystal.[490] (Reprinted from ref 490. Copyright 1985 American Chemical Society.)

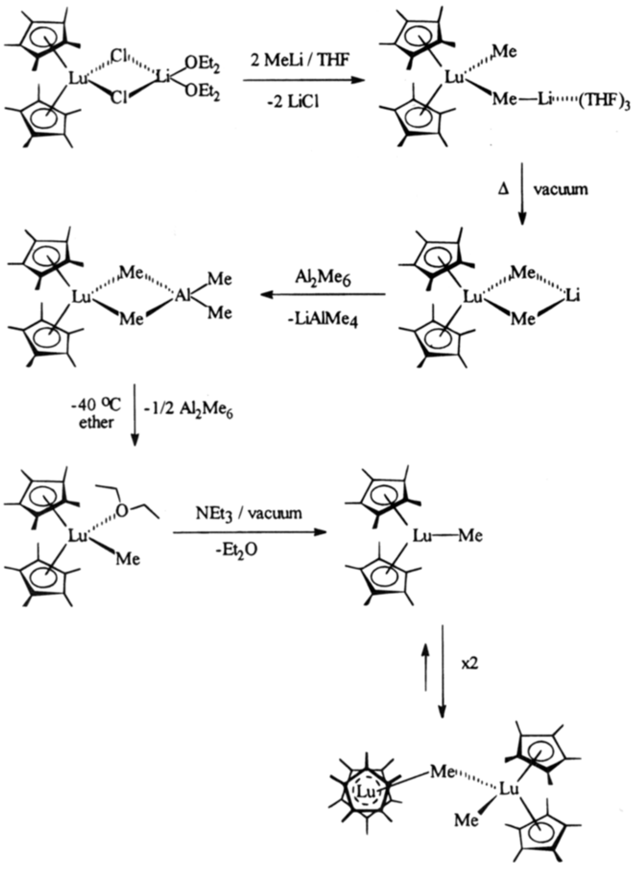
In addition, thermolysis of **76a** at 80 °C in cyclohexane evolved methane and formed a yellow insoluble product whose identity was established by X-ray crystallography as $[(C_5Me_5)Sc(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)]_2$.[514] This ring metalation, due to intramolecular activation of a ring methyl C–H bond, can explain the observed rate law for reaction 97, which is first order in **76a**. Thus, a generation of $[(C_5Me_5)Sc(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)]_2$ is the slow kinetic step and its dimerization is fast, as indicated in eq 101:[265,272]



(101)

The experimental details in this field are vast but they all are consistent with reactions occurring by σ-bond metathesis transition states.[265,272,488a]

Before the rich chemistry of **76a** was developed, Watson[358–360,488b,490] showed that $[(C_5Me_5)_2LuMe]_2$ (**76r**) undergoes a variety of reactions involving C–H and C–C bond activation. Even though **76a** is difficult to prepare the synthesis of **76r** is even more complicated. The labor-intensive multistage synthesis is depicted in eq 102:[490]



76r

(102)

Unlike the scandium species **76a**, the analogous lutetium complex **76r** is dimeric in solid state but ^{1}H-NMR studies, in cyclohexane-d_{12}, show a rapid monomer–dimer equilibrium (15% dissociation). The molecular structure analysis of **76r** revealed an unsymmetric dimer with one bridging and one terminal methyl group (Figure 89).[488b,490]

In sharp contrast to the previously discussed symmetrically methyl-bridged complexes of the type $[(C_5H_5)_2Ln(\mu\text{-}Me)]_2$ (**73**), the interactions between the bridging methyl group and Lu(2) in this asymmetric complex should be regarded as intermolecular agostic Lu–C–H···Lu contacts. This clearly demonstrates the exceedingly high Lewis acidity of the coordinatively unsaturated $(C_5Me_5)_2LuMe$ (**76r**) species which coordinates C–H σ-bonds in the absence of classical donors. In view of this result, complexation of alkanes by **76r** seems possible. Indeed, in a sealed NMR tube a solution of **76r** in cyclohexane-d_{12} reacts at 70 °C under an atmosphere of $^{13}CH_4$ to form the corresponding ^{13}C-labeled complex that is in equilibrium with the unlabeled methyl compound (eq 103).[488b,490]

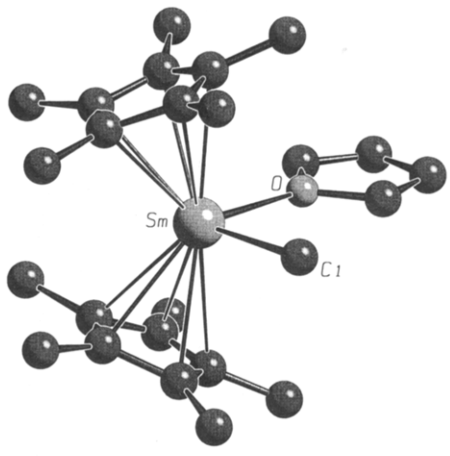


Figure 90. Structure of $(C_5Me_5)_2SmMe(THF)$ in the crystal.[404]

However, the ease with which the methane exchange reaction proceeds depends dramatically on the ionic radius of the metal ion. In the order of increasing ionic radius of the rare earth ion bis(pentamethylcyclopentadienyl) methyl complexes of Sc (monomer,[265,272] **76a**), Lu (dimer,[490] **76r**) and Y (dimer,[456,488b] **76b**) show the following relative methane exchange rates: 1:50:250. Higher alkanes such as ethane and propane also react but at much smaller rates and the resulting ethyl and propyl complexes are reported to decompose by β-hydrogen transfer.[488b] Furthermore, bulkier alkanes do not react at all because these molecules cannot enter the narrow wedge between the canted (C_5Me_5) rings which is a requirement for the reaction to occur.

$$\underset{\textbf{76r}}{(C_5Me_5)_2LuMe} + {}^{13}CH_4 \rightleftharpoons (C_5Me_5)_2Lu^{13}CH_3 + CH_4 \quad (103)$$

Naturally hard Lewis bases bind strongly to the lanthanide ion and a number of monomeric adducts $(C_5Me_5)_2LnMe(LB)$ with LB = THF,[208,265,272,295,297,404,456,489,491] Et_2O,[287,358,456] NEt_3,[359] and pyridine[358] have been reported. The THF adducts were characterized by spectroscopic methods and by crystal structure analysis of the yttrium[489] and samarium[404] derivative. These compounds can be prepared by way of ionic metathesis from appropriate bis(pentamethylcyclopentadienyl)lanthanide chlorides and MeLi[208,297,489] or by cleaving tetramethylaluminate complexes such as $[(C_5Me_5)_2Sm(\mu\text{-}Me)_2AlMe_2]_2$ with THF.[404] The structure of $(C_5Me_5)_2SmMe(THF)$ is typical for metallocenes of eight-coordinated lanthanides and exhibits no unusual features (Figure 90).[404]

Despite the presence of THF, $(C_5Me_5)_2SmMe(THF)$ was reported to react with various organic substrates in reactions which were typical for solvent-free species.[404] Although the scandium derivative of this series, $(C_5Me_5)_2ScMe(THF)$, can be isolated in pure form,[272] only NMR data have been reported.[265] However, it was noted that the THF molecule was not as tightly bound as expected which is indicative of the severe steric constraints imposed by the bulky pentamethylcyclopentadienyl rings on the scandium ion.

When bis(pentamethylcyclopentadienyl)lanthanide halides are allowed to react with a 2-fold molar amount of MeLi in THF, methyl complexes of the general formula $(C_5Me_5)_2Ln(\mu\text{-}Me)_2Li(LB)_n$ ($n = 0$;[358] $(LB)_n = (THF)_2$,[268,463] $(THF)_3$,[358] (tmed),[61,268,294,463,465]

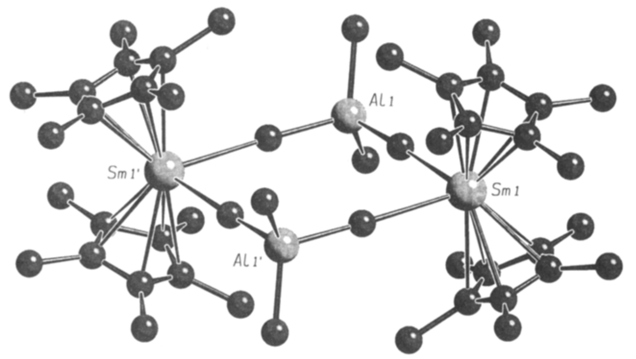


Figure 91. Structure of [(C$_5$Me$_5$)$_2$Sm(μ-Me)$_2$AlMe$_2$]$_2$ (**77h**) in the crystal.[404]

(Et$_2$O),[295] and (Et$_2$O)$_2$[297]) may result depending on the added bases and work-up procedures. Although these complexes were only characterized spectroscopically there is little, if any, doubt about the correctness of the proposed structures which is expected to be similar to that of their parent compounds (C$_5$H$_5$)$_2$Ln(μ-Me)$_2$Li(LB)$_n$. However, base-free (C$_5$Me$_5$)$_2$Lu(μ-Me)$_2$Li, an important intermediate in the synthesis of **76r**, probably has a more complicated structure.

Unlike the monomeric parent compounds (C$_5$H$_5$)$_2$Ln(μ-Me)$_2$AlMe$_2$, the analogous bis(pentamethylcyclopentadienyl) complexes **77** exist in a dimer–monomer equilibrium[404,456] in solution and are dimers in the solid state. Tetramethylaluminate complexes (Ln = Y,[295,456] Sm,[404] Yb,[358] Lu[358,456]) may be prepared in reactions outlined in eqs 104–106:

$$(C_5Me_5)_2Ln(Me)_2Li + Al_2Me_6 \rightarrow \tfrac{1}{2}\underset{\textbf{77q, 77r}}{[(C_5Me_5)_2Ln(Me)_2AlMe_2]_2} + LiAlMe_4 \quad (104)$$

Ln = Yb, Lu

$$(C_5Me_5)_2YCl(THF) + LiAlMe_4 \rightarrow \tfrac{1}{2}\underset{\textbf{77b}}{[(C_5Me_5)_2Y(Me)_2AlMe_2]_2} + LiCl \quad (105)$$

$$(C_5Me_5)_2Sm(THF)_2 + (AlMe_3)_2 \rightarrow \tfrac{1}{2}\underset{\textbf{77h}}{[(C_5Me_5)_2Sm(Me)_2AlMe_2]_2} + \text{“Al”} \quad (106)$$

The solid-state structures of the isomorphous molecules **77b**[456] and **77h**[404] confirm their dimeric nature. Figure 91 shows a perspective drawing of **77h**. The structure analysis revealed two eight-coordinate Sm^{3+} ions which are symmetrically bridged by two μ-bis-η^1 AlMe$_4^-$ anions. The bent metallocene moieties (C$_5$Me$_5$)Sm and the tetrahedral AlMe$_4^-$ unit displayed no unusual feature. Furthermore, allowing for a difference of 22 pm in bond lengths between terminal and bridging methyl groups, the averaged bond distance d(Sm–μ-CH$_3$) = 274.6(16) Å falls in the usual range. (The value of 22 pm was derived experimentally from several crystal structure determinations.) More interestingly, the linear Sm–C–Al angle (averaged to 176.5(9)°) raises the question regarding the position of the methyl hydrogen atoms, because the normal Sm–methyl distances require that a model is proposed that is different from the two-electron, three-center bonding mode in (C$_5$H$_5$)$_2$Y(μ-Me)$_2$AlMe$_2$ and the agostic bonding situation in **76r**. An alternative would be a methyl carbon atom in a center of a trigonal bipyramid in which the Sm and Al may occupy the apices and the hydrogen atoms the equatorial positions. The correctness of this proposal awaits further evidence, especially by a highly accurate X-ray or neutron diffraction study which could reveal the position of hydrogen atoms.

Due to interest in the catalytic and stoichiometric reactions of organolanthanides, e.g. reactions of bis(pentamethylcyclopentadienyl)lanthanide methyl and hydride complexes with alkenes under conditions in which α-olefin insertion as well as σ-bond metathesis can occur, many (C$_5$Me$_5$)Ln alkyl (ethyl,[265,488a,492] propyl,[265,352,446,488a] *n*-butyl,[265,363,488a] *sec*-butyl,[265,358,359,363] *n*-pentyl,[352,488a] *n*-hexyl,[488a] (trimethylsilyl)methyl,[268,294,360,465] 2-phenylethyl,[299,488a] *para*-substituted 2-phenylethyl,[488a] benzyl,[265,272,295,403,404,442,493,494,503] and substituted benzyl,[278,411]) complexes, allylic derivatives,[265,295,271,304,359,503] 2-butynyl complexes,[510] and ylidic species (C$_5$Me$_5$)$_2$Ln(μ-CH$_2$)$_2$PR$_2$ (R = Me,[308,496] ^{t}Bu$_2$, Ph[308]) have been prepared.

Olefin insertion into a M–H or M–C bond is the key step in polymerization processes and has therefore been extensively investigated. Olefins readily insert into Ln–H or Ln–C bonds, giving rise to the alkyl compounds as outlined in eqs 107,[265] 108,[358,359] and 109:[299]

$$(C_5Me_5)_2ScH + CH_2{=}CMe_2 \rightarrow (C_5Me_5)_2ScCH_2CHMe_2 \quad (107)$$

$$\underset{\textbf{76r}}{(C_5Me_5)_2LuMe} + CH_2{=}CHMe \rightarrow (C_5Me_5)_2LuCH_2CHMe_2 \quad (108)$$

$$\underset{\textbf{76a}}{(C_5Me_5)_2ScMe} \xrightarrow{H_2/H_2C=CHPh} (C_5Me_5)_2ScCH_2CH_2Ph \quad (109)$$

Some of the alkyl species have only transient stability due to the reverse reaction, and other decomposition routes, and they were only characterized spectroscopically. Reaction 108 is particularly interesting, because the decomposition of the isobutyl product allowed the direct observation of β-methyl elimination by NMR.[359] It is interesting to note that the latter process is a factor of 100 times faster than β-hydride transfer. Benzyl complexes may be prepared by C–H activation of the methyl group in toluene according to eq 110.[404] As there is a preference of C(sp^2)–H over primary C–H bonds to undergo bond disruption by organolanthanide hydride systems, mixtures of benzyl and tolyl derivatives are obtained.[265] Clean conversion of organolanthanide halides to benzyl complexes was achieved by metathesis as in eq 111.[265]

$$\tfrac{1}{2}[(C_5Me_5)_2SmH]_2 + MePh \xrightarrow[\text{(2) THF}]{\text{(1) cyclohexene, 10 min}} (C_5Me_5)_2SmCH_2Ph(THF) \quad (110)$$

$$(C_5Me_5)_2ScCl + KCH_2Ph \xrightarrow[-KCl]{\text{THF/hexane}} (C_5Me_5)_2ScCH_2Ph \quad (111)$$

Apart from their importance as initial reaction products of olefin insertion, alkyl complexes have a long-standing history as precursors in the synthesis of organolanthanide hydrides. They can be prepared conveniently by cleaving the Ln−C bond by molecular hydrogen as shown in eq 112:

$$(C_5Me_5)_2LnR + H_2 \rightarrow (C_5Me_5)_2LnH + RH \quad (112)$$

It is clear that the synthesis of well-defined hydrides require that the alkyl species meet certain conditions such as kinetic stability, high purity, and good solubility even in hydrocarbon solvents. Furthermore, if the absence of any coordinating base is added to the list of restrictions and if complexes with a low coordination number are anticipated, the choice of suitable alkyl ligands is limited to those without β-hydrogens and bulky alkyl ligands. A ligand that satisfies all the requirements is the bis(trimethylsilyl)methyl anion, because the trimethylsilyl groups provide for good solubility in aliphatic solvents and the absence of β-hydrogen atoms as well as the lack of β-C atoms preclude decomposition by way of β-H or β-Me extrusion. The latter process would be thermodynamically unfavorable, because of the formation of a carbon−silicon double bond. Moreover the steric bulk of this ligand effectively prevents the attack of Lewis bases on the lanthanide ion. Stoichiometric amounts of [bis(trimethylsilyl)methyl]lithium react with bis(pentamethylcyclopentadienyl)lanthanide chlorides giving rise to $(C_5Me_5)_2LnCH(SiMe_3)_2$ in good yields (eqs 113−115).

$$(C_5Me_5)_2LnCl(THF)_n + LiCH(SiMe_3)_2 \xrightarrow[-LiCl]{} (C_5Me_5)_2LnCH(SiMe_3)_2 \quad (113)$$

$Ln = Sc\ (n = 0)$,[299] $Y\ (n = 1)$[275]

$$[(C_5Me_5)_2LnCl]_n + LiCH(SiMe_3)_2 \xrightarrow[-LiCl]{toluene} (C_5Me_5)_2LnCH(SiMe_3)_2 \quad (114)$$

$Ln = Ce$[284]

$$(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li(Et_2O)_2 + LiCH(SiMe_3)_2 \xrightarrow[-2LiCl]{toluene} (C_5Me_5)_2LnCH(SiMe_3)_2 \quad (115)$$

$Ln = La, Nd, Sm, Lu$[304]

These compounds are soluble in THF, ether and aliphatic solvents and can be recrystallized from saturated pentane solutions at low temperature. They have been characterized by common spectroscopical methods as well as by X-ray structure determination of the colorless yttrium,[275] bright red cerium,[284] and blue-green neodymium[304,362b] (Figure 92) compound.

Allowing for differences in the ionic radii of the lanthanides, the three crystallographically determined structures have the same overall geometry. The most important feature is the unusually unsymmetrical conformation of the bis(trimethylsilyl)methyl residue. One methyl group has a short contact to Nd ($d_{Nd\cdots C(2)}$ = 289.5(7) pm) as can be seen by inspecting Figure 92, which shows a plot of neodymium complex perpendicular to the plane defined by Nd, Si_1 and Si_2. This apparent intramolecular γ-agostic Me−Ln interaction is clearly a result of the coordinatively unsaturated, seven-coordinate Nd^{3+} ion. Moreover the planarity of atoms Nd, Si_1, Si_2, and C_2 within 2(1) pm and the significant lengthening of the Si_1-C_2 (d = 189.0(9) pm; compare Si_1-C_3, 184.7(13) pm) is suggestive of a model for an incipient β-methyl elimination. This minimum conformation does not seem to lie in a deep potential well because the low-temperature (T = −90 °C) NMR spectra in toluene-d_8 did not unambiguously show resonances which could be assigned to an unsymmetrically bound $CH(SiMe_3)_2$ residue.[362b] Although this agostic metal··methyl contact is to weak to be observed in solution on the NMR time scale, this type of secondary interaction[275,284,304,354,356,362b,498] has become an integral part of the picture developed to explain the initial step in C−H activation and homogeneous catalysis by strongly electrophilic organolanthanide compounds.

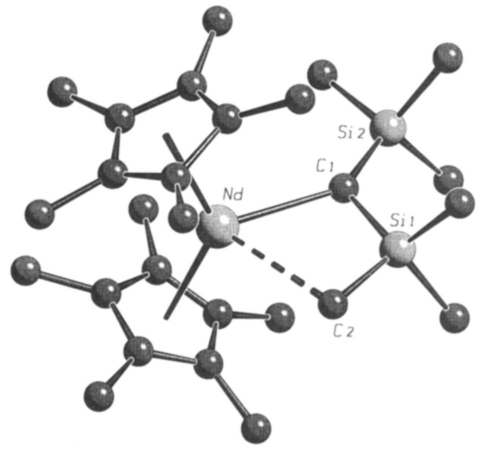


Figure 92. Structure of $(C_5Me_5)_2NdCH(SiMe_3)_2$ in the crystal.[304,362b]

Although the steric bulk of the $CH(SiMe_3)_2$ group in $(C_5Me_5)_2LnCH(SiMe_3)_2$ shields the metal ion from attack of coordinating bases such as THF or ether, some small molecules such as NC^tBu and CN^tBu were shown to react, yielding $(C_5Me_5)_2CeCH(SiMe_3)_2(NC^tBu)$[284] and $(C_5Me_5)_2YCH(SiMe_3)_2(CN^tBu)$,[411] respectively. By contrast, NC^tBu is reported to insert into the Y−C bond of $(C_5Me_5)_2YCH(SiMe_3)_2$ forming the imide complex $(C_5Me_5)_2Y[N{=}C(^tBu)CH(SiMe_3)_2](NC^tBu)$.[411] Additional bis(pentamethylcyclopentadienyl)lanthanide imides and iminoacyls are dicussed earlier within the chapter of bis(pentamethylcyclopentadienyl)lanthanide pnicogenides (see, for example, eqs 70 and 71 and Figure 69.)[411]

Unlike NC^tBu, acetonitrile reacts as a proton acid with bis(trimethylsilyl)methyl complexes, yielding $[(C_5Me_5)_2LnCH_2CN]_2$ and $CH_2(SiMe_3)_2$ (eq 116):[495]

$$(C_5Me_5)_2LnCH(SiMe_3)_2 + MeCN \rightarrow {}^1/_2[(C_5Me_5)_2LnCH_2CN]_2 + CH_2(SiMe_3)_2 \quad (116)$$

$Ln = La, Ce$

Besides the synthesis of dimeric $(C_5Me_5)_2Sm[(^tBu)CPPC(^tBu)]Sm(C_5Me_5)_2$ (Figure 93) by reductive dimerization of phosphaalkine $^tBuC{\equiv}P$ with $(C_5Me_5)_2Sm$-

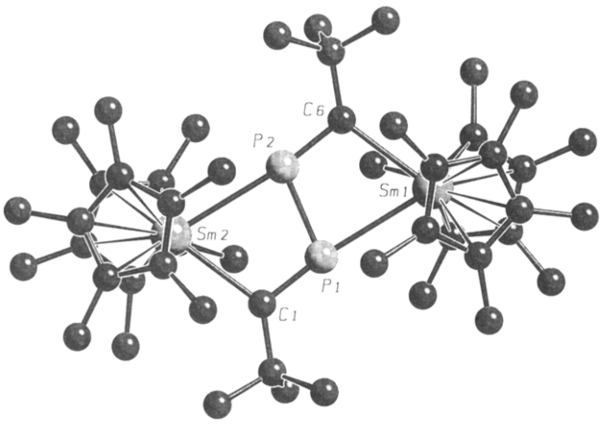


Figure 93. Structure of $(C_5Me_5)_2Sm[(^tBu)CPPC(^tBu)]Sm(C_5Me_5)_2$ in the crystal.[500]

$(THF)_2$ in toluene,[500] (trimethylsilyl)diazomethyl complexes $(C_5Me_5)_2LnC(=N_2)SiMe_3$ (Ln = Y, Yb, Lu) are known,[499] as well as a bis(pentamethylcyclopentadienyl)samarium derivative with the bulky 2-(dimethylaminomethyl)ferrocenyl ligand.[501]

Most of the known bis(pentamethylcyclopentadienyl)lanthanide aryl compounds and vinyl derivatives[265,488a] have been studied in the context of the C−H activation reaction. There are reports[265,274,360] on the reversible reaction of benzene with $[(C_5Me_5)_2LnH]_2$ generating corresponding phenyl complexes **78** as shown in eq 117.

$$\tfrac{1}{2}[(C_5Me_5)_2LnH]_2 + C_6H_6 \rightarrow \underset{\textbf{78}}{(C_5Me_5)_2LnPh} + H_2 \qquad (117)$$

When the evolving H_2 is purged from the reaction mixture the corresponding phenyl derivatives were obtained in good yield. The lutetium complex **78r** is reported[360,490] to undergo a second activation of a remote C−H bond leading to the dimer $[(C_5Me_5)_2Lu]_2C_6H_4$. Naturally classical methods involving reagents such as LiPh[265,272] and $HgPh_2$[502] can also be utilized to produce phenyl derivatives as outlined in eqs 118 and 119.

$$\underset{\textbf{20a}}{(C_5Me_5)_2ScCl} + LiPh \xrightarrow{\text{toluene}} \underset{\textbf{78a}}{(C_5Me_5)_2ScPh} + LiCl \qquad (118)$$

$$(C_5Me_5)_2Sm(THF) + \tfrac{1}{2}HgPh_2 \rightarrow (C_5Me_5)_2SmPh(THF) + \tfrac{1}{2}Hg \qquad (119)$$

The majority of phenyl complexes have been characterized by spectroscopic means. Only the Sm−THF−adduct has been subjected to an X-ray structure analysis.[502] In addition to these phenyl derivatives, some tolyl,[265,442] *ortho*-substituted phenyl,[493] and pentafluorophenyl[262] complexes have been reported.

The reaction of pyridine with hydride and alkyl complexes (notably **76a**, **76b** and **76r**) bears resemblance to that in eq 117 inasmuch as C−H activation readily occurs, this time promoted by the nucleophilic nitrogen atom which stabilizes the transition state and the reaction product. Further information is available in the section on bis(pentamethylcyclopentadienyl)lanthanide pnictogenides: eq 72.[265,272,278,360]

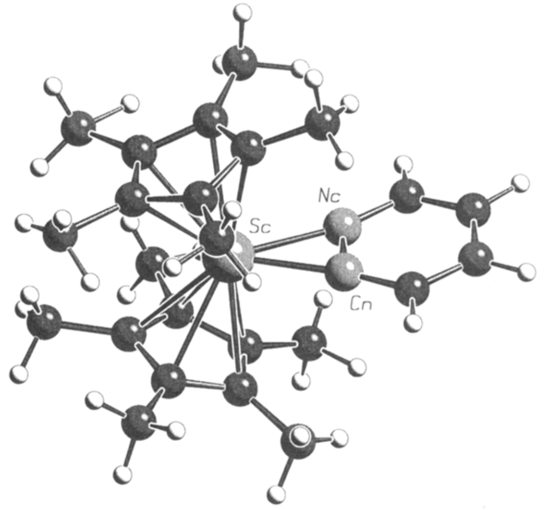


Figure 94. Structure of $(C_5Me_5)_2Sc[\eta^2\text{-N,C-}(NC_5H_4)]$ in the crystal.[272,265]

The X-ray structure analysis of the scandium compound $(C_5Me_5)_2Sc[\eta^2\text{-N,C-}(NC_5H_4)]$ reveals a monomer in the solid state as shown in Figure 94.[265,272] The pyridyl ring lies normal to the plane defined by the centroids of (C_5Me_5) and scandium and is η^2-bound to the Sc^{3+} ion with the nitrogen and an adjacent carbon atom.

The study of alkynyl complexes of the bis(pentamethylcyclopentadienyl) lanthanide fragment, aimed at a deeper understanding of the frequently observed alkynyl coupling and oligomerizations reactions, has attracted much attention in recent years. Methods of preparation of terminal alkynyl complexes involve both ionic metathesis (e.g. eqs 120[513] and 121[208]), protonation of organolanthanide compounds (e.g. eqs 122,[265] 123,[409] and 124[440]), as well as oxidation processes (e.g. eq 125[440]):

$$(C_5Me_5)_2YCl(THF) + 2LiC{\equiv}C^tBu \xrightarrow[-LiCl]{THF} (C_5Me_5)_2Y(\mu\text{-}C{\equiv}C^tBu)_2Li(THF) \qquad (120)$$

$$[(C_5Me_5)_2Sm(THF)_2][BPh_4] + KC{\equiv}CR \xrightarrow[-K[BPh_4]]{THF} (C_5Me_5)_2Sm(C{\equiv}CR)(THF) \qquad (121)$$

$R = {}^tBu$, Ph

$$(C_5Me_5)_2ScMe + HC{\equiv}CMe \rightarrow (C_5Me_5)_2ScC{\equiv}CMe + CH_4 \qquad (122)$$

$$(C_5Me_5)_2LnCH(SiMe_3)_2 + HC{\equiv}CR \xrightarrow[-CH_2(SiMe_3)_2]{THF} 1/n[(C_5Me_5)_2LnC{\equiv}CR]_n \qquad (123)$$

Ln = La, Ce: R = Me

Ln = Ce: $R = {}^tBu$

$$(C_5Me_5)_2LnN(SiMe_3)_2 + HC{\equiv}CPh \xrightarrow[-HN(SiMe_3)_2]{THF} (C_5Me_5)_2Ln(C{\equiv}CPh)(THF) \qquad (124)$$

Ln = Ce, Nd

$$(C_5Me_5)_2Sm(THF) + HC{\equiv}CR \xrightarrow{\text{toluene}} (C_5Me_5)_2Sm(C{\equiv}CPh)(THF) \qquad (125)$$

$R = (CH_2)_2Ph,\ CH_2NEt_2,\ (CH_2)_2CHMe_2,\ {}^iPr,\ {}^tBu$

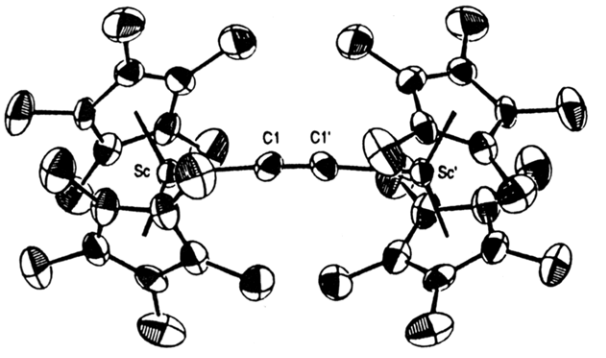


Figure 95. Structure of $(C_5Me_5)_2ScC{\equiv}CSc(C_5Me_5)_2$ in the crystal.[511] (Reprinted from ref 511. Copyright 1991 American Chemical Society.)

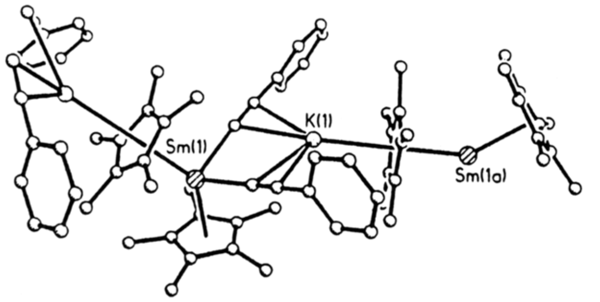


Figure 96. Structure of $\{K[(C_5Me_5)_2Sm(C{\equiv}CPh)_2]\}_n$ in the crystal.[440] (Reprinted from ref 440. Copyright 1993 American Chemical Society.)

Terminal alkynes such as propyne, ${}^nPrC{\equiv}CH$, ${}^tBuC{\equiv}CH$, $Me_3SiC{\equiv}CH$, and ${}^nPrC{\equiv}CH$ react with $(C_5Me_5)_2LnMe$[265] and $(C_5Me_5)_2LnCH(SiMe_3)_2$[278,512] within minutes to afford the corresponding alkynyl complexes. With excess alkyne these compounds promote catalytically alkyne coupling reactions to either dimers (for Ln = Sc, Y) or a mixture of dimers and higher oligomers (for Ln = La, Ce). The dependence of the reaction product on the metal ion radii demonstrates that steric effects may play an important role. Possible mechanisms for the catalytical dimerization/oligomerization of terminal alkynes by lanthanide carbyls (alkynyl formation and insertion into Ln−C(sp) bonds) have been described, for example, by Heeres et al.[510,512] and den Haan et al.[278] It is interesting to note that the regioselectivity depends on the nature of the alkyne. Thus, propyne, ${}^nPrC{\equiv}CH$, and ${}^tBuC{\equiv}CH$ were dimerized to head-to-tail dimers, whereas $Me_3SiC{\equiv}CH$ and ${}^nPrC{\equiv}CH$ gave mixtures of isomers.

Owing to their high reactivity and low solubility most of the base-free alkynyl complexes have defied characterization by single-crystal X-ray structure determination. Whereas the structures of $[(C_5Me_5)_2Sm(C{\equiv}C^tBu)]_2$,[440] $(C_5Me_5)_2ScC{\equiv}CSc(C_5Me_5)_2$[511] (Figure 95) and $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}C^tBu)_2Li(THF)$,[513] $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$,[208] and polymeric $\{K[(C_5Me_5)_2Ln(C{\equiv}CPh)_2]\}_n$ (Ln = Ce, Sm (Figure 96))[440] exhibit basically no unusual features, it is the structure of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_4Ph)$[505,506] that is unusual (see Figure 97).

This complex is prepared from $(C_5Me_5)Sm(THF)_2$ and the diyne $PhC{\equiv}CC{\equiv}CPh$;[505] it also can be obtained from thermolysis of $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$ or by reacting the samarium complexes $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$, $(C_5Me_5)_2Sm$, or $(C_5Me_5)_2SmCH(SiMe_3)_2$, for example, with $HC{\equiv}CPh$.[506] These reactions could have led to "simple" dimeric phenylethynyl complexes, but instead, the X-ray structure showed that coupling of the terminal alkyne occurred. The alkyne coupling mediated by organolanthanide compounds has been discussed in detail recently:[440] Up to now, five further coupled trienediyl products $[(C_5Me_5)_2Nd]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_4Ph)$,[440] $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}RC_4R)$ (R = $(CH_2)_2CHMe_2$ and $(CH_2)_2Ph$)[440] as well as $[(C_5Me_5)_2Ce]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}RC_4R)$ (R = Me and ${}^tBu$)[409] have been identified by X-ray crystallography.

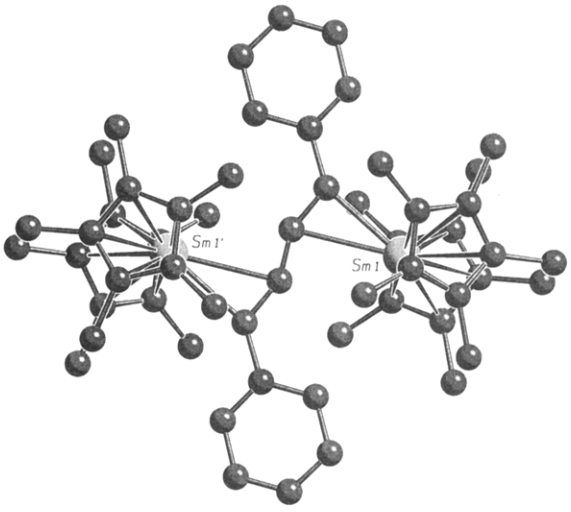


Figure 97. Structure of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_4Ph)$ in the crystal.[505,506]

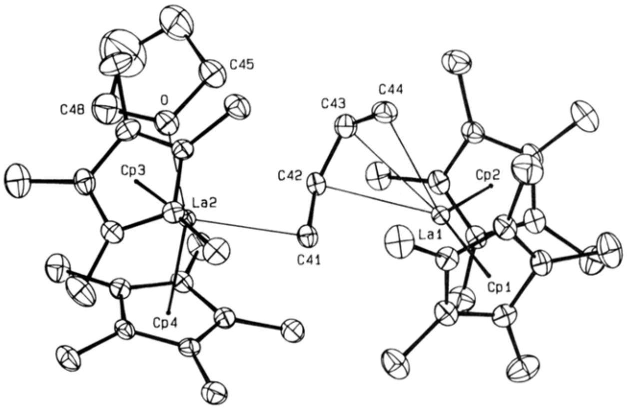


Figure 98. Structure of $(C_5Me_5)_2La(THF)(\mu\text{-}\eta^1,\eta^3\text{-}C_4H_6)\text{-}La(C_5Me_5)_2$ in the crystal.[504]

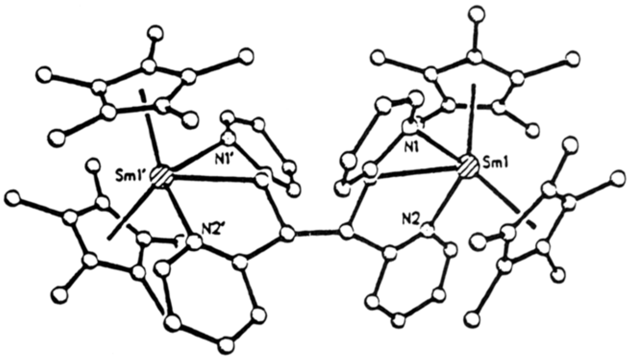


Figure 99. Structure of $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}1,2,3,4\text{-}(py_4)C_4H_4]$ in the crystal.[507] (Reprinted from ref 507. Copyright 1993 American Chemical Society.)

Reaction of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ with ${}^tBuC{\equiv}CH$ generates not only the already mentioned $[(C_5Me_5)_2Sm(C{\equiv}C^tBu)]_2$, but also another unusual product, the formally 1,3-di-*tert*-butyl-substituted butadienyl spe-

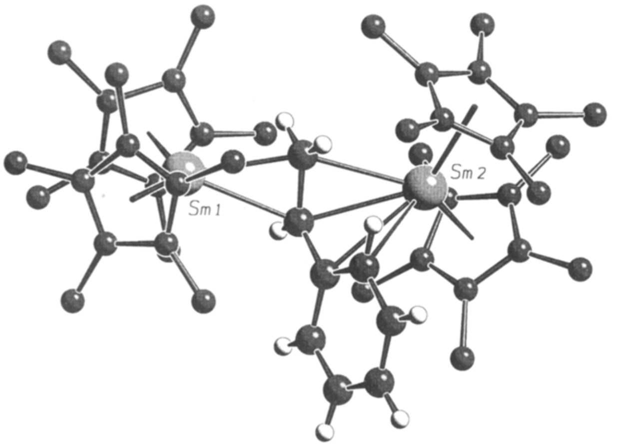


Figure 100. Structure of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$ in the crystal.[503,509]

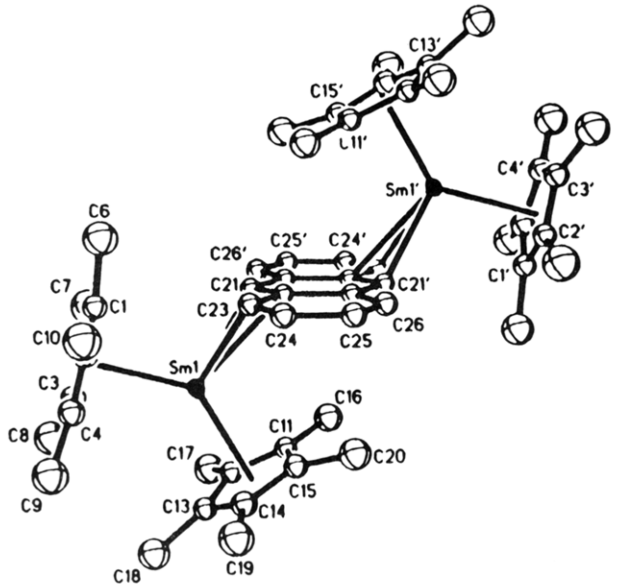


Figure 101. Structure of $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{10}H_{14})]$ in the crystal.[733] (Reprinted from ref 733. Copyright 1994 American Chemical Society.)

cies $(C_5Me_5)_2Sm[(^tBu)CH{=}CC(^tBu){=}CH_2]$.[440] The use of magnesium butadiene, $[Mg(C_6H_4)(THF)_2]$, as diene carrier, together with $(C_5Me_5)_2La(\mu\text{-}Cl)_2K(DME)_2$ as lanthanide reagent resulted in the synthesis and first X-ray structurally characterized "pure" butadiene complex $(C_5Me_5)_2La(THF)(\mu\text{-}\eta^1,\eta^3\text{-}C_4H_6)La(C_5Me_5)_2$ (Figure 98). Astonishingly the compound is thermally stable up to 200 °C.[504]

As long ago as 1983, black $[(C_5Me_5)_2Sm]_2(PhC{=}CPh)$ was reported to be formed by reaction of $(C_5Me_5)_2Sm(THF)_2$ and $PhC{\equiv}CPh$ in pentane and its enediyl structure was derived from NMR and IR spectra.[508] Divalent $(C_5Me_5)_2Sm(THF)_2$ with 1,2-di-2-pyridyl)ethene yields either $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-pyCHCHpy})$ (ratio 2:1) or the reductive coupling product $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}1,2,3,4\text{-}(py_4)C_4H_4]$ (ratio 1:1) whose structure is shown in Figure 99.[507] These results illustrate the importance of stoichiometry on synthetic reactions.

Solvent-free divalent bis(pentamethylcyclopentadienyl)samarium generates, in a stoichiometric reaction with stilbene, $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-PhCHCHPh})$ while with styrene $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$ forms (Figure 100).[503,509] In both bimetallic complexes, phenyl carbon atoms are oriented to interact with one of the samarium centers and the two $(C_5Me_5)_2Sm$ units of each molecule coordinate to the carbon−carbon alkene bond.

Decamethylsamarocene reacts with polycyclic aromatic hydrocarbons like anthracene, pyrene, 2,3-benzanthracene, 9-methylanthracene, and acenaphthylene to form the binuclear samarium complexes $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{10}H_{14})]$ (Figure 101), $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{16}H_{10})]$, $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{18}H_{12})]$, $[(C_5Me_5)_2Sm]_2[(C_{15}H_{12})]$, and $[(C_5Me_5)_2Sm]_2[(C_{12}H_8)]$, respectively.[733]

Last but not least, the tetranuclear species $\{(C_5Me_5)_3[\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Ln_2\}_2$ (Ln = La, Ce (Figure 102)) has to be mentioned. It is formed by thermolysis of $(C_5Me_5)_2LnCH(SiMe_3)_2$ in cyclohexane with extrusion of $CH_2(SiMe_3)_2$ via intermolecular hydrogen transfer.[494]

iii. Derivatives with Other Substituted Cyclopentadienyl Rings. Compared to the large number of available ring-substitued bis(cyclopentadienyl)lanthanide halides, only a small number of derivatives have been reported in which the ring is partially substituted with sterically small alkyl groups. Most

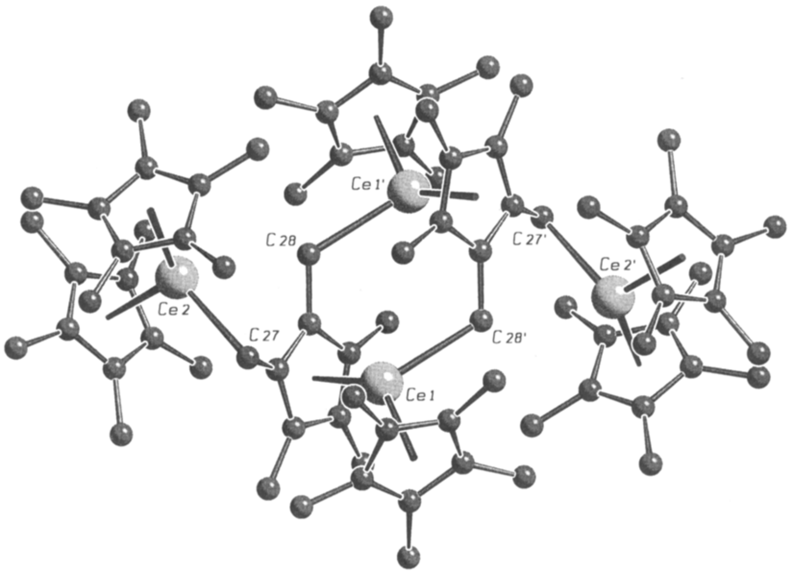


Figure 102. Structure of $\{(C_5Me_5)_3[\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Ce_2\}_2$ in the crystal.[494]

Table 20. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Complexes Containing Other Substituted Cyclopentadienyl Ligands and Lanthanide to Carbon Bonds

compound	Ln		color, characterization, etc.
$(MeC_5H_4)_2LnMe$	Y		NMR;[6c,178,435,519] complex with THF: NMR[178]
	Tb		yellow, IR, lumines.; complex with THF: lumines.[104]
	Er		catalysis[519]
	Yb		synthesis,[483] catalysis[519]
$(MeC_5H_4)_2Ln(\mu\text{-}Me)_2AlMe_2$	Y		synthesis, catalysis[519]
	Ho		synthesis, catalysis[519]
	Er		synthesis, catalysis[519]
	Yb		synthesis, catalysis[519]
$(MeC_5H_4)_2LnEt$	Y		NMR[435]
$(MeC_5H_4)_2LnPr$	Y		NMR[435]
$(MeC_5H_4)_2Ln^nBu$	Y		NMR, catalysis[519]
$(MeC_5H_4)_2Ln^tBu$	Y		complex with THF: yellow, IR[314]
	Er		complex with THF: pink[314]
	Lu		complex with THF: white, NMR, IR[314,459]
$(MeC_5H_4)_2LnC_8H_{17}$	Y		NMR, catalysis[519]
$(MeC_5H_4)_2LnCH_2CHMeCH_2NMe_2$	Lu		colorless, NMR, MS, melt./dec.[389]
$(MeC_5H_4)_2LnCH_2SiMe_3$	Y		complex with THF: NMR, IR[459]
$(MeC_5H_4)_2LnCH_2CH{=}CH_2$	Y		complex with THF: NMR[435]
$(MeC_5H_4)_2LnC(Et){=}CHEt$	Y		complex with THF: NMR[435]
$(MeC_5H_4)_2LnC{\equiv}C^tBu$	Y		NMR[178,435]
	Sm		yellow, X-ray, NMR, IR, UV, magn. d.[315a]
	Yb		bright orange, IR, UV[483]
$(MeC_5H_4)_2LnC_6H_4Me\text{-}4$	Er		light pink, melt./dec., magn. d.; complex with THF: orange red, MS, IR, melt./dec.[83]
$(MeC_5H_4)Ln(\mu\text{-}C_5H_3Me)_2Ln(MeC_5H_4)$	Y		NMR[519]
$(^tBuC_5H_4)_2LnMe$	Y		reactions[428,430]
	Ce		orange, X-ray, NMR, IR, MS, melt./dec.[520]
	Nd		purple, X-ray, IR[521]
	Gd		colorless, IR[521]
	Lu		reactions[428]
$(^tBuC_5H_4)_2LnC{\equiv}CPh$	Sm		yellow, X-ray, IR, melt./dec.[319]
$[Li(THF)_4]\{[(C_{14}H_{10})CMe_2C_5H_3{}^tBu]_2Ln\}$	Nd		yellow[522]
$[Li(THF)_4]\{[(C_{14}H_{10})CMe_2C_5H_4]_2Ln\}$	Nd		brown yellow, X-ray[522]
$(Me_3SiC_5H_4)_2LnMe$	Y		catalysis[519]
	Er		catalysis[519]
$(Me_3SiC_5H_4)_2Ln(\mu\text{-}Me)_2AlMe_2$	Y		synthesis, catalysis[519]
$(Me_3SiC_5H_4)_2LnBu$	Er		catalysis[519]
$(Me_2C_5H_3)_2LnMe$	Y		X-ray, NMR, IR[328]
$(C_5Me_4Et)_2LnMe$	Y		catalysis[519]
$(C_5Me_4Et)_2LnPh$	Sm		orange, NMR, IR, magn. d.; complex with THF: orange, NMR, IR, magn. d.[502]
$[C_5H_4(CH_2)_3C_5H_4]Ln^tBu$	Y		complex with THF: yellow, NMR, IR, melt./dec.[523]
	La		complex with THF: pale yellow, IR, melt./dec.,[523] NMR[241,523,524]
	Nd		complex with THF: pale green, NMR, IR, melt./dec.[523]
$[C_5H_4(CH_2)_3C_5H_4]LnCH_2CMe_3$	La		complex with THF: yellow, NMR, IR, melt./dec.[523]
$[C_5H_4(CH_2)_3C_5H_4]LnC{\equiv}CPh$	La		tan,[57] melt./dec., NMR, IR[57,344a]
	Ce		brown, NMR,[57] melt./dec., IR[57,344a]
	Nd		complex with THF: yellow green, IR, melt./dec.[244]
$[C_5H_4(CH_2)_3C_5H_4]LnPh$	La		complex with THF: yellow, NMR, IR, melt./dec.[523]
	Pr		complex with THF: pale yellow, IR, melt./dec.[523]
$[C_5H_4(CH_2)_3C_5H_4]LnC_6H_4Me\text{-}4$	La		complex with THF: orange yellow, NMR, IR, melt./dec.[523]
	Pr		complex with THF: pale yellow, IR, melt./dec.[523]
$[Me_2Si(C_5Me_4)_2]LnMe$	Sc		NMR; complex with PMe_3: orange-yellow, NMR, reactions[747]
$[Me_2Si(C_5Me_4)_2]LnC_3H_7$	Sc		synthesis; complex with PMe_3: NMR[747]
$[Me_2Si(C_5Me_4)_2]Ln^iC_3H_7$	Sc		NMR[747]
$[Me_2Si(C_5Me_4)_2]Ln^iBu$	Sc		complex with PM_3: NMR[747]
$[Me_2Si(C_5Me_4)_2]LnC_5H_{11}$	Sc		synthesis; complex with PMe_3: synthesis[747]
$[Me_2Si(C_5Me_4)_2]LnCH_2CHMeC_3H_7$	Sc		complex with PMe_3: NMR[747]
$[Me_2Si(C_5Me_4)_2]LnCH_2CHEt_2$	Sc		orange-yellow, NMR; complex with PMe_3: NMR[747]
$[Me_2Si(C_5Me_4)_2]LnCH_2PMe_2$	Sc		NMR[747]
$[Me_2Si(C_5Me_4)_2]Ln(CH_2)_3OCH_2CH{=}CH_2$	Sc		synthesis[352]
$[Me_2Si(C_5Me_4)_2]LnCMe{=}CHMe$	Sc		complex with PMe_3: NMR[747]
$[Me_2Si(C_5Me_4)_2]LnCMe{=}CMe_2$	Sc		NMR; complex with PMe_3: synthesis[747]
$[Me_2Si(C_5Me_4)_2]LnCH(SiMe_3)_2$	Sc	**79a**	synthesis[352]
	Y	**79b**	catalysis[517]
	La	**79c**	PE[743]
	Nd	**79f**	blue green,[305] green, X-ray, NMR, IR,[362a] PE,[743] catalysis[517]
	Sm	**79h**	red brown,[305] orange, NMR, IR[362a] PE,[743] catalysis[517]
	Lu	**79r**	colorless,[305,362a] IR, NMR[362a] PE,[743] catalysis[517]
$[Li(tmed)_3]\{[Me_2Si(C_5Me_4)_2]Ln[\eta^2\text{-}CH(SiMe_3)Si(Me_2)CH_2]\}$	Lu		colorless, NMR, IR[362a]
$[Me_2Si(C_5H_3{}^tBu)_2]LnCH_2SiMe_3$	Sc		synthesis,[351,352] catalysis[732]
$[Me_2Si(C_5H_3{}^tBu)_2]Ln(CH_2CH{=}CHMe)$	Sc		synthesis[351]

Table 20 (Continued)

compound	Ln		color, characterization, etc.
$[Me_2Si(C_5H_3{}^tBu)_2]Ln(CH_2CMe{=}CHMe)$	Sc		synthesis[351]
$[Me_2Si(C_5H_3{}^tBu)_2]Ln(CH_2CMe{=}CMe_2)$	Sc		synthesis[351]
$[Me_2Si(C_5H_3{}^tBu)_2]Ln(CH_2CH{=}CHPr)$	Sc		synthesis[351]
$[Me_2Ge(C_5Me_4)_2]LnCH(SiMe_3)_2$	Nd	**80f**	blue, NMR[356]
	Ho	**80n**	yellow, X-ray, NMR, MS[356]
$(C_5Me_5)_2Ln(Me)_2Ln(C_5H_5)_2$	Y		NMR[456]
	Lu		NMR[456]
$(C_5H_5)(C_5Me_5)LnMe$	Sc		complex with PMe_3: synthesis[352]
$(C_5Me_5)(C_5Me_4Pr)LnMe$	Sc		synthesis[363]
$(C_5Me_5)(C_5Me_4Pr)LnPh$	Sc		NMR[363]
$(C_5Me_5)(H_2C_5Me_3\text{-}1,3,4)LnMe$	Sc		complex with PMe_3: synthesis[352]
$(C_5Me_5)(C_5Me_4CH_2Ph)LnC{\equiv}C^tBu$	Sc		NMR[363]
$(C_5Me_4CH_2C_6H_4Me\text{-}3)(C_5Me_4CH_2C_6H_4CF_3\text{-}3)LnPh$	Sc		off-white, NMR[363]
$(C_5Me_4CH_2C_6H_4Me\text{-}3)(C_5Me_4CH_2C_6H_4NMe_2\text{-}3)LnPh$	Sc		NMR[363]
$[Me_2Si(C_5H_4)(C_5Me_4)]LnCH(SiMe_3)_2$	Lu	**81r**	colorless, X-ray, NMR, IR[354]
$\{Me_2Si(C_5Me_4)[C_5H_3(C_{10}H_{18})]\}LnCH(SiMe_3)_2$	Y		colorless,[726] X-ray,[726,355] NMR, CD,[726] catalysis[735]
($C_{10}H_{18}$ = (−)-menthyl and (+)-neomenthyl)	La		synthesis, catalysis[735]
	Nd		green, NMR,[726] catalysis[735]
	Sm		red-orange,[726] X-ray,[355,726] NMR, CD,[726] catalysis[355,449,735]
	Lu		colorless, NMR,[726] catalysis[735]
$\{Me_2Si(C_5Me_4)[C_5H_3(C_{10}H_{18})]\}LnC_6H_4CH_2NMe_2\text{-}2$ ($C_{10}H_{18}$ = (+)-neomenthyl)	Lu		colorless, NMR, CD[726]
$\{Me_2Si(C_5Me_4)[C_5H_3(C_{10}H_{18})]\}Ln(CH_2)_2PMe_2$ ($C_{10}H_{18}$ = (+)-neomenthyl)	Lu		colorless, NMR, CD[726]
$\{Me_2Si(C_5Me_4)[C_5H_3(C_{16}H_{22})]\}LnCH(SiMe_3)_2$ ($C_{16}H_{22}$ = (−)-phenylmenthyl)	Y		colorless, NMR, CD,[726] catalysis[735]
$\{Me_2Si(C_5Me_4)[C_5H_3(CH_2CH_2P^tBu_2)]\}LnCH(SiMe_3)_2$	Sc		X-ray[525]
$[Et_2Si(C_5H_4)(C_5Me_4)]LnCH(SiMe_3)_2$	Y	**82b**	colorless, NMR, IR,[354] catalysis[517]
	Lu	**82r**	colorless, NMR, IR,[354] catalysis[517]
$[(C_5Me_5)Ln(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)]_2$	Sc		yellow,[265,514] X-ray,[514] NMR[265]
$(C_5Me_5)Ln[\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)_3]$	Sc		pale yellow, NMR[363]
$(C_5Me_5)Ln(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}C_6H_4)$	Sc		colorless, NMR[363]
$(C_5Me_5)Ln[\eta^5{:}\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}(C_6H_3Me\text{-}p)]$	Sc		NMR[363]
$(C_5Me_4CH_2Ph)Ln[\eta^5{:}\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}(C_6H_3Me\text{-}p)]$	Sc		NMR[363]
$(C_5Me_4CH_2C_6H_4Me\text{-m})Ln(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}C_6H_4)$	Sc		NMR[363]
$(C_5Me_4CH_2C_6H_4Me\text{-m})Ln[\eta^5{:}\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}(C_6H_3CF_3\text{-}p)]$	Sc		NMR[363]
$(C_5Me_4CH_2C_6H_4Me\text{-m})Ln[\eta^5{:}\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}(C_6H_3NMe_2\text{-}p)]$	Sc		NMR[363]
$(C_5Me_4CH_2C_6H_4CF_3\text{-m})Ln[\eta^5{:}\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}(C_6H_3Me\text{-}p)]$	Sc		NMR[363]
$(C_5Me_4CH_2C_6H_4NMe_2\text{-m})Ln[\eta^5{:}\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}(C_6H_3Me\text{-}p)]$	Sc		NMR[363]

of the research has been confined to complexes of the methylcyclopentadienyl series and bridged cyclopentadienyl ligand systems. The latter ones may become very important for asymmetric catalysis. For a comprehensive survey see also Table 20.

Reactions of bis(methylcyclopentadienyl)lanthanide chlorides in ether with MeLi followed by extraction of the residue yield complexes of the composition $[(MeC_5H_4)_2LnMe]_2$ (eq 126):

$$^1/_2[(MeC_5H_4)_2LnCl]_2 + MeLi \rightarrow [(MeC_5H_4)_2LnMe]_2 + LiCl \quad (126)$$

Ln = Y,[178,435] Tb[104]

Other alkyl, aryl, and alkynyl complexes may be prepared as shown in eqs 127,[435] 128,[314] 129,[83] 130,[315a] and 131 (see also section II.B.3.a.iii and Table 16):[433,434]

$$^1/_2[(MeC_5H_4)_2YH(THF)]_2 + CH_2{=}CHR \rightarrow (MeC_5H_4)_2YCH_2CH_2R \quad (127)$$

R = H, Me

$$^1/_2[(MeC_5H_4)_2LnCl]_2 + {}^tBuLi \xrightarrow[-LiCl]{THF} (MeC_5H_4)_2Ln^tBu(THF) \quad (128)$$

Ln = Y, Er, and Lu

$$^1/_2[(MeC_5H_4)_2ErCl]_2 + LiC_6H_4Me\text{-}4 \xrightarrow[-LiCl]{THF} (MeC_5H_4)_2ErC_6H_4Me\text{-}4(THF) \quad (129)$$

$$2(MeC_5H_4)_2SmCl(THF) + 2LiC{\equiv}C^tBu \xrightarrow[-2LiCl]{} [(MeC_5H_4)_2SmC{\equiv}C^tBu]_2 \quad (130)$$

$$[(MeC_5H_4)_2YH(THF)]_2 + 2CN^tBu \rightarrow \{(MeC_5H_4)_2Y[\mu\text{-}\eta^2\text{-}(CH{=}N^tBu)]\}_2 \quad (131)$$

These complexes strongly resemble the analogous bis(cyclopentadienyl)lanthanide derivatives and it appears that in most cases, the intention was to prepare $(MeC_5H_4)_2LnX$ compounds in order to amplify the results already obtained from their C_5H_5 analogues. However, better solubility and crystal quality also played a role. Unfortunately, the ring substituted compounds are characterized, although a number of alkyl species have been utilized as ethylene polymerization catalysts.[519] These investigations revealed (by ^1H- and ^{13}C-NMR spectroscopy) that the major deactivation step severely limiting the lifetime of the catalyst, is a sp^2-C−H bond disruption of the MeCp ring, yielding the "tucked-in" complex $\{\eta^5\text{-}(MeC_5H_4)Y[\eta^5{:}\eta^1\text{-}(MeC_5H_4)]\}_2$. This discouraging outcome was overcome by using permethylated cyclopentadienyl ligand systems as described in the previous section.

Besides the intramolecularly stabilized, base-free lutetium alkyl complex $(MeC_5H_4)_2LuCH_2CHMeCH_2NMe_2$, which is accessible from stoichiometric reaction of $LuCl_3$, the lithium salt $LiCH_2CHMeCH_2NMe_2$ and $Na(MeC_5H_4)$ in THF,[389] there are a few other bis(methylcyclopentadienyl)lanthanide complexes $(MeC_5H_4)_2YR$ (R = $CH_2CH{=}CH_2$, C(Et)=CHEt,[435] CH_2SiMe_3[459]) that exist as THF adducts. Whithin the context of homogeneous ethylene polymerization catalysts, some attention has been made to the dimeric species $[(MeC_5H_4)_2YR]_2$ (R = ^{n}Bu, C_8H_{17}), their thermolysis product $(MeC_5H_4)Y(\mu\text{-}C_5H_3Me)_2Y(MeC_5H_4)$, and the trimethylaluminum adducts $(MeC_5H_4)_2Ln(\mu\text{-}Me)_2AlMe_2$ (Ln = Y, Ho, Er, Yb).[519]

In addition to bis(methylcyclopentadienyl)lanthanide methyl complexes four further types of methyl complexes with ancillary bis(1,3-dimethylcyclopentadienyl),[328] bis(*tert*-butylcyclopentadienyl),[520,521] bis(ethylcyclopentadienyl),[519] or bis(trimethylsilylcyclopentadienyl)[519] ligand environments have been reported. These compounds are dimeric and the lanthanide ions are symmetrically bridged by methyl groups as shown by X-ray crystallography of $[(Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$[328] and $[(^tBuC_5H_4)_2Ln(\mu\text{-}Me)]_2$ (Ln = Ce,[520] Nd[521]). While other derivatives like $[(Me_3SiC_5H_4)_2ErBu]_2$,[519] $(C_5Me_4Et)_2SmPh(THF)$,[502] and $[Li(THF)_4]\{[(C_{14}H_{10})CMe_2C_5H_3{}^tBu]_2Nd\}$[522] have been characterized at most by spectroscopic means, the structures of $[(^tBuC_5H_4)_2Sm(\mu\text{-}C{\equiv}CPh)]_2$[319] and of the 9-(cyclopentadienyl-1-methylethyl)-9,10-dihydroanthracene derivative $[Li(THF)_4]\{[(C_{14}H_{10})CMe_2C_5H_4]_2Nd\}$[522] (Figure 103) were confirmed by X-ray crystallography.

Ring-bridged bis(cyclopentadienyl)lanthanide derivatives are very well known. Just as a 1,3-propanediyl chain can kinetically stabilize bis(cyclopentadienyl)lanthanide chlorides, notably those of the large lanthanide ions (La, Ce, Nd, and Pr), this chelating ligand also allows the preparation of alkyl, aryl, and alkynyl complexes of the general formula $[C_5H_4(CH_2)_3C_5H_4]_2LnR(THF)_n$ by way of simple metathetical reactions as shown in eq 132:

$$\underset{\mathbf{30}}{[C_5H_4(CH_2)_3C_5H_4]_2LnCl(THF)} + RM \xrightarrow[-MCl]{THF} [C_5H_4(CH_2)_3C_5H_4]_2LnR(THF)_n \quad (132)$$

M = Li:[523] R = ^{t}Bu, Ln = Y, La, Nd ($n = 1$); R = CH_2CMe_3, Ln = La ($n = 1$); R = Ph, Ln = La, Pr ($n = 1$); R = C_6H_4Me-4, Ln = La, Pr ($n = 1$)

M = Na:[57,244,344a] R = $C{\equiv}CC_6H_5$, Ln = La, Ce ($n = 0$); Ln = Nd ($n = 1$)

All compounds have been examined by spectroscopic means such as ^{1}H- and ^{13}C-NMR and IR techniques as well as by elemental analyses, so that little, if any, doubt exists concerning their compositions, despite the absence of structural data.

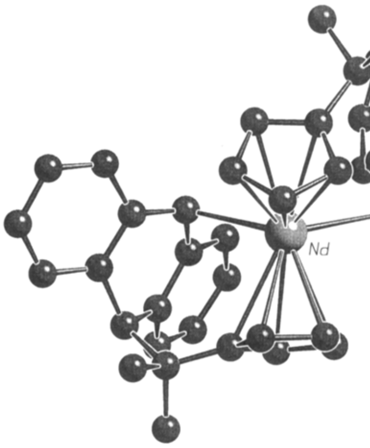


Figure 103. Structure of the anion of $[Li(THF)_4]\{[(C_{14}H_{10})CMe_2C_5H_4]_2Nd\}$ in the crystal.[522]

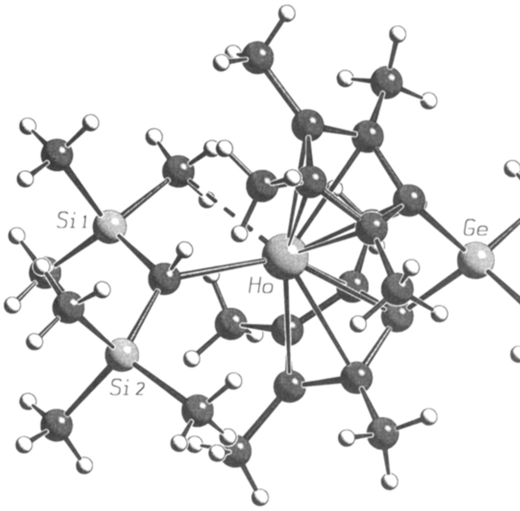


Figure 104. Structure of $[Me_2Ge(C_5Me_4)_2]HoCH(SiMe_3)_2$ (**80n**) in the crystal.[356]

Permethylated ring-bridged cyclopentadienes have been synthesized to replace the bis(pentamethylcyclopentadienyl) system as an ancillary ligand, aiming at complexes having on the one hand essentially the same properties (high solubility in pentane, steric bulk) as $(C_5Me_5)_2Ln{-}C$ compounds but displaying on the other hand a much higher catalytic activity due to the more open coordination sphere of the lanthanide ion. The most frequently utilized alkyl ligand that allows access to the catalytically active hydrides is again the bis(trimethylsilyl)methyl group. Thus, appropriate halide precursors like $[Me_2E(C_5Me_4)_2]Ln(\mu\text{-}Cl)_2Li(LB)_2$ (E = Si, Ge; LB = Et_2O, THF) and $[R_2Si(C_5H_4)(C_5Me_4)]Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$ (R = Me, Et) react with $LiCH(SiMe_3)_2$ in toluene giving rise to $[Me_2Si(C_5Me_4)_2]LnCH(SiMe_3)_2$ (Ln = Sc (**79a**),[352] Nd (**79f**), Sm (**79h**), Lu (**79r**)[305,362a]), $[Me_2Ge(C_5Me_4)_2]LnCH(SiMe_3)_2$ (Ln = Nd (**80f**), Ho (**80n**)),[356] $[Me_2Si(C_5H_4)(C_5Me_4)]LuCH(SiMe_3)_2$ (**81r**),[354] and $[Et_2Si(C_5H_4)(C_5Me_4)]LnCH(SiMe_3)_2$ (Ln = Y (**82b**), Lu (**82r**)),[354] respectively. All reactions proceed under essentially the same conditions and the resulting alkyls are isolated in good yields. The resulting complexes are soluble in pentane, toluene, and polar solvents, and they have been examined by NMR and IR spectroscopy. Since these compounds crystallize very nicely from saturated pentane solutions **79f**,[362a] **80n**,[356] (Figure 104), and **81r**[354] have been subjected to X-ray structure analysis. In view of the solid-state structure of $(C_5Me_5)_2NdCH(SiMe_3)_2$[304,362b] it is not surprising that the $CH(SiMe_3)_2$ group adopts the unusual planar geometry with a close lanthanide–methyl contact which is reminiscent of the transition state for β-methyl elimination.

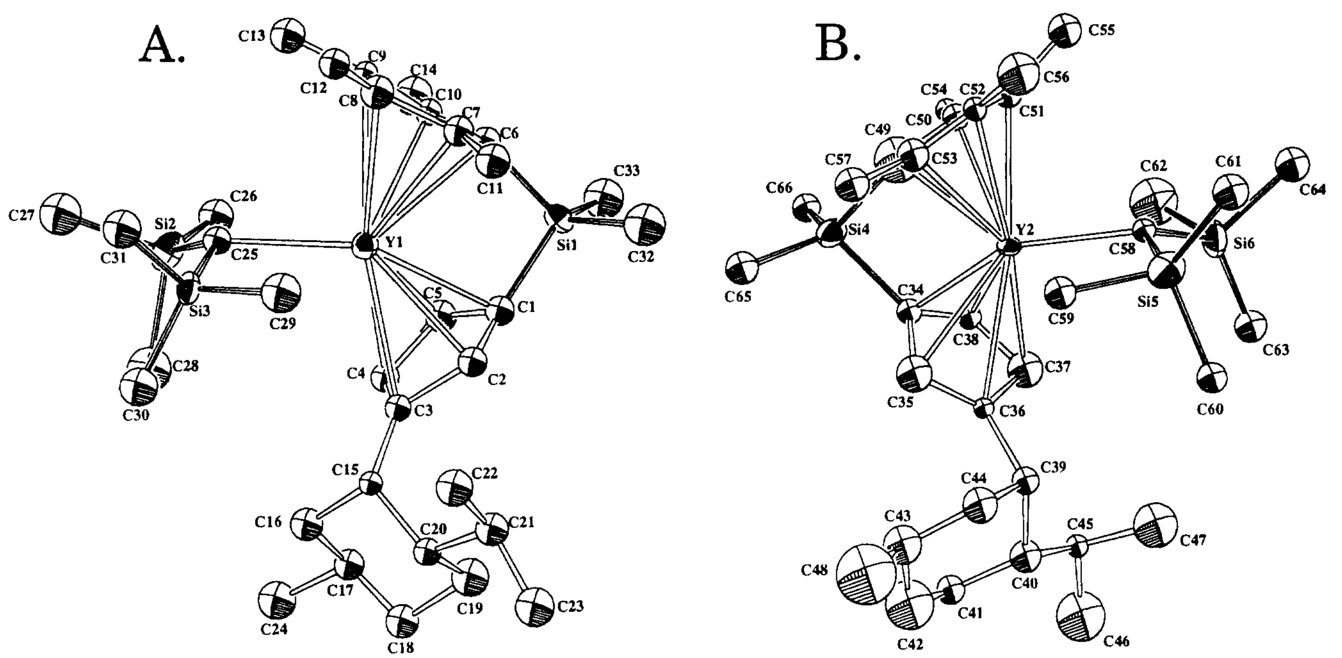


Figure 105. Perspective ORTEP drawing of the structures of (*R*)-{$Me_2Si(C_5Me_4)[C_5H_3$(+)-neomenthyl]}$YCH(SiMe_3)_2$ (**A**) and of (*S*)-{$Me_2Si(C_5Me_4)[C_5H_3$(+)-neomenthyl]}$YCH(SiMe_3)_2$ (**B**) in the crystal.[726] (Reprinted from ref 726. Copyright 1994 American Chemical Society.)

Table 21. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Complexes Containing Lanthanide to Silicon, Germanium, and Tin Bonds, Respectively

compound	Ln	color, characterization, etc.
$(C_5H_5)_2LnSiPh_3$	Sc	complex with THF: yellow, NMR[381]
$(C_5H_5)_2LnSi^tBuPh_2$	Sc	complex with THF: yellow, NMR, IR, melt./dec.[381]
$(C_5H_5)_2LnSi(SiMe_3)_2Ph$	Sc	complex with THF: yellow, NMR, IR, melt./dec.[381]
$(C_5H_5)_2LnSi(SiMe_3)_3$	Sc	complex with THF: yellow, X-ray, NMR, IR, melt./dec.[381]
$[Li(DME)_x][(C_5H_5)_2Ln(SiMe_3)_2]$	Sm	$x = 2$ (**83h**): yellow;[153] $x = 3$ (**84h**): yellow, NMR, melt./dec.[153,526]
	Dy	$x = 2$ (**83m**): brownish, NMR, melt./dec.[153]
	Ho	$x = 2$ (**83n**): yellow, NMR, melt./dec.[153]
	Er	$x = 2$ (**83o**): yellow, NMR, melt./dec.[153]
	Tm	$x = 2$ (**83p**): green, NMR, melt./dec.[153]
	Lu	$x = 2$ (**83r**): yellowish, melt./dec.;[153] $x = 3$ (**84r**): yellow, NMR,[153,233,526] X-ray,[233] melt./dec.[153,526]
$(C_5Me_5)_2LnSiH(SiMe_3)_2$	Y	yellow, reactions[742]
	Nd	bluegreen,[742] IR[529]
	Sm	red, X-ray, IR[529,742]
$(C_5H_5)_2LnGePh_3$	Er	pink, melt./dec., magn. d.[530]
$(C_5H_5)_2LnGe(SiMe_3)_3$	Sc	complex with THF: yellow, NMR, IR, melt./dec.[381]
$(C_5H_5)_2LnSnPh_3$	Er	pink, melt./dec., magn. d.[530]
	Yb	yellow, melt./dec.[530]

With $[Me_2Si(C_5Me_4)_2]Sc(CH_2)_3OCH_2CH{=}CH_2$,[352] $[Me_2Si(C_5H_3{}^tBu)_2]LnR$ (R = alkyl, allyl),[351,352] and the ionic species $[Li(tmed)_3]\{[Me_2Si(C_5Me_4)_2]Lu[\eta^2\text{-}CH(SiMe_3)Si(Me_2)CH_2]\}$[362a] further symmetrical dimethylsilyl-bridged cyclopentadienyl ligand systems, chelating the Ln–C fragment in $\eta^5{:}\eta^5$-fashion, have been mentioned in the literature. The chiral organolanthanides $[Me_2Si(C_5Me_4)(C_5H_3R^*)]LnCH(SiMe_3)_2$ (Ln = Y, La, Nd, Sm, Lu; R* = (−)-menthyl, (+)-neomenthyl, (−)-phenylmenthyl) are of interest as precatalysts for catalytic enantioselective olefin hydrogenation.[355,449,726,735] These complexes, like the yttrium derivative with R* = (+)-neomenthyl (Figure 105) are configurationally stable in toluene at 60 °C but they epimerize in the presence of primary alkyl amines.[726]

Examining the role of phosphines in Ziegler–Natta polymerization processes Schaefer et al.[525] prepared $\{Me_2Si(C_5Me_4)[C_5H_3(CH_2CH_2P^tBu_2)]\}ScCH(SiMe_3)_2$, a scandium alkyl with a well-defined, high effective phosphine concentration.[525] Furthermore, dealing with relative bond dissociation energies of early transition metal compounds a great many of new organoscandium species with two differently substituted cyclopentadienyl ligand systems have been synthesized.[363] $[(C_5Me_5)Sc(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)]_2$, the decomposition product of $(C_5Me_5)_2ScMe$ (**76a**), has already been discussed in detail within the previous chapter.[265,514]

b. Compounds with Rare Earth to Silicon, Germanium, and Tin Bonds. In comparison to the abundant alkyl complexes described in the preceding section, lanthanide compounds with bonds to silicon, germanium, or tin are rare (Table 21).

In fact there are only two crystallographically characterized bis(cyclopentadienyl)lanthanide complexes having unsubstituted C_5H_5 ligands and Ln–Si bonds.[233,381,526] The lack of further examples can be ascribed to experimental difficulties which arise in the preparation of stable MR_3^- anions (M = Si, Ge, or Sn; R = alkyl or aryl) and also to the decreased propensity of lanthanide ions to form bonds to soft

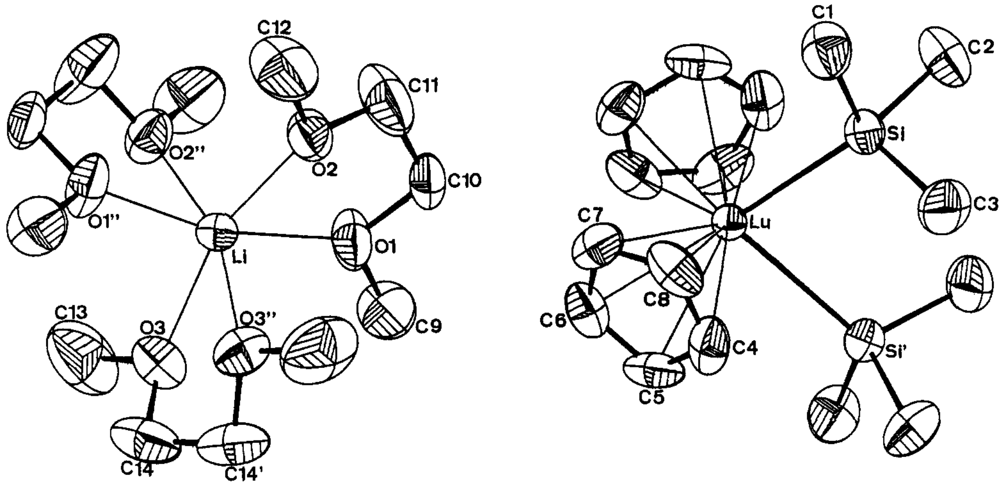


Figure 106. Structure of $[Li(DME)_3][(C_5H_5)_2Lu(SiMe_3)_2]$ in the crystal.[233]

donors. Complexes of the type $[Li(DME)_x][(C_5H_5)_2Ln(SiMe_3)_2]$ (**83** and **84**) may be prepared in reactions between $(C_5H_5)_2LnCl_2Na(DME)$ and $LiSiMe_3$ as outlined in eq 133:[153,233,526]

$$(C_5H_5)_2Ln(\mu\text{-}Cl)_2Na(DME) + 2LiSiMe_3 \xrightarrow{\text{pentane, DME}} \underset{\textbf{83, 84}}{[Li(DME)_x][(C_5H_5)_2Ln(SiMe_3)_2]} + NaCl + LiCl \quad (133)$$

$x = 2$: Ln = Sm (**83h**), Dy (**83m**), Ho (**83n**), Er (**83o**), Tm (**83p**), Lu (**83r**)

$x = 3$: Ln = Sm (**84h**), Lu (**84r**)

These complexes are extremely moisture- and air-sensitive and slowly decompose at room temperature. Thermolysis of neat **83** occurs at elevated temperatures (73 to 96 °C). Complexes with $x = 3$ (**84**) are reported[153] to lose one molecule DME in vacuum generating compounds of the type **83**. Characterization of **83** and **84** was achieved by NMR and IR spectroscopy. Structural evidence for the existence of Ln–Si bonds was first obtained by X-ray crystallography of a complex with the proposed composition $[Li(DME)_3][Cp_2$"Sm"$(SiMe_3)_2]$ (**84h**).[526] Unexpectedly, the solid-state structure of **84** (Figure 106) shows the lutetium compound $[Li(dme)_3][(C_5H_5)_2Lu(SiMe_3)_2]$ (**84r**)[233] consisting of well separated cation–anion pairs. (This case of mistaken identity is due to a mislabeling.) While three bidentate DME molecules coordinate to the central metal ion Li^+ of the cationic moiety in an octahedral fashion, the two centroids of the cyclopentadienyl and the two Me_3Si^- anions describe a distorted tetrahedron around the lanthanide ion Ln^{3+} which resides in the center of the counteranion.

However, in **84h** unusual short Sm to carbon bond distances (roughly 10 pm shorter than expected) gave rise to some speculation[153,526] about a seemingly high degree of covalency which might be induced by the strongly donating Me_3Si^- groups. Interestingly, a reinvestigation of the structural results[233] using a single crystal of $[Li(DME)_3][(C_5H_5)_2Lu(SiMe_3)_2]$ (**84r**) revealed exactly the same unit cell parameters and bond lengths within the error limits. As Lu^{3+} is smaller than Sm^{3+} by 10 pm,[527] the former questionable Sm–C bond distances fell precisely in the range of cyclopentadienyl–carbon–lutetium bond lengths. From this it can readily be inferred that all ambiguities in the structure of **84h**[526] could be eliminated if samarium was replaced by lutetium. The assumption that the lutetium compound was confused with the samarium complex receives further support by the fact that both compounds have the same yellow color and also by the fact that the heavy metal elements Sm and Lu diffract X-rays nearly equally well, so that an error in the choice of the lanthanide atom might remain undiscovered.

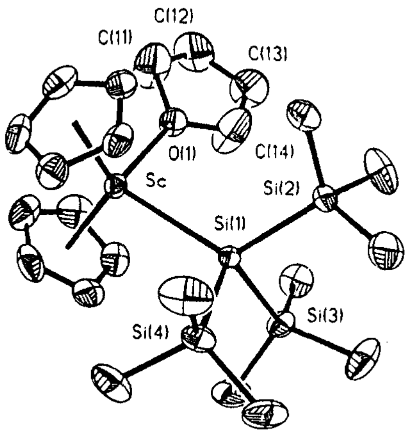


Figure 107. Structure of $(C_5H_5)_2ScSi(SiMe_3)_3(THF)$ in the crystal.[381] (Reprinted from ref 381. Copyright 1993 American Chemical Society.)

Very recently, a small number of scandocene silyl complexes $(C_5H_5)_2Sc(SiR_3)(THF)$ ($SiR_3 = Si(SiMe_3)_3$ (see Figure 107), $Si(SiMe_3)_2Ph$, Si^tBuPh_2, $SiPh_3$) as well as one scandocene germyl complex $(C_5H_5)_2Sc[Ge(SiMe_3)_3](THF)$ have been obtained after reaction of dimeric scandocene chloride (**20a**) with appropriate

$$\underset{\textbf{20a}}{{}^1/_2[(C_5H_5)_2ScCl]_2} + (THF)_3LiER_3 \xrightarrow[-2THF,\ -LiCl]{} (C_5H_5)_2Sc(ER_3)(THF) \quad (134)$$

$ER_3 = Si(SiMe_3)_3$, $Si(SiMe_3)_2Ph$, Si^tBuPh_2, $SiPh_3$, $Ge(SiMe_3)_3$

silyl and germyl lithium reagents (eq 134). These yellow crystalline d^0 metal silyl species are very air-

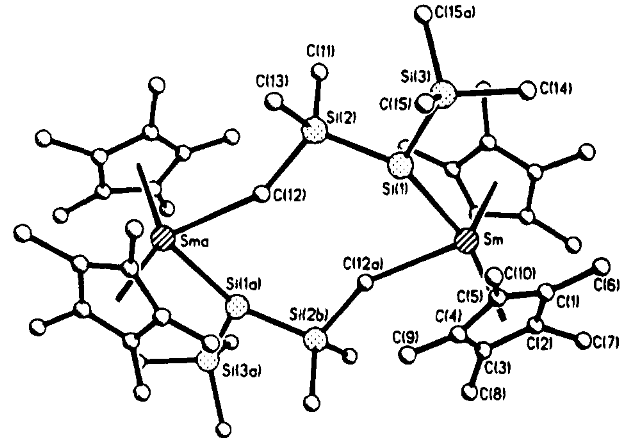


Figure 108. Structure of $[(C_5Me_5)_2SmHSi(SiMe_3)_2]_2$ in the crystal.[529] (Reprinted from ref 529. Copyright 1992 American Chemical Society.)

and moisture-sensitive, soluble in most organic solvents, and react with alkenes, alkynes, carbon monoxide, and xylyl isocyanide.[381]

In 1991, interest in the chemistry of organolanthanide complexes with lanthanide to silicon bonds developed because of their potential and utility as catalysts for hydrosilylation of olefins[307] and dehydrocoupling of silanes to polysilanes.[528] The catalytically active species with Ln–Si bond were prepared in situ by reacting bis(pentamethylcyclopentadienyl)lanthanide alkyl compounds with alkyl or aryl silanes. One year later, in 1992, isolation and structural characterization of the first bis(pentamethylcyclopentadienyl)lanthanide silyl compounds was reported.[529] According to eq 135, $(C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = Nd, Sm) react at 85 °C with excess $H_2Si(SiMe_3)_2$ to form isolable silyl complexes.

$$(C_5Me_5)_2LnCH(SiMe_3)_2 \xrightarrow[-CH_2(SiMe_3)_2]{H_2Si(SiMe_3)_2} (C_5Me_5)_2LnHSi(SiMe_3)_2 \quad (135)$$

Ln = Nd, Sm

Spectroscopic evidence shows that these complexes are monomeric in solution while the solid-state structure consists of dimers as shown in Figure 108. It has been found that a variety of silanes react with lanthanide alkyl complexes to form corresponding silyl species, which however, tend to undergo further reaction with silanes ending up in the formation of disilanes and organolanthanide hydrides. Thus the proper choice of the lanthanide alkyl and the organosilane appears to be crucial for the preparation of stable and isolable silyl complexes.

By 1978, metathesis of $LiGePh_3$ and $LiSnPh_3$ with $[(C_5H_5)_2LnCl]_2$ (**20**) in THF solution had been reported to afford the bis(cyclopentadienyl)lanthanide triphenylgermyl and triphenylstannyl compounds, respectively.[530] Characterization was achieved by elemental analyses, molecular weight determinations, IR spectroscopy, and measurements of their magnetic susceptibilities although no structural data are yet available.

5. Bis(cyclopentadienyl) Rare Earths Hydrides

a. Cyclopentadienyl Compounds. The initial report[258] on the thermolysis of $(C_5H_5)_2Lu^tBu(THF)$ (and related alkyl and aryl compounds) at 200 °C suggested that the decomposition proceeds by way of β-H elimination and the formation of an organolanthanide hydride. In the ensuing years, methods have been developed to synthesize and isolate these sensitive and reactive hydride complexes. Many of them have been fully structurally characterized by single-crystal X-ray crystallography (compare Table 22), but the hydride–hydrogen atoms are usually not located nor refined.

There are basically three methods which proved most useful in generating discrete organolanthanide hydrides: hydrogenolysis[314,459] of lanthanide to carbon bonds, carefully controlled thermolysis[157] of lanthanide alkyl complexes, and substitution of halide ion X^- in $(C_5H_5)_2LnX(THF)$ by hydride ions.[149]

Cleavage of Ln–C bonds by molecular hydrogen at ambient pressure and room temperature has found wide application especially in the synthesis of solvent-free (and in many instances ring-substituted (*vide infra*)) bis(cyclopentadienyl)lanthanide hydrides. In a series of experiments, Evans et al.[314,459] showed that the ease with which the hydrogenolysis of bis(cyclopentadienyl)lanthanide alkyl complexes occurs, critically depends on the nature of the solvent (i.e. polarity) and to some extent on the steric bulk of the alkyl residue. While $[(C_5H_5)_2Ln(\mu\text{-}Me)]_2$ (**73**) reacts fastest with H_2 in a mixture of 10:1 toluene/THF (eq 136), $(C_5H_5)_2Ln^tBu(THF)$ (**74**) exhibited the highest reaction rates in pure toluene according to eq 137.

$$\underset{\mathbf{73}}{[(C_5H_5)_2Ln(\mu\text{-}Me)]_2} + H_2 \xrightarrow[\text{ambient pressure}]{\text{toluene/THF}} \underset{\mathbf{85}}{[(C_5H_5)_2Ln(\mu\text{-}H)(THF)]_2} + 2CH_4 \quad (136)$$

Ln = Y (**85b**), Er (**85o**), Yb (**85q**), Lu (**85r**)

$$2\underset{\mathbf{74}}{(C_5H_5)_2Ln^tBu(THF)} + H_2 \xrightarrow{\text{toluene}} \underset{\mathbf{85}}{[(C_5H_5)_2Ln(\mu\text{-}H)(THF)]_2} + 2HCMe_3 \quad (137)$$

Ln = Y (**85b**), Er (**85o**), Lu (**85r**)

By contrast, no reaction was observed in the systems **73**/toluene, **73**/THF, and **74**/THF. Thus tightly bound donor molecules such as THF as well as noncoordinating solvents such as toluene may hamper reactivity, either by firmly occupying a coordination site on the lanthanide ion as in the latter cases or by disallowing dissociation of dimeric molecules such as **73**. In other words, the solvent must support the formation of coordinatively unsaturated lanthanide–alkyl intermediates which then undergo hydrogenolysis. Characterization of these extremely air- and moisture-sensitive dimeric complexes **85** was achieved by IR and ^1H-NMR spectroscopy. Infrared bands within the region of 1350 cm^{-1} were assigned to Ln–(μ-H)–Ln vibrations by evaluating the isotope shift of deuterated analogues. NMR spectroscopy also proved useful as a diagnostic tool in cases where Ln = yttrium, since the nucleus ^{89}Y (100% natural abundance) is magnetically active ($I = {}^1/_2$) and coupling with bridging and terminal hydrogen atoms gives rise to characteristic multiplets.[102]

Table 22. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Hydrides

compound	Ln		color, characterization, etc.
$(C_5H_5)_2LnH$	Y	**85b**	complex with THF: white, IR,[314] NMR;[314,240] with DME: NMR, IR;[459] with dioxane: IR;[459] with py: yellow, IR[435]
	Nd	**85f**	complex with THF: blue, NMR, IR, melt./dec.[106,157]
	Sm	**85h**	complex with THF: yellow, NMR, IR;[106] with NEt_3: green, IR[248]
	Er	**85o**	complex with THF: pink,[314] IR[314,459]
	Yb	**85q**	complex with THF: yellow, NMR, IR[459]
	Lu	**85r**	colorless, X-ray;[531] complex with THF: colorless, NMR,[106,149,254,258,314,376] X-ray,[149,254,532] IR,[149,254,258,314] melt./dec.;[149,376] with NEt_3: colorless[531]
$(C_5H_5)_2LnD$	Y		complex with THF: white, IR[314]
	Er		complex with THF: pink, IR[314]
	Yb		complex with THF: IR[459]
	Lu		complex with THF: IR[149,314] NMR, melt./dec.[149]
$[Li(THF)_x]\{[(C_5H_5)_2LnH]_3H\}$	Y		$x = 0$: yellow;[102] $x = 4$: yellow,[102] NMR,[102,178,240,398] IR[102,398]
	Yb		$x = 4$: orange opaque, NMR, IR[459]
	Lu		$x = 3$: colorless, NMR, IR,[149,533] IR, melt./dec.[149]
$[Li(THF)_x]\{[(C_5H_5)_2LnD]_3D\}$	Yb		$x = 4$: NMR, IR[459]
$[Na(THF)_6]\{[(C_5H_5)_2LnH]_3H\}$	Lu		colorless, NMR, IR[149]
$[Li(THF)_4]\{[(C_5H_5)_2LnH]_3Cl\}$	Er		pink, X-ray, IR[533]
$(C_5H_5)_2LnBH_4$	Sc		colorless, IR, MS, melt./dec.,[534] NMR[41,534]
	Sm		yellow;[248] complex with THF: yellow, IR[535]
	Er		pink, IR; complex with THF: peach colored, IR[535]
	Yb		orange, NMR, IR; complex with THF: orange, IR[535]
	Lu		colorless, IR,[375] NMR[258,375]
$(C_5H_5)_2LnBD_4$	Sm		complex with THF: IR[535]
	Er		complex with THF: IR[535]
	Yb		IR; complex with THF: IR[535]
$[(C_5H_5)_2LnAlH_4]_x(LB)_n$	Y		LB = Et_2O ($x = 2$, $n = 1$): colorless, X-ray, IR;[536] ($x = 2$, $n = 2$): colorless,[536] IR;[218,536] LB = THF ($x = 2$, $n = 2$): colorless, IR,[536] X-ray;[537] LB = NEt_3 ($x = 2$, $n = 2$): white, IR, X-ray[536]
	Sm		LB = NEt_3 ($x = 2$, $n = 2$): yellow green, X-ray[247]
	Yb		LB = NEt_3 ($x = 2$, $n = 2$) (with C_6H_6): yellow, X-ray[531]
	Lu		($x = 2$, $n = 0$): IR;[255] LB = NEt_3 ($x = 1$, $n = 1$): X-ray;[538] ($x = 2$, $n = 2$) (without C_6H_6): colorless, X-ray, IR;[538] (with C_6H_6): colorless, X-ray;[531] LB = Et_2O ($x = 2$, $n = 2$): white, IR; LB = THF ($x = 2$, $n = 2$): X-ray, IR[538]
$[(C_5H_5)_2Ln]_2AlH_4Cl$	Y		complex with 2THF: IR; with NEt_3 (C_6H_6): X-ray, IR[539]
$(C_5H_5)_2LnAlH_2Et_2$	Lu		IR[255]
$(C_5H_5)_2LnAlH_3(C_6H_{13})$	Lu		IR[255]
$(C_5H_5)_2LnAlH_2(C_6H_{13})_2$	Lu		IR[255]
$(C_5H_5)_2LnH_4Re(PPhMe_2)_3$	Y		complex with THF: yellow, X-ray, NMR, IR[540]
	Lu		complex with THF: NMR, IR[540]
$(C_5H_5)_2LnH_4Re(PPh_3)_3$	Y		complex with THF: NMR[540]
$(C_5H_5)_2LnH_6Re(PPh_3)_2$	Y		complex with THF: pale yellow, X-ray, NMR, IR[540]
	Lu		complex with THF: NMR, IR[540]
$(C_5H_5)_2LnH_7Re_2(PMe_2Ph)_4$	Y		NMR;[457] complex with THF: bright red,[540] X-ray, NMR, IR[457,540]
	Lu		dark brown,[540] X-ray, NMR, IR[457,540]
$[Li(THF)_4]\{[(C_5H_5)_2Ln(\mu\text{-}H)]_2[(C_5H_5)_2Ln(\mu\text{-}OMe)](\mu^3\text{-}H)\}$	Y		NMR, IR[398]
$[Li(THF)_4]\{[(C_5H_5)_2Ln(\mu\text{-}H)][(C_5H_5)_2Ln(\mu\text{-}OMe)]_2(\mu^3\text{-}H)\}$	Y		NMR, IR[398]
$[Li(THF)_4]\{[(C_5H_5)_2Y(\mu\text{-}OMe)]_3(\mu^3\text{-}H)\}$	Y		NMR, IR[398]
$[Li(THF)_3]_2\{[(C_5H_5)_2Y(\mu\text{-}OMe)]_3(\mu^3\text{-}H)\}_2$	Y		X-ray[398]

The structure of **85r** has been determined by X-ray diffraction studies.[149,254,532] The centrosymmetric molecule (Figure 109) is reminiscent of dimeric bis(cyclopentadienyl)lanthanide halide $[(C_5H_5)_2Sc(\mu\text{-}Cl)]_2$ (**20a**)[211] and alkyl $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$ (**73b**)[234] complexes inasmuch as two $(C_5H_5)_2Ln^+$ moieties are bridged in a symmetrical fashion. Unlike the majority of halide ions and alkyl groups, the small hydride ions allow the coordination of an additional molecule of THF, leading to formally nine-coordination at the lanthanide ions.

The accuracy of the structure determination was sufficient to reveal the μ-H atoms at distances of 198(6) and 231(6) pm from Lu^{3+}.[149] **85f** and **85r** can also be obtained by thermal decomposition (β-H elimination) of $(C_5H_5)_2Ln(^sBu)(THF)$ at temperatures between −30 °C and 0 °C.[106,157] (Trimethylsilyl)methyl complexes $(C_5H_5)_2Ln(CH_2SiMe_3)(THF)$ (Ln = Sm, Lu) have also been used successfully as starting materials in hydride synthesis.[106] However, the triethylamine adduct $[(C_5H_5)_2Sm(\mu\text{-}H)(NEt_3)]_2$ was prepared by reaction of $(C_5H_5)_2SmCl$ (**20h**) with $LiAlH_4$ and excess NEt_3 in diethyl ether.[248]

The structural chemistry of organolanthanide hydrides is not restricted to the above, comparatively simple neutral dimers, but rather dominated by anionic, trimetallic units which crystallize with a solvated alkali metal ion as countercation. $[Li(THF)_4]\{[(C_5H_5)_2ErH]_3Cl\}$ was the first complex of this family to be structurally characterized.[533] The anion presented in Figure 110 consists of three $(C_5H_5)_2Er^+$ units bridged by two $\mu_2\text{-}H^-$ and one $\mu_2\text{-}Cl^-$ anions as well as one central $\mu_3\text{-}H^-$ ion. The similar structural type in the anion has been established for $[Li(THF)_x]\{[(C_5H_5)_2LnH]_3H\}$ (Ln = Y,[102,178,240,398] Yb,[459] Lu[149,533]), $[Na(THF)_6]\{[(C_5H_5)_2LuH]_3H\}$,[149] $[Li(THF)_4]\{[(C_5H_5)_2Y$-

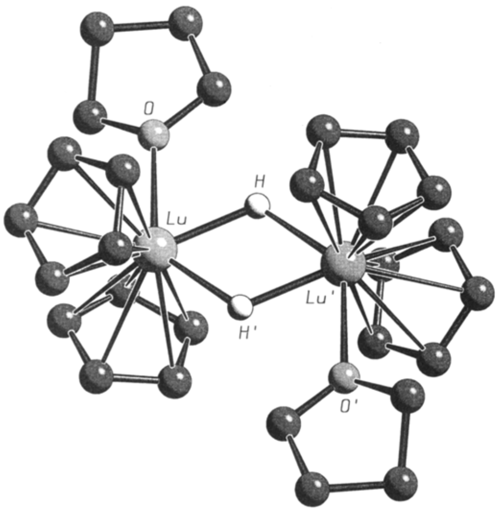


Figure 109. Structure of $[(C_5H_5)_2Lu(\mu\text{-}H)(THF)]_2$ (**85r**) in the crystal.[149]

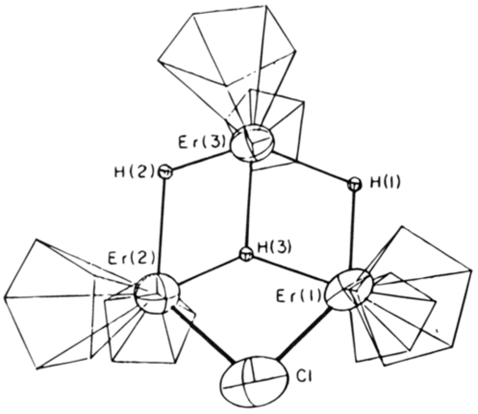


Figure 110. Structure of $\{[(C_5H_5)_2ErH]_3Cl\}^-$ in the crystal.[533] (Reprinted from ref 533. Copyright 1982 American Chemical Society.)

$(\mu_2\text{-}H)]_x[(C_5H_5)_2Y(\mu_2\text{-}OMe)]_{3-x}(\mu_3\text{-}H)\}$ (x = 2, 1, 0),[398] and $[Li(THF)_3]_2\{[(C_5H_5)_2Y(\mu_2\text{-}OMe)]_3(\mu_3\text{-}H)\}_2$[398] (see also section II.B.2.a bis(cyclopentadienyl)lanthanide chalcogenides).

These complexes have been synthesized by a variety of methods which include thermolysis of *tert*-butyl complexes (**74**) in toluene in the presence of alkali halides (eq 138),[533] reaction of metallic sodium (or sodium amalgam) with $(C_5H_5)_2LnCl(THF)$ (**21**) in THF (eq 139),[149] or by rearrangement of dimeric hydrides **85** to trimeric ones induced by strongly nucleophilic reagents (eq 140).[102]

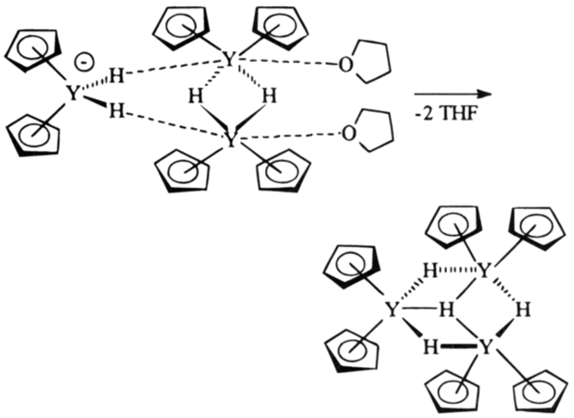
$$\underset{\textbf{74r}}{3(C_5H_5)_2Lu^tBu(THF)} \xrightarrow[\text{LiCl}]{\text{toluene, 75 °C}} [Li(THF)_3]\{[(C_5H_5)_2LuH]_3H\} \quad (138)$$

$$\underset{\textbf{21r}}{3(C_5H_5)_2LuCl(THF)} \xrightarrow{\text{Na/THF}} [Na(THF)_6]\{[(C_5H_5)_2LuH]_3H\} \quad (139)$$

$$\underset{\textbf{85b}}{4[(C_5H_5)_2YH(THF)]_2} + 2^tBuLi \xrightarrow[\substack{-(C_5H_5)_2Y^tBu(THF)/\\ -(C_5H_5)_3Y(THF)}]{\text{THF}} 2[Li(THF)_4]\{[(C_5H_5)_2YH]_3H\} \quad (140)$$

Unlike reactions 138 and 139 whose mechanisms are unknown, the proposed mechanism of reaction 140 begins by a nucleophilic attack of a $^tBu^-$ anion on **85b**, β-elimination of isobutene and generating $[(C_5H_5)_2YH_2]^-$ ion which may then react with dimer **85b** to form the triangular-shaped anion $\{[(C_5H_5)_2Y(\mu_2\text{-}H)]_3(\mu_3\text{-}H)\}^-$ as outlined in eqs 141 and 142:

$$\underset{\textbf{85b}}{[(C_5H_5)_2YH(THF)]_2} + {}^tBu^- \rightarrow \underset{\textbf{74b}}{(C_5H_5)_2Y^tBu(THF)} + [(C_5H_5)_2YH_2]^- \quad (141)$$



(142)

The remarkable stability of such a trimetallic structure has been demonstrated by Evans et al.[398] who conducted a series of methanolysis experiments on $[Li(THF)_4]\{[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}$. In accord with their anionic nature the bridging hydrogen atoms of the latter complex react with protons of 1−3 equiv of MeOH, giving rise to three discrete and isolable μ_2-methoxy-bridged complexes which were identified by NMR, IR (see eq 143, x = 2, 1, 0) and X-ray structure analysis of $[Li(THF)_3]_2\{[(C_5H_5)_2Y(\mu_2\text{-}OMe)]_3(\mu_3\text{-}H)\}_2$.

$$[Li(THF)_4]\{[(C_5H_5)_2Y(\mu_2\text{-}H)]_3(\mu_3\text{-}H)\} + nMeOH \xrightarrow[-78\text{ to }0\text{ °C}]{\text{THF}} [Li(THF)_4]\{[(C_5H_5)_2Y]_3(\mu_2\text{-}OMe)_{3-x}(\mu_2\text{-}H)_x(\mu_3\text{-}H)\} + n/2H_2 \quad (143)$$

Interestingly, all μ_2-H$^-$ ions can be displaced by μ_2-OMe$^-$ ions leaving the entire trimetallic structure intact. Furthermore, the central, triply bridging H$^-$ ion could not be replaced even under rigorous conditions (temperature as high as 65 °C for 30 min). This suggests that the trimetallic structure has superior stability which might be attributable to the additional negative charge which reduces the inherent electron deficiency of lanthanide complexes.

Tetrahydroborate complexes of the bis(cyclopentadienyl)lanthanide system with bridging hydrogen atoms have been known since 1976.[535] Metathesis of stoichiometric amounts of $NaBH_4$ and $(C_5H_5)_2LnCl(THF)$ (**21**) (eq 144) affords complexes of the type $(C_5H_5)_2LnBH_4(THF)$ which lose THF under dynamic vacuum at elevated temperatures.[41,534,535]

$$\underset{\textbf{21}}{(C_5H_5)_2LnCl(THF)} + MBH_4 \xrightarrow{\text{THF}} (C_5H_5)_2LnBH_4(THF) + MCl \quad (144)$$

M = Na: L = Sm, Er, Yb[535]

M = Li: Ln = Sc[534]

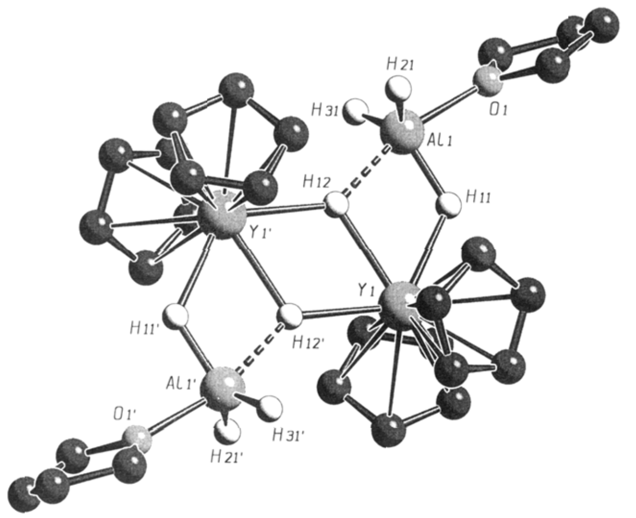


Figure 111. Structure of $[(C_5H_5)_2YH]_2(AlH_3{\cdot}THF)_2$ in the crystal.[537]

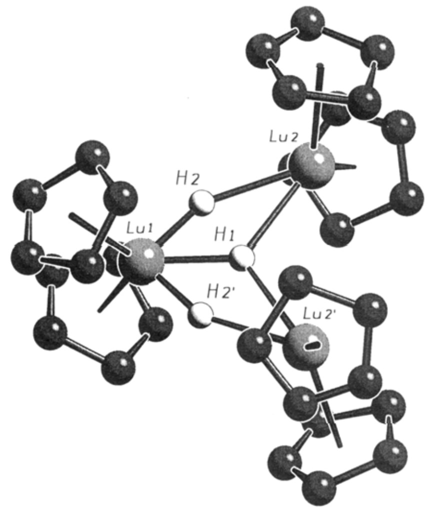


Figure 112. Structure of $[(C_5H_5)_2Lu]_3(\mu_2\text{-}H)_2(\mu_3\text{-}H)$ in the crystal.[531]

Infrared spectra of the unsolvated complexes $(C_5H_5)_2LnBH_4$ exhibit three bands which are characteristic of a H-bridged structure with a tridentate BH_4^- ligand, whereas the spectra of the corresponding THF adducts were suggestive of a bidentate tetrahydroborate ligand.

A number of tetrahydroaluminate complexes have been prepared and characterized by complete X-ray structure determination.[247,531,536,537,538,539] Bis(cyclopentadienyl)lanthanide chlorides react in benzene (in the presence of excess Lewis base), diethyl ether, or THF with a suspension of $LiAlH_4$ (or $NaAlH_4$) to form compounds of the general formulae: $[(C_5H_5)_2LnAlH_4]_2(LB)_n$ (Ln = Lu (n = 0);[255] Ln = Y, LB = Et_2O (n = 1);[536] Ln = Y, Lu, LB = Et_2O (n = 2);[218,536,538] Ln = Y, Lu, LB = THF (n = 2);[536–538] Ln = Y, Sm, Yb, Lu, LB = NEt_3 (n = 2)[247,531,536,538]). Equation 145 shows the formation of the latter triethylamine adducts:

$$\underset{\mathbf{20}}{[(C_5H_5)_2LnCl]_2} + 2MAlH_4 + 2NEt_3 \xrightarrow[-2MCl]{} [(C_5H_5)_2LnH]_2(AlH_3{\cdot}NEt_3)_2 \quad (145)$$

M = Li, Na

Depending on the stoichiometry and reaction conditions, slightly different structures have been observed.[247,531,536,537,538] Figure 111 presents the structure of $[(C_5H_5)_2YH]_2(AlH_3{\cdot}THF)_2$ which may serve as an explanatory example.[537] The core of this complex is made up of a centrosymmetric $[(C_5H_5)_2YH]_2$ unit which is essentially identical to that of **85r**.[149,254,532] While in the latter complex, THF molecules provide a formal coordination number of nine for each Lu^{3+} ion, the coordination spheres of the Y atoms are coordinated by two ($AlH_3{\cdot}THF$) ligands. The coordination geometry of aluminum is best described as a distorted trigonal bipyramid in which three hydrogen atoms lie in the equatorial plane and one hydrogen and the oxygen atom occupy the axial positions. One of the equatorial H atoms bridges yttrium (d(Y–H) = 217(6) pm) and aluminum (d(Al–H) = 157(6) pm), whereas the remaining equatorial hydrogen atoms are terminal. Accordingly, their bond distances are much shorter, $d(\text{Al–H}_{\text{terminal}})$ = 149(6) and 146(8) pm, respectively. Compared to this, the distance between the Y-bridging hydride ion and the adjacent Al atom is long (200(1) pm) and the interaction must be considered weak. Nevertheless, the same structure type has been established for $[(C_5H_5)_2YH]_2(AlH_3{\cdot}NEt_3)_2$,[536] and the benzene-free lutetium complexes $[(C_5H_5)_2LuH]_2(AlH_3{\cdot}LB)_2$ (LB = NEt_3, THF),[538] whereas the related samarium complex[247] exhibits NEt_3-stabilized AlH_3 molecules which coordinate to both samarium ions via two independent hydrogen bridges. Furthermore, the environment of Al resembles a distorted tetrahedron rather than a bipyramid because the Sm-bridging hydride ion seems to be too remote to coordinate to Al.

Exposure of a single crystal of the 18-electron complex $[(C_5H_5)_2LuH]_2(AlH_3{\cdot}NEt_3)_2$ to hard X-rays (Mo Kα, λ = 0.7106 nm) resulted in dissociation of the dimer and formation of monomeric $(C_5H_5)_2Lu(\mu\text{-}H)AlH_3(NEt_3)$, a species with a monodentate alumohydride group and a 14-electron configuration at the rare earth metal.[538] Resistance to X-ray radiation can be achieved by inclusion of noncoordinated benzene molecules in the crystal lattice. While the structure of the Yb derivative $[(C_5H_5)_2Yb(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)AlH_2{\cdot}NEt_3]_2{\cdot}C_6H_6$ is, in general, identical to the already discussed Y systems $[(C_5H_5)_2YH]_2(AlH_3{\cdot}LB)_2$ (LB = THF, NEt_3)[536,537] the corresponding heavy metal Lu complex (with C_6H_6 in the crystal lattice) can be described best as $[(C_5H_5)_2Lu(\mu_2\text{-}H)]_2[(\mu_2\text{-}H)_2AlH{\cdot}NEt_3]_2{\cdot}C_6H_6$.[531] The latter compound decomposes with excess NEt_3 to yield a mixture of $[(C_5H_5)_2Lu(\mu\text{-}H)(NEt_3)]_2$ and trimetallic $[(C_5H_5)_2Lu]_3(\mu_2\text{-}H)_2(\mu_3\text{-}H)$ (Figure 112).[531] Also with one molecule benzene in the lattice crystallizes the bis(cyclopentadienyl)yttrium hydridochloride $[(C_5H_5)_2Y]_2(AlH_4Cl)(NEt_3){\cdot}C_6H_6$.[539]

Methyl complexes such as $(C_5H_5)_2LuMe(THF)$ and $(C_5H_5)_2YMe(THF)$ are capable of abstracting acidic hydrogen atoms even those of transition metal hydride complexes generating novel mixed polymetallic hydride species as shown by Alvarez et al.[457]

$$(C_5H_5)_2LnMe(THF) + Re_2H_8(PMe_2Ph)_4 \xrightarrow[-CH_4]{THF} (C_5H_5)_2Ln(THF)_nRe_2H_7(PMe_2Ph)_4 \quad (146)$$

Ln = Y (n = 1), Lu (n = 0)

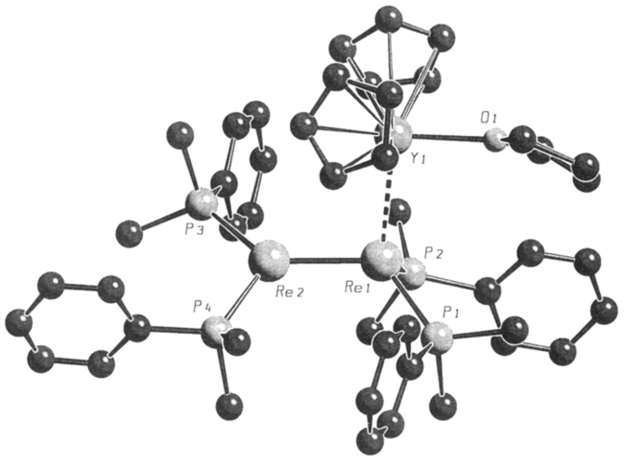


Figure 113. Structure of $(C_5H_5)_2Y(THF)H_6Re(PPh_3)_2$ in the crystal.[540]

The structures of both complexes was deduced by common spectrocopic methods and X-ray crystallography.[457,540] Using again the reaction of $(C_5H_5)_2LnMe(THF)$ (Ln = Y, Lu) and rhenium polyhydrides $ReH_5(PPh_3)_3$, $ReH_5(PMe_2Ph)_3$, and $ReH_7(PPh_3)_2$, respectively, five other heterobimetallic hydrides have been synthesized in good yields: $(C_5H_5)_2Ln(THF)H_4Re(PPh_3)_3$ (Ln = Y), $(C_5H_5)_2Ln(THF)H_4Re(PPhMe_2)_3$ (Ln = Y, Lu) and $(C_5H_5)_2Ln(THF)H_6Re(PPh_3)_2$ (Ln = Y (Figure 113), Lu). The structure of the latter two yttrium compounds was verified by single-crystal X-ray determinations.[540]

b. Pentamethylcyclopentadienyl Compounds. Since the discovery[358,359] in 1982 of bis(pentamethylcyclopentadienyl)lutetium hydride $[(C_5Me_5)_2LuH]_2$ (**86r**) which exhibits a remarkable reaction chemistry[360,490] with chemically "inert" substrates such as benzene, tetramethylsilane, and methane, the interest in hydride complexes of the other members of the rare earth group[265,272−274,278,284,304,362b,403,508] has grown steadily. The synthesis of such highly reactive, solvent-free hydrides is best achieved by hydrogenolysis of solvent-free alkyl complexes in nonpolar solvents as shown in eq 147:

$$n(C_5Me_5)_2LnCH(SiMe_3)_2 + 2H_2 \xrightarrow[\text{ambient pressure}]{\text{pentane}} \underset{\mathbf{86}}{[(C_5Me_5)_2LnH]_n} + nCH_2(SiMe_3)_2 \quad (147)$$

$n = 2$: Ln = Y (**86b**), La (**86c**), Ce (**86d**), Nd (**86f**), Sm (**86h**), Lu (**86r**)

$n = ?$: Ln = Sc (**86a**)

The lutetium complex **86r** was first prepared by hydrogenolysis of the methyl complex $[(C_5Me_5)_2LuMe]_2$ (**76r**)[359] which is much harder to prepare than the bis(trimethylsilyl)methyl analogue. The orange samarium hydride **86h** may also be prepared by hydrogenolysis of $[(C_5Me_5)_2Sm]_2C_2Ph_2$ (eq 148) which is precipitated as a black substance from the reaction of $(C_5Me_5)_2Sm(THF)_2$ and PhC≡CPh in toluene.[508]

$$[(C_5Me_5)_2Sm]_2C_2Ph_2 + 2H_2 \rightarrow \underset{\mathbf{86h}}{[(C_5Me_5)_2SmH]_2} + C_2H_2Ph_2 \quad (148)$$

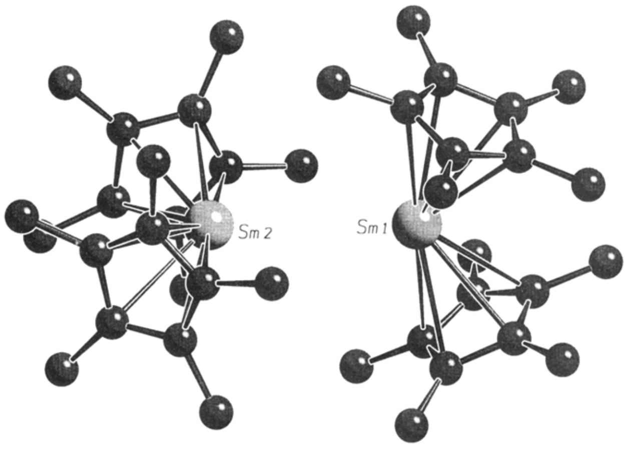


Figure 114. Structure of $[(C_5Me_5)_2SmH]_2$ (**86h**) in the crystal.[508]

In all cases, hydride complexes **86** form as sparingly soluble, exceedingly moisture- and air-sensitive solids on the wall of the flask. These compounds have been mainly characterized by NMR and IR spectroscopy. Only **86h** was subjected to a single-crystal X-ray diffraction analysis; Figure 114 shows the molecular structure of **86h**.[508]

Two $(C_5Me_5)_2Sm$ moieties are oriented in a way that minimizes mutual steric repulsion by adopting a nearly tetrahedral arrangement of the rings about the center of the Sm−Sm axis. Although the positions of hydride ions could not be determined by the X-ray diffraction study, it can be assumed that at least one of them bridges the two metal centers. This would lead to a structure in accord with that of $(C_5Me_5)_2Lu(\mu\text{-}Me)(Me)Lu(C_5Me_5)_2$ (**76r**).[490] Nevertheless, it is also conceivable that both of hydrogen atoms bridges the samarium atoms.[541]

The molecularity of the highly sensitive scandium hydride $[(C_5Me_5)_2ScH]_n$ (**86a**) is unknown, because it is unstable in the absence of an atmosphere of H_2. The solvent adduct $(C_5Me_5)_2ScH(THF)$ is monomeric and can be stored infinitely in the dark at −10 °C.[265,272] However, **86a** is a valuable synthetic reagent when generated *in situ* and readily inserts into the double bond of olefins as outlined in eqs 149 and 150:[265,272,352]

$$\underset{\mathbf{86a}}{\text{“}(C_5Me_5)_2ScH\text{”}} + CH_2{=}CHR \xrightarrow{\text{toluene}} (C_5Me_5)_2ScCH_2CH_2R \quad (149)$$

$$\underset{\mathbf{86a}}{\text{“}(C_5Me_5)_2ScH\text{”}} + CH_2{=}C{=}CH_2 \xrightarrow{-80\ ^\circ C} (C_5Me_5)_2ScC_3H_5 \quad (150)$$

These highly reactive solvent-free and, in contrast to their unsubstituted analogous in nonpolar solvents, moderately soluble bis(pentamethylcyclopentadienyl)lanthanide hydrides have been employed in a variety of stoichiometric and catalytic reactions such as oligomerization of olefins, hydrogenation, and activation of C−H bonds. Most of the reaction chemistry has been described in refs 265, 304, 305, 352, 360−362, 490, and 542.

Thermolysis of $[(C_5Me_5)_2YH]_2$ (**86b**) at 100 °C in *n*-octane, cyclohexane, or benzene yields a "tucked-

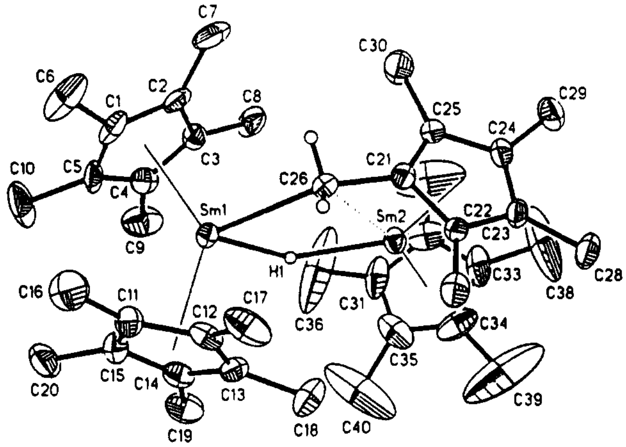


Figure 115. Structure of $(C_5Me_5)_2Sm(\mu\text{-H})(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$ in the crystal.[403] (Reprinted from ref 403. Copyright 1991 American Chemical Society.)

over" bimetallic red metallocene (eq 151) which was identified as $(C_5Me_5)_2Y(\mu\text{-H})(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)$.[493,543] Analogously, the samarium hydride **86h**

$$\underset{\mathbf{86}}{[(C_5Me_5)_2LnH]_2} \xrightarrow[-H_2]{} (C_5Me_5)_2Ln(\mu\text{-H})(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5) \qquad (151)$$

$$Ln = Y, Sm$$

converts via an internal metalation in alkanes or benzene at room temperature over a period of several days (eq 151) into the corresponding complex $(C_5Me_5)_2Sm(\mu\text{-H})(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$. Single crystals of the dark brown Sm complex were structurally characterized by X-ray crystallography which revealed the molecular structure presented in Figure 115.[403]

References to spectroscopic and other data of known bis(pentamethylcyclopentadienyl) rare earth hydrides are given in Table 23.

c. Derivatives with Other Substituted Cyclopentadienyl Rings. Parallel with the development of bis(cyclopentadienyl)lanthanide hydrides (*vide supra*) a variety of ring-substituted analogues thereof have been prepared and analyzed (Table 24). Methyl, *tert*-butyl, and trimethylsilyl substituents on the cyclopentadienyl rings provide for good solubility in aromatic and to a lesser extent in aliphatic solvents which is essential for studying their reactions and for growing X-ray quality single crystals. Despite the principal difficulty of X-ray diffraction studies to locate hydrogen atoms due to their small contributions to the electron density, this technique has been widely used to characterize hydride complexes, since NMR spectroscopy also often fails to give well-resolved spectra.

$(MeC_5H_4)_2Ln^tBu(THF)$ (Ln = Y, Er, and Lu)[314] reacts with H_2 to generate the corresponding $[(MeC_5H_4)_2LnH(THF)]_2$ which are soluble in THF and partly soluble in toluene and which can be recrystallized from THF/hexane. The molecular structure[314] of $[(MeC_5H_4)_2YH(THF)]_2$ is virtually identical to that of $[(C_5H_5)_2LuH(THF)]_2$ (**85r**).

The assumption that trimetallic hydride complexes form by interaction of anionic $[(C_5H_5)_2LnH_2]^-$ and the neutral dimer **85** (compare eq 142) was further supported by an experiment in which $[(MeC_5H_4)_2YH_2]^-$ had been replaced by an isolobal $(MeC_5H_4)_2ZrH_2$ molecule. Expectedly, a neutral (hetero) trimetallic complex was generated in 32% yield according to eq 152:[102]

$$[(MeC_5H_4)_2YH(THF)]_2 + {}^1/_2[(MeC_5H_4)_2ZrH_2]_2 \xrightarrow{\text{THF/hexane}} [(MeC_5H_4)_2YH]_2[(MeC_5H_4)_2ZrH](\mu^3\text{-H}) \qquad (152)$$

Like bis(methylcyclopentadienyl)lanthanide hydride complexes, which show much the same structural types as their unsubstituted cyclopentadienyl analogues, the bis(1,3-dimethylcyclopentadienyl) system exhibit similar structures. Thus, $[Li(THF)_4]\{[(Me_2C_5H_3)_2LnH]_3H\}$ could be synthesized[328] and hydrogenolysis[328] of $[(Me_2C_5H_3)_2YMe]_2$ dissolved in a mixture of THF and hexane affords the unsolvated trimeric complex $[(Me_2C_5H_3)_2YH]_3$ (eq 153) which recalls the trimeric decomposition product[531] $[(C_5H_5)_2Lu]_3(\mu_2\text{-H})_2(\mu_3\text{-H})$.

$${}^3/_2[(Me_2C_5H_3)_2Y(\mu\text{-Me})]_2 + 3H_2 \rightarrow [(Me_2C_5H_3)_2Y(\mu\text{-H})]_3 + 3CH_4 \qquad (153)$$

Dissolution of $[(Me_2C_5H_3)_2Y(\mu\text{-H})]_3$ in pure THF generates $[(Me_2C_5H_3)_2Y(\mu\text{-H})(THF)]_2$ which belongs to the well-known structure type of **85r**. Both compounds, $[(Me_2C_5H_3)_2Y(\mu\text{-H})]_3$ (hydrogen atoms could not be located) and $[(Me_2C_5H_3)_2Y(\mu\text{-H})(THF)]_2$ have been characterized by standard instrumental methods and by X-ray crystallography.[328]

Just as two methyl substituents on the cyclopentadienyl rings can decrease the coordination number of the central metal to eight, *tert*-butyl groups are even more effective in doing so. Thus the solvent-

Table 23. Spectroscopic and Other Data of Bis(pentamethylcyclopentadienyl)lanthanide Hydrides

compound	Ln		color, characterization, etc.
$(C_5Me_5)_2LnH$	Sc	**86a**	NMR; with THF: yellow,[265] NMR, IR[265,272]
	Y	**86b**	white, IR,[278] NMR;[274,278] with THF: white, NMR, IR,[278] reactions[734,739,740,742,746]
	La	**86c**	colorless, NMR, IR, D-deriv.[304]
	Ce	**86d**	green, NMR, IR,[273,284] D-deriv.[284]
	Nd	**86f**	blue green, NMR, IR,[304,362b] D-deriv.[304]
	Sm	**86h**	orange, X-ray, NMR, IR;[508] with THF: yellow, NMR,[403] reactions[742,746]
	Lu	**86r**	colorless, NMR,[304,359] IR, D-derivative[304,360]
$(C_5Me_5)_2Ln(\mu\text{-H})_2BMes_2$	Y		yellow, NMR[742]
	Sm		red, NMR[742]
$(C_5Me_5)_2Ln(\mu\text{-H})(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)$	Y		(with C_6H_6): red, NMR, IR,[493,543] X-ray[493]
	Sm		brown, X-ray, NMR, IR, magn. d.[403]

Table 24. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Hydrides Containing Other Substituted Cyclopentadienyl Ligands

compound	Ln		color, characterization, etc.
$(MeC_5H_4)_2LnH$	Y		complex with THF: colorless, X-ray, IR, D-deriv.,[314] NMR;[178,314] with py: yellow, NMR[435]
	Er		IR;[2i] complex with THF: pink, X-ray, IR[314]
	Lu		complex with THF: colorless, NMR, IR[314]
$[(MeC_5H_4)_2LnH]_2[(MeC_5H_4)_2ZrH]H$	Y		colorless, NMR, IR, melt./dec.[102]
$(^tBuC_5H_4)_2LnBH_4$	Sm		yellow green[248]
$[(^tBuC_5H_4)_2Ln]_2H(AlH_4\cdot tmed)$	Sm		green, X-ray[247]
$(^tBuC_5H_4)_2LnH(AlH_3\cdot THF)$	Sm		X-ray[544]
$[MeO(CH_2)_2C_5H_4]_2LnH$	Y		white,[545,725] X-ray, MS,[725] NMR, IR[545,725]
	La		white, NMR, MS, IR[725]
	Pr		yellow, IR, MS[725]
	Ho		pale brown[725]
$[MeO(CH_2)_2C_5H_4]_2LnBH_4$	Y		X-ray, NMR, IR[545]
	La		colorless, MS, NMR, IR, melt./dec.[546]
	Pr		green, X-ray, MS, IR, melt./dec.[546]
	Nd		blue, X-ray, MS, IR, melt./dec.[546]
	Sm		yellow, MS, IR, melt./dec.[546]
	Gd		colorless, MS, IR, melt./dec.[546]
$[MeO(CH_2)_2C_5H_4]_2LnAlH_4$	Y		white, NMR, IR[545]
$(Me_2C_5H_3)_2LnH$	Y		X-ray, NMR, IR, melt./dec., complex with THF: colorless, X-ray, NMR, IR[328]
$[Li(THF)_4]\{[(Me_2C_5H_3)_2LnH]_3H\}$	Y		NMR, IR[328]
$(^tBu_2C_5H_3)_2LnH$	Ce		X-ray[248]
	Sm		X-ray[248]
	Lu		colorless, X-ray[334]
$(^tBu_2C_5H_3)_2LnBH_4$	Ce		orange, X-ray[329]
	Sm		yellow orange, X-ray[248]
$(^tBu_2C_5H_3)_2LnAlH_4$	Lu		white; complex with THF: yellow[337]
$[(Me_3Si)_2C_5H_3]_2LnBH_4$	Sc		white, X-ray, NMR, IR, melt./dec.[547]
	Y		complex with THF: white, IR, melt./dec.[547]
	La		complex with THF: white, IR, melt./dec.[547]
	Pr		complex with THF: green, IR, melt./dec.[547]
	Nd		complex with THF: blue violet, IR, melt./dec.[547]
	Sm		complex with THF: yellow, IR, melt./dec.[547]
	Yb		complex with THF: maroon, IR, melt./dec.[547]
$[(Me_3Si)_2C_5H_3]_2LnBPh_4$	Ce		complex with NCMe, DME: yellow brown, NMR, IR[313]
$[(C_5H_4(CH_2)_3C_5H_4]LnH$	Y	**87b**	complex with THF: white, NMR, IR, MS, melt./dec.[548]
	Dy	**87m**	complex with THF: yellow, IR, MS, melt./dec.[548]
	Er	**87o**	complex with THF: pink, IR, MS, melt./dec.[548]
	Lu	**87r**	complex with THF: white, NMR, IR, MS, melt./dec.[548]
$[O(CH_2CH_2C_5H_4)_2]LnH$	Y		colorless, NMR, MS, IR, D-deriv.[549]
	Gd		white, MS, IR[549]
	Er		orange, MS, IR[549]
	Yb		red, MS, IR[549]
	Lu		colorless, NMR, MS, IR, D-deriv.[549]
$[Me_2Si(C_5H_4)_2]LnH$	Y		complex with THF: MS[550]
$\{[Me_2Si(C_5H_4)_2]_2Ln\}_2(\mu\text{-}H)(\mu\text{-}Cl)$	Yb		complex with 2THF: reddish, X-ray, MS[550]
$[Me_2Si(C_5H_3{}^tBu)_2]LnH$	Sc		NMR,[351] catalysis[732]
$[Me_2Si(C_5H_2(^tBu)SiMe_3)]LnH$	Y		colorless, catalysis[686]
$[Me_2Si(C_5Me_4)_2]LnH$	Sc		complex with PMe_3: catalysis[352,518,747]
	Nd		green, NMR, IR, D-deriv.,[362a] catalysis[361,362a]
	Sm		orange, NMR, IR, D-deriv.,[362a] catalysis[361,362a]
	Lu		colorless, NMR, IR, D-deriv.,[362a] catalysis[361,362a]
$(C_5Me_4CH_2C_6H_4Me\text{-}3)(C_5Me_4CH_2Ph)LnH$	Sc		NMR[363]
$[Me_2Si(C_5H_4)(C_5Me_4)]LnH$	Lu		colorless, NMR, IR[354]
$\{Me_2Si(C_5Me_4)[C_5H_3(C_{10}H_{18})]\}LnH$ ($C_{10}H_{18}$ = (+)-neomenthyl)	Y		NMR[726]
$[Et_2Si(C_5H_4)(C_5Me_4)]LnH$	Y		colorless, NMR, IR[354]
	Lu		colorless, X-ray, NMR, IR, D-deriv.[354]
$\{[Et_2Si(C_5H_4)(C_5Me_4)]Ln\}_2(\mu\text{-}H)(\mu\text{-}Et)$	Y		NMR, D-deriv.[354]
	Lu		white, X-ray, NMR, IR, D-deriv.[354]
$\{[Et_2Si(C_5H_4)(C_5Me_4)]Ln\}_2(\mu\text{-}H)(\mu\text{-}Pr)$	Y		white, NMR, IR[354]
	Lu		off-white[354]
$\{[Et_2Si(C_5H_4)(C_5Me_4)]Ln\}_2(\mu\text{-}H)(\mu\text{-}C_6H_{13})$	Lu		off-white, NMR, IR[354]

free dimers $[(^tBu_2C_5H_3)_2LnH]_2$ were obtained as outlined in eq 154:

$$[(^tBu_2C_5H_3)_2LnCl]_2 + 2MAlH_4 \xrightarrow[-2MCl]{LB} [(^tBu_2C_5H_3)_2LnH]_2 + 2AlH_3(LB)_n \quad (154)$$

Ln = Lu:[334] M = Li, LB = Et_2O

Ln = Ce, Sm:[248] M = Na, LB = NEt_3

The shielding effect of the *tert*-butyl groups is reported to be so pronounced that the intermediate $[(^tBu_2C_5H_3)_2LuH]_2(AlH_3\cdot OEt_2)_2$ is not observed. In addition, crystals of $[(^tBu_2C_5H_3)_2LuH]_2$ exhibit enhanced stability against oxygen and moisture so that they do not deteriorate on exposure to air within a 3 to 5 min period—a behavior that is completely unknown for all hydride complexes discussed so far. The X-ray diffraction study revealed a crowded dimer

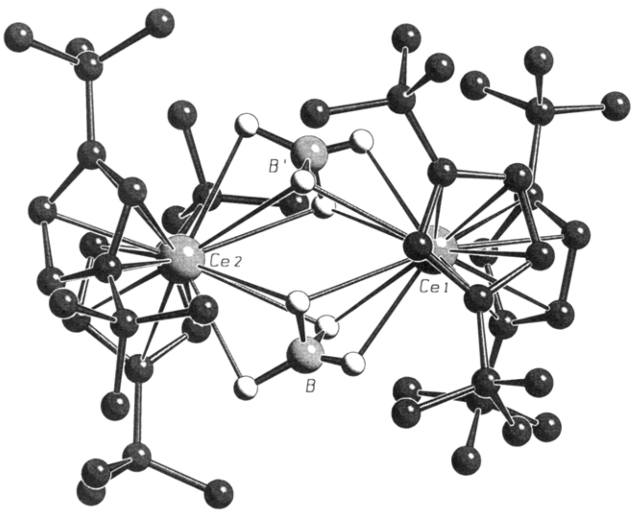


Figure 116. Structure of $[(^tBu_2C_5H_3)_2Ce(BH_4)]_2$ in the crystal.[329]

with d(Lu−H) = 232(1) and 227(1) pm.[334] The Sm species can also be obtained by redox reaction of the divalent samarocene $(^tBu_2C_5H_3)_2Sm(THF)$ with $AlH_3{\cdot}NEt_3$.[248]

A bis(di-*tert*-butylcyclopentadienyl)ligand system also supports the formation of solvent-free dimeric tetrahydroborate complexes.[248,329] The structure of $[(^tBu_2C_5H_3)_2Ce(BH_4)]_2$ (Figure 116) reveals that the BH_4^- anion acts as a bridge between two Ce^{3+} ions in a μ-η^3:η^3 fashion.[329] Interestingly, $[(^tBu_2C_5H_3)_2Ce(BH_4)]_2$ is isostructural to $[(^tBu_2C_5H_3)_2CeCl]_2$[329] and in fact the Ce⋯B separation (293(2) pm) is in agreement with the Ce−Cl bond distance of 289.8(4) pm in the chloride suggesting that a BH_4^- ion occupies roughly the same size as a Cl^- anion. A further increase in steric bulk of the Cp substituents leads to monomeric tetrahydroborates[547] as shown by the crystal structure of bis[(trimethylsilyl)cyclopentadienyl]scandium tetrahydroborate $[(Me_3Si)_2C_5H_3]_2ScBH_4$.

The use of a substituted cyclopentadienyl system with a pending ether function has also enabled isolation of monomeric tetrahydroborates $[MeO(CH_2)_2C_5H_4]_2LnBH_4$ (Ln = Y,[545] La, Pr, Nd, Sm, Gd[546]). Single-crystal X-ray structures of the Y,[545] Pr, and Nd[546] derivatives support intramolecular stabilization of the rare earth element by lone pair of the oxygen atoms.

The chemistry of tetrahydroaluminates seems to be dominated by bimetallic species; some recent examples include the dimers $[(^tBuC_5H_4)_2SmH(AlH_3{\cdot}THF)]_2$,[544] $[(^tBuC_5H_4)_2Sm]_2H(AlH_4{\cdot}tmed)$,[247] and $[(^tBu_2C_5H_3)_2LnAlH_4(LB)]_2$[337] as well as monomeric $[MeO(CH_2)_2C_5H_4]_2YAlH_4$.[545] Treatment of the latter compound with triethylamine at 50 °C leads to elimination of AlH_3 and formation of the symmetric dimer $\{[MeO(CH_2)_2C_5H_4]_2Y(\mu\text{-}H)\}_2$ in moderate yield.[545]

There has been considerable interest in organolanthanide hydrides with bridged ancillary π-ligands whose structural features differ in both, length of the ring-bridging chain and in the nature and number of further substituents attached to the cyclopentadienyl ring. Butyl complexes of the type $[C_5H_4(CH_2)_3C_5H_4]Ln^tBu(THF)$ are useful starting materials and readily undergo hydrogenolysis of the Ln−C bond generating the desired hydrides **87** as shown in eq 155:[548,551]

$$2[C_5H_4(CH_2)_3C_5H_4]Ln^tBu(THF) \xrightarrow[-2HCMe_3]{H_2} \underset{\mathbf{87}}{\{[C_5H_4(CH_2)_3C_5H_4]LnH(THF)\}_2} \quad (155)$$

Ln = Y (**87b**), Dy (**87m**), Er (**87o**), Lu (**87r**)

Although no structural data are available there is mass and NMR spectroscopic evidence that the dimeric formulation is correct.[548] Since a 1,3-propanediyl chain does not impose severe steric constraints on the complex, the structure of **87** should be similar to that of $[(C_5H_5)_2LuH(THF)]_2$[149,254,532] (**85r**). Recently, however, it was shown that chelating π-ligands can convert into metal-bridging ones after dimerization (*vide infra*).[354] Complexes **87** were obtained in low to moderate yield (18−30%). They are soluble in THF and insoluble in aliphatic and aromatic solvents. These hydrides are capable of hydrogenating olefins such as 1-hexene catalytically.[548] Similar results, as far as the hydrogenation of olefins is concerned, were obtained with 1,1′-(3-oxapentamethylene)dicyclopentadienyl lanthanide hydride complexes which were prepared from $[O(CH_2CH_2C_5H_4)_2]LnCl$ and sodium hydride in THF (eq 156).[549]

$$2[O(CH_2CH_2C_5H_4)_2]LnCl + 2NaH \xrightarrow[-2NaCl]{toluene} \{[O(CH_2CH_2C_5H_4)_2]LnH\}_2 \quad (156)$$

Ln = Y, Gd, Er, Yb, Lu

The complexes were characterized by elemental analyses and NMR and infrared spectroscopy. Unfortunately, the deuterated species failed to show Ln−D absorption bands characteristically shifted to lower wavenumbers, so that no assignments of bands could be made. This was explained by accidental overlap of bands or more likely by H−D exchange.[549]

In the hope of finding catalysts with enhanced reactivity, singly heteroatom bridged complexes of the types $\{[Me_2Si(C_5H_3{}^tBu)_2]LnH\}_2$,[351,352] $\{[Me_2Si(C_5Me_4)_2]LnH\}_2$ (Ln = Nd, Sm, Lu),[361,362a] $\{[Me_2Si(C_5H_4)(C_5Me_4)]LnH\}_2$, and $\{[Et_2Si(C_5H_4)(C_5Me_4)]LnH\}_2$ (Ln = Y and Lu)[354] have been synthesized and intensively investigated. These complexes were expected to be less sterically crowded than their bis(pentamethylcyclopentadienyl) analogues and as a result, may show higher rates of reaction and turnover numbers. Comparisons across the lanthanide series between $[(C_5Me_5)_2LnH]_2$ (**86**) and $\{[Me_2Si(C_5Me_4)_2]LnH\}_2$ have been made and published in a series of three papers.[304,361,362a] The solvent-free hydrides are best prepared by hydrogenolysis of the corresponding bis(trimethylsilyl)methyl derivatives **79** as outlined in eq 157:[362a]

$$\underset{\mathbf{79}}{2[Me_2Si(C_5Me_4)_2Ln]CH(SiMe_3)_2} + 2H_2 \xrightarrow[-2CH_2(SiMe_3)_2]{pentane} \{[Me_2Si(C_5Me_4)_2]LnH\}_2 \quad (157)$$

Ln = Nd, Sm, Lu

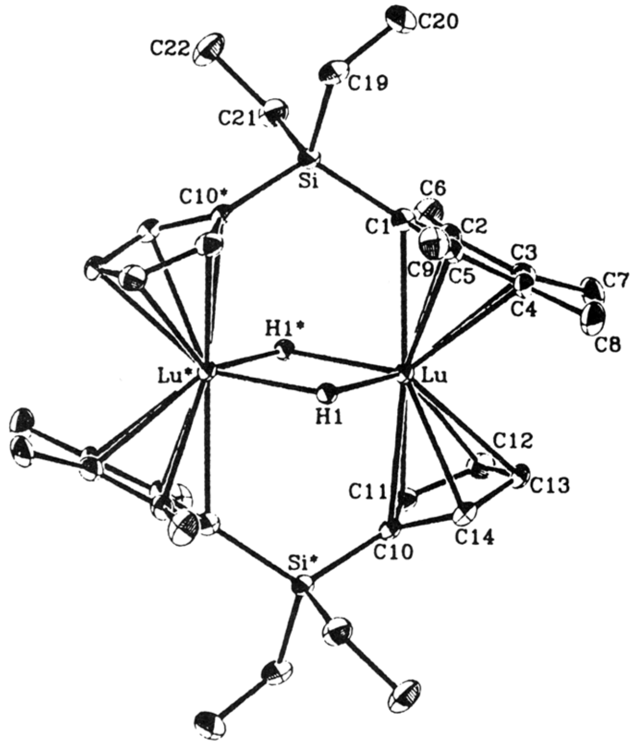


Figure 117. Structure of $\{[Et_2Si(C_5H_4)(C_5Me_4)]LuH\}_2$ in the crystal.[354] (Reprinted from ref 354. Copyright 1990 American Chemical Society.)

These dimeric hydrides (by cryoscopy and mass spectrometry) can be collected as microcrystalline materials which are reported to be markedly less soluble in aliphatic solvents than their nonbridged pentamethylcyclopentadienyl analogues **86**. Thus, ethylene polymerization suffers from catalyst poisoning caused by trace impurities, but yields of propylene polymerization are roughly 10 times those catalyzed by **86**. Similarly, the insertion of bulky olefins such as cyclohexene into Ln−H bonds is sensitive to the ligand environment and was shown to be the rate-limiting factor in the homogeneous hydrogenation. Thus, the catalyst offering the most accessible surface area reacts fastest. However, it would be misleading to assume that enhanced reactivity of a catalyst always goes along with a reduction in steric bulk of the metal supporting π-ligand system. By contrast, hydrogenolysis of small olefins such as 1-hexene is fastest when catalyzed with **86** which offers less space to bind the hexyl group and possesses the weakest Ln−C bond. The reversed behavior here reflects the fact that α-olefin insertion for small substrates is fast and instead the cleavage of the Ln−C bond by molecular hydrogen becomes the rate limiting step. Hence, the complex with the weakest Ln−C bond reacts fastest.[304,361,362a]

A further extension of the concept to enhance reactivity, by reducing steric demand of the ligands attached to the metal ion, consists in the utilization of partially substituted or completely unsubstituted ring-bridged ligands of the types $[R_2Si(C_5H_4)(C_5Me_4)]^{2-}$ (R = Me, Et)[354] and $[Me_2Si(C_5H_4)_2]^{2-}$.[550] Unfortunately, the attempt turned out to be counterproductive at least to some extent. The hydrogenolysis of $[R_2Si(C_5H_4)(C_5Me_4)]LnCH(SiMe_3)_2$ (R = Me (**81**), Et (**82**)) led to dimeric hydride complexes $\{[R_2Si(C_5H_4)(C_5Me_4)]LnH\}_2$ (Ln = Y, Lu) with rearranged π-ligands (μ-η^5:η^5), effectively preventing the complex from dissociation. $\{[Et_2Si(C_5H_4)(C_5Me_4)]LuH\}_2$ has been structurally characterized and consists of a centrosymmetric dimer as shown in Figure 117.[354]

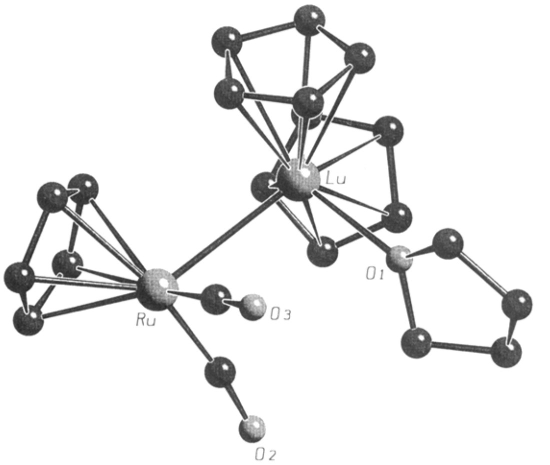


Figure 118. Structure of $(THF)(C_5H_5)_2LuRu(CO)_2(C_5H_5)$ (**88r**) in the crystal.[146c,256]

The comparatively slow hydrogenolysis of **81** and **82**, respectively, is remarkable in that it constitutes a rare example of an observable process in which a distinctly monomeric species with a chelating ligand changes into a dimer with two metal-bridging ligands. Despite the noticeably depressed reactivity, olefins such as ethylene, propylene, and 1-hexene insert into one of the LnHLn bonds of $\{[Et_2Si(C_5H_4)(C_5Me_4)]LnH\}_2$ (Ln = Y, Lu) yielding unsymmetrical compounds $\{[Et_2Si(C_5Me_4)(C_5H_4)]Ln\}_2(\mu\text{-H})(\mu\text{-R})$ (R = Et, Pr, C_6H_{13}).[354] Very recently, synthesis of a similar unsymmetrically bridged Yb−chloro−hydride has been reported which crystallizes from THF as the solvent−adduct $\{[Me_2Si(C_5H_4)_2]_2Yb(THF)\}_2(\mu\text{-H})(\mu\text{-Cl})$ with two nonchelating, metal-bridging $[Me_2Si(C_5H_4)_2]^{2-}$ ligand systems.[550]

6. Bis(cyclopentadienyl) Rare Earth Complexes with Rare Earth to Other Element Bonds

A direct bond between a rare earth ion and a transition metal atom was first reported in 1990.[256] Metathesis of $Na[(C_5H_5)Ru(CO)_2]$ and $(C_5H_5)_2LuCl(THF)$ (**21r**) in THF results with 62% yield in the formation of a molecular complex (eq 158) which composition of $(THF)(C_5H_5)_2LuRu(CO)_2(C_5H_5)$ (**88r**) was determined by an X-ray structure investigation (Figure 118).[146c,256]

$$\underset{\mathbf{21r}}{(C_5H_5)_2LuCl(THF)} + Na[(C_5H_5)Ru(CO)_2] \xrightarrow{THF/20\ °C} \underset{\mathbf{88r}}{(THF)(C_5H_5)_2LuRu(CO)_2(C_5H_5)} + NaCl \quad (158)$$

This structure is remarkable in both the fact that there is a direct bond between Lu and Ru (d(Lu−Ru) = 295.5(2) pm) and the observation that both carbonyl groups are strictly bonded to Ru in a terminal fashion. This contrasts with a number of bimetallic lanthanide complexes with anionic transition metal carbonyl fragments in which CO ligands always serve as a bridging isocarbonyl group. In these species the partially negatively charged oxygen atoms constitute a hard Lewis base which forms

Table 25. Spectroscopic and Other Data of Bis(cyclopentadienyl)lanthanide Complexes Containing Rare Earth to Other Element Bonds

compound	Ln		color, characterization, etc.
$(C_5H_5)_2LnRu(CO)_2(C_5H_5)$	La	**88c**	complex with THF: NMR[146c]
	Lu	**88r**	complex with THF: colorless, NMR, IR, melt./dec.,[146c] X-ray[146c,256]
$(C_5Me_5)_2LnRu(CO)_2(C_5H_5)$	Lu		colorless, NMR, IR, melt./dec.[146c]
$[(1,3\text{-}Me_3Si)_2C_5H_3]_2LnRu(CO)_2(C_5H_5)$	Lu		complex with THF: colorless, NMR, IR, melt./dec.[146c]

Table 26. Spectroscopic and Other Data of Cationic Bis(cyclopentadienyl)lanthanide Complexes

compound	Ln	color, characterization, etc.
$[(C_5Me_5)_2Ln][BPh_4]$	Ce	complex with 2THF: orange, NMR, IR; with $2SC_4H_8$: blue green, X-ray, NMR, IR[552]
	Sm	complex with 2THF: red orange, X-ray, NMR, IR, magn. d.;[208] with THF, H_2NNH_2: X-ray, NMR[445]
$\{[(1,3\text{-}Me_3Si)_2C_5H_3]_2Ln\}[BPh_4]$	La	complex with DME, NCMe (+0.5DME): colorless, X-ray, NMR[313]
	Ce	complex with DME, NCMe (+0.5DME): yellow brown, IR, NMR[313]

strong bonds with the lanthanide ion as dicussed in detail within the section on bis(cyclopentadienyl) rare earth chalcogenides (IIB2a).

Very recently, three further heterobimetallic bis(cyclopentadienyl) species containing a direct lanthanide–metal bond have been published:[146c] $(C_5Me_5)_2LuRu(CO)_2(C_5H_5)$, $(THF)[(1,3\text{-}Me_3Si)_2C_5H_3]_2LuRu(CO)_2(C_5H_5)$, and the lanthanum complex $(THF)(C_5H_5)_2LaRu(CO)_2(C_5H_5)$ (**88c**). For both the Lu derivatives the synthetic pattern is based on metathetical reactions similar to those in eq 158. The starting materials are the salt $Na[(C_5H_5)Ru(CO)_2]$ and common rare earth chlorides $(C_5Me_5)_2Lu(\mu\text{-}Cl)_2Na(THF)_2$ and $\{[(1,3\text{-}Me_3Si)_2C_5H_3]_2Lu(\mu\text{-}Cl)\}_2$ (**29r**), respectively. Equimolar reactions are carried out in THF at 20 °C and both compounds can be isolated after work-up procedures as microcrystalline, extremely air- and moisture-sensitive solids in yields of more than 50%. The lanthanum analogue to **88r** has been derived from ^{139}La-NMR spectroscopy as one disproportionation product of the unstable mono(cyclopentadienyl) complex $(THF)_2(C_5H_5)(I)LaRu(CO)_2(C_5H_5)$.

Table 25 summarizes some important data of bis(cyclopentadienyl) lanthanide complexes which contain a direct lanthanide to other element bond.

7. Cationic Bis(cyclopentadienyl) Rare Earth Complexes

The steadily growing interest in the development of cationic compounds of the rare earth elements is due to the assumption that cationic species are of importance in olefin polymerization processes by Ziegler–Natta and Kaminsky type catalysts. However, bis(cyclopentadienyl)lanthanides with a rare earth metal in the cation can still be counted on one's fingers (Table 26).

With exception of $[(C_5Me_5)_2Ce(THF)_2][BPh_4]$[552] and $\{[(1,3\text{-}Me_3Si)_2C_5H_3]_2Ce(DME)(NCMe)\}[BPh_4]\cdot0.5(DME)$[313] all of them have been characterized by single-crystal X-ray structure analysis.[208,313,445,552] It is striking that in all cases the counterion consists of the bulky, unreactive tetraphenylborate anion; in addition no unsubstituted cyclopentadienyl systems have been reported to be part of such cationic bis(cyclopentadienyl)lanthanides. The cerium complex $[(C_5Me_5)_2Ce(THF)_2][BPh_4]$ as well as its tetrahydrothiophene derivative have been prepared by protolysis of the lanthanide alkyl $(C_5Me_5)_2CeCH(SiMe_3)_2$ with triethylammonium tetraphenylborate in THF and tetrahydrothiophene, respectively, at room temperature according to eq 159:[552]

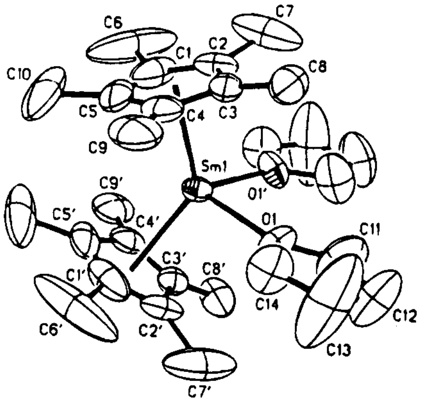


Figure 119. Structure of $[(C_5Me_5)_2Sm(THF)_2]^+$ in the crystal.[208] (Reprinted from ref 208. Copyright 1990 American Chemical Society.)

$$(C_5Me_5)_2CeCH(SiMe_3)_2 + (HNEt_3)BPh_4 \xrightarrow{LB} [(C_5Me_5)_2Ce(LB)_2][BPh_4] + CH_2(SiMe_3)_2 + NEt_3 \quad (159)$$

$LB = THF, SC_4H_8$

The samarium analogue, $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$, is formed in high yield on oxidation reaction of the strong reductant $(C_5Me_5)_2Sm(THF)_2$ with $AgBPh_4$ in THF. The structure of the cation, which is depicted in Figure 119, possesses an overall geometry similar to that of divalent, neutral $(C_5Me_5)_2Sm(THF)_2$.[208] Reaction of $[(C_5Me_5)_2(THF)Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2H_2)$ with 2 equiv of $(HNEt_3)BPh_4$ in THF affords under expulsion of triethylamine the well-known THF adduct $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ and the hydrazine complex $[(C_5Me_5)_2Sm(\eta^2\text{-}N_2H_4)(THF)][BPh_4]$.[445]

The lanthanide iodide $[(1,3\text{-}Me_3Si)_2C_5H_3]_2LnI(NCMe)_2$ provides a good precursor for synthesis of the ionic mixed DME/NCMe adducts $\{[(1,3\text{-}Me_3Si)_2C_5H_3]_2Ln(DME)(NCMe)\}[BPh_4]\cdot0.5DME$ (Ln = Ce, La); it reacts smoothly with suspensions of $AgBPh_4$ in THF to give the desired cationic compounds.[313]

C. Mono(cyclopentadienyl) Rare Earth Complexes

The previously reviewed chemistry deals exclusively with metallorganic compounds of trivalent rare earths made up of either unsubstituted, permethyl-

Table 27. Spectroscopic and Other Data of Mono(cyclopentadienyl)lanthanide Halides and Pseudohalides

compound	Ln		color, characterization, etc.
$(C_5H_5)LnCl_2$	Y	**89b**	colorless, X-ray[748]
	La	**89c**	complex with 3THF: melt./dec.[25]
	Ce	**89d**	yellow green; complex with THF: white[100]
	Pr	**89e**	light green, IR; complex with HCl: light green; with THF: yellowish green; with 2THF: yellowish green; with 2THF, HCl: green[100]
	Nd	**89f**	reddish; complex with HCl: light purple; with THF: purple; with 2 THF: purple;[100] with 3THF: purple, IR, elec. d.;[100] X-ray;[145,553] with THF, HCl: purple; with 2THF, HCl: purple; with 3THF, HCl: purple[100]
	Sm	**89h**	complex with 3THF: beige,[554] melt./dec.[25,554]
	Eu	**89i**	complex with 2THF: melt./dec.;[25] with 3THF: purple,[554] X-ray, Möβb.,[692] magn. d., melt./dec.[554]
	Gd	**89k**	elec. d.; complex with 3THF: elec. d.,[81] lavender, magn. d., melt./dec.[554]
	Dy	**89m**	complex with 3THF: colorless, magn. d., melt./dec.[554]
	Ho	**89n**	complex with 3THF: yellow, melt./dec.[554]
	Er	**89o**	complex with 3THF: pink, melt./dec.[554] X-ray,[555] magn. d.[250,554]
	Tm	**89p**	complex with 3THF: melt./dec.;[25] with 4THF: melt./dec.[556]
	Yb	**89q**	complex with THF: yellow, NMR, UV;[364] with 3THF: orange, magn. d.,[554] X-ray,[261,364] NMR,[364] melt./dec.[25,554]
	Lu	**89r**	complex with 3THF: colorless, melt./dec.[554]
$[Li(THF)_2]_2(\mu\text{-}Cl)_4[(C_5H_5)Ln(THF)]$	La		X-ray,[145,557,558] IR[559]
	Pr		X-ray[561]
	Nd		X-ray,[145,557–559] IR,[559,560] NMR[560]
$(C_5H_5)LnCl(THF)_2(\mu\text{-}Cl)_2LnCl_2(THF)_3$	Sm		yellow green, X-ray[562]
$(C_5H_5)LnBr_2$	Yb		complex with 3THF: X-ray[261]
$(C_5H_5)Ln(NCO)_2$	Eu		complex with 3THF: Möβb.[692]
$(C_5H_5)Ln(NCS)_2$	Eu		complex with 3THF: Möβb.[692]

ated, or partly substituted tris- and bis(cyclopentadienyl)lanthanide species. The presence of two or even three of these more or less bulky aromatic ligand systems results in enhancement of stability; however, the steric congestion around the metal center results in a significant reduction in reactivity. Nevertheless, the reactivity of bis(cyclopentadienyl)lanthanide derivatives with alkyl bonds is extensive. In order to relax the steric constraint, interest in the spatial less-demanding mono(cyclopentadienyl)lanthanide unit grows steadily, particularly since organolanthanides containing only one cyclopentadienyl group on the rare earth metal center results in not only one, but two highly reactive bonds.

1. Mono(cyclopentadienyl) Rare Earth Halides

Due to the broad area of application which is generally offered by metal halides synthesis of halides of mono(cyclopentadienyl)lanthanide complexes are the key starting materials. The synthetic routes are outlined below.

a. Cyclopentadienyl Derivatives. Rare earth organyls with only one cyclopentadienyl ligand were first described in 1963 by Manastyrskyj et al.,[554] who succeeded in preparing the chloro complexes by three different synthetic routes (eqs 160–162). A short summary of known mono(cyclopentadienyl)lanthanide halides is given in Table 27.

$$LnCl_3 + NaC_5H_5 \xrightarrow{THF} \underset{\mathbf{89}}{(C_5H_5)LnCl_2(THF)_3} + NaCl \quad (160)$$

Ln = Sm (**89h**), Eu (**89i**), Gd (**89k**), Dy (**89m**), Ho (**89n**), Er (**89o**), Lu (**89r**)

$$\underset{\mathbf{1o}}{(C_5H_5)_3Er} + 2ErCl_3 \xrightarrow{THF} \underset{\mathbf{89o}}{3(C_5H_5)ErCl_2(THF)_3} \quad (161)$$

$$\underset{\mathbf{21q}}{(C_5H_5)_2YbCl(THF)} + HCl \xrightarrow{THF} \underset{\mathbf{89q}}{(C_5H_5)YbCl_2(THF)_3} + C_5H_6 \quad (162)$$

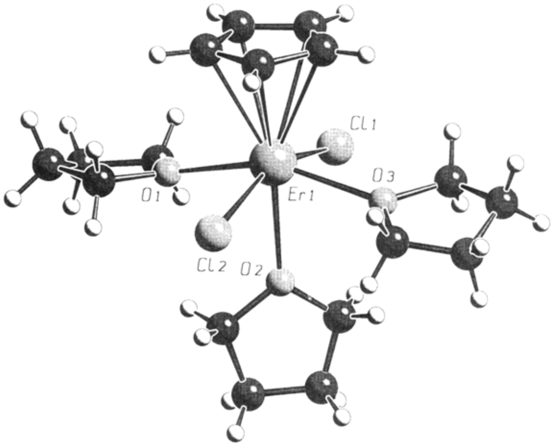


Figure 120. Structure of $(C_5H_5)ErCl_2(THF)_3$ (**89o**) in the crystal.[555]

About 20 years later, syntheses of mono(cyclopentadienyl)dichloro compounds were reported for some lower rare earth elements.[100,103,151] They are accessible by reaction of the corresponding trichlorides with sodium cyclopentadienide in THF as both solvent free and with one to three solvent molecules in the coordination sphere: $(C_5H_5)LnCl_2(THF)_n$ (Ln = Ce, $n = 0, 1$; Pr, $n = 0, 1, 2$; Nd, $n = 0, 1, 2, 3$ (**89f**)). In addition the hydrogen chloride derivatives $(C_5H_5)LnCl_2(HCl)(THF)_n$ (Ln = Pr, $n = 0, 2$; Nd, $n = 0, 1, 2, 3$) have been prepared, using appropriate lanthanide chlorides mixed with hydrogen chloride in THF.[100] The first reports on the yttrium complex $(C_5H_5)YCl_2(THF)_3$ (**89b**) came from the work of Jamerson et al.[563] During extensive studies whether 4f orbitals of organolanthanide compounds display covalent bonding the X-ray photoelectron spectrum of $(C_5H_5)GdCl_2$ was recorded.[81]

X-ray crystallographic data, for the organolanthanide chlorides and bromides $(C_5H_5)LnX_2(THF)_3$ (X = Cl, Ln = Nd (**89f**),[145,553] Er (**89o**) (Figure 120),[555]

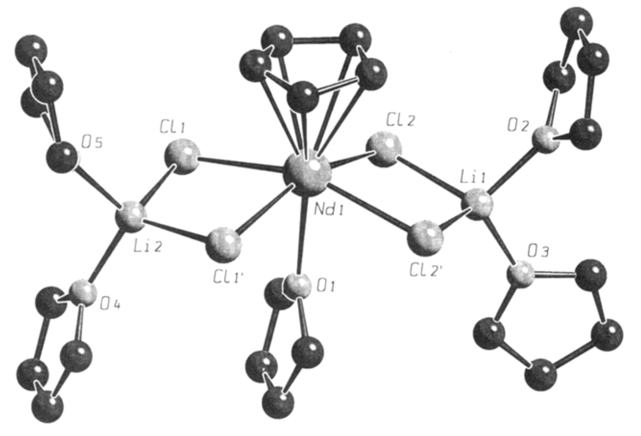


Figure 121. Structure of $[Li(THF)_2]_2(\mu\text{-}Cl)_4[(C_5H_5)Nd(THF)]$ in the crystal.[557-559]

Yb (**89q**);[261,364] X = Br, Ln = Yb[261]) show that these molecules are monomeric with a pseudo-octahedral coordination geometry around the rare earth metal, considering the η^5-bonded cyclopentadienyl ligand as occupying a single octahedral site. Exposure of **89q** to high vacuum results in the formation of the mono-THF adduct $(C_5H_5)YbCl_2(THF)$.[364]

In the early 1980s, zerovalent lanthanides activated by amalgamation were shown to be useful starting materials in the synthesis of mono(cyclopentadienyl)dichlorolanthanide THF adducts (eq 163):[25,556]

$$5Ln + 3HgCl_2 \xrightarrow{THF} 3Ln/Hg + 2LnCl_3\cdot n(THF) \xrightarrow{Hg(C_5H_5)_2} \underset{\mathbf{89}}{2(C_5H_5)LnCl_2(THF)_n} \qquad (163)$$

Ln = La, Sm, Eu, Tm, Yb; $n = 2, 3, 4$

A completely new structural type was discovered in 1987 for the light rare earths lanthanum and neodymium.[557] Reaction of $LnCl_3\cdot n(LiCl)\cdot n(THF)$ with one equivalent of NaC_5H_5 yielded $[Li(THF)_2]_2(\mu\text{-}Cl)_4[(C_5H_5)Ln(THF)]$ (Ln = La, Nd (Figure 121)), in which the pseudo-octahedral geometry is achieved by coordination to an η^5-cyclopentadienyl group which is *trans* to tetrahydrofuran and the two *cis* sites are filled by $(THF)_2Li(\mu\text{-}Cl)_2$, forming the, by now, common $Ln(\mu\text{-}Cl)_2Li$ unit.[145,557-559] Recently, praseodymium was shown to form a tetrachloride with a similar structure.[561]

In contrast, addition of NaC_5H_5 to a THF solution of pure samarium trichloride in the stoichiometrical ratio 0.6:1 generated the binuclear, mono(cyclopentadienyl)samarium species $(C_5H_5)SmCl(THF)_2(\mu\text{-}Cl)_2SmCl_2(THF)_3$ (Figure 122). In this complex, samarium is at the center of a pseudo-octahedron of which two positions are occupied by bridging chlorine atoms, forming the connection between the other pentagonal–bipyramidal-coordinated samarium atom.[562] The structure of $(C_5H_5)LnCl_2(THF)(\mu\text{-}Cl)_2Li(THF)_4$ has been mentioned, although no details are available.[151]

b. Pentamethylcyclopentadienyl Derivatives. With the isolation of "$Li[(C_5Me_5)YbI_3](Et_2O)_2$", suggested to have the structure shown in eq 164, Watson first introduced in 1980 the pentamethylcyclopentadienyl anion into the mono(cylcopentadienyl) chemistry of trivalent rare earths. Stirring for at least a further day afforded conversion to the bridged bis(pentamethylcyclopentadienyl)ytterbium iodide.[282,297]

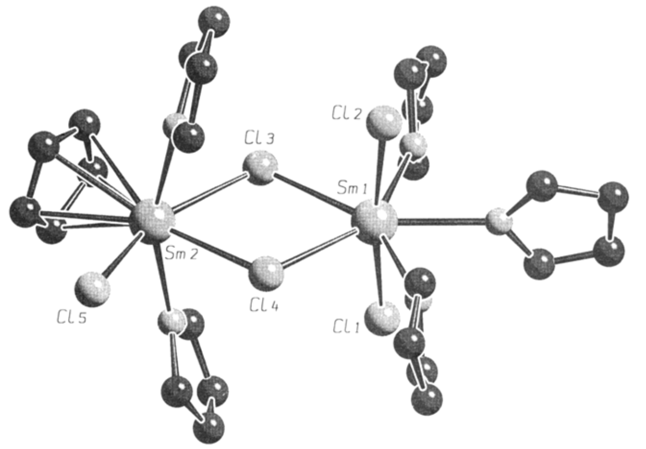
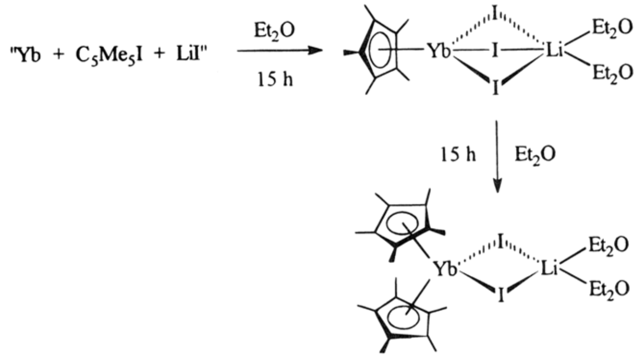


Figure 122. Structure of $(C_5H_5)SmCl(THF)_2(\mu\text{-}Cl)_2SmCl_2(THF)_3$ in the crystal.[562]



(164)

In the past decade, this series has been extended to those compounds shown in eq 165. Unfortunately, no single-crystal X-ray diffraction analysis has been performed but the structures are probably similar to the C_5H_5 derivatives.

$$LnX_3 + MC_5Me_5 \xrightarrow{S'} (C_5Me_5)LnX_3M(S')_n \qquad (165)$$

Ln = La, Ce: X = Cl, M = Li, S′ = THF ($n = 2$)[441]

Ln = Pr: X = Cl, M = Na, S′ = Et_2O ($n = 1$)[294,564]

Ln = Nd: X = Cl, M = Na, S′ = Et_2O ($n = 2$)[280]

Ln = Yb: X = I, M = Li, S′ = Et_2O ($n = 2$);[282,297]
X = Cl, M = Li, S′ = THF ($n = 1$)[282]

Ln = Lu: X = Cl, M = Li, S′ = Et_2O ($n = 1$);[282]
X = Cl, M = Na, S′ = Et_2O ($n = 2$);[564] X = Cl,
M = Na, S′ = $THF\cdot Et_2O$ ($n = 1$)[565,566]

The praseodymium derivative slowly liberates sodium chloride at room temperature over a period of several days to give $(C_5Me_5)PrCl_2(Et_2O)$.[564] Crystals, which were isolated by addition of dimethoxyethane to an equimolar mixture of $YbCl_3$ and KC_5Me_5 in

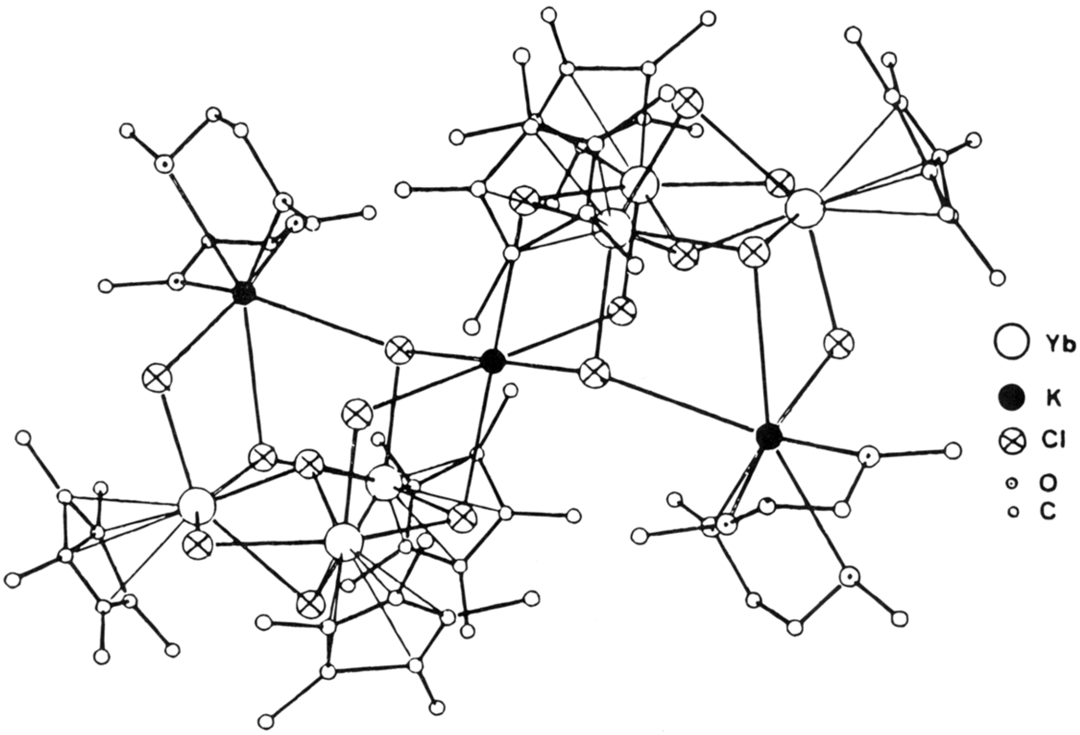


Figure 123. Structure of $\{\mathrm{K[((C_5Me_5)Yb)_3Cl_8K(DME)_2]_2}\}^-$ in the crystal.[564]

THF, have been identified as $\mathrm{[K(DME)_3]\{K[((C_5Me_5)Yb)_3Cl_8K(DME)_2]_2\}}$, shown in Figure 123.[564]

It has been shown that treatment of the tetravalent cerium complex $\mathrm{(C_5H_6N)_2CeCl_6}$ with a 4-fold molar excess of $\mathrm{LiC_5Me_5}$ did not afford an organo-$\mathrm{Ce^{IV}}$ species but rather the trivalent reduction product $\mathrm{(C_5Me_5)CeCl_3Li(py)_2}$.[567]

The reaction shown in eq 166 shows, once again, how the outcome of an experiment depends upon the lanthanide metal, the halide, and alkali metal metallocene. Using $\mathrm{KC_5Me_5}$ and $\mathrm{LaI_3(THF)}_x$ gives $\mathrm{(C_5Me_5)LnI_2(THF)_3}$ (Ln = La (**90c**), Ce (**90d**)) as shown.[306] It is assumed that the higher lattice energy of potassium iodide is the reason for the clean separation. Very recently, **90c** has been obtained in nearly quantitative yield from the exchange reaction of $\mathrm{LaI_3(THF)_3}$ and $\mathrm{C_5Me_5Tl}$ in THF.[146c]

$$\mathrm{LnI_3(THF)}_x + \mathrm{KC_5Me_5} \xrightarrow{\mathrm{THF}} \underset{\mathbf{90}}{\mathrm{(C_5Me_5)LnI_2(THF)_3}} + \mathrm{KI} \quad (166)$$

Ln = La (**90c**), Ce (**90d**)

The X-ray structure determination of yellow-green **90d** confirms its monomeric nature and the pseudo-octahedral mer,trans geometry (Figure 124),[306] which is analogous to that of the unsubstituted mono(cyclopentadienyl)lanthanide analogues $\mathrm{(C_5H_5)LnCl_2(THF)_3}$ (**89**) and $\mathrm{(C_5H_5)LnBr_2(THF)_3}$.

A convenient method for removal of the coordinated THF molecules of **90** is by its treatment with trimethylsilyl iodide, since cyclic ethers such as THF undergo ring opening by trimethylsilyl iodide. Thus, using the lanthanum species **89c** these ring opening reactions result in the formation of $\mathrm{Me_3SiO(CH_2)_4I}$ and base-free $\mathrm{[(C_5Me_5)LaI_2]}_n$.[566,568]

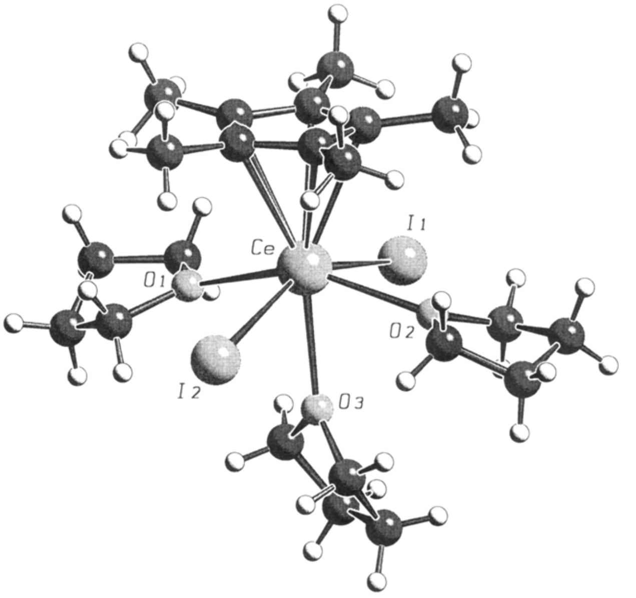


Figure 124. Structure of $\mathrm{(C_5Me_5)CeI_2(THF)_3}$ in the crystal.[306]

Prolonged exposure of **89** to vacuum leads to loss of some THF and conversion to the less soluble $[\mathrm{(C_5Me_5)LnI_2(THF)}_x]_y$ ($x < 1$).[306] Synthesis of the corresponding chloride species $[\mathrm{(C_5Me_5)CeCl_2(THF)}_x]_y$ has been accomplished from $\mathrm{CeCl_3}$ by conproportionation with $\mathrm{[Li(Et_2O)_2][(C_5Me_5)_2CeCl_2]}$ or by reaction with $\mathrm{MC_5Me_5}$ (M = K, Li). It was shown by cryoscopy that "$[\mathrm{(C_5Me_5)CeCl_2(THF)}_x]_y$" is monomeric in THF although it was suggested that it was oligomeric in other solvents. Thus, at room temperature the following monomer–oligomer equilibrium is proposed (eq 167):[306]

$$y\mathrm{(C_5Me_5)CeCl_2(THF)_3} \rightleftharpoons [\mathrm{(C_5Me_5)CeCl_2(THF)}_x]_y + y(3-x)\mathrm{THF} \quad (167)$$

Luminescence spectra have been determined for the cerium–THF species $\mathrm{(C_5Me_5)CeCl_2(THF)}_n$,[289] $\mathrm{(C_5Me_5)CeI_2(THF)_3}$ (**90d**),[61,289] or $[\mathrm{(C_5Me_5)CeI_2(THF)}_x]_y$,[61]

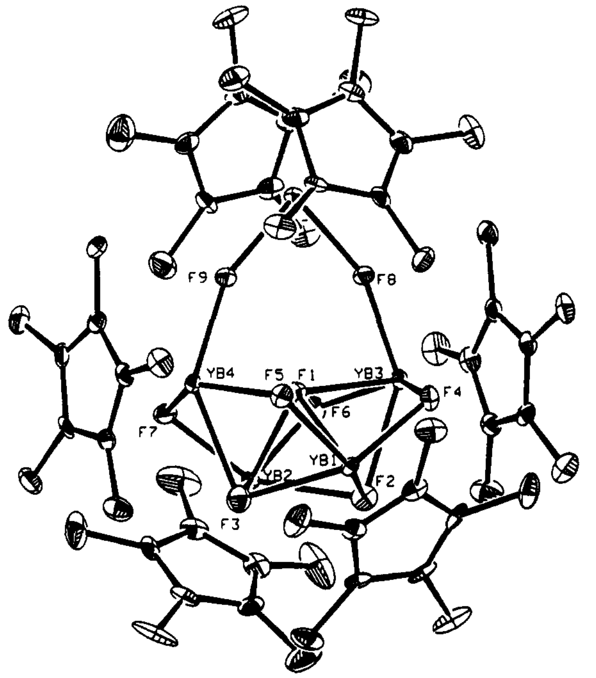


Figure 125. Structure of $[Yb_5(C_5Me_5)_6(\mu_4\text{-}F)(\mu_3\text{-}F)_2(\mu\text{-}F)_6]^-$ in the crystal.[264] (Reprinted from ref 264. Copyright 1990 American Chemical Society.)

and for the mono(pentamethylcyclopentadienyl)dichlororoceriumacetonitrile adduct $(C_5Me_5)CeI_2(NCMe)_n$.[289]

Two lutetium species, formulated as $(C_5Me_5)Lu_2Cl_5(THF)_2$ and $[(C_5Me_5)LuCl_2]_n$, have been mentioned as resulting from the workup of $(C_5Me_5)LuCl_3Na(THF{\cdot}Et_2O)$.[565] Likewise, by accident, the dichlorocerium pyridine adduct $(C_5Me_5)CeCl_2(py)$ was formed from $(C_5H_6N)_2CeCl_6$ and the 3 molar equiv of NaC_5Me_5.[567]

The first monomeric salt- and solvent-free mono(pentamethylcyclopentadienyl)lanthanide dihalide was prepared in 1986: A study of the one-electron oxidation of alkyl and aryl chlorides RCl with divalent $(C_5Me_5)_2Yb(Et_2O)$ lead to $(C_5Me_5)YbCl_2$.[286] It was postulated that the species $(C_5Me_5)_2YbR$ was formed by trapping of R$^\bullet$ by $(C_5Me_5)_2Yb$ which then, along with $(C_5Me_5)_2YbCl$, rearranges to give $(C_5Me_5)YbCl_2$, C_5Me_5R, and R–R. Additional studies on mechanisms of these atom-abstraction oxidative additions, as well as the extension to the corresponding fluoride, bromide, and iodide systems, including the independent synthesis of $(C_5Me_5)YbX_2$ (X = Cl, Br), are summarized in yet another article.[287] Similar reactions with samarium and europium species have also been dicussed.[285] The oxidation of divalent permethylytterbocene by titanium tetrachloride or trimethylchlorsilane gives $(C_5Me_5)YbCl_2$ or $[(C_5Me_5)YbCl]_n$, respectively.[301]

The formation of the X-ray crystallographically characterized pentaytterbium cluster $[Yb_5(C_5Me_5)_6(\mu_4\text{-}F)(\mu_3\text{-}F)_2(\mu_2\text{-}F)_6]$ (Figure 125) results from defluorination of the fluorocarbon perfluoro-2,4-dimethyl-3-ethylpent-2-ene by $(C_5Me_5)_2Yb(Et_2O)$.[264]

Recently, a totally different preparative pathway has been discovered by reacting 1 equiv of mono(pentamethylcyclopentadienyl)bis(acetylacetonato)scandium with 2 equiv of aluminum trichloride in toluene. Transfer of the acetylacetonato anions to aluminum generates oligomeric $[(C_5Me_5)ScCl_2]_n$ as shown in eq 168:[569]

$$n(C_5Me_5)Sc(acac)_2 + 2nAlCl_3 \xrightarrow[-2nCl_2Al(acac)]{\text{toluene}} [(C_5Me_5)ScCl_2]_n \qquad (168)$$

Reaction between $GdCl_3$ and NaC_5Me_5 give $(C_5Me_5)GdCl_2(THF)_3$ and $\{Na(\mu_2\text{-}THF)[(C_5Me_5)Gd(THF)]_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2\}_2$ (Figure 126); the latter compound represents the first species in which two organolanthanide moieties are bridged by the oxygen atoms of two molecules of tetrahydrofuran.[570] The oxo-bridged pentaytterbium species $[(C_5Me_5)YbCl]_5Cl_3O(Et_2O)_2$ was identified by X-ray structure analysis.[571]

References to spectroscopic and other data for mono(pentamethylcyclopentadienyl) halides of the rare earth elements are given in Table 28.

Table 28. Spectroscopic and Other Data of Mono(pentamethylcyclopentadienyl)lanthanide Halides

compound	Ln		color, characterization, etc.
$[Ln_5(C_5Me_5)_6(\mu^4\text{-}F)(\mu^3\text{-}F)_2(\mu^2\text{-}F)_6]$	Yb		(+PhMe): red, X-ray[264]
$(C_5Me_5)LnCl_2$	Sc		NMR[569]
	Y		complex with $KCl(THF)_2$: reactions[501]
	La		complex with $LiCl(THF)_2$: colorless, NMR, IR[441]
	Ce		complex with THF: yellow, IR,[306] lumines.;[289] with py: yellow brown, IR, melt./dec.;[567] with $LiCl(THF)_2$: green, NMR, IR;[441] with $LiCl(py)_2$: pale yellow, IR, melt./dec.[567]
	Pr		complex with Et_2O: synthesis;[564] with $NaCl(Et_2O)$: synthesis[294,564]
	Nd		complex with $NaCl(Et_2O)_2$: blue, IR, melt./dec.[280]
	Gd		complex with 3THF: white, IR[570]
	Yb		blue, NMR,[286,287,301] UV;[286,287] complex with LiCl(THF): blue, IR, UV[282]
	Lu		complex with $LiCl(Et_2O)$: white, NMR;[282] with $NaCl(Et_2O)_2$: synthesis;[564] with $NaCl(THF{\cdot}Et_2O)$: white, NMR,[565] synthesis[566]
$(C_5Me_5)_3Ln_2Cl_3$	Sm		NMR[285]
$[K(DME)_3]\{K[((C_5Me_5)Ln)_3Cl_8K(DME)_2]_2\}$	Yb		X-ray[564]
$\{Na(\mu^2\text{-}THF)[(C_5Me_5)Ln(THF)]_2(\mu^2\text{-}Cl)_3(\mu^3\text{-}Cl)_2\}_2$	Gd		(+6THF): white, X-ray, IR[570]
$[(C_5Me_5)LnCl]_5Cl_3O(Et_2O)_2$	Yb		X-ray[571]
$(C_5Me_5)LnBr_2$	Yb		blue[287]
$(C_5Me_5)LnI_2$	La	**90c**	colorless;[306] complex with 3THF: colorless, melt./dec.,[146c] NMR,[146c,306] IR[306]
	Ce	**90d**	complex with 3THF: yellow green, X-ray,[306] lumines.;[61,289] with CNMe: lumines.[289]
	Yb	**90q**	complex with $LiI(Et_2O)_2$: green, UV[282,297]

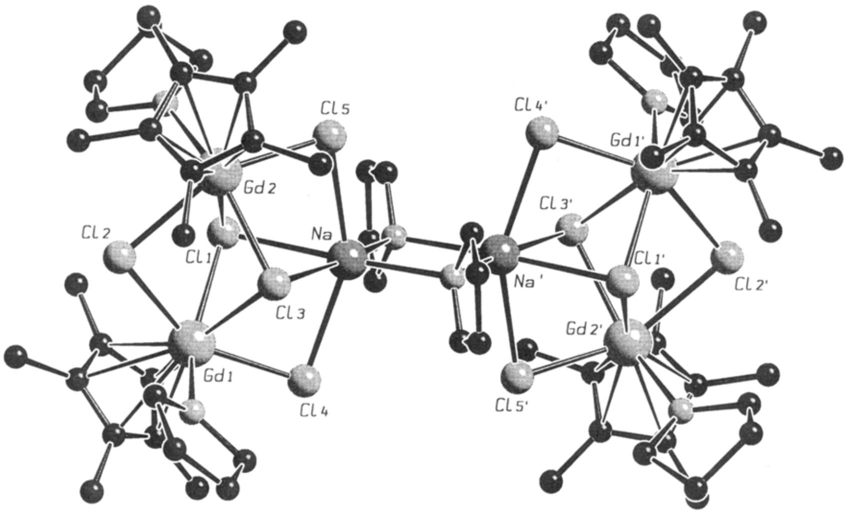


Figure 126. Structure of $\{Na(\mu_2\text{-}THF)[(C_5Me_5)Gd(THF)]_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2\}_2$ in the crystal.[570]

Table 29. Spectroscopic and Other Data of Mono(cyclopentadienyl)lanthanide Halides Containing Other Substituted Cyclopentadienyl Ligands

compound	Ln	color, characterization, etc.
$[Li(THF)_2]_2(\mu\text{-}Cl)_4[(MeC_5H_4)Ln(THF)]$	La	yellow, NMR, IR[572]
	Nd	X-ray, IR,[572,573] purple, melt./dec.[572]
$(^tBuC_5H_4)LnCl_2$	Lu	complex with 2THF: white, NMR, IR[196]
$(^tBuC_5H_4)LnI_2$	Sm	complex with 3THF: X-ray[341]
$(PhCH_2C_5Me_4)LnCl_2$	Nd	complex with THF: IR; with 2THF: IR[574]
	Sm	complex with THF: IR; with 2THF: IR[574]
	Gd	complex with THF: IR; with 2THF: IR[574]
	Er	complex with 3THF: synthesis[575]
	Yb	complex with 3THF: synthesis[575]
$(C_5H_9C_5H_4)LnCl_2$	Nd	complex with 3THF: NMR, IR[576]
	Sm	complex with 2THF: NMR, IR[576]
	Gd	complex with THF: NMR, IR; with 2THF: NMR, IR; with 3THF: NMR, IR[576]
$\{[(C_5H_9C_5H_4)Ln(THF)]_2(\mu^2\text{-}Cl)_3(\mu^3\text{-}Cl)_2Na(THF)_2\}$	Er	(+THF): pink, X-ray, IR[577]
$(C_3H_5C_5H_4)LnCl_2$	Nd	complex with THF: NMR, IR[576]
	Sm	complex with 2THF: NMR, IR[576]
	Gd	complex with THF: NMR, IR; with 2THF[576]
$(Me_3SiC_5H_4)LnCl_2$	Nd	IR; complex with THF: synthesis; with 2THF: synthesis[578]
	Sm	synthesis; complex with THF: synthesis[578]
	Gd	complex with THF: synthesis[578]
$(C_3H_7C_5Me_4)LnCl_2$	Ce	complex with $LiCl(py)_2$: pale yellow, IR, melt./dec.[567]
$(Me_4C_5CH_2Ph)LnCl_2$	Sc	NMR[363]
$(Me_4C_5CH_2C_6H_4Me\text{-}3)LnCl_2$	Sc	NMR[363]
$(Ph_2C_5Me_3)LnCl_2$	Lu	complex with $(THF{\cdot}Et_2O)$: brown, NMR[565]
$(C_5Ph_5)LnCl_2$	Lu	complex with THF: orange, NMR, MS, UV, IR, melt./dec.[340]
$(CO)_3MnC_5H_4LnI_2$	Yb	complex with 3THF: yellowish, IR, melt./dec.[327]
$(2,4\text{-}C_7H_{11})LnCl_2$	Nd	complex with THF: ruby-red, X-ray[209b]
$(2,5\text{-}^tBu_2C_4H_2)YbCl_2$	Yb	complex with 2THF: orange, X-ray, melt./dec.[749]

c. Derivatives with Other Substituted Cyclopentadienyl Rings. A large number of these compounds have been prepared and they are listed in Table 29.

The incorporation of an alkalimetal halide, e.g. LiCl or NaCl, occurs when monosubstituted cyclopentadienyl ligands are used in much the same way as that obtained with permethylated cyclopentadienyl. For example, the tetranuclear oxocomplex $[Li(THF)_4]_2\{[(MeC_5H_4)NdCl(\mu^2\text{-}Cl)NdCl_2(MeC_5H_4)]_2(\mu^4\text{-}O)\}$ (for more details see the chalcogenide section II.C.2.c), crystallized from a THF solution of $NdCl_3{\cdot}2(LiCl){\cdot}n(THF)$ and 2 equiv of $NaMeC_5H_4$.[579] Changing the stoichiometry from 1:2 to 1:1 led to $[Li(THF)_2]_2(\mu\text{-}Cl)_4[(MeC_5H_4)Ln(THF)]$ (Ln = La,[572] Nd[572,573]). Reaction of $ErCl_3$ with an equimolar amount of the cyclopentane-substituted cyclopentadienyl sodium salt, $C_5H_9C_5H_4Na$, yielded $\{[(C_5H_9C_5H_4)Er(THF)]_2(\mu^2\text{-}Cl)_3(\mu^3\text{-}Cl)_2Na(THF)_2\}{\cdot}(THF)$ (Figure 127).[577]

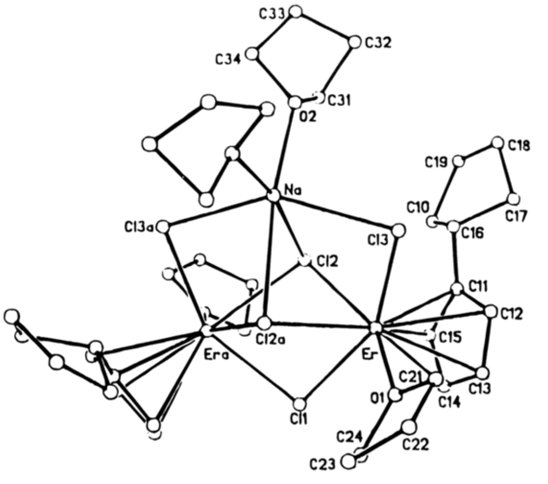


Figure 127. Structure of $\{[(C_5H_9C_5H_4)Er(THF)]_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2Na(THF)_2\}$ in the crystal.[577] (Reprinted from ref 577. Copyright 1992 Pergamon.)

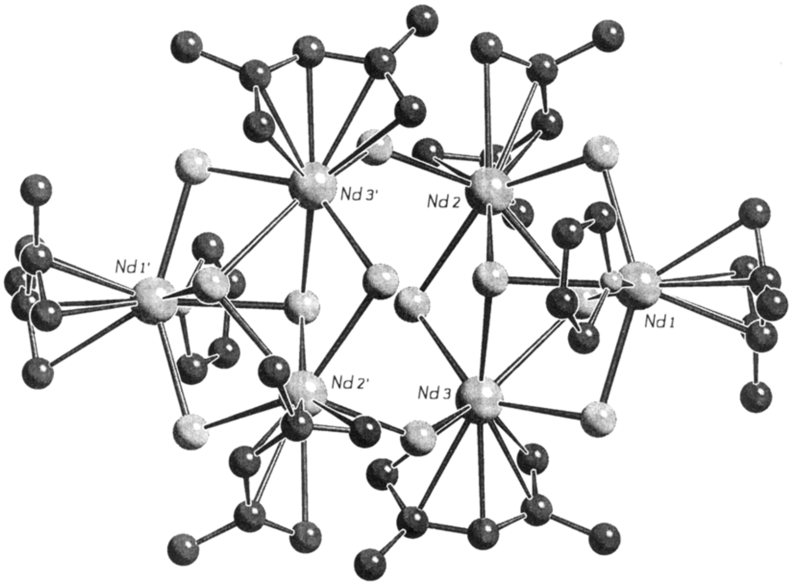


Figure 128. Structure of $(2,4\text{-}C_7H_{11})_6Nd_6Cl_{12}(THF)_2$ in the crystal.[209b]

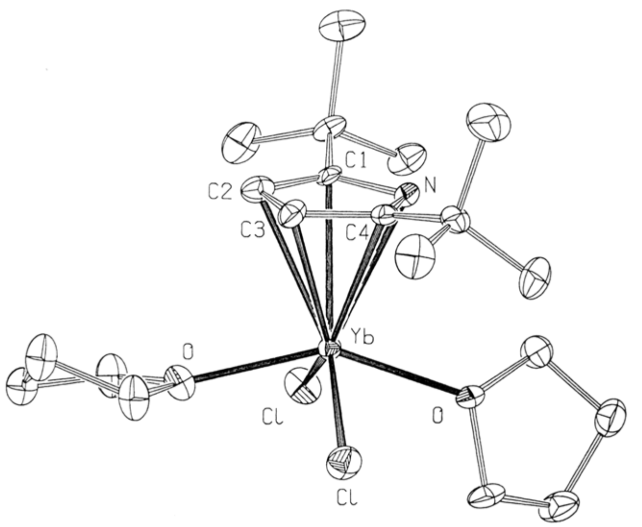


Figure 129. Structure of $(2,5\text{-}{}^tBu_2C_4H_2N)YbCl_2(THF)_2$ in the crystal.[749]

Except for $(C_3H_7C_5Me_4)CeCl_3Li(py)_2$,[567] $(Me_4C_5CH_2Ph)ScCl_2$, and $(Me_4C_5CH_2C_6H_4Me\text{-}3)ScCl_2$,[363] all additional examples of known chloride complexes $({}^tBuC_5H_4)LuCl_2(THF)_3$,[196] $(Ph_2C_5Me_3)LuCl_2(THF\cdot Et_2O)$,[565] $(PhCH_2C_5H_4)LnCl_2(THF)_n$ (Ln = Er, Yb,[575] $n = 3$; Ln = Nd, Sm, Gd,[574] $n = 1, 2$), $(RC_5H_4)LnCl_2(THF)_n$ (R = C_3H_5, C_5H_9, Ln = Nd, Sm, Gd; $n = 0, 1, 2, 3$),[576] $(Me_3SiC_5H_4)LnCl_2(THF)_n$ (Ln = Nd, Sm, Gd, $n = 0, 1, 2$),[578] and $(C_5Ph_5)LuCl_2(THF)$[340] have been obtained by metathesis of the corresponding anhydrous lanthanide chloride with the respective sodium organyl in THF. Dichloroscandium derivatives $(Me_4C_5CH_2C_6H_4R\text{-}3)ScCl_2$ (R = H, Me) have been prepared in a similar manner as its permethylated congener $[(C_5Me_5)ScCl_2]_n$ (eq 168).[363]

The number of mono(cyclopentadienyl)lanthanide iodides is limited to one example, $({}^tBuC_5H_4)SmI_2(THF)_3$.[341]

Studying the catalytic activity of the "open-Cp" compound tris(2,4-dimethylpentadienyl)neodymium for 1,4-polymerization of butadiene in the presence of halide containing Lewis acids, Taube et al.[209b] synthesized "$(2,4\text{-}C_7H_{11})NdCl_2(THF)_{0.33}$" by heating a toluene solution of $(2,4\text{-}C_7H_{11})_3Nd$ and neodymium trichloride $NdCl_3\cdot 2(THF)$. The reaction product crystallizes as the hexameric species $(2,4\text{-}C_7H_{11})_6Nd_6Cl_{12}(THF)_2$ (Figure 128) showing two Nd_3Cl_5 trimers held together by two chloro bridges. The pentadienyl systems coordinate the neodymium atoms of the Nd_3Cl_5 units (which form coordination polyhedrons of the appearence of distorted hexagonal bipyramids) in η^5 fashion.

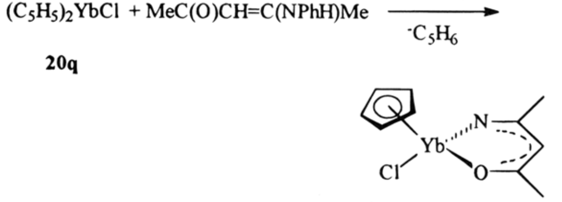
The reaction between $YbCl_3(THF)_3$ and $Na[NC_4H_2\text{-}{}^tBu_2\text{-}2,5]$ yields the monopyrrolyl complex $(2,5\text{-}{}^tBu_2C_4H_2N)YbCl_2(THF)_2$, the first organolanthanide halide containing a η^5-bonded azacyclopentadienyl ligand (Figure 129).[749]

2. Mono(cyclopentadienyl) Rare Earth Chalcogenides

The number of mono(cyclopentadienyl) rare earth oxygen compounds is rather large, but complexes of this type with metal sulfur, selenium, or even tellurium bonds are largely unknown.

a. Cyclopentadienyl Derivatives. Available data for monocyclopentadienyl rare earth chalcogenides are given in Table 30.

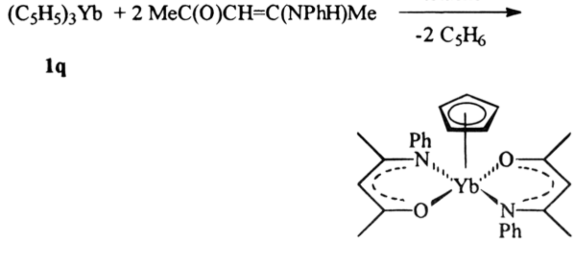
The first report on complexes with chelating agents such as β-amino ketones dates from Bielang and Fischer.[382] After reactions of bis- and tris(cyclopentadienyl)ytterbium compounds (**20q** and **1q**) with the protonic acid, 4-anilino-3-penten-2-one, they obtained the products shown in eqs 169 and 170.



$$(C_5H_5)_2YbCl + MeC(O)CH{=}C(NPhH)Me \xrightarrow[\text{-}C_5H_6]{\text{toluene}}$$

20q

(169)



$$(C_5H_5)_3Yb + 2\ MeC(O)CH{=}C(NPhH)Me \xrightarrow[\text{-2}\ C_5H_6]{\text{toluene}}$$

1q

(170)

Table 30. Spectroscopic and Other Data of Mono(cyclopentadienyl)lanthanide Chalcogenides

compound	Ln		color, characterization, etc.
$(C_5H_5)_5Ln_5(\mu^2\text{-}OMe)_4(\mu^3\text{-}OMe)_4(\mu^5\text{-}O)$	Y		X-ray, melt./dec.,[373] NMR, IR[226,373]
	Gd		white, X-ray, MS, IR, melt./dec.[580]
$(C_5H_5)Ln(O^tBu)_2$	Y		yellow, X-ray, NMR[581]
$(C_5H_5)_2Ln(\mu\text{-}O^tBu)_2Ln(O^tBu)(C_5H_5)$	Y		X-ray, NMR[581]
$(C_5H_5)Ln[OCH_2(C_4H_3O)]_2$	Nd		blue, MS, IR, XPS, melt./dec.[377]
	Yb		yellow, MS, IR, XPS, melt./dec.[377]
$[(C_5H_5)Ln_2(OPh)_3(\mu\text{-}OPh)_2(DME)_2]$	Lu		(+DME): X-ray, NMR, IR, melt./dec.[582]
$(C_5H_5)Ln(OC_6H_4NH_2\text{-}2)_2$	Yb		pink, NMR, MS, IR, XPS, melt./dec.[161]
$(C_5H_5)Ln(OC_6H_4CHO\text{-}2)_2$	Nd		yellow, MS, IR, XPS, melt./dec.[377]
	Yb		yellow, MS, IR, XPS, melt./dec.[377]
$(C_5H_5)Ln(OC_9H_6N)_2$; (OC_9H_6N) =	Nd		yellowish green, NMR, MS, IR, XPS, melt./dec.[161]
8-hydroxiisoquinoline	Yb		yellow, NMR, MS, IR, XPS, melt./dec.[161]
$(C_5H_5)Ln(acac)_2$	Nd	**91f**	purple, MS, IR, melt./dec.[160]
	Sm	**91h**	pale yellow, MS, IR, melt./dec.[160]
	Gd	**91k**	pale yellow, MS, IR, melt./dec.[160]
	Dy	**91m**	yellow, MS, IR, melt./dec.[160]
	Er	**91o**	pink, MS, IR, melt./dec.[160]
	Yb	**91q**	orange, melt./dec.,[383] MS,[383,385] thermo. d.[52d]
$[(C_5H_5)_2Co][(C_5H_5)Ln(acac)_3]$	Ce		blue green, magn. d.[109]
$(C_5H_5)Ln[OC(Me){=}CHCO_2Et]_2$	Yb		thermo. d.[52d]
$(C_5H_5)Ln[OC(Me){=}CHC(O)CF_3]_2$	Yb		orange, melt./dec.,[383] MS[383,385]
$(C_5H_5)Ln[OC(^tBu){=}CHC(O)^tBu]_2$	Yb		pale yellow, melt./dec.,[383] MS[383,385]
$(C_5H_5)Ln[OC(Ph){=}CHC(O)Me]_2$	Yb		yellow, melt./dec.,[383] MS[383,385]
$(C_5H_5)Ln[OC(CF_3){=}CHC(O)(C_4H_3S)]_2$	Yb		yellow, IR, melt./dec.,[383] MS[383,385]
$(C_5H_5)Ln[OC(Ph){=}C(C_4H_8N_2O)]_2$	Yb		gray yellow, IR, melt./dec.,[383] MS[383,385]
$(C_5H_5)Ln[OC(Me){=}CHC(Me){=}NPh]_2$	Yb		yellow, UV, melt./dec.[382]
$(C_5H_5)Ln(Cl)[OC(Me){=}CHC(Me){=}NPh]$	Yb		red brown, UV, melt./dec.[382]
$(C_5H_5)Ln(OSO_2CF_3)_2$	Lu	**92r**	complex with THF: colorless, NMR; with 3THF: colorless, X-ray, NMR[392]
$(C_5H_5)Ln(Cl)(O_2CPh)$	Sm		orange, MS, IR, melt./dec.[583]
	Yb		orange, MS, IR, melt./dec.[583]
$(C_5H_5)Ln(Cl)(O_2CC_6H_4OMe\text{-}2)$	Sm		orange, MS, IR, melt./dec.[583]
	Yb		orange, MS, IR, melt./dec.[583]
$(C_5H_5)Ln(Cl)(O_2CC_6H_4F\text{-}2)$	Sm		orange, MS, IR, melt./dec.[583]
	Yb		orange, MS, IR, melt./dec.[583]
$(C_5H_5)Ln(Cl)(O_2CC_6H_4Br\text{-}2)$	Sm		orange, MS, IR, melt./dec.[583]
	Yb		orange, MS, IR, melt./dec.[583]
$C_5H_5)Ln(Cl)(O_2CC_6H_4I\text{-}2)$	Sm		orange, MS, IR, melt./dec.[583]
	Yb		orange, MS, IR, melt./dec.[583]

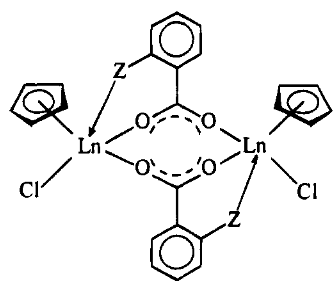
Analogous reactions of tris(cyclopentadienyl)lanthanides **1** with pure acetylacetone occur smoothly to give $(C_5H_5)Ln(acac)_2$ (**91**) (Ln = Nd (**91f**), Sm (**91h**), Gd (**91k**), Dy (**91m**), Er (**91o**),[160] Yb (**91q**)[383,385]) in acceptable yields. A large number of similar mono(cyclopentadienyl) compounds of the rare earths are reported in the literature. In most cases, they have been prepared by reactions of **1** with 2 equiv of a substituted β-diketones and β-ketoimine,[72,383,385] or related chelating reagent such as salicylaldehyde, furfuryl alcohol,[377] 8-hydroxyquinoline, or *o*-aminophenol[161] and the "double-chelate" $[MeC(O)CHC(Me)NHCH_2CH_2NHCH(Me)C(O)Me]$.[72] In connection with mono(cyclopentadienyl)lanthanide acetylacetonates, it should be mentioned that the ionic cobalticinium salt $[(C_5H_5)_2Co][(C_5H_5)Ce(acac)_3]$ contains three acetylacetonate groups ligated to a mono(cyclopentadienyl)cerium unit. An attempt to transform the trivalent THF adduct $(C_5H_5)_3Ce(THF)$ (**2d**) with the strong oxidant, cobalt(III) acetylacetonate failed to oxidize Ce, but the salt, $[(C_5H_5)_2Co^{III}][(C_5H_5)Ce^{III}(acac)_3]$, was isolated.[109]

$$\underset{\mathbf{2d}}{(C_5H_5)_3Ce(THF)} + Co(acac)_3 \xrightarrow{THF} [(C_5H_5)_2Co][(C_5H_5)Ce(acac)_3] \quad (171)$$

Equimolar treatment of bis(cyclopentadienyl)lanthanide chlorides **20** with benzoic acid, or some of its substituted derivatives, yielded chloromono(cyclopentadienyl)lanthanide carboxylates. Spectrometrical investigations (IR, MS, and XPS) indicate that the carboxylates are dimeric (eq 172). The donor atoms in ortho position of the phenyl groups are assumed to interact with the rare earth metals.[583]

$$\underset{\mathbf{20}}{2\ (C_5H_5)_2LnCl} + 2\ HO_2CC_6H_4Z\text{-}2 \xrightarrow[-2\ C_5H_6]{THF}$$

Ln = Sm, Yb: Z = F, Br, I, OMe



(172)

X-ray crystallography showed the cyclopentadienylyttrium methoxide complex $(C_5H_5)_5Y_5(\mu_2\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)$ made from a mixture of $(C_5H_5)_2YCl(THF)$ (**21b**) and KOH in methanol contains an interstitial oxygen dianion.[226,373] The corresponding gadolinium complex $(C_5H_5)_5Gd_5(\mu_2\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)$ (Figure 130) was obtained from $(C_5H_5)GdCl_2$-

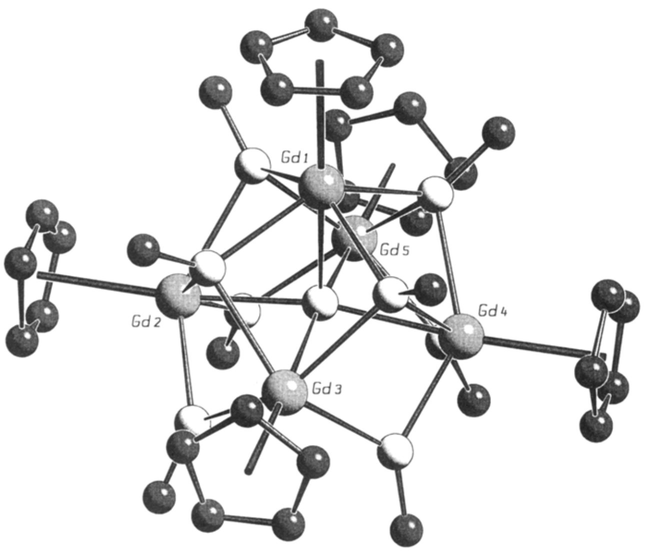
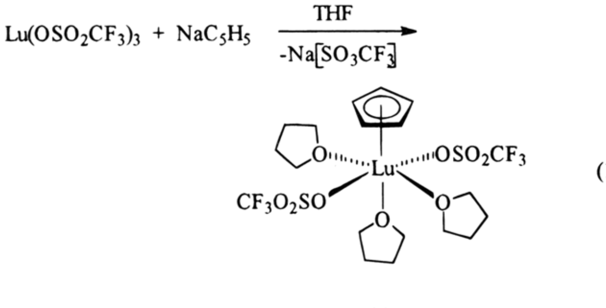


Figure 130. Structure of $(C_5H_5)_5Gd_5(\mu_2\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)$ in the crystal.[580]

$(THF)_3$ (**89k**) and 2 equiv of NaOMe.[580] Furthermore, it has been observed that a suspension of $LuCl_3$ in DME reacts with NaC_5H_5 and NaOPh, in the molar ratio of 1:1:2, generating $[(C_5H_5)Lu_2(OPh)_3(\mu\text{-}OPh)_2(DME)_2]{\cdot}(DME)$.[582]

Very recently, the dimeric type complexes $[(C_5H_5)Y(\mu\text{-}O^tBu)(O^tBu)]_2$ (Figure 131) and $(C_5H_5)_2Y(\mu\text{-}O^tBu)_2Y(O^tBu)(C_5H_5)$ have been isolated and structurally characterized. Both yttrium *tert*-butoxy species were obtained as a part of an investigation on the reactivity of the trimetallic alkoxide $Y_3(O^tBu)_7Cl_2(THF)_2$ with alkali metal cyclopentadienyl reagents.[581]

Research has focused on the development of new synthetic strategies. The application of the easily available rare earth tris(trifluoromethanesulfonates) as starting materials is one strategy. Indeed, addition of an equimolar amount of sodium cyclopentadienyl to a THF solution of lutetium triflate gave the mono(cyclopentadienyl)bis(triflato)lanthanide **92r** as outlined in eq 173:[392]



(173)

92r

In order to elucidate the solid state structure of this organolutetium triflate, X-ray quality single crystals of **92r** were grown from THF and a diffraction study (Figure 132) was undertaken. It confirms the predicted monomeric structure with a pseudo-octahedrally surrounded rare earth metal with two monodentate triflato ligands, a η^5-cyclopentadienyl group, and three meridionally arranged tetrahydrofuran molecules. In vacuum, crystalline **92** liberates two THF molecules.[392]

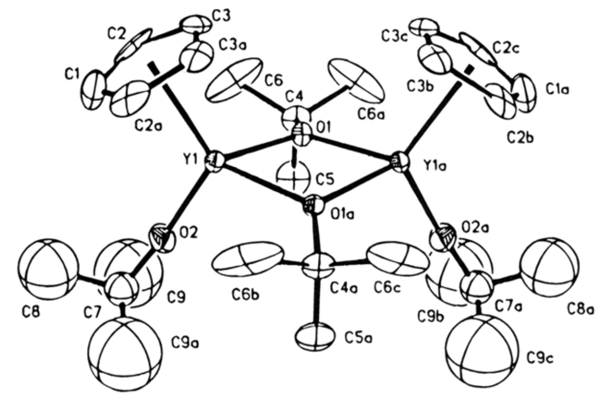


Figure 131. Structure of $[(C_5H_5)Y(\mu\text{-}O^tBu)(O^tBu)]_2$ in the crystal.[581] (Reprinted from ref 581. Copyright 1993 American Chemical Society.)

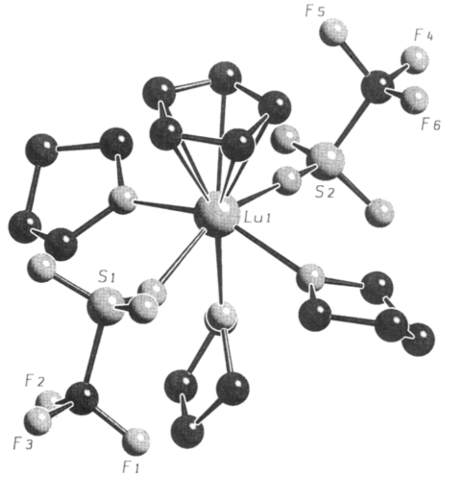


Figure 132. Structure of $(C_5H_5)Lu(OSO_2CF_3)_2(THF)_3$ (**92r**)in the crystal.[392]

b. Pentamethylcyclopentadienyl Derivatives. The first examples of mono(pentamethylcyclopentadienyl)lanthanide chalcogenides appeared in 1985. The initial product of a redox reaction between divalent $[(C_5Me_5)Sm(I)(THF)_2]_2$ and $Co_2(CO)_8$ was thought to be $(C_5Me_5)(I)(THF)_2SmOCCo(CO)_3$, but the isolated products are $(C_5Me_5)_2(THF)SmOCCo(CO)_3$ and $[SmI_2(THF)_5][Co(CO)_4]$.[422] In the same year, alcoholysis (eq 174) of mono(pentamethylcyclopentadienyl)trimethyllutetate by *tert*-butyl alcohol or *tert*-butyl mercaptan, afforded the doubly bridged alkoxo species $(C_5Me_5)Lu(\mu\text{-}O^tBu)_2(O^tBu)Li(tmed)$ and mono(cyclopentadienyl)lanthanide thiolate $(C_5Me_5)Lu(\mu\text{-}S^tBu)_2(S^tBu)Li(tmed)$, respectively.[405] NMR investigations of both species indicate a fast exchange between the terminal E^tBu groups and the corresponding bridging groups.

$$[Li(tmed)_2][(C_5Me_5)LuMe_3] + 3\,{}^tBuEH \xrightarrow{Et_2O}$$
$$(C_5Me_5)Lu(\mu\text{-}E^tBu)_2(E^tBu)Li(tmed) + 3CH_4 \quad (174)$$

$$E = O, S$$

Neutral alkyls $(C_5Me_5)_2LnCH(SiMe_3)_2$ react, according to Heeres et al.,[408] with *tert*-butyl alcohol in the ratio 1:2 to give dimeric mono(pentamethylcyclopentadienyl)alkoxolanthanide compounds as in eq 175.

$$(C_5Me_5)_2LnCH(SiMe_3)_2 + 2HO^tBu \xrightarrow{\text{pentane}} \underset{\mathbf{93}}{[(C_5Me_5)Ln(\mu\text{-}O^tBu)(O^tBu)]_2} + C_5Me_5H + CH_2(SiMe_3)_2 \quad (175)$$

Ln = La (**93c**), Ce (**93d**)

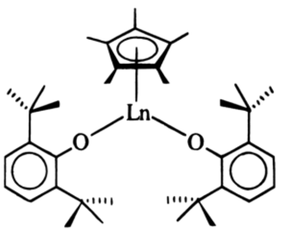
Two methods have been developed recently to prepare the *tert*-butoxide yttrium[581] and europium[584] derivatives **93b** and **93i**. Reaction of the trimetallic alkoxides $Ln_3(O^tBu)_7Cl_2(THF)_2$ (Ln = Y, Eu) with MC_5Me_5 (M = Na, K) in toluene gives the appropriate dimers. The dark purple europium alkoxide $[(C_5Me_5)Eu(\mu\text{-}O^tBu)(O^tBu)]_2$ (**93i**) represents the first pentamethylcyclopentadienyl complex of trivalent europium.[584] **93b** can also be synthesized directly from solvated yttrium trichloride, NaO^tBu, and KC_5Me_5 according to eq 176:[581]

$$YCl_3(THF)_x + 2NaO^tBu + KC_5Me_5 \xrightarrow[-2\,NaCl/-KCl]{\text{toluene}} \underset{\mathbf{93b}}{{}^1/_2[(C_5Me_5)Y(\mu\text{-}O^tBu)(O^tBu)]_2} \quad (176)$$

X-ray crystallographic studies of **93b**,[581] **93d**,[408] and **93i** (Figure 133)[584] show them to be isostructural with the unsubstituted cyclopentadienyl congener $[(C_5H_5)Y(\mu\text{-}O^tBu)(O^tBu)]_2$.[581] The two symmetrical alkoxo bridges as well as the two terminal *tert*-butoxo ligands are arranged in a cis configuration.

Monomeric **94** have been prepared by the reaction shown in eq 177, starting from tris(2,6-di-*tert*-butylphenoxo)cerium,[585,586] -yttrium,[497] or -lanthanum.[407]

$$Ln(OC_6H_3{}^tBu_2\text{-}2,6)_3 + MC_5Me_5 \xrightarrow[-MOC_6H_3{}^tBu_2\text{-}2,6]{\text{toluene}}$$



(177)

94

Ln = La, Ce: M = Li
Ln = Y: M = K

The solvent-free structures of the unsaturated alkoxides **94d** (Figure 134)[585,586] and **94b**[497] have been obtained by single-crystal X-ray analyses. Addition of THF to a toluene solution of **94c** yields the THF adduct $(C_5Me_5)La(OC_6H_3{}^tBu_2\text{-}2,6)_2(THF)_2$. A solution of **94c** in benzene has been observed to disproportionate slowly to $Ln(OC_6H_3{}^tBu_2\text{-}2,6)_3$ and the bis(pentamethylcyclopentadienyl)lanthanum aryloxide, $(C_5Me_5)_2LaOC_6H_3{}^tBu_2\text{-}2,6$.[407]

Lithium chloride containing chloromono(pentamethylcyclopentadienyl)scandium aryloxides are obtainable (eq 178) by slow addition of an equimolar amount of butylated lithium phenolates to a toluene solution of oligomeric scandium chloride $[(C_5Me_5)ScCl_2]_n$ in the presence of trimethylphosphine (to increase the solubility of the oligomer in the aliphatic solvent via formation of the adduct $(C_5Me_5)ScCl_2(PMe_3)$).[569]

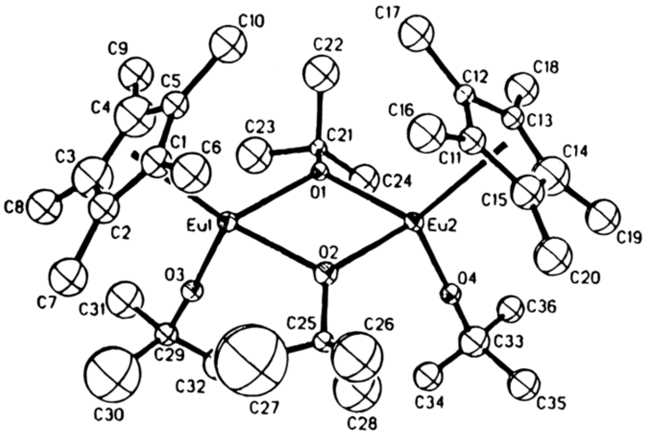


Figure 133. Structure of $[(C_5Me_5)Eu(\mu\text{-}O^tBu)(O^tBu)]_2$ in the crystal.[584] (Reprinted from ref 584. Copyright 1994 American Chemical Society.)

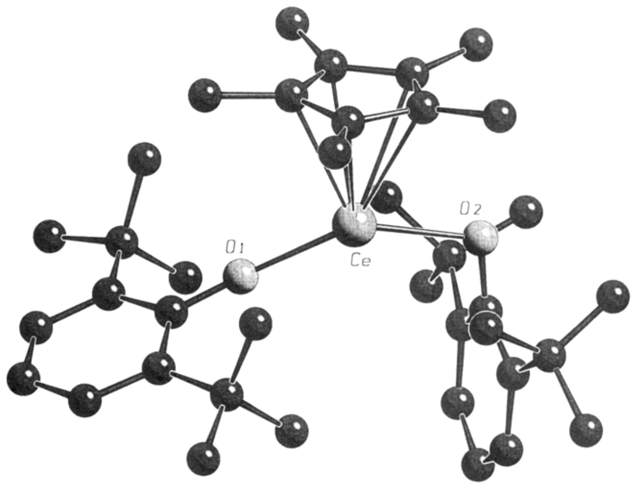


Figure 134. Structure of $(C_5Me_5)Ce(OC_6H_3{}^tBu_2\text{-}2,6)_2$ (**94d**) in the crystal.[585,586]

$$1/n[(C_5Me_5)ScCl_2]_n + LiOR \xrightarrow{\text{toluene/PMe}_3} (C_5Me_5)Sc(OR)(Cl){\cdot}(LiCl) \quad (178)$$

$R = OC_6H_2{}^tBu_3\text{-}2,4,6;\ OC_6H_3{}^tBu_2\text{-}3,5$

The latter two reaction products (eq 178) are suggested to exist as symmetrical dimers of the formula $[(C_5Me_5)Sc(\mu\text{-}OR)(\mu\text{-}Cl)Li(\mu\text{-}Cl)]_2$. Absence of trimethylphosphine, under otherwise the same conditions, gives a 1:1 mixture of $[(C_5Me_5)ScCl_2]_n$ and $[(C_5Me_5)Sc(OR)_2]_n$. The use of THF, in which $[(C_5Me_5)ScCl_2]_n$ dissolves freely, instead of PMe_3 leads to the corresponding salt-free, monomeric THF adducts $(C_5Me_5)Sc(OR)(Cl)(THF)$.[569] In the same article, Bercaw et al. reported the preparation of $(C_5Me_5)Sc(acac)_2$ from scandium acetylacetonate and a pentamethylcyclopentadienyl Grignard reagent according to eq 179:

$$Sc(acac)_3 + (C_5Me_5)MgCl(THF) \xrightarrow[-ClMg(acac)(THF)]{\text{toluene}} (C_5Me_5)Sc(acac)_2 \quad (179)$$

Very recently, the analogous Y–acac complex $(C_5Me_5)Y(acac)_2$ has been synthesized from $(C_8H_8)Ln$-

Table 31. Spectroscopic and Other Data of Mono(pentamethylcyclopentadienyl)lanthanide Chalcogenides

compound	Ln		color, characterization, etc.
$(C_5Me_5)Ln(O^tBu)_2$	Y	**93b**	colorless, X-ray, NMR, IR[581]
	La	**93c**	NMR, IR[408]
	Ce	**93d**	yellow, X-ray, NMR, IR[408]
	Eu	**93i**	purple, X-ray, NMR, IR, UV, magn. d.[584]
$(C_5Me_5)Ln(\mu\text{-}O^tBu)_2(O^tBu)Li(tmed)$	Lu		colorless, NMR, melt./dec.[405]
$(C_5Me_5)Ln(OC_6H_3{}^tBu_2\text{-}2,6)_2$	Y	**94b**	X-ray, NMR[497]
	La	**94c**	white, IR; complex with 2THF: white, NMR, IR[407]
	Ce	**94d**	yellow orange, X-ray, NMR, IR[585,586]
$(C_5Me_5)Ln(acac)_2$	Sc		yellow, NMR[569]
	Y		white, NMR, MS, melt./dec.[587]
$(C_5Me_5)Ln(Cl)(OC_6H_2{}^tBu_3\text{-}2,4,6)$	Sc		with LiCl: synthesis[569]
$(C_5Me_5)Ln(Cl)(OC_6H_3{}^tBu_2\text{-}3,5)$	Sc		with LiCl: white, NMR[569]
$(C_5Me_5)(I)LnOCCo(CO)_3$	Sm		NMR[422]
$(C_5Me_5)Ln(\mu\text{-}S^tBu)_2(S^tBu)Li(tmed)$	Lu		colorless, NMR, melt./dec.[405]
$(C_5Me_5)Ln[S_2P(OMe)_2]_2$	Sm		dimer, red, X-ray, NMR, IR, MS, melt./dec.[729]
$[(C_5Me_5)Ln]_6Se_{11}$	Sm		X-ray[730]

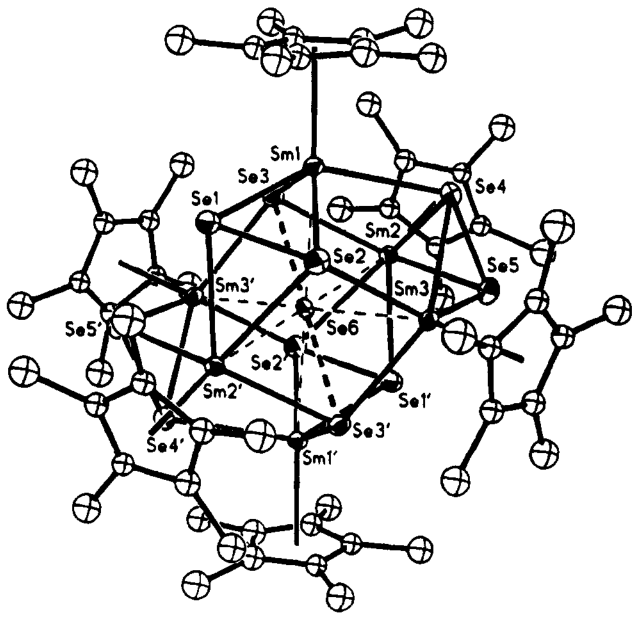


Figure 135. Structure of $[\{(C_5Me_5)Sm\}_6Se_{11}]$ in the crystal.[730] (Reprinted from ref 730. Copyright 1994 VCH.)

(C_5H_5) and a 2-fold amount of acetylacetone in hexane,[587] and a polynuclear samarium selenide, $[\{(C_5Me_5)Sm\}_6Se_{11}]$ (Figure 135) was found in an NMR tube containing $[\{(C_5Me_5)_2Sm\}_2(\mu\text{-}\eta^1{:}\eta^3\text{-}Se_3)(THF)]$ in toluene.[730]

Table 31 gives the data of known mono(pentamethylcyclopentadienyl)lanthanide chalcogenides.

c. Derivatives with Other Substituted Cyclopentadienyl Rings. A whole series of substituted bis(cyclopentadienyl)scandium alkyls has been reported and investigated in detail in the course of studies aimed at determining the relative bond dissociation energies. The synthetic route used to make these complexes is shown in eq 180:[363]

$$Sc(acac)_3 + Li(Me_4C_5CH_2C_6H_4R\text{-}3) \xrightarrow[-Li(acac)]{\text{toluene}} (Me_4C_5CH_2C_6H_4R\text{-}3)Sc(acac)_2 \quad (180)$$

R = H, Me

The preparation of $[(RC_5H_4)Y(\mu\text{-}O^tBu)(O^tBu)]_2$ (R = Me, $SiMe_3$) was obtained from $Y_3(O^tBu)_7Cl_2(THF)_2$ and NaC_5H_4Me and $KC_5H_4SiMe_3$, respectively. The latter trimethylsilyl-substituted cyclopentadienyl compound has also been obtained from $YCl_3(THF)_x$, $KC_5H_4SiMe_3$, and 2 equiv of NaO^tBu although in a slightly lower yield.[581]

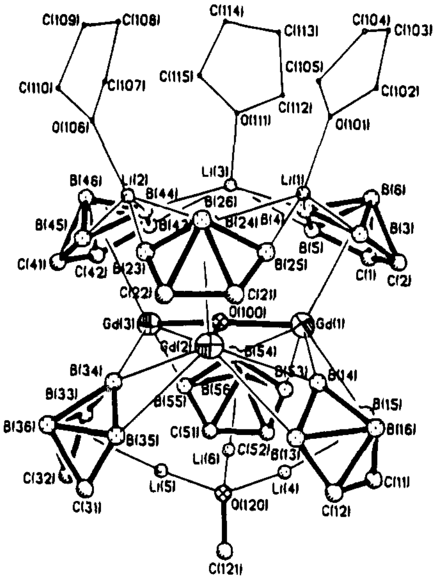


Figure 136. Structure of $\{[(Me_3Si)_2C_2B_4H_4]Gd\}_3\{[(Me_3Si)_2C_2B_4H_4]Li\}_3[Li(THF)_3](\mu^3\text{-}OMe)(\mu^3\text{-}O)$ in the crystal ($C_{cage}-SiMe_3$ groups are omitted for clarity).[588] (Reprinted from ref 588. Copyright 1992 VCH.)

Metathesis of $NdCl_3{\cdot}(LiCl)_2{\cdot}(THF)_n$ with a 2-fold molar equivalent of methylcyclopentadienyl sodium in THF allowed isolation of air and moisture sensitive crystals of the tetranuclear oxo species $[Li(THF)_4]_2\{[(MeC_5H_4)NdCl(\mu_2\text{-}Cl)NdCl_2(MeC_5H_4)]_2(\mu_4\text{-}O)\}$.[579] Another cluster worth mentioning at this point has been isolated recently by reaction of $GdCl_3$ with the THF-solvated carborane salt $Li_2[2,3\text{-}(SiMe_3)_2C_2B_4H_4]$:[588] The first trinuclear μ_3-oxygen bridged half-sandwich π-complex of Gd^{III} with the formula $\{[(Me_3Si)_2C_2B_4H_4]Gd\}_3\{[(Me_3Si)_2C_2B_4H_4]Li\}_3[Li(THF)_3](\mu_3\text{-}OMe)(\mu_3\text{-}O)$ (Figure 136) consists of six closo-carborane cages, three THF molecules, and three Gd and six Li atoms. The origin of the μ_3-OMe ligand and the μ_3-O atom is unknown. The reproducibility of the reaction and the fact that $SmCl_3$ reacts completely analogously led to the assumption that THF cleavage might occur; however, the presence of water was not excluded.

Table 32 summarizes important data of mono(cyclopentadienyl) rare earth chalcogenides with other substituted cyclopentadienyl rings.

Table 32. Spectroscopic and Other Data of Mono(cyclopentadienyl)lanthanide Chalcogenides Containing Other Substituted Cyclopentadienyl Ligands

compound	Ln	color, characterization, etc.
$(MeC_5H_4)Ln(O^tBu)_2$	Y	yellow, NMR[581]
$[Li(THF)_4]_2\{[(MeC_5H_4)LnCl(\mu^2\text{-}Cl)LnCl_2(MeC_5H_4)]_2(\mu^4\text{-}O)\}$	Nd	X-ray[579]
$(Me_3SiC_5H_4)Ln(O^tBu)_2$	Y	white, X-ray, NMR[581]
$(C_5Me_4Et)Ln(acac)_2$	Lu	colorless, X-ray, NMR, MS, melt./dec.[750]
$(Me_4C_5CH_2Ph)Ln(acac)_2$	Sc	NMR[363]
$(Me_4C_5CH_2C_6H_4Me\text{-}3)Ln(acac)_2$	Sc	pale yellow, NMR[363]
$\{[(Me_3Si)_2C_2B_4H_4]Ln\}_3\{[(Me_3Si)_2C_2B_4H_4]Li\}_3[Li(THF)_3](\mu^3\text{-}OMe)(\mu^3\text{-}O)$	Gd	light yellow, X-ray, IR[588]

Table 33. Spectroscopic and Other Data of Mono(cyclopentadienyl)lanthanide Pnicogenides

compound	Ln	color, characterization, etc.
$[(C_5H_5)Ln]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2)_2$	Yb	complex with 2 THF: purple, X-ray[108]
$(C_5H_5)Ln(^tBuNCH{=}CHN^tBu)$	Yb	yellow green, NMR, IR, melt./dec.[380]
$(C_5H_5)Ln(OEP)$	Sc	X-ray,[589] dark red, NMR, MS, UV,[589,590] IR, melt./dec.[590]
$(C_5H_5)LnP^cC_6H_{11}$	Yb	orange, MS[89]
$(C_5H_5)LnPPh$	Yb	orange, MS[89]

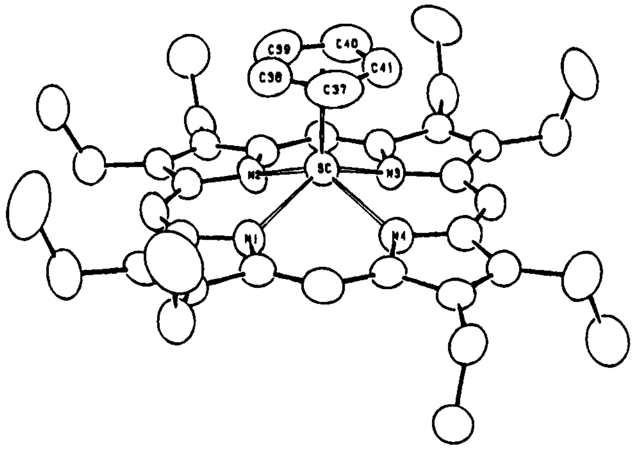


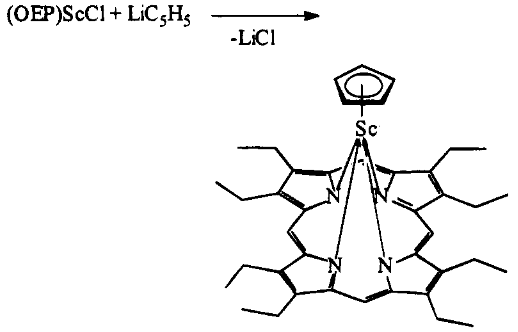
Figure 137. Structure of $(C_5H_5)Sc(OEP)$ in the crystal.[589] (Reprinted from ref 589. Copyright 1990 American Chemical Society.)

3. Mono(cyclopentadienyl) Rare Earth Pnicogenides

Except for the ytterbium systems "$(C_5H_5)YbPR$" (R = $^cC_6H_{11}$, Ph),[89] no mono(cyclopentadienyl) compounds of rare earth metals with bonds to the soft pnicogenides phosphorous, arsenic, antimony, or even bismuth have been described. In contrast several examples are known with the lightest homologue, nitrogen.

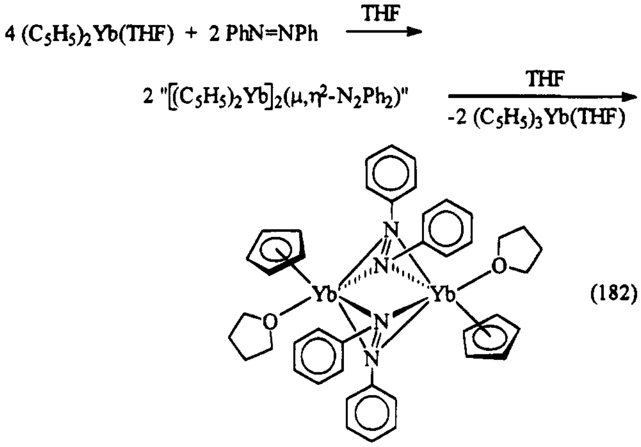
a. Cyclopentadienyl Derivatives. Apart from the mono(cyclopentadienyl)ytterbium β-amino ketonates mentioned earlier (see section II.C.2.a),[382] only three complexes have been identified as containing lanthanide–nitrogen bonds in complexes with only one unsubstituted cyclopentadienyl ligand (Table 33).

Studying metalloporphyrin derivatives, Arnold et al.[589,590] succeeded in 1990 in the synthesis of the first mono(cylcopentadienyl)lanthanide sandwich compound containing the dianion of octaethylporphyrin (Figure 137). This bulky dianion is able to stabilize the mono(cyclopentadienyl)scandium unit as outlined in eq 181. This compound is soluble in various polar and nonpolar solvents and in the solid state it is air stable.[563]



(181)

Reaction of azobenzene with 2 molar equiv of divalent ytterbocene $(C_5H_5)_2Yb(THF)$ in THF gives the redistribution products $(C_5H_5)_3Yb(THF)$ (**2q**) and $[(C_5H_5)(THF)Yb]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2)_2$. Intermediate formation of "$[(C_5H_5)_2Yb]_2(\mu,\eta^2\text{-}N_2Ph_2)$" with subsequent ligand redistribution is proposed (eq 182):[108]



(182)

The structure of the latter mono(cyclopentadienyl) compound (Figure 138), which precipitates with one molecule of toluene of crystallization, contains two fully reduced $N_2Ph_2^{2-}$ ligands. The two different sets of Yb–N distances observed for both ligand systems have to be assigned to Yb–NR_2 single bonds and Yb←NR_3 donor bonds in such a way that each rare earth metal center is involved in two single bonds (one to each $N_2Ph_2^{2-}$) and two donor bonds (one to each $N_2Ph_2^{2-}$).[108]

Recently, $[(C_5H_5)Yb(^tBuNCH{=}CHN^tBu)]_n$ was synthesized in good yield from $(C_5H_5)YbCl(THF)_3$ (**89q**) with a mixture of $C_2H_2(N^tBu)_2$ and 2 equiv of potassium in THF.[380]

b. Pentamethylcyclopentadienyl Derivatives. The pentamethylcyclopentadienyl–samarium analogue of $[(C_5H_5)(THF)Yb]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2)_2$ was ob-

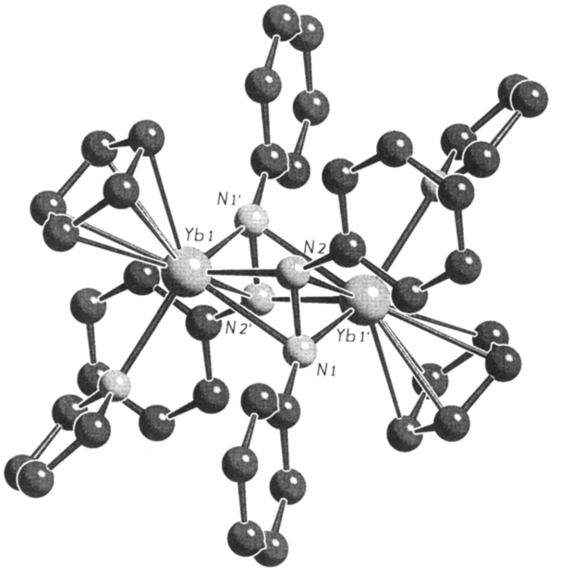


Figure 138. Structure of $[(C_5H_5)(THF)Yb]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2Ph_2)_2$ in the crystal.[108]

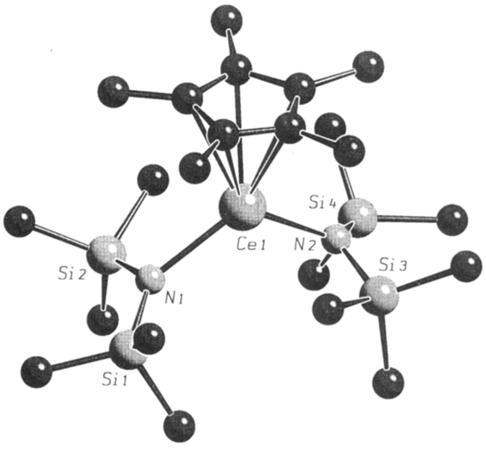


Figure 139. Structure of $(C_5Me_5)Ce[N(SiMe_3)_2]_2$ (**95d**) in the crystal.[586]

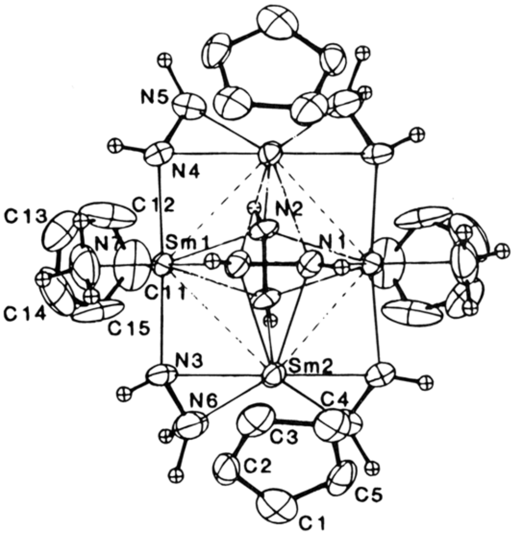


Figure 140. Structure of $[(C_5Me_5)Sm]_4(NHNH_2)_4(NHNH)_2$ in the crystal (Me groups of C_5Me_5 are omitted for clarity).[591] (Reprinted from ref 591. Copyright 1992 American Chemical Society.)

tained from $[(C_5Me_5)_2Sm]_2(\mu,\eta^2\text{-}N_2Ph_2)$ which slowly rearranges to bimetallic $[(C_5Me_5)(THF)Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2Ph_2)_2$, two Sm^{3+}, and six $C_5Me_5^-$. $(C_5Me_5)_3Sm$ (**16h**) could not be identified. The single-crystal X-ray structure determination of orange $[(C_5Me_5)(THF)Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2Ph_2)_2$ revealed the presence of two molecules THF of solvation per lanthanide organyl.[108]

Monomeric mono(pentamethylcyclopentadienyl)lanthanide−nitrogen compounds of the type $(C_5Me_5)Ln[N(SiMe_3)_2]_2$ (**95**) have been prepared by two different synthetical pathways, either by metathesis of a lanthanide chloride (eq 183)[280,441] or an aryloxide (eq 184).[586]

$$(C_5Me_5)LnCl_3M(S')_2 + 2Na(SiMe_3)_2 \xrightarrow[-MCl,\ -2NaCl]{} \underset{\mathbf{95}}{(C_5Me_5)Ln[N(SiMe_3)_2]_2} \quad (183)$$

Ln = Ce (**95d**):[441] M = Li; S′ = THF

Ln = Nd (**95f**):[280] M = Na; S′ = Et_2O

$$\underset{\mathbf{94d}}{(C_5Me_5)Ce(OC_6H_3{}^tBu_2\text{-}2,6)_2} + 2NaN(SiMe_3)_2 \xrightarrow{\text{toluene}} (C_5Me_5)Ce[N(SiMe_3)_2]_2 + \underset{\mathbf{95d}}{2NaOC_6H_3{}^tBu_2\text{-}2,6} \quad (184)$$

Additionally, the ^{1}H-NMR data of the yttrium and lanthanum derivatives **95b** and **95c** are reported.[441] The structure of **95d** was elucidated by an X-ray diffraction analysis and shown by Heeres et al.[586] to consist of a pentamethylcyclopentadienyl ligand and the two amide ligands in which a carbon atom of a trimethylsilyl group is within bonding distance of the cerium metal center (Figure 139).

Reaction of permethylated divalent samarocene $(C_5Me_5)_2Sm$ with excess hydrazine in benzene affords a yellow crystalline hydrazido samarium complex of overall formula $[(C_5Me_5)Sm]_4(NHNH_2)_4(NHNH)_2$ (eq 185). The tetranuclear compound has the samarium atoms arranged in a distorted tetrahedron with bridging hydrazido anions, $NHNH_2^-$, on four edges of the tetrahedron while two hydrazido dianions,

$$4(C_5Me_5)_2Sm + 6N_2H_4 \xrightarrow[-4C_5Me_5H,\ -2H_2]{\text{benzene}} [(C_5Me_5)Sm]_4(NHNH_2)_4(NHNH)_2 \quad (185)$$

$NHNH^{2-}$, are located on the crystallographic 2-fold axis which are on the remaining opposite edges of the tetrahedron (Figure 140).[591]

The permethylated congener of the metalloporphyrin−cyclopentadienyl sandwich complex $(C_5Me_5)Sc(OEP)$, was synthesized by metathesis of the chloride, (OEP)ScCl, with an alkali metal pentamethylcyclopentadienide.[589,590]

Important spectroscopic and other data of mono(pentamethylcyclopentadienyl)lanthanide pnicogenides are shown in Table 34.

c. Derivatives with Other Substituted Cyclopentadienyl Rings. Similar to $(C_5H_5)Sc(OEP)$ and $(C_5Me_5)Sc(OEP)$, the sandwich compound $(MeC_5H_4)Sc(OEP)$ has been formed on reaction of methylcyclopentadienylsodium[589] or lithium[590] and the octaethylporphyrinscandium chloride (OEP)ScCl.

The rather uncommon use of the doubly negatively charged cyclopentadienyl amido chelate $Li_2[Me_4C_5$-

Table 34. Spectroscopic and Other Data of Mono(pentamethylcyclopentadienyl)lanthanide Pnicogenides

compound	Ln		color, characterization, etc.
$(C_5Me_5)Ln[N(SiMe_3)_2]_2$	Y	**95b**	NMR[441]
	La	**95c**	NMR[441]
	Ce	**95d**	orange, X-ray, IR,[586] NMR[441,586]
	Nd	**95f**	blue, IR, melt./dec.[280]
$[(C_5Me_5)Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2Ph_2)_2$	Sm		complex with 2 THF (+2THF): orange, X-ray, NMR, IR[108]
$[(C_5Me_5)Ln]_4(NHNH_2)_4(NHNH)_2$	Sm		$(+2NH_3)$: yellow, X-ray, NMR, IR, magn. d.[591]
$(C_5Me_5)Ln(OEP)$	Sc		NMR, MS, UV,[589,590] bright red, IR, melt./dec.[590]

Table 35. Spectroscopic and Other Data of Mono(cyclopentadienyl)lanthanide Pnicogenides Containing Other Substituted Cyclopentadienyl Ligands

compound	Ln	color, characterization, etc.
$[Li(THF)_4][(^tBuC_5H_4)Ln(NPh_2)_3]$	Yb	red, X-ray, NMR, IR[751]
$[Li(DME)_3][(MeC_5H_4)Ln(NPh_2)_3]$	La	bright yellow,[572] X-ray, NMR, IR, melt./dec.[572,593]
	Pr	yellow green,[572] IR, melt./dec.[572,593]
	Nd	blue purple,[572] IR, melt./dec.[572,593]
$(MeC_5H_4)Ln(OEP)$	Sc	bright red, IR, melt./dec.,[590] NMR, UV[589,590]
$[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]LnCl$	Sc	white,[352,592,752] NMR, IR, catalysis[752]

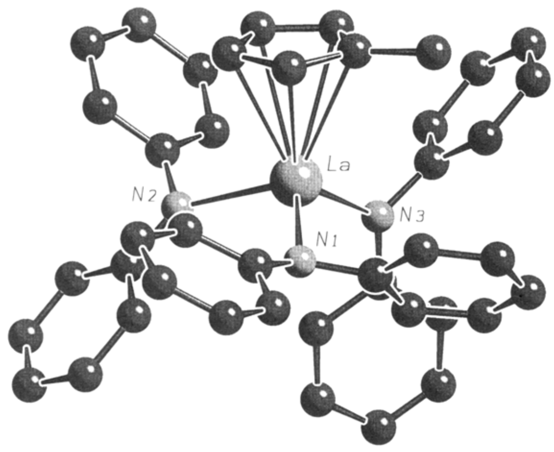


Figure 141. Structure of the anion of $[Li(DME)_3][(MeC_5H_4)La(NPh_2)_3]$ in the crystal.[572,593]

$Si(Me)_2NCMe_3]$ in organometallic chemistry of the rare earths has enabled the preparation of the scandium derivative, $[Me_4C_5Si(Me)_2(\eta^1\text{-}NCMe_3)]ScCl$, from $ScCl_3(THF)_3$. The formal coordination number of five for Sc^{3+} in the latter product ensues from combining one π-bonded, substituted anionic cyclopentadienyl system (which contributes three electron pairs) with one σ-bonded chloride anion and an amido–scandium σ-bond. The dianionic $[Me_4C_5SiMe_2NR]$ group is therefore an eight-electron chelating ligand.[352,592] More detailed information concerning synthesis and structure of the amidoscandium alkyls $[Me_4C_5Si(Me)_2(\eta^1\text{-}NCMe_3)]ScCH(SiMe_3)_2$, $\{[Me_4C_5Si(Me)_2(\eta^1\text{-}NCMe_3)]Sc(\mu\text{-}^nPr)\}_2$, and the amidoscandium hydride $\{[Me_4C_5Si(Me)_2(\eta^1\text{-}NCMe_3)]Sc(PMe_3)(\mu\text{-}H)\}_2$ are given in the following sections.[352,592]

The synthesis of ionic compounds $[Li(DME)_3][(MeC_5H_4)Ln(NPh_2)_3]$ (Ln = La, Pr, Nd) has been recently accomplished by reaction of the *in situ* prepared chloride precursors $[Li(THF)_2]_2(\mu\text{-}Cl)_4[(MeC_5H_4)Ln(THF)]$ of lighter lanthanides with a 2-fold amount of $LiNPh_2$ (eq 186). A single-crystal X-ray structure analysis of the lanthanum species shows the anion to form a distorted tetrahedron of three diphenylamido groups and one methylcyclopentadienyl ligand surrounding the central rare earth metal (Figure 141).[572,593]

$$[Li(THF)_2]_2(\mu\text{-}Cl)_4[(MeC_5H_4)Ln(THF)] + 2LiNPh_2 \xrightarrow[\text{DME}]{\text{THF/hexane/toluene}} [Li(DME)_3][(MeC_5H_4)Ln(NPh_2)_3] + 4LiCl \quad (186)$$

Ln = La, Nd, Pr

A short summary of important data of mono(cyclopentadienyl)lanthanide pnicogenides containing other substituted cyclopentadienyl rings is given in Table 35.

4. *Mono(cyclopentadienyl) Rare Earth Complexes with Rare Earth to Element Group 14 Bonds*

Neither lanthanide–silicon bonds nor bonds of the rare earths to the elements that follow silicon in group 14 of the periodic table are known, but many are known with the congener of silicon, carbon.

a. Cyclopentadienyl Derivatives. Well-defined mono(cyclopentadienyl)lanthanide complexes with two σ-carbyl ligands are scarce owing to the low degree of steric saturation of the lanthanide ion by the unsubstituted cyclopentadienyl group (Table 36). Two approaches have been taken to address the problems associated with the insufficient steric saturation of the highly reactive mono(cyclopentadienyl)lanthanide unit; on the one hand bulky hydrocarbyl ligands were used, and, on the other hand ligands with heteroatom lone pairs connected to the cyclopentadienyl groups were studied.

In the mid-1970s Tsutsui et al.[250] described the preparation of solvent-free mono(cyclopentadienyl)holmium bis(phenylacetylide) from the appropriate lanthanide chloride **89n**, although the sand-colored solid was poorly characterized (eq 187).

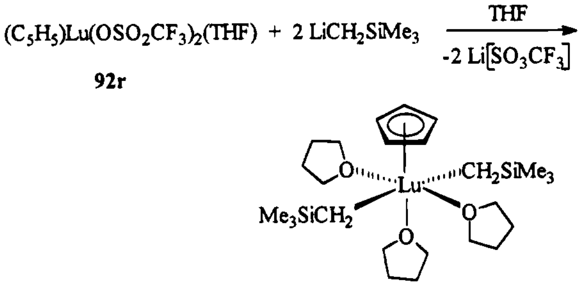
$$\underset{\textbf{89n}}{(C_5H_5)HoCl_2(THF)_3} + 2LiC{\equiv}CPh \xrightarrow{\text{THF}} (C_5H_5)Ho(C{\equiv}CPh)_2 + 2LiCl \quad (187)$$

However, synthesis of the mono(cyclopentadienyl)dialkyllutetium THF adduct $(C_5H_5)Lu(CH_2SiMe_3)_2(THF)_3$ (**96r**) has been accomplished by reaction of a THF solution of mono(cylcopentadienyl)lutetium bis(triflate) (**92r**) with 2 equiv of lithium (trimethylsilyl)methyl, according to eq 188.[392] Unfortunately, all attempts to obtain single crystals of **96r**, suitable for

Table 36. Spectroscopic and Other Data of Mono(cyclopentadienyl)lanthanide Complexes Containing Lanthanide to Element Group 14 Bonds

compound	Ln		color, characterization, etc.
$(C_5H_5)Ln(CH_2SiMe_3)_2$	Lu	**96r**	complex with 3THF: pale yellow, NMR[392]
$(C_5H_5)Ln[(CH_2)_3AsMe_2]_2$	Lu		yellow orange, NMR[594]
$(C_5H_5)Ln[(CH_2)_3As^tBu_2]_2$	Lu		yellow, NMR, MS[594]
$(C_5H_5)Ln[(CH_2)_3NMe_2](Cl)$	Lu		complex with 2THF: colorless, NMR[594]
$(C_5H_5)Ln[CH_2CH(Me)CH_2NMe_2](Cl)$	Lu		complex with 2THF: colorless, X-ray, NMR, melt./dec.[594]
$(C_5H_5)Ln(CH_2CH{=}CH_2)_2$	Nd		complex with THF: IR, MS[479]
$[Li(dioxane)_2][(C_5H_5)Ln(CH_2CH{=}CH_2)_3]$	Nd		IR, MS[479]
$(C_5H_5)Ln(\eta^2\text{-}C_4Ph_4)$	Gd		complex with 3THF: IR[595]
$(C_5H_5)Ln(C{\equiv}CPh)_2$	Ho		sand, IR, UV, magn. d., melt./dec.[250]
$(C_5H_5)Ln(C_{10}H_8)$	Lu		complex with DME: X-ray,[596a,b] purple black, IR, melt./dec.[596b]
$(C_5H_5)Ln(C_{14}H_{10})$	Lu		complex with 2THF: red orange, NMR[481]
$(C_5H_5)Ln\{[C_5H_3(CH_2NMe_2)]Fe(C_5H_5)\}_2$	Yb		sand, IR, MS, melt./dec.[482]
$(C_5H_5)Ln(Cl)[C_5H_3(CH_2NMe_2)]Fe(C_5H_5)$	Sm		yellow brown, NMR, MS, IR, UV, magn. d., melt./dec.[501]
$[Li(DME)_3]_2\{[(C_5H_5)Ln]_4(\mu^2\text{-}Me)_2(\mu^4\text{-}O)(\mu^2\text{-}Cl)_6\}$	Nd		X-ray[597]

a X-ray diffraction study, failed as the crystals are extremly thin and needlelike in shape.

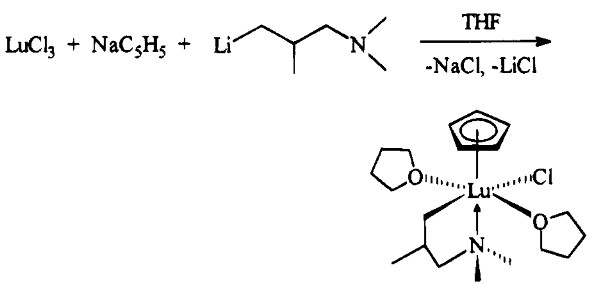


(188)

96r

The use of the bidentate, bulky 1,2,3,4-tetraphenylbutadienedi-1,4-yl ligand system has been reported to allow the isolation of a mono(cyclopentadienyl)gadolinium THF adduct of the formula $(C_5H_5)Gd(\eta^2\text{-}C_4Ph_4)(THF)_3$.[595] Two mono(cyclopentadienyl)lanthanide allyl compounds could be prepared by metathesis. Spectra of both complexes, $(C_5H_5)Nd(CH_2CH{=}CH_2)_2(THF)$ as well as $[Li(dioxane)_2][(C_5H_5)Nd(CH_2CH{=}CH_2)_3]$, show bands characteristic of η^3-allyl groups.[479]

The first X-ray crystallographic data on a monomeric lanthanide organyl containing, in addition to one unsubstituted cyclopentadienyl anion, a Ln–C σ-bond has become available for the intramolecularly stabilized species $(C_5H_5)Lu[CH_2CH(Me)CH_2NMe_2](Cl)(THF)_2$. It was formed on metathesis of *in situ* prepared mono(cyclopentadienyl)lutetium dichloride **89r** with 1 equiv of lithium 3-(dimethylamino)-2-methylpropyl in THF as outlined in eq 189:[594]



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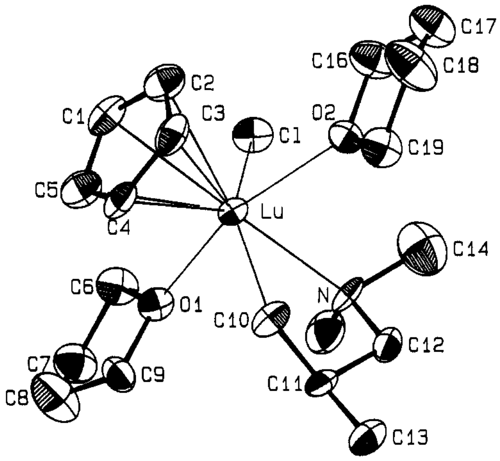
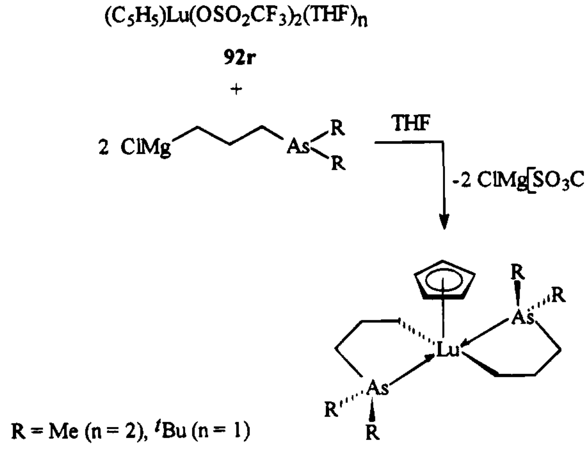


Figure 142. Structure of $(C_5H_5)Lu[CH_2CH(Me)CH_2NMe_2](Cl)(THF)_2$ in the crystal.[594]

The molecular structure of the latter product (Figure 142) shows a distorted pseudo-octahedral geometry around the rare earth metal with two molecules of tetrahydrofuran located in the coordination sphere of the lutetium. The centroid of the η^5-cyclopentadienyl group and the intramolecularly dative amino function occupy the imaginary, axial sites of the distorted octahedron.[594]

Equimolar reaction of isolated **89q** and the non-methyl-substituted salt lithium 3-(dimethylamino)propyl proceeds analogously to yield the closely related chloromono(cyclopentadienyl)lutetium alkyl $(C_5H_5)Lu[(CH_2)_3NMe_2](Cl)(THF)_2$. Although bonds between the hard lanthanide lutetium and the soft donor atom arsenic are not necessarily obvious, As–Lu interactions of corresponding 3-(dialkylarsano)propyl systems are assumed to effect a similar coordinative stabilization of the (C_5H_5)–Lu unit in dialkylated products described below (eq 190):[594]



(190)

Table 37. Spectroscopic and Other Data of Mono(pentamethylcyclopentadienyl)lanthanide Complexes Containing Lanthanide to Element Group 14 Bonds

compound	Ln		color, characterization, etc.
$(C_5Me_5)LnMe_2$	Sc		white, NMR[569]
	Y		white, NMR[598]
$[Li(tmed)_2][(C_5Me_5)LnMe_3]$	Yb	**97q**	yellow, NMR,[294,463,465] melt./dec.[294,465]
	Lu	**97r**	colorless,[463,465] X-ray,[294,465] NMR,[294,463] IR, melt./dec.[465]
$(C_5Me_5)Ln^tBu_2$	Lu		complex with THF: NMR[565]
$[Li(tmed)_2][(C_5Me_5)Ln^tBu_2Cl]$	Yb		wine red, melt./dec.[599]
$[Li(THF)_n][(C_5Me_5)Ln^tBu_2Cl]$	Lu		$n = 2$: NMR;[565] $n = 3$: colorless, NMR, melt./dec.[599]
$(C_5Me_5)Ln(CH_2{}^tBu)_2$	Lu		complex with THF: NMR[565]
$(C_5Me_5)Ln(CH_2SiMe_3)[CH(SiMe_3)_2]$	Lu		complex with THF: NMR[565]
$[Li(THF)_3][(C_5Me_5)Lu(CH_2SiMe_3)[CH(SiMe_3)_2]Cl]$	Lu		X-ray[565]
$(C_5Me_5)Ln[CH(SiMe_3)_2]_2$	La	**98c**	X-ray,[566,568] NMR;[441,498,568] complex with THF: X-ray, NMR[568]
	Ce	**98d**	orange, X-ray,[586] NMR,[441,585,586] IR[585,586]
$(C_5Me_5)Ln[CH(SiMe_3)_2](BPh_4)$	La		yellow, NMR; complex with 3THF: yellow, NMR[600]
$(C_5Me_5)Ln[CH(SiMe_3)_2][B(C_6H_4F\text{-}4)_4]$	La		NMR, melt./dec.[600]
$(C_5Me_5)Ln[C_6H_4CH_2NMe_2)_2$	Y		X-ray,[601] white, NMR, IR[441]
$(C_5Me_5)Ln[o\text{-}C_6H_4CH_2NMe(CH_2\text{-}\mu)]\text{-}[\mu\text{-}o\text{-}C_6H_4CH_2NMe(CH_2\text{-}\mu)]Ln(C_5Me_5)$	Y		complex with THF: white, X-ray, NMR, IR[601]
$(C_5Me_5)Ln[(\mu\text{-}CH_2)_2PMe_2]_2$	Lu		colorless, NMR, IR[496]
$[(C_5Me_5)_2Ln(\mu\text{-}C{\equiv}CPh)_2]_2Ln$	Yb		red, X-ray, NMR, IR, melt./dec.[602]
$(C_5Me_5)(C_2B_9H_{11})Ln$	Sc		complex with 3THF: yellow, NMR[603]
$[Li(THF)_3][(C_5Me_5)(C_2B_9H_{11})LnCH(SiMe_3)_2]$	Sc		NMR[603]
$[Li(THF)_3]\{Li[(C_5Me_5)(C_2B_9H_{11})LnCH(SiMe_3)_2]_2\}$	Sc		yellow, X-ray[603,604]
$(C_5Me_5)Ln(Me)(OC_6H_3{}^tBu_2\text{-}3,5)$	Sc		white, NMR[569]
$(C_5Me_5)Ln(Me)(OC_6H_3{}^tBu_2\text{-}2,6)$	Y		white,[598] NMR;[598,605] complex with 2THF: NMR[598]
$(C_5Me_5)Ln[CH(SiMe_3)_2](OC_6H_3{}^tBu_2\text{-}2,6)$	Y		white,[598] NMR[497,598]
	La		NMR[600]
	Ce		orange, NMR, IR[586]
$(C_5Me_5)Lu[CH(SiMe_3)_2]Cl_2Li(LB)_n$	Lu		$(LB)_n = (THF)_2$: white, NMR; $(LB)_n = (tmed)$: white, NMR, X-ray[565]
$(C_5Me_5)Ln(C{\equiv}CSiMe_3)(OC_6H_3{}^tBu_2\text{-}2,6)$	Y		yellow, NMR; complex with 2 THF: white, NMR[598]
$(C_5Me_5)Ln(Cl)[C_5H_3(CH_2NMe_2)]Fe(C_5H_5)$	Y		brown red, NMR, MS, IR, UV−vis, melt./dec., magn. d.[501]

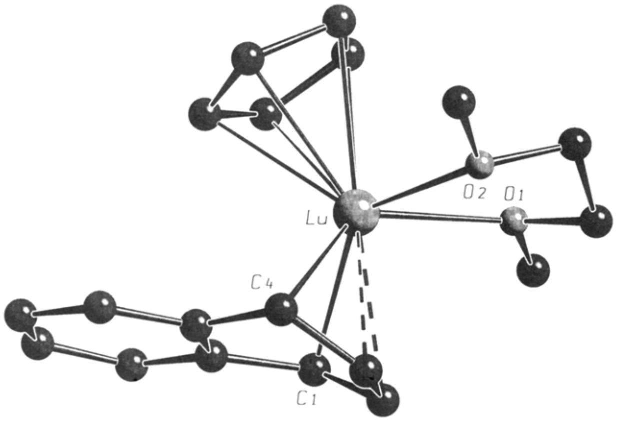
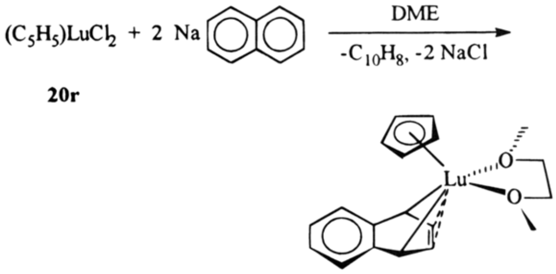


Figure 143. Structure of $(C_5H_5)Lu(\eta^4\text{-}C_{10}H_8)(DME)$ in the crystal.[596]

Taking advantage of the chelate effect two thermally stable 2-[(dimethylamino)methyl]ferrocenyl compounds $(C_5H_5)Yb\{[C_5H_3(CH_2NMe_2)]Fe(C_5H_5)\}_2$ (a dialkyl)[482] and $(C_5H_5)Sm(Cl)[C_5H_3(CH_2NMe_2)]Fe(C_5H_5)$ (a monoalkyl)[501] have successfully been employed to stabilize the mono(cyclopentadienyl)lanthanide unit.

Very recently, some approaches to mono(cyclopentadienyl)lanthanide alkyls have been made using bulky aromatic systems such as the anthracene dianion ($C_{14}H_{10}{}^{2-}$)[481] and the naphthalide ligand ($C_{10}H_8{}^{2-}$).[596] However, only the structure of the lutetium naphthalene complex $(C_5H_5)Lu(\eta^4\text{-}C_{10}H_8)$-(DME) (eq 191) could be elucidated by a single-crystal X-ray analysis (Figure 143).[596]



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Finally, a tetranuclear neodymium cluster has to be mentioned which acquires stabilization by incorporation of an oxygen dianion in the molecular unit. $[Li(DME)_3]_2\{[(C_5H_5)Nd]_4(\mu_2\text{-}CH_3)_2(\mu_4\text{-}O)(\mu_2\text{-}Cl)_6\}$ has been crystallized from DME after reaction of $(C_5H_5)_2NdCl{\cdot}2(LiCl){\cdot}n(THF)$ and lithium methyl in the molar ratio 1:1.[597]

b. Pentamethylcyclopentadienyl Derivatives. In view of the sterically larger permethylated cyclopentadienyl group $C_5Me_5{}^-$ compared to the unsubstituted aromatic ligand system $C_5H_5{}^-$ quite a few mono(pentamethylcyclopentadienyl)lanthanide species containing additionally at least one η^1-Ln−C bond have been described (Table 37).

Alkylmono(pentamethylcyclopentadienyl)lanthanide complexes were first prepared 1984 in form of the phosphorus ylide $(C_5Me_5)Lu[(\mu\text{-}CH_2)_2PMe_2]_2$. This ylide complex has been obtained by reaction of lutetium trichloride with 1 equiv of sodium pentamethylcyclopentadienyl and 2 equiv of the chelating ligand $Li(\mu\text{-}CH_2)_2PMe_2$ as in eq 192:[496]

$$LuCl_3 + NaC_5Me_5 + 2Li(\mu\text{-}CH_2)_2PMe_2 \xrightarrow[-NaCl,\ -2LiCl]{} (C_5Me_5)Lu[(\mu\text{-}CH_2)_2PMe_2]_2 \quad (192)$$

In the same year Schumann et al.[465] also reported the synthesis and structure of the ionic complex type $[Li(tmed)_2][(C_5Me_5)LnMe_3]$ (**97**) with only terminal methyl groups (eq 193). The single-crystal X-ray

$$\mathrm{LnCl_3 + NaC_5Me_5 + 2tmed + 3LiMe \xrightarrow[-NaCl,\ -2LiCl]{THF/Et_2O} \underset{\mathbf{97}}{[Li(tmed)_2][(C_5Me_5)LnMe_3]}} \quad (193)$$

Ln = Yb (**97q**), Lu (**97r**)[294,463,465]

diffraction study of the lutetate **97r** (Figure 144) showed that the molecule is composed of one π-bonded pentamethylcyclopentadienyl ligand and three σ-bonded methyl groups in a distorted pseudotetrahedral arrangement.[294,465]

Initial efforts toward the synthesis of neutral compounds of the general monomeric formula, $(C_5Me_5)LnR_2$, showed that two *tert*-butyl groups together with the pentamethylcyclopentadienyl anion are not bulky enough to give isolable compounds of even small lanthanides like ytterbium and lutetium. Thus, treatment of $LnCl_3$ with NaC_5Me_5 and lithium *tert*-butyl in the molar ratio 1:1:2 yielded again cation–anion pairs as in eqs 194 and 195.[565,599] However, it was reported that the reaction illustrated in eq 195 also gives the salt-free THF adduct $(C_5Me_5)Lu^tBu_2(THF)$ as a byproduct.[565]

$$\mathrm{YbCl_3 + NaC_5Me_5 + 2Li^{\mathit{t}}Bu \xrightarrow[-NaCl,\ -LiCl]{THF/Et_2O/tmed} [Li(tmed)_2][(C_5Me_5)Yb^{\mathit{t}}Bu_2Cl]} \quad (194)$$

$$\mathrm{LuCl_3 + NaC_5Me_5 + 2Li^{\mathit{t}}Bu \xrightarrow[-NaCl,\ -LiCl]{THF/Et_2O} [Li(THF)_{\mathit{n}}][(C_5Me_5)Lu^{\mathit{t}}Bu_2Cl]} \quad (195)$$

$n = 2,^{565}\ 3^{599}$

While the anion of $[Li(tmed)_2][(C_5Me_5)Yb^tBu_2Cl]$ contains a cation with tetracoordinated lithium, the THF analogue, $[Li(THF)_3][(C_5Me_5)Lu(^tBu)_2Cl]$ contains only three-coordinate lithium. It is thought that the lithium is coordinated to the chloride, thereby increasing its coordination number to four.[599]

First reports on salt- and solvent-free mono(pentamethylcyclopentadienyl)lanthanide dialkyls date back to 1988. Teuben et al.[585] obtained $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$ (**98d**) by reacting mono(pentamethylcyclopentadienyl)cerium aryloxide **94d** with 2 molar equiv of the corresponding lithium alkyl (eq 196). Thermolysis of **98d** begins at room temperature and slowly proceeds to generate $CH_2(SiMe_3)_2$ and a mixture of unidentified organocerium materials.

$$\mathrm{\underset{\mathbf{94d}}{(C_5Me_5)Ce(OC_6H_3{}^{\mathit{t}}Bu_2\text{-}2,6)_2} + 2LiCH(SiMe_3)_2 \xrightarrow{pentane} \underset{\mathbf{98d}}{(C_5Me_5)Ce[CH(SiMe_3)_2]_2} + 2LiOC_6H_3{}^{\mathit{t}}Bu\text{-}2,6} \quad (196)$$

One year later, the solid-state structure of **98d** proved the existence of the monomeric complex. The high-electron deficiency at the formally five-coordinate rare earth metal center is alieviated by the formation of a variety of secondary interactions with the α-C–H or even β-Si–CH_3 bonds.[586] The X-ray crystal structure of the lanthanum congener, $(C_5Me_5)La[CH(SiMe_3)_2]_2$ (**98c**) (Figure 145), published by Schaverien et al.,[566,568] gave similar results. The coordination geometry of the complexes **98** is described best as a two-legged piano stool.

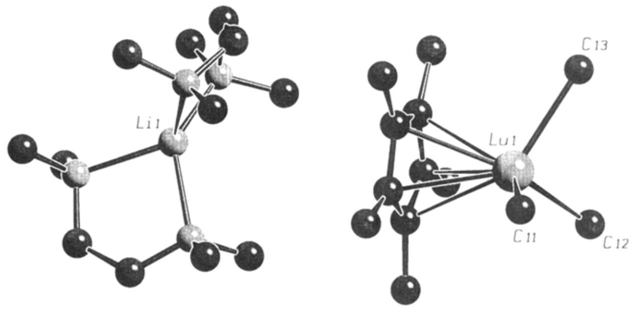


Figure 144. Structure of $[Li(tmed)_2][(C_5Me_5)LuMe_3]$ (**97r**) in the crystal.[294,465]

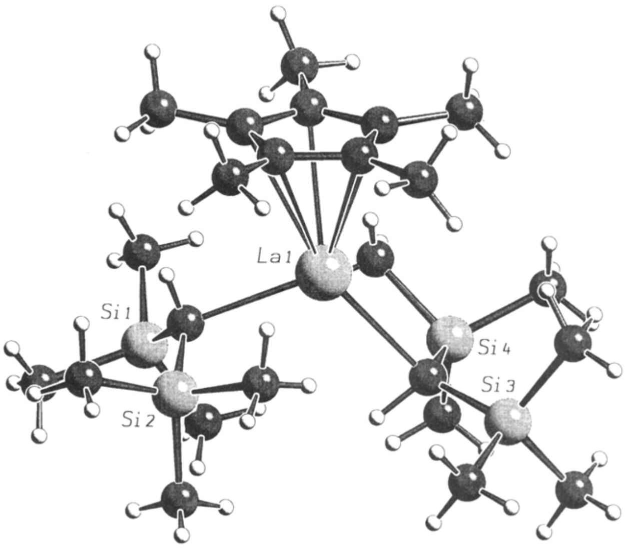


Figure 145. Structure of $(C_5Me_5)La[CH(SiMe_3)_2]_2$ (**98c**) in the crystal.[566,568]

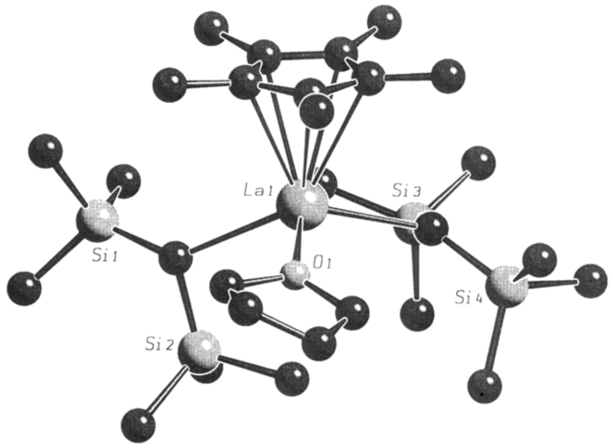
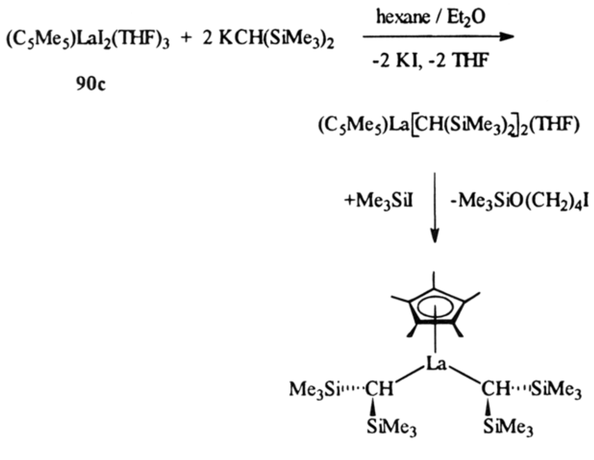


Figure 146. Structure of $(C_5Me_5)La[CH(SiMe_3)_2]_2(THF)$ in the crystal.[568]

The lanthanum derivative **98c** was prepared by metathesis of $(C_5Me_5)LaI_2(THF)_3$ (**90c**) with 2 equiv of potassium bis(trimethylsilyl)methyl, followed by removal of THF from the THF adduct (Figure 146) via cleavage of the cyclic ether tetrahydrofuran by trimethylsilyl iodide (eq 197).[566,568] Higher yields of **98c** are available by direct treatment of the THF-free iodide $[(C_5Me_5)LaI_2]_n$, with 2 equiv of $KCH(SiMe_3)_2$ in diethyl ether. Addition of THF regenerates the THF adduct quantitatively.[566,568]



(197)

98c

Incorporation of salts can be avoided by using neutral homoleptic lanthanide alkyl complexes in acid–base reactions with pentamethylcyclopentadiene as in eq 198:[441,601]

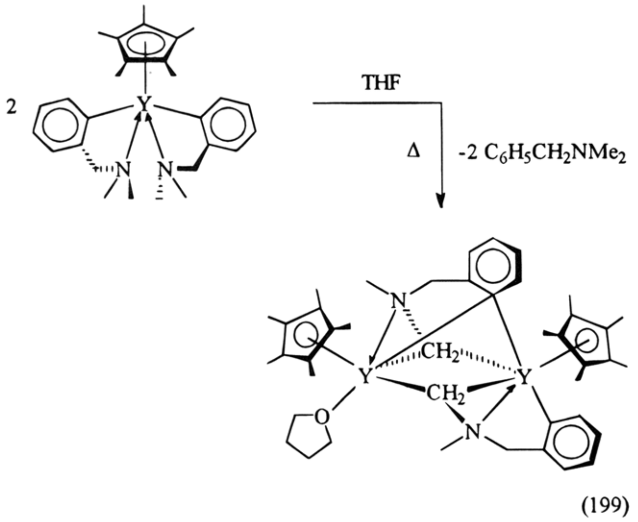
$$\mathrm{LnR_3 + C_5Me_5H \rightarrow (C_5Me_5)LnR_2 + RH} \quad (198)$$

$$\mathrm{R = C_6H_4(CH_2NMe_2)\text{-}2:\ Ln = Y}$$

$$\mathrm{R = CH(SiMe_3)_2:\ Ln = La\ (\mathbf{98c}),\ Ce\ (\mathbf{98d})}$$

The introduction of a single pentamethylcyclopentadienyl ligand occurs cleanly with the starting material $Y[C_6H_4(CH_2NMe_2)\text{-}2]_3$. However, analogous reactions of the homoleptic species $Ln[CH(SiMe_3)_2]_3$ give product mixtures comprised of **98**, $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$ and $Ln[CH(SiMe_3)_2]_3$.[441] The single-crystal X-ray structure determination of the 14-electron system $(C_5Me_5)Y[C_6H_4(CH_2NMe_2)]_2$ (Figure 147) unambiguously demonstrates the presence of agostic Y···C–H and unique Y···C–N interactions in addition to intramolecular coordination of the dimethylamino group.[601]

Thermal decomposition of a THF solution of $(C_5Me_5)Y[C_6H_4(CH_2NMe_2)]_2$ (eq 199) gives the species depicted in Figure 148. Its asymmetrical structure has been demonstrated by a X-ray diffraction study.[601]



(199)

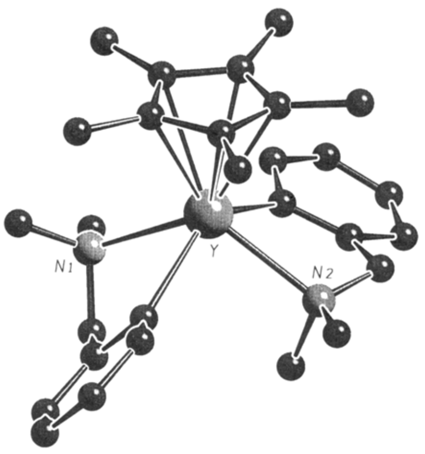


Figure 147. Structure of $(C_5Me_5)Y[C_6H_4CH_2NMe_2]_2$ in the crystal.[601]

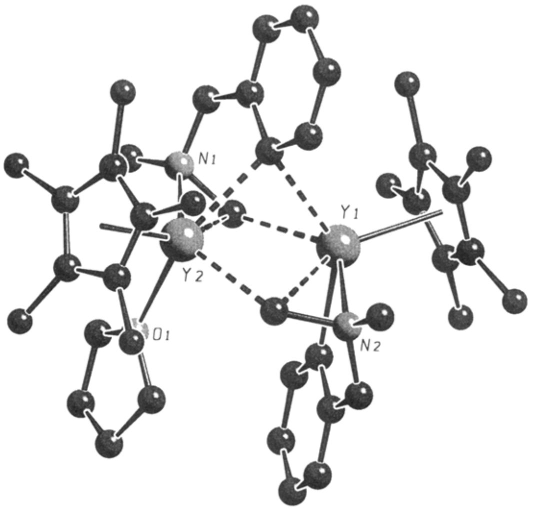


Figure 148. Structure of $(C_5Me_5)Y[o\text{-}C_6H_4CH_2NMe(CH_2\text{-}\mu)][\mu\text{-}o\text{-}C_6H_4CH_2NMe(CH_2\text{-}\mu)]Y(C_5Me_5)(THF)$ in the crystal.[601]

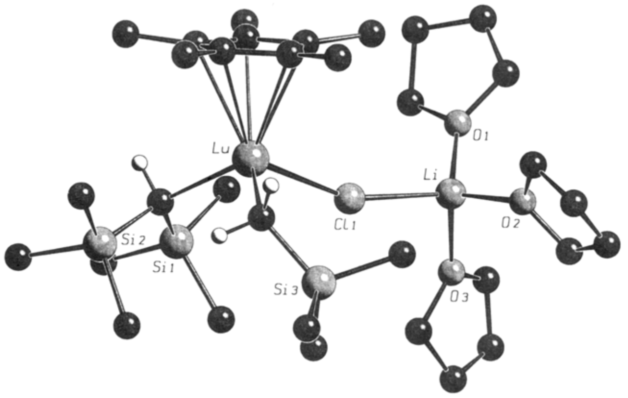


Figure 149. Structure of $(C_5Me_5)Lu(CH_2SiMe_3)[CH(SiMe_3)_2](\mu\text{-}Cl)Li(THF)_3$ in the crystal.[565]

Intramolecular coordination of the nitrogen lone pairs to the rare earth metal center was suggested for the ferrocenyl derivative $(C_5Me_5)Y(Cl)[C_5H_3(CH_2NMe_2)]Fe(C_5H_5)$.[501]

The dialkyl derivative $(C_5Me_5)La[CH(SiMe_3)_2]_2$ (**98c**) is a useful precursor for synthesis of cationic mono(pentamethylcyclopentadienyl)lanthanide alkyl complexes. Compound **98c** reacts with $[PhNMe_2H]BPh_4$ to give zwitterionic $(C_5Me_5)La[CH(SiMe_3)_2]_2(\mu\text{-}\eta^x\text{-}Ph)_2BPh_2$. Irreversible reaction of the latter compound with THF generates the solvated cationic species $\{(C_5Me_5)La[CH(SiMe_3)_2](THF)_3\}(BPh_4)$.[600] The zwitterionic lanthanoorganyl can also be used as starting

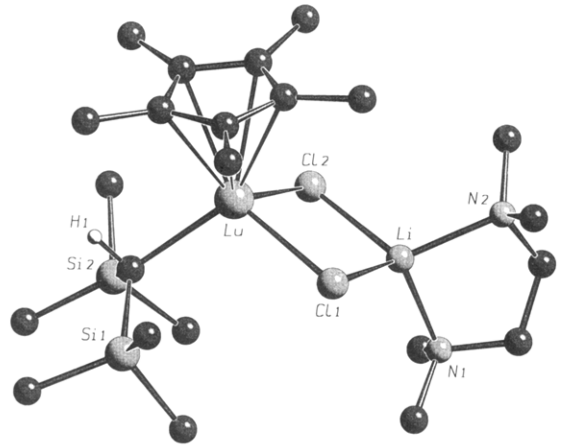
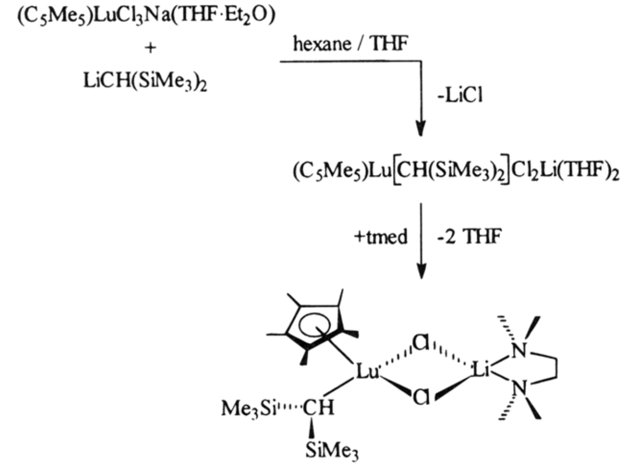


Figure 150. Structure of $(C_5Me_5)Lu[CH(SiMe_3)_2](\mu\text{-}Cl)_2\text{-}Li(tmed)$ in the crystal.[565]

material for mixed species such as $(C_5Me_5)La[CH(SiMe_3)_2](OC_6H_3{}^tBu_2\text{-}2,6)$.[600]

A respectable number of alkyllanthanide chlorides with only one pentamethylcyclopentadienyl ligand has been prepared in course of the reaction sequence, illustrated in eq 200:[565,566]



(200)

Addition of [bis(trimethylsilyl)methyl]lithium to a diethyl ether solution of $(C_5Me_5)Lu[CH(SiMe_3)_2]Cl_2\text{-}Li(THF)_2$ yields the chiral, LiCl-free, mixed-dialkylated compound $(C_5Me_5)Lu(CH_2SiMe_3)[CH(SiMe_3)_2]\text{-}(THF)$ which is contaminated with a small amount of the lithium chloride adduct $(C_5Me_5)Lu(CH_2SiMe_3)\text{-}[CH(SiMe_3)_2]ClLi(THF)_3$.[565,566] Single-crystal X-ray structure determinations show that the THF complex (Figure 149) and the tmed complex $(C_5Me_5)Lu[CH(SiMe_3)_2]Cl_2Li(tmed)$ (Figure 150) have tetracoordinated lithium linked to lutetium by two or one bridging chloro ligands, repectively. In each case the overall geometry corresponds roughly to a three-legged piano stool.[565]

In addition, syntheses of two other salt-containing and salt-free complex combinations are described in the same article:[565] $(C_5Me_5)LuR_2ClLi(THF)_2/(C_5Me_5)\text{-}LuR_2(THF)$ ($R = {}^tBu$ and $CH_2{}^tBu$). The equilibrium outlined in eq 201 is suggested to exist in the presence of lithium chloride, which is solvated by THF, in hexane solutions.

$$(C_5Me_5)LuR_2ClLi(THF)_2 \rightleftharpoons (C_5Me_5)LuR_2(THF) + LiCl{\cdot}(THF) \quad (201)$$

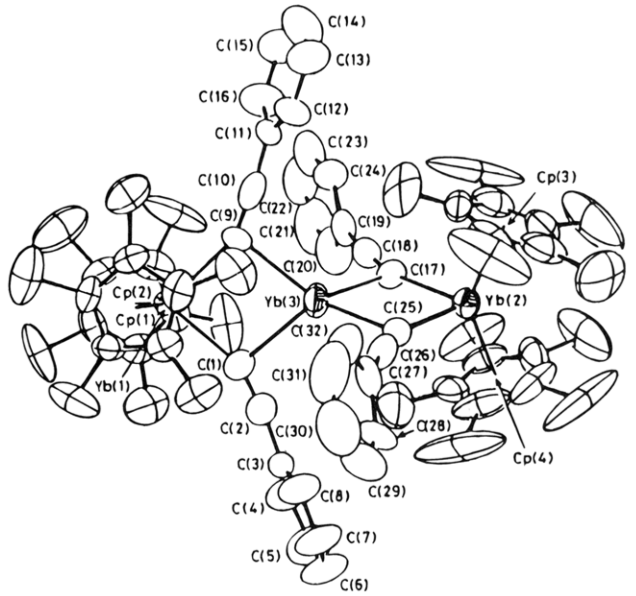


Figure 151. Structure of $[(C_5Me_5)_2Yb(\mu\text{-}C{\equiv}CPh)_2]_2Yb$ in the crystal.[602] (Reprinted from ref 602. Copyright 1984 Chemical Society of London.)

Some (aryloxo)mono(pentamethylcyclopentadienyl)lanthanide alkyl species are known. Solvent-free organolanthanides $(C_5Me_5)Ln[CH(SiMe_3)_2](OC_6H_3\text{-}{}^tBu_2\text{-}2,6)$ are accessible by metathesis of the corresponding pure mono(pentamethylcyclopentadienyl)lanthanide aryloxides **94** with an alkalimetal bis(trimethylsilyl)methyl salt in toluene or pentane, respectively (eq 202).

$$\underset{\mathbf{94}}{(C_5Me_5)Ln(OC_6H_3{}^tBu_2\text{-}2,6)_2} + MCH(SiMe_3)_2 \xrightarrow[-MOC_6H_3{}^tBu_2\text{-}2,6]{} (C_5Me_5)Ln(OC_6H_3{}^tBu_2\text{-}2,6)[CH(SiMe_3)_2] \quad (202)$$

$Ln = Y$: $M = Li$,[497] K[598]

$Ln = Ce$: $M = K$[586]

The mixed phenoxomethylscandium derivative, prepared by the two different pathways shown in eqs 203 and 204, is thought to be dimeric with bridging alkoxo units.[569] The synthesis of oligomeric mono-

$$2(C_5Me_5)Sc(OC_6H_3{}^tBu_2\text{-}3,5)Cl{\cdot}(LiCl) + 2LiMe \xrightarrow[-4LiCl]{Et_2O} [(C_5Me_5)Sc(Me)(\mu\text{-}OC_6H_3{}^tBu_2\text{-}3,5)]_2 \quad (203)$$

$$2/n[(C_5Me_5)ScMe_2]_n + 2HOC_6H_3{}^tBu_2\text{-}3,5 \xrightarrow[-2CH_4]{benzene\text{-}d_6} [(C_5Me_5)Sc(Me)(\mu\text{-}OC_6H_3{}^tBu_2\text{-}3,5)]_2 \quad (204)$$

(pentamethylcyclopentadienyl)dimethylscandium $[(C_5Me_5)ScMe_2]_n$ is achieved by reaction of an ethereal suspension of $[(C_5Me_5)ScCl_2]_n$ with two equivalents of $LiMe{\cdot}(LiBr)$.[569] Very recently, the corresponding Y−Me species has been synthesized from mono(pentamethylcyclopentadienyl)lanthanide aryloxides and NMR data are suggestive of a trimeric constitution, $[(C_5Me_5)YMe_2]_3$.[598]

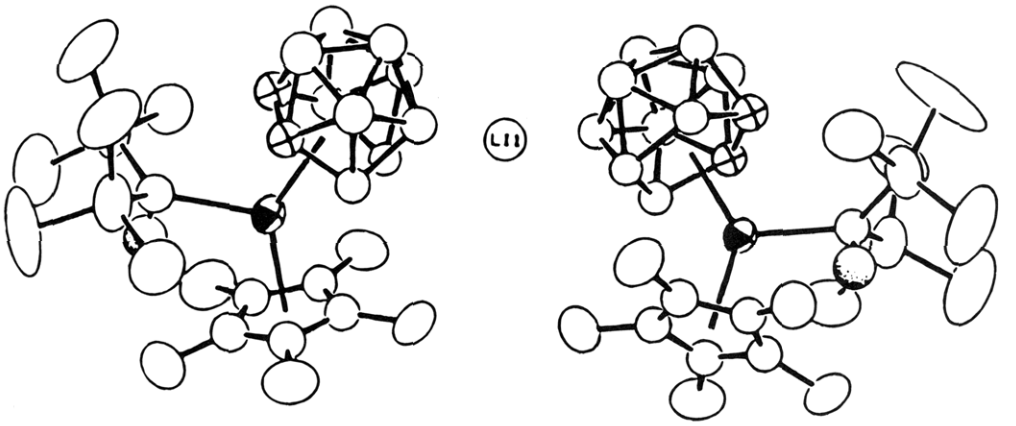


Figure 152. Structure of $[Li(THF)_3]\{Li[(C_5Me_5)(C_2B_9H_{11})ScCH(SiMe_3)_2]_2\}$ in the crystal, showing the two anions and the bridging lithium atom.[603,604] (Reprinted from ref 603. Copyright 1993 American Chemical Society.)

The preparation of dimeric $[(C_5Me_5)Y(Me)(\mu\text{-}OC_6H_3{}^t\text{-}Bu_2\text{-}2,6)]_2$ proceeds in a manner analogous to that in eq 203. The dimers are cleaved by THF to give the monomeric THF adduct $(C_5Me_5)Y(Me)(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$.[598,605]

Evidently, mono(pentamethylcyclopentadienyl)lanthanide alkyls do not tend to form clusters in order to saturate the coordination sphere of the rare earth metal. Only one, mixed-valence $Yb^{III}Yb^{II}Yb^{III}$ cluster has appeared in the literature. Permethylated, divalent ytterbocene reacts with phenylacetylene in the molar ratio 3:4 to afford the phenylacetylide derivative $[(C_5Me_5)_2Yb(\mu\text{-}C{\equiv}CPh)_2]_2Yb$ (Figure 151) which crystallizes with one molecule benzene of solvation. Magnetic susceptibility studies reveal that no electron exchange occurs between the two Yb^{III} centers.[602]

Recently, some research has centered on pentamethylcyclopentadienyl dicarbolide complexes of the rare earth scandium:[603,604] Alkylation of $(C_5Me_5)(C_2B_9H_{11})Sc(THF)_3$ with $LiCH(SiMe_3)_2$ yields essentially quantitatively $[Li(THF)_3][(C_5Me_5)(C_2B_9H_{11})ScCH(SiMe_3)_2]$. Recrystallization of the latter complex by pentane diffusion into a concentrated toluene solution gives $[Li(THF)_3]\{Li[(C_5Me_5)(C_2B_9H_{11})ScCH(SiMe_3)_2]_2\}$ whose structure has been determined by single-crystal X-ray diffraction analysis (Figure 152).

c. Derivatives with Other Substituted Cyclopentadienyl Rings. Application of the sterically congested cyclopentadienyl derivative, 1,3-diphenyl-2,4,5-trimethylcyclopentadienyl, leads to a discernible enhancement in thermal stability of the resulting metallorganic rare earth species. In contrast to their permethylated relatives, the lutetium organyls $(Ph_2C_5Me_3)Lu(CH_2SiMe_3)_2(THF)$ and $[K(Et_2O)_{0.5}][(Ph_2C_5Me_3)Lu\{CH(SiMe_3)_2\}Cl_2]$ are stable in solution at 50–60 °C for short periods of time.[565,566] While the latter compound has been isolated after treatment of $(Ph_2C_5Me_3)LuCl_2(THF)(Et_2O)$ with 1 equiv of $KCH(SiMe_3)_2$, the potassium organyl KCH_2SiMe_3 reacts with $(Ph_2C_5Me_3)LuCl_2(THF)(Et_2O)$ in a 2:1 molar ratio to give $(Ph_2C_5Me_3)Lu(CH_2SiMe_3)_2(THF)$.[565]

In studying catalytically active scandium hydrides, Bercaw et al. reported the metathetical synthesis of the intramolecularly chelated amidoscandium complex $[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]ScCH(SiMe_3)_2$ prepared from $[Me_4C_5Si(Me_2)(\eta^1\text{-}N^tBu)]ScCl$ with an equimolar amount of lithium bis(trimethylsilyl)methyl.[352,592] Recently, the same group succeeded in the isolation of the highly active dimer $\{[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]Sc(\mu\text{-}{}^nPr)\}_2$ (Figure 153) after reaction of the hydridic phosphine adduct $\{[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]Sc(PMe_3)(\mu\text{-}H)\}_2$ with 2 equiv of propene at low temperatures[352] as well as some more of these derivatives.[752]

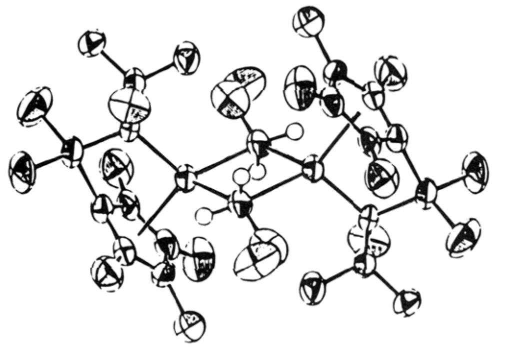


Figure 153. Structure of $\{[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]Sc(\mu\text{-}{}^nPr)\}_2$ in the crystal.[352] (Reprinted from ref 352. Copyright 1990 Thieme.)

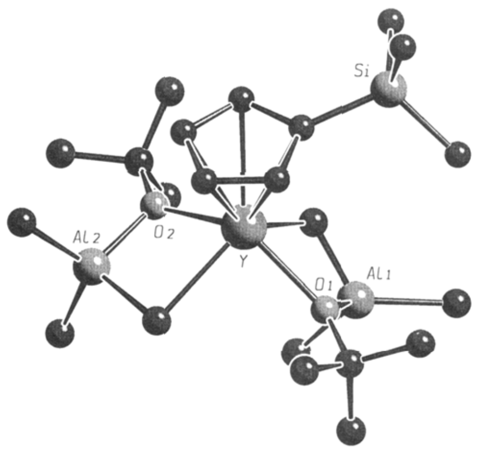


Figure 154. Structure of $(Me_3SiC_5H_4)Y[(\mu\text{-}O^tBu)(\mu\text{-}Me)AlMe_2]_2$ in the crystal.[606]

Studies on the reactivity of the alkoxide $[(Me_3SiC_5H_4)Y(\mu\text{-}O^tBu)(O^tBu)]_2$ with trimethylaluminum resulted in cleavage of the dimeric precursor and affording the mixed-ligand complex $(Me_3SiC_5H_4)Y[(\mu\text{-}O^tBu)(\mu\text{-}Me)AlMe_2]_2$. X-ray crystallographic data from the latter monomer confirm a formally seven-coordinated yttrium atom which is linked to two four-coordinate aluminum atoms by bridging *tert*-butoxide and methyl groups (Figure 154).[606]

Important data on reported mono(cyclopentadienyl)lanthanide alkyls containing a differently sub-

Table 38. Spectroscopic and Other Data of Mono(cyclopentadienyl)lanthanide Complexes Containing Lanthanide to Element Group 14 Bonds and Other Substituted Cyclopentadienyl Ligands

compound	Ln	color, characterization, etc.
$(Me_3SiC_5H_4)Ln[(\mu\text{-}O^tBu)(\mu\text{-}Me)AlMe_2]_2$	Y	X-ray, NMR, IR[606]
$(Ph_2C_5Me_3)Ln(CH_2SiMe_3)_2$	Lu	complex with THF: NMR[565]
$[K(Et_2O)_{0.5}][(Ph_2C_5Me_3)Ln\{CH(SiMe_3)_2\}Cl_2]$	Lu	NMR[565]
$[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]LnC_3H_7$	Sc	dimer: white, X-ray,[352,752] NMR, IR; complex with PMe_3: NMR[752]
$[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]LnC_4H_9$	Sc	dimer: NMR, IR[752]
$[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]Ln^iC_4H_9$	Sc	complex with PMe_3: cream, NMR[752]
$[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]Ln^iC_6H_{11}$	Sc	complex with PMe_3: white, NMR, IR[752]
$[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]LnCHPh(CH_2)_3Ph$	Sc	complex with PMe_3: yellow, NMR, IR[752]
$[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]LnCH(SiMe_3)_2$	Sc	white, NMR, IR, catalysis[352,752]
$[\{Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)\}Ln]_2(\mu,\eta^2,\eta^2\text{-}C_2H_4)$	Sc	complex with 2PMe_3: orange, X-ray, NMR[752]

stituted cyclopentadienyl ring are surveyed in Table 38.

5. Mono(cyclopentadienyl) Rare Earth Hydrides

Up to now, only three different cyclopentadienyl ligand systems have been used in the synthesis of mono(cyclopentadienyl) rare earth hydride compounds: disubstituted $^tBu_2C_5H_3^-$, bulky $C_5Me_5^-$, and chelating $[Me_4C_5Si(Me_2)(NCMe_3)]^-$. The interest in these compounds centers around their potential as catalysts.

The initial report in this area dates back to 1989: Lobkovskii et al.[336] prepared $\{[(^tBu_2C_5H_3)LuH]_4(AlH_4)_2[AlH_4(Et_2O)]_2\}\cdot Et_2O$, a polynuclear lutetium etherate with a tetralanthanide metal skeleton, by reaction of $[(^tBu_2C_5H_3)_2LuCl]_2$ with $LiAlH_4$ in a pentane–ether mixture. This hydride differs from the one reported two years later by the presence of one molecule of ether of crystallization. Both complexes are assumed to be generated by decomposition of dimeric bis(cyclopentadienyl)lutetium hydride $\{[(^tBu_2C_5H_3)_2LuH]_2(AlH_3\cdot LB)_2\}$.[337] The synthesis of the octanuclear aluminohydride, $(^tBu_2C_5H_3)_5Sm_4(AlH_4)_4H_3(tmed)_2$, has been accomplished by reaction of divalent $(^tBu_2C_5H_3)_2Sm$ with AlH_3 in Et_2O or its THF adduct with AlH_3 in THF and excess tmed. The cyclic metal core of this cluster resembles a sitting frog with three Sm atoms coordinated to one $^tBu_2C_5H_3^-$ ligand each and a $(^tBu_2C_5H_3)_2Sm$ unit; all Sm atoms are connected via μ_2- and μ_3-bridging hydrogens.[607]

The influence of ancillary hard ligands such as alkoxides in the catalytic behavior of organolanthanide hydrides has been studied by Schaverien et al. They developed mono(pentamethylcyclopentadienyl)alkoxoyttrium hydride species of the type $[(C_5Me_5)(2,6\text{-}^tBu_2C_6H_3O)Y(\mu\text{-}H)]_2$ (**99b**)[497,598,605] and $[(C_5Me_5)(2,6\text{-}^tBu_2C_6H_3O)Y]_2(\mu\text{-}H)(\mu\text{-}R)$ where R = Et, ^{n}Pr, ^{n}Bu, C_6H_{13}, as well as $C{\equiv}CSiMe_3$.[598,605] The latter

$$2(C_5Me_5)Y(OC_6H_3{}^tBu_2\text{-}2,6)[CH(SiMe_3)_2] + 2H_2 \xrightarrow{\text{hexane}} \underset{\mathbf{99b}}{[(C_5Me_5)(2,6\text{-}^tBu_2C_6H_3O)Y(\mu\text{-}H)]_2} + CH_2(SiMe_3)_2 \quad (205)$$

$$\underset{\mathbf{99b}}{[(C_5Me_5)(2,6\text{-}^tBu_2C_6H_3O)Y(\mu\text{-}H)]_2} + H_2C{=}CHR \rightarrow [(C_5Me_5)(2,6\text{-}^tBu_2C_6H_3O)Y]_2(\mu\text{-}H)(\mu\text{-}R) \quad (206)$$

$R = H, Me, Et, {}^nBu$

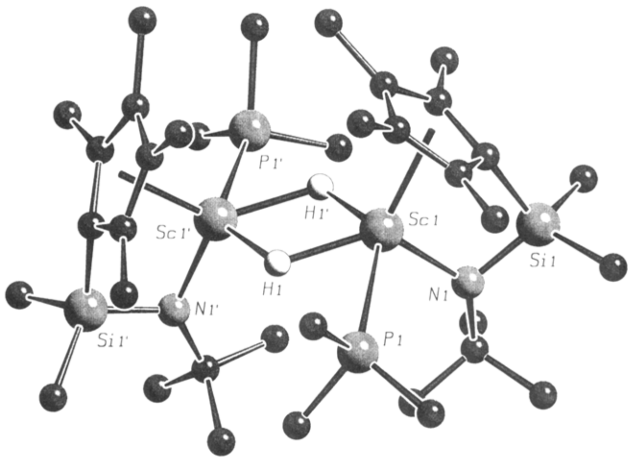


Figure 155. Structure of $\{[Me_4C_5Si(Me_2)(\eta^1\text{-}N^tBu)]Sc(PMe_3)(\mu\text{-}H)\}_2$ in the crystal.[352,592]

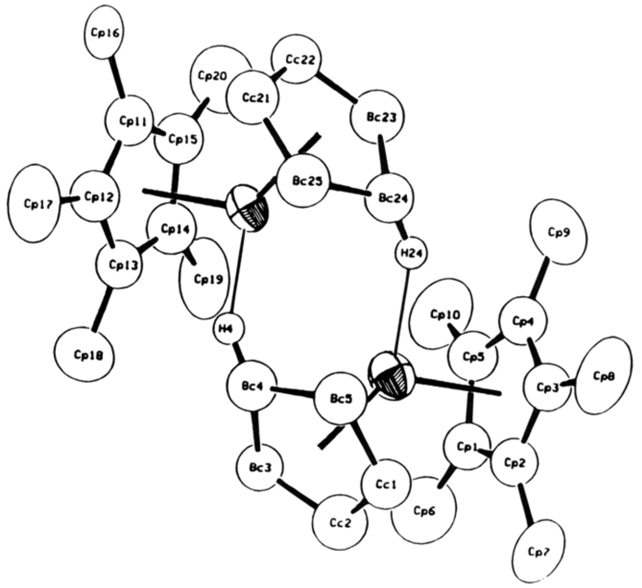


Figure 156. Structure of the anion of $[Li(THF)]_2[(C_5Me_5)(C_2B_9H_{11})ScH]_2$ in the crystal (only the pentagonal faces of the dicarbolloide ligands are shown).[603]

alkyl derivatives may serve as models for the first insertion step in alkene polymerization processes.[598,605] Hydrogenation of $(C_5Me_5)Y(OC_6H_3{}^tBu_2\text{-}2,6)[CH(SiMe_3)_2]$ in hexane affords the *trans* dimer **99b** (eq 205) which reacts regiospecifically with terminal olefins $H_2C{=}CHR$ (R = H, Me, Et, ^{n}Bu) or (trimethylsilyl)acetylene $HC{\equiv}SiMe_3$ to yield corresponding μ-hydride-μ-alkyl (eq 206) and μ-hydride-μ-acetylide species, respectively.[497,598,605]

The structurally characterized single-component organoscandium compound $\{[Me_4C_5Si(Me)_2(\eta^1\text{-}N^tBu)]Sc(PMe_3)(\mu\text{-}H)\}_2$ (Figure 155) also provides a regiospecific catalyst for clean polymerization of α-olefins.[352,592,752]

Table 39. Spectroscopic and Other Data of Mono(cyclopentadienyl)lanthanide Hydrides

compound	Ln		color, characterization, etc.
$(C_5Me_5)(2,6\text{-}^tBu_2C_6H_3O)LnH$	Y	**99b**	white,[598] NMR[497,598]
$[(C_5Me_5)(2,6\text{-}^tBu_2C_6H_3O)Ln]_2(\mu\text{-H})(\mu\text{-Et})$	Y		NMR[598,605]
$[(C_5Me_5)(2,6\text{-}^tBu_2C_6H_3O)Ln]_2(\mu\text{-H})(\mu\text{-}^nPr)$	Y		white,[598] NMR[598,605]
$[(C_5Me_5)(2,6\text{-}^tBu_2C_6H_3O)Ln]_2(\mu\text{-H})(\mu\text{-}^nBu)$	Y		white, NMR[598]
$[(C_5Me_5)(2,6\text{-}^tBu_2C_6H_3O)Ln]_2(\mu\text{-H})(\mu\text{-}C_6H_{13})$	Y		yellow,[598] NMR[598,605]
$[(C_5Me_5)(2,6\text{-}^tBu_2C_6H_3O)Ln]_2(\mu\text{-H})(\mu\text{-C}{\equiv}CSiMe_3)$	Y		NMR[598]
$[Li(THF)]_2[(C_5Me_5)(C_2B_9H_{11})LnH]_2$	Sc		$(+^3/_2$toluene): X-ray, NMR[603]
$[(tBu_2C_5H_3)LnH]_4(AlH_4)_2[AlH_4(Et_2O)]_2$	Lu		X-ray;[337] complex with Et_2O: X-ray[336]
$(^tBu_2C_5H_3)_5Ln_4(AlH_4)_4H_3(tmed)_2$	Sm		yellow green, X-ray[607]
$\{[Me_4C_5Si(Me_2)(\eta^1\text{-N}^tBu)]Ln(\mu\text{-H})\}_2$	Sc		complex with $2PMe_3$: white,[752] X-ray,[352,592] NMR[592,752] IR[752]

Table 40. Spectroscopic and Other Data of Mono(cyclopentadienyl)lanthanide Complexes Containing Rare Earth to Other Element Bonds

compound	Ln	color, characterization, etc.
$[(C_5H_5)Ln]\{(C_5H_5)Lu[W(CO)_5]_2\}$	Lu	synthesis[608]
$[Na(THF)_2][(C_5H_5)Ln\{Ru(CO)_2(C_5H_5)\}(THF)(\mu\text{-I})_2]$	La	colorless, NMR, IR[146c]

The high stability of the pentamethylcyclopentadienyl-dicarbollide scandium hydride, $[Li(THF)]_2[(C_5Me_5)(C_2B_9H_{11})ScH]_2$, augurs ill for its utility as an olefin polymerization catalyst. The dimeric complex consists of two anionic $[(C_5Me_5)(C_2B_9H_{11})ScH]^-$ fragments held together by two, $2e^-$, dative bonds between an electron-rich boron hydride and the electron-deficient rare earth scandium (Figure 156).[603]

Important data of hydridic mono(cyclopentadienyl)-lanthanides are given in Table 39.

6. Mono(cyclopentadienyl) Rare Earth Complexes with Rare Earth to Other Element Bonds

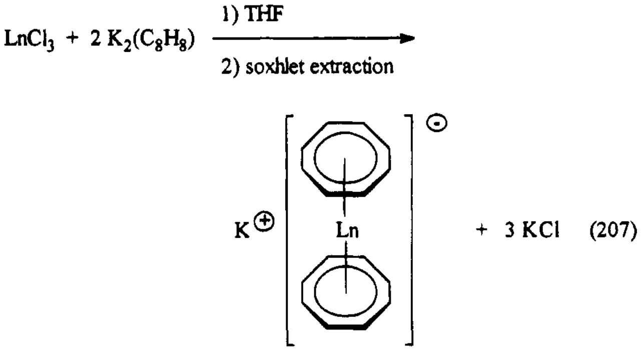
The lanthanum−ruthenium compound $(THF)(C_5H_5)La[Ru(CO)_2(C_5H_5)](\mu\text{-I})_2Na(THF)_2$ and the ionic lutetium−tungsten complex $[(C_5H_5)Lu]\{(C_5H_5)Lu[W(CO)_5]_2\}$ are the only mono(cyclopentadienyl)-lanthanides reported to possess direct lanthanide−transition metal bonds (see Table 40). The latter complex is formed as the main product when equimolar amounts of the chloride $(C_5H_5)LuCl_2$ (**89r**) and the carbonyl $Na_2W(CO)_5$ are allowed to react in DME at −78 °C. The resulting reactive intermediate $\{(C_5H_5)Lu{-}W(CO)_5\}$ dimerizes immediately to give $[(C_5H_5)Lu]\{(C_5H_5)Lu[W(CO)_5]_2\}$.[608] In contrast, $[Na(THF)_2][(THF)(C_5H_5)La\{Ru(CO)_2(C_5H_5)\}(\mu\text{-I})_2]$ results from mixing an equimolar mixture of the iodide $(C_5H_5)LaI_2(THF)_3$ with $Na[(C_5H_5)Ru(CO)_2]$ in THF at −20 °C.[146c] While no spectroscopic data are given for $[(C_5H_5)Lu][(C_5H_5)Lu\{W(CO)_5\}_2]$,[608] the La−Ru bond of crystalline $[Na(THF)_2][(THF)(C_5H_5)La\{Ru(CO)_2(C_5H_5)\}(\mu\text{-I})_2]$ was supported by IR and NMR spectra.[146c]

III. Cyclooctatetraenyl Rare Earth Compounds

A. Cyclooctatetraenyl and Cyclooctatetraenyl−Cyclopentadienyl Rare Earth Complexes

Owing to their large size and possibly due to the availability of f orbitals of suitable symmetry, the lanthanide and actinide ions form many complexes with the 10 π-electron planar aromatic cyclooctatetraene dianion $(C_8H_8{}^{2-})$. Many sandwich complexes of the rare earth elements have been isolated and these containing either exclusively the cyclooctatetraenyl ligand or a cyclooctatetraenyl and a cyclopentadienyl ligand within in one compound are listed in Tables 41 and 42.

Shortly after the synthesis of "uranocene" $(C_8H_8)_2U$ by Streitwieser et al.[631] in 1968, Hayes and Thomas[632] reported the successful isolation of lanthanide(II) cyclooctatetraene complexes in 1969. One year later Mares, Hodgson, and Streitwieser[613] prepared complexes of the type $K[(C_8H_8)_2Ln]$ (**100**) using the methodology developed for the synthesis of uranocene (eq 207).



100

Ln = Y (**100b**), Gd (**100k**),[611] La (**100c**),[611,612] Ce (**100d**), Pr (**100e**), Nd (**100f**), Sm (**100h**), Tb (**100l**)[611,613]

In contrast, the scandium derivative **100a** was isolated in the equimolar reaction of $(C_8H_8)ScCl(THF)$ with $K_2(C_8H_8)$ in THF at room temperature in almost quantitative yield.[609] These complexes **100** are air- and moisture-sensitive and decompose without melting about 160 °C. They are insoluble in hexane, benzene, toluene, ether, CCl_4, $CHCl_3$, and acetonitrile, but moderately soluble in dioxane and THF. The similarities of the IR spectra of uranocene and **100** suggested that in the latter compounds the two $(C_8H_8)^{2-}$ rings are η^8-bound to the lanthanide ion with local D_{8h} symmetry as is the case for $(C_8H_8)_2U$.[633] Unequivocal structural proof was achieved in the solvated heterobimetallic sandwich species $[K(diglyme)][(C_8H_8)_2Ln]$ (Ln = Ce (Figure 157)[616], Yb[619]) in which the counter cation is coordinated by a chelating ether molecule and one bridging cyclooctatetraenyl ring system. The latter compounds are described more precisely as $(diglyme)K(\mu\text{-}C_8H_8)Ln(C_8H_8)$.

Table 41. Spectroscopic and Other Data of Cyclooctatetraenyllanthanide Complexes

compound	Ln	color, characterization, etc.
$[M(LB)_n][(C_8H_8)_2Ln]$	Sc	M = K ($n = 0$) (**100a**): yellow brown, IR[609]
	Y	M = Li (LB = THF, $n = x$): NMR;[610] M = K ($n = 0$) (**100b**): yellow, IR[611]
	La	M = K ($n = 0$) (**100c**): green,[611] IR,[611,612]
	Ce	M = Li (LB = THF, $n = 4$): green, X-ray, NMR, IR, melt./dec.; M = Na (LB = THF, $n = 3$): green, X-ray, NMR, IR, melt./dec.;[634b] M = K ($n = 0$) (**100d**): pale green, IR,[611] UV,[611,613] melt./dec., magn. d.,[613] lumines.,[289] MO;[614] (LB = DME, $n = 1$): green, IR;[615] (LB = diglyme, $n = 1$): X-ray,[616] lumines.[61]
	Pr	M = K ($n = 0$) (**100e**): yellow gold, IR,[611] UV,[611,613] melt./dec., magn. d.[613]
	Nd	M = K ($n = 0$) (**100f**): pale green, IR,[611] UV, magn. d., melt./dec.;[613] complex with 2THF: M = Li (LB = THF, $n = 4$): X-ray[145]
	Sm	M = Li (LB = THF, $n = x$): NMR;[610] M = Na (LB = THF, $n = x$): synthesis;[617] M = K ($n = 0$) (**100h**): brown, IR,[611] UV, melt./dec., magn. d.[613]
	Gd	M = K ($n = 0$) (**100k**): yellow, IR, UV, magn. d.[611]
	Tb	M = K ($n = 0$) (**100l**): yellow brown, IR, UV;[611] melt./dec., magn. d.[613]
	Yb	M = K (LB = DME, $n = 1$): blue, NMR, IR;[618] (LB = diglyme, $n = 1$): blue, X-ray[619]
	Lu	M = Li (LB = THF, $n = x$): NMR[610]
$(C_8H_8)_3Ln_2$	Ce	green, MS, IR[615]
$[(C_8H_8)Ln(THF)_2][Ln(C_8H_8)_2]$	Ce	gold, IR, magn. d.[620]
	La	gold, IR[620]
	Nd	X-ray,[620,621] green, IR, magn. d.[620]
	Er	reddish brown, IR, magn. d.[620]
$(C_8H_8)Ln(\mu\text{-}C_8H_8)K(\mu\text{-}C_8H_8)Ln(\mu\text{-}C_8H_8)K(THF)_4$	Er	yellow, X-ray, NMR, IR[575]

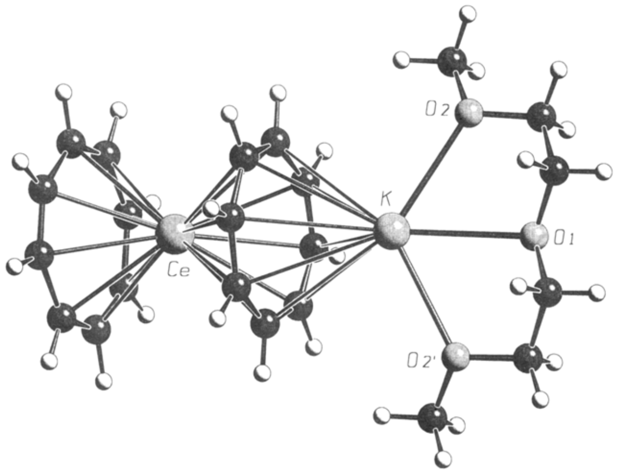


Figure 157. Structure of $[K(diglyme)][(C_8H_8)_2Ce]$ in the crystal.[616]

Despite the striking similarities between actinide and lanthanide complexes as far as the structure is concerned, the lanthanide compounds are much more sensitive toward oxygen which is attributable to the ionic nature of their bondings.[619] The readiness of ligand exchange is typical for lanthanide complexes and this behavior is exemplified by the reaction of $K[(C_8H_8)_2Ce]$ (**100d**) and UCl_4 which results in the formation of uranocene, $CeCl_3$, and KCl in nearly quantitative yield.[611] Resurgence of interest in metallocenes in general and in lanthanide complexes (including oxidation states +4 and +2) in particular led to the synthesis of $[Li(THF)_4][(C_8H_8)_2Nd](THF)_2$,[145] $(C_8H_8)Ln(\mu\text{-}C_8H_8)K(\mu\text{-}C_8H_8)Ln(\mu\text{-}C_8H_8)K(THF)_4$ (Ln = Er, Yb[575]), and $[K(diglyme)][(^tBuC_8H_7)_2Yb]$[634a] as well as the very recently isolated $[M(THF)_n][(C_8H_8)_2Ce]$ with M = Li and $n = 4$ (separated ion pairs) or M = Na and $n = 3$ (linear $Na(\mu\text{-}C_8H_8)Ce(C_8H_8)$ arrangement).[634b] Figure 158 presents a perspective plot of the tetradecker complex $(C_8H_8)Er(\mu\text{-}C_8H_8)K(\mu\text{-}C_8H_8)\text{-}Er(\mu\text{-}C_8H_8)K(THF)_4$.[575]

Cocondensation of cyclooctadiene and lanthanide atoms in the ratio 10−20:1 results in binary cyclooc-

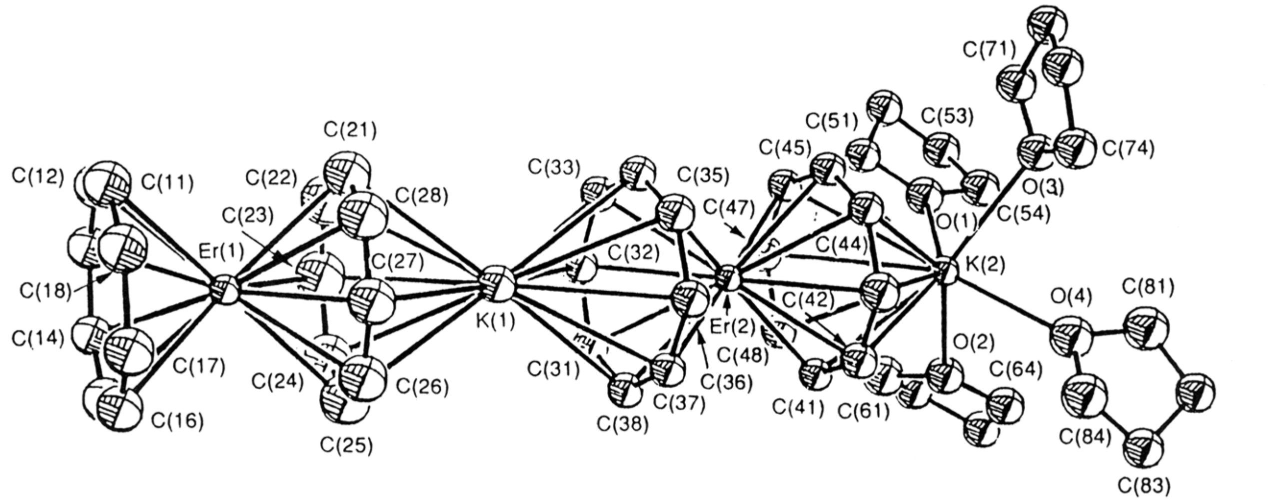


Figure 158. Structure of $(C_8H_8)Er(\mu\text{-}C_8H_8)K(\mu\text{-}C_8H_8)Er(\mu\text{-}C_8H_8)K(THF)_4$ in the crystal.[575] (Reprinted from ref 575. Copyright 1991 Chemical Society of London.)

Table 42. Spectroscopic and Other Data of Cyclooctatetraenylcyclopentadienyllanthanide Complexes

compound	Ln		color, characterization, etc.
$(C_8H_8)Ln(C_5H_5)$	Sc	**101a**	IR, MS, melt./dec.,[609] PE[237]
	Y	**101b**	IR; complex with THF; complex with py: IR[563]
	Pr	**101e**	complex with 2THF: yellow, X-ray[622]
	Nd	**101f**	IR;[563] complex with 2THF: purple[622]
	Sm	**101h**	synthesis[563]
	Gd	**101k**	complex with THF: colorless[622]
	Ho	**101n**	IR, MS; complex with THF: IR; with NH_3: IR; with $CN^cC_6H_{11}$: IR[563]
	Er	**101o**	synthesis[563]
$(C_8H_8)Ln(C_5Me_5)$	Sc		white, NMR, MS, IR, melt./dec., elec. d.[623]
	Y		colorless,[624] white,[623] NMR, melt./dec.,[623,624] IR, elec. d.[623]
	La		pale yellow, IR, melt./dec.,[623] NMR;[441,623] complex with THF: white, IR, elec. d.,[623] yellowish,[624] NMR[623,624]
	Ce		brown, NMR, IR[441]
	Pr		complex with THF: yellow, NMR[624]
	Sm		orange, NMR, IR;[201] complex with THF: red,[624,625] NMR, melt./dec.[624]
	Gd		complex with THF: yellowish, NMR, melt./dec.[624]
	Tb		yellowish, NMR[624]
	Dy		yellow, NMR, melt./dec.[624]
	Er		pink, NMR[624]
	Lu		colorless, X-ray, NMR, melt./dec.[624]
$(C_8H_8)(C_5Me_5)Ln(CH_2{=}C_3N_2Me_4)$	Y		yellow, X-ray, NMR, melt./dec.[753]
$(C_8H_8)Ln(MeC_5H_4)$	Y		complex with THF: colorless, X-ray, MS, NMR, melt./dec.[626]
$(C_8H_8)Ln(C_5H_4PPh_2)$	Sm		complex with 2THF: blue, X-ray, NMR[627]
$(C_8H_8)Ln(C_5H_4PPh_2)Rh(C_5H_5)(CO)$	Sm		pink grey, NMR, IR[627]
$(C_8H_8)Ln(C_5H_3{}^tBu_2)$	Tb		yellow, X-ray, NMR, melt./dec.[587]
$(C_8H_8)Ln(C_5H_3(SiMe_3)_2)$	Pr		green-yellow, NMR, MS, melt./dec.[750]
	Dy		yellow, NMR, MS, melt./dec.[750]
$(C_8H_8)Ln(C_5Me_4H)$	Y		complex with nTHF($n \leq 2$): colorless, NMR, MS, melt./dec.[628]
	La		complex with 2THF: colorless, X-ray, NMR, MS, melt./dec.[628]
	Pr		complex with nTHF($n \leq 2$): yellow, NMR, MS, melt./dec.[628]
	Sm		complex with nTHF($n \leq 2$): dark red, NMR, MS, melt./dec.[628]
	Gd		complex with nTHF($n \leq 2$): colorless, MS, melt./dec.[628]
	Dy		complex with nTHF($n \leq 2$): yellow, MS, melt./dec.[628]
	Er		pink, MS, melt./dec.[628]
	Lu		colorless, X-ray, NMR, MS, melt./dec.[628]
$(C_8H_8)Ln(C_5Me_4Et)$	Y		complex with THF: colorless, NMR, melt./dec.[750]
	La		complex with THF: white, NMR, melt./dec.[750]
	Nd		complex with THF: green, melt./dec.[750]
	Sm		complex with THF: dark red, NMR, melt./dec.[750]
	Gd		complex with THF: colorless, melt./dec.[750]
	Tm		yellow, melt./dec.[750]
	Lu		colorless, X-ray, NMR, melt./dec.[750]
$(C_8H_8)Ln(C_5Me_4PMe_2)$	Sm		dark green, NMR[627]
$(C_8H_8)Ln(C_5Me_4PMe_2)Rh(C_5H_5)(CO)$	Sm		red, NMR[627]
$(C_8H_8)Ln(C_5Me_4PPh_2)$	Sm		red brown, NMR[627]
$(C_8H_8)Ln(C_5Me_4PPh_2)Rh(C_5H_5)(CO)$	Sm		brown, NMR, IR[627]
$(C_8H_8)Ln[C_5(CH_2Ph)_5]$	Lu		white, X-ray, NMR[629]
$(C_8H_8)Ln(C_5Ph_5)$	Pr		yellow, MS, melt./dec.[750]
$(C_8H_8)Ln(2,4\text{-}C_7H_{11})$	Nd		complex with THF: green, X-ray, MS, IR[754]
	Sm		complex with THF: red brown, X-ray, IR,[630] NMR[706]
	Er		complex with THF: deep red, X-ray, MS, IR[754]

tatetraenyl complexes which after extraction with THF gives the THF adducts according eq 208:

$$C_8H_8(g) + Ln(g) \xrightarrow[p\,<\,4\,\times\,10^{-4}\ \text{Torr}]{\text{cocondensation}} (C_8H_8)_3Ln_2 \xrightarrow{\text{THF}} [(C_8H_8)Ln(THF)_2][(C_8H_8)_2Ln] \quad (208)$$

Ln = Ce, La, Er,[620] Nd[620,621]

The unsolvated complexes are extremely sensitive to air and moisture, pyrophoric, and insoluble in nonpolar solvents. The neodymium complex has been examined by X-ray analysis.[620,621] Figure 159 shows two different environments around the Nd atoms. The molecule is composed of a cationic $(C_8H_8)Nd(THF)_2^+$ unit which is η^3 bound to one cyclooctatetraenyl ring of the well-known $(C_8H_8)_2Ln^-$ (Ln = Nd) sandwich.

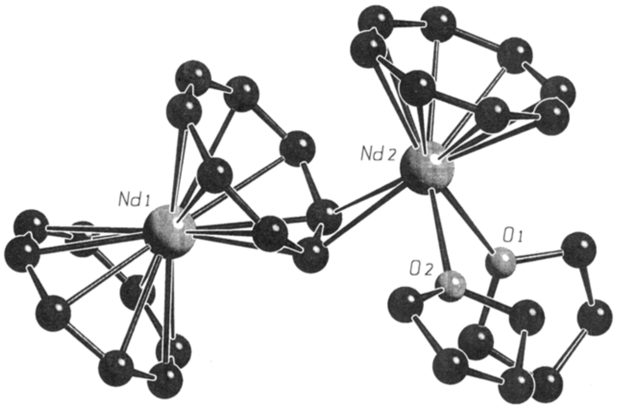


Figure 159. Structure of $[(C_8H_8)Nd(THF)_2][(C_8H_8)_2Nd]$ in the crystal.[620,621]

Since the first preparation of neutral mixed sandwich complexes of the type $(C_8H_8)Ln(C_5H_5)$ by Jamerson et al.[563] in 1974 much interest has been directed at these and related derivatives. Metathetical reactions of either $[(C_8H_8)LnCl(THF)_2]_2$ and NaC_5H_5 (eq

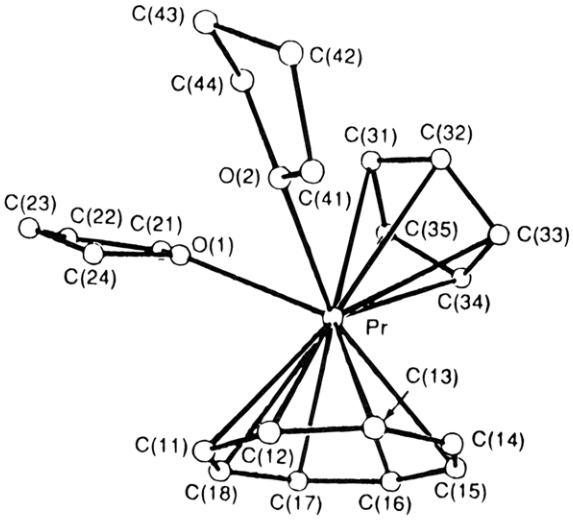


Figure 160. Structure of $(C_8H_8)Pr(C_5H_5)(THF)_2$ (**101e**) in the crystal.[622] (Reprinted from ref 622. Copyright 1991 Chemical Society of London.)

209) or $(C_5H_5)LnCl_2(THF)_3$ (**89**) and $K_2(C_8H_8)$ (eq 210) result in the formation of $(C_8H_8)Ln(C_5H_5)(THF)_n$ (n = 0−2) (**101**):

$$[(C_8H_8)LnCl(THF)_2]_2 + 2NaC_5H_5 \xrightarrow[-2NaCl]{THF} 2(C_8H_8)Ln(C_5H_5)(THF)_n \quad (209)$$

101

Ln = Sc (**101a**),[237,609] Y (**101b**), Nd (**101f**)[563]

$$(C_5H_5)LnCl_2(THF)_3 + K_2(C_8H_8) \xrightarrow[-2KCl]{} (C_8H_8)Ln(C_5H_5)(THF)_n \quad (210)$$

89 **101**

Ln = Y (**101b**), Sm (**101h**), Ho (**101n**),
Er (**101o**),[563] Nd (**101f**),[622] Pr (**101e**),
Gd (**101k**)[622]

The THF is lost upon heating in vacuo; compounds **101** are remarkably thermally stable and can be sublimed under reduced pressure (for instance $(C_8H_8)Sc(C_5H_5)$[609] sublimes at 120 °C/0.1 Torr). Nevertheless, they are extremely sensitive toward oxygen and ignite in contact with air. The volatile sandwiches give molecular ions in their mass spectra.[563,609] Evidence for π-bonded $C_8H_8^{2-}$ and $C_5H_5^-$ rings comes also from infrared spectra, but it was not before 1991 when the crystal structure of $(C_8H_8)Pr(C_5H_5)(THF)_2$ (**101e**) was published:[622] Figure 160 shows a formally nine-coordinate Pr^{3+} ion to which both the $C_8H_8^{2-}$ and the $C_5H_5^-$ ligand is η^8 and η^5 bound, respectively. The centroids of the eight- and five-membered rings and Pr^{3+} make an angle of 138°.

Many examples have been prepared in which the $C_8H_8^{2-}$ ring is unsubstituted while the substitutions on the cyclopentadienyl ring are varied. Complexes with $MeC_5H_4^-$,[626] $C_5Me_4H^-$,[628] $C_5Me_5^-$,[201,441,623−625] $^tBu_2C_5H_3^-$,[587] $C_5H_4PPh_2^-$ (see Figure 161),[627] $C_5Me_4PMe_2^-$,[627] $C_5Me_4PPh_2^-$,[627] and $C_5(CH_2Ph)_5$[629] have been prepared in similar ways as their unsubstituted analogues. The solvent-free species exhibit the expected linear arrangement about the center lanthanide ion ($(C_8H_8)-Ln-(C_5H_5)$) in $(C_8H_8)Lu(C_5Me_4H)$,[628] $(C_8H_8)Lu(C_5Me_5)$,[624] $(C_8H_8)Tb(^tBu_2C_5H_3)$,[587] and $(C_8H_8)Lu[C_5(CH_2Ph)_5]$ (Figure 162).[629] The $(C_8H_8)_{centroid}-M-Cp_{centroid}$ angles are 176.3(4)/175.4(3)°, 173.0°, 177.8°, and 167.7°.

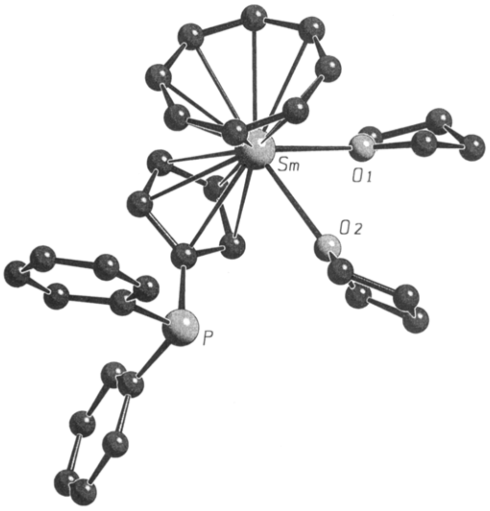


Figure 161. Structure of $(C_8H_8)Sm(C_5H_4PPh_2)(THF)_2$ in the crystal.[627]

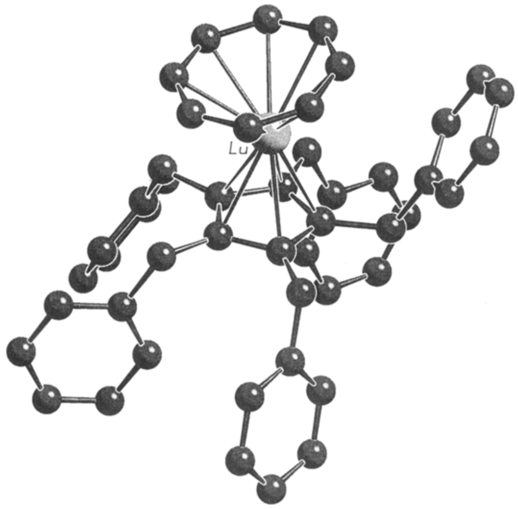


Figure 162. Structure of $(C_8H_8)Lu[C_5(CH_2Ph)_5]$ in the crystal.[629]

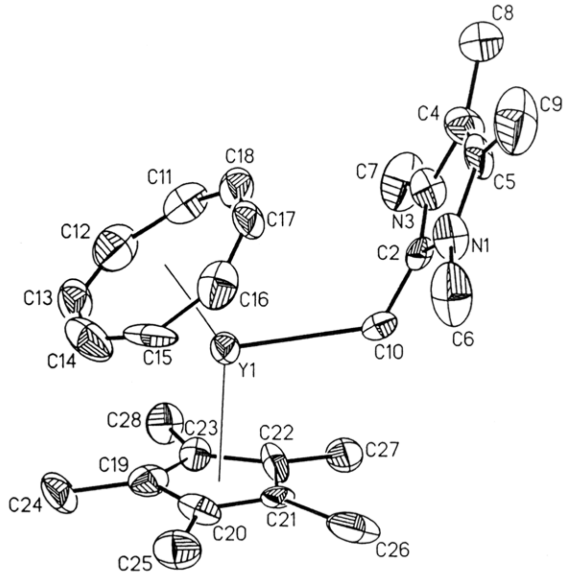


Figure 163. Structure of $(C_8H_8)(C_5Me_5)Y(CH_2{=}CC_2N_2Me_4)$ in the crystal.[753]

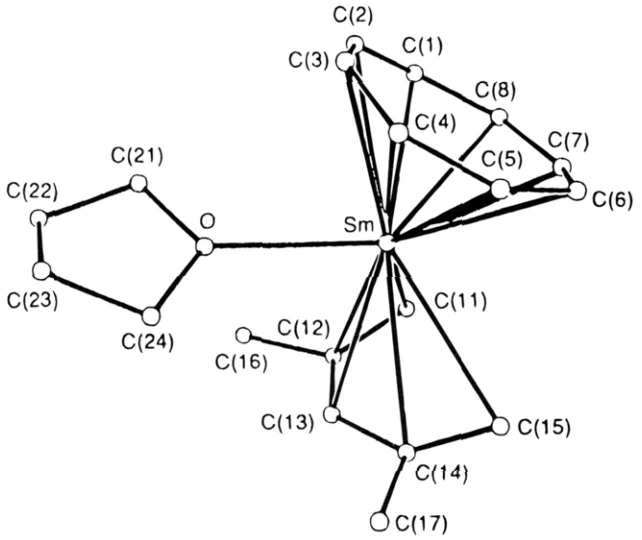
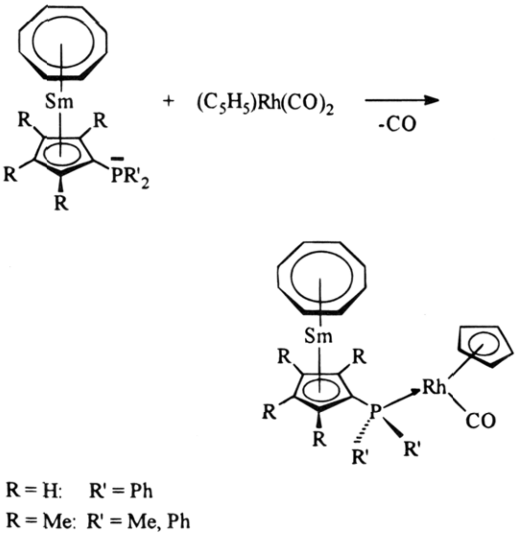


Figure 164. Structure of $(C_8H_8)Sm(2,4\text{-}C_7H_{11})(THF)$ in the crystal.[630] (Reprinted from ref 630. Copyright 1991 Chemical Society of London.)

$(C_8H_8)Y(C_5Me_5)$ reacts with 1,2,3,4-tetramethyl-2-methyleneimidazoline with formation of a 1:1 complex in which the olefin is "end-on" coordinated via the CH_2 carbon of the olefin. There is a $Y-CH_2-C$ angle of 123.1° (Figure 163).[753]

The high solubility in aliphatic and aromatic solvents of pentamethylcyclopentadienyl compounds $(C_8H_8)Lu(C_5Me_5)$ and their high volatility makes them valuable sources of rare earth metals for the production of thin films by CVD methods.[635] Further applications exist in the preparation of novel heterobimetallic complexes[627] when the cyclopentadienyl ring bears a donor group (such as PR_2) which will bind transition metal atoms. Very recently, a couple of heterobimetallic rhodium complexes have been prepared by reacting $(C_8H_8)Sm(C_5R_4PR'_2)$ (R = H, CH_3; R' = Me, Ph) with $(C_5H_5)Rh(CO)_2$ in refluxing THF or toluene as outlined in eq 211:[627]



(211)

Mixed π-complexes have also been obtained from 2,4-dimethylpentadienyl (as an example for an open pentadienyl system), such as $(C_8H_8)Sm(2,4\text{-}C_7H_{11})(THF)$[630] and indenyl anions as in $(C_8H_8)Pr(C_9H_7)(THF)_2$.[622] The η^5 coordination of the former ligands have been confirmed by X-ray crystallography (Figure 164).

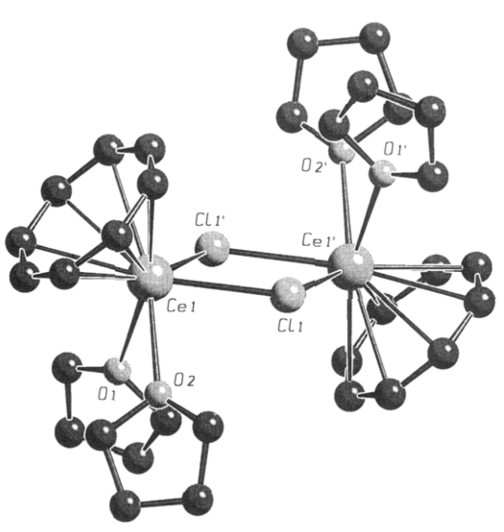


Figure 165. Structure of $[(C_8H_8)CeCl(THF)_2]_2$ (**102d**) in the crystal.[637,638]

B. Cyclooctatetraenyl Rare Earth Halides

Cyclooctatetraenyl lanthanide halide complexes (Table 43), in particular $[(C_8H_8)LnCl(THF)_2]_2$ (**102**), are useful precursors for the synthesis of a variety of lanthanide complexes.

Although several different synthetic methods have been employed,[145,639,640] the most straightforward and useful route is the ionic metathesis between $K_2(C_8H_8)$ and $LnCl_3$ illustrated by eq 212. The byproduct

$$2LnCl_3 + 2K_2(C_8H_8) \xrightarrow{THF} \underset{\mathbf{102}}{[(C_8H_8)LnCl(THF)_n]_2} + 4KCl \quad (212)$$

$n = 1$: Ln = Sc (**102a**),[609] Er (**102o**),[636] Lu (**102r**)[636,641]

$n = 2$: Ln = La (**102c**),[636] Ce (**102d**),[611,637,638] Pr (**102e**), Sm (**102h**), Nd (**102f**)[611,637]

$K[(C_8H_8)_2Ln]$ (**100**), which is also formed in the reaction, can be removed by washing with THF because the halide complexes **102** are even less soluble in THF than **100** and virtually insoluble in all common aromatic and aliphatic solvents.[637] Single-crystal X-ray structure analyses of **102d**[637,638] and **102f**[145,639] show that these compounds were dimeric. As can be readily inferred from Figure 165 molecules of **102d** are composed of two $(C_8H_8)CeCl(THF)_2$ moieties which are related by a center of symmetry. The two cerium atoms are asymmetrically bridged by two Cl^- ions at distances of 285.5(2) and 293.5(2) pm, respectively. Bridging chloride ions are also present in $\{[1,4\text{-}(Me_3Si)_2C_8H_6]Sc(\mu\text{-}Cl)\}_2(\mu\text{-}THF)$ but the small size of Sc^{3+} only allows the coordination of one semibridging THF molecule (Figure 166).[643]

As the size of the halide ion increases the complexes become monomeric (eq 213), as can be seen in Figure 167 which shows the results of an X-ray structure determination of $(C_8H_8)CeI(THF)_3$.[642a] The THF adducts $(C_8H_8)LnI(THF)_n$ (Ln = Nd, Sm) are

Table 43. Spectroscopic and Other Data of Cyclooctatetraenyllanthanide Halides

compound	Ln		color, characterization, etc.
$(C_8H_8)LnCl$	Sc	**102a**	complex with THF: yellow, IR[609]
	Y	**102b**	complex with THF: reactions[624,627]
	La	**102c**	complex with 2THF: yellow, NMR, IR[636]
	Ce	**102d**	complex with 2THF: yellow green, IR,[611] X-ray,[637,638] magn. d.[637]
	Pr	**102e**	complex with 2THF: pale green, IR,[611] magn. d.[637]
	Nd	**102f**	complex with 2THF: bright green,[611,639] X-ray,[145,639] IR,[611,640] UV,[611,637] magn. d.[637]
	Sm	**102h**	complex with 2THF: purple,[611,755] NMR,[755] IR,[611,640] UV,[611,637] magn. d.[637]
	Gd	**102k**	complex with THF: reactions[624]
	Tb	**102l**	complex with THF: reactions[624]
	Dy	**102m**	complex with THF: reactions[624]
	Er	**102o**	complex with THF: pink,[636] reactions[624]
	Lu	**102r**	complex with THF: white,[636] NMR,[636,641] reactions[624]
$(C_8H_8)LnBr$	Sm		complex with THF: purple, NMR, melt./dec.[755]
$(C_8H_8)LnI$	La		complex with 3THF: pale yellow, NMR, melt./dec.[642a,755]
	Ce		complex with 3THF: bright yellow, X-ray, melt./dec.[642a,755]
	Pr		complex with 3THF: greenish yellow, melt./dec.[642a,755]
	Nd		complex with 2THF: green, melt./dec;[642a,755] with 3THF: green, X-ray, NMR, IR, melt./dec.[642b]
	Sm		complex with THF: purple, melt./dec.;[642a,755] with 3THF: violet, NMR, IR, melt./dec.[642b]

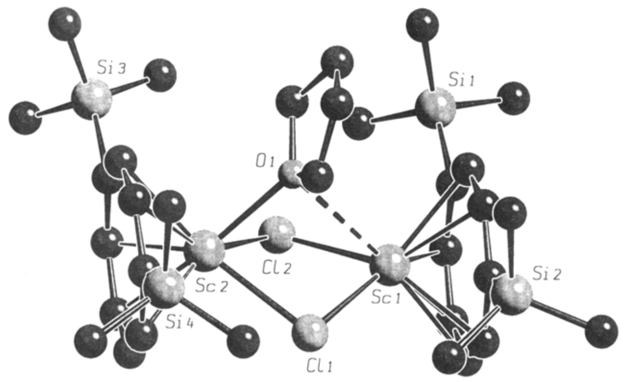


Figure 166. Structure of $\{[1,4\text{-}(Me_3Si)_2C_8H_6]Sc(\mu\text{-}Cl)\}_2(\mu\text{-}THF)$ in the crystal.[643]

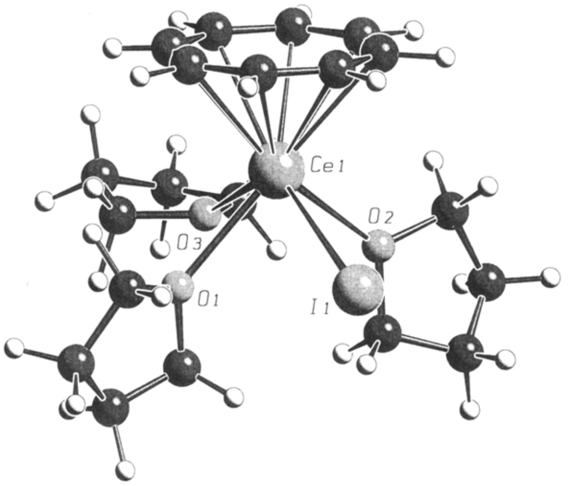


Figure 167. Structure of $(C_8H_8)CeI(THF)_3$ in the crystal.[642a]

also available by reaction of $LnI_3(THF)_3$ with $K_2(C_8H_8)$ in THF.[642b]

$$2Ln + 2C_8H_8 + I_2 \xrightarrow{THF} 2(C_8H_8)LnI(THF)_n \quad (213)$$

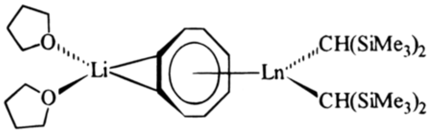
$$Ln = La, Ce, Pr\ (n = 3), Nd\ (n = 2), Sm\ (n = 1)$$

C. Cyclooctatetraenyl Rare Earth Complexes with Rare Earth to Element Group 14, 15, or 16 Bonds

By far the synthetically most challenging task in this area is the synthesis of cyclooctatetraenyl derivatives with σ-bonded ligands such as alkyl, aryl, amide, alkoxide, or aryloxide. This is propably due to the fact that the dinegative, planar C_8H_8 ligand is sterically smaller than, for example, two $C_5H_5^-$ ligands, and rearrangement pathways that are prevented in the latter are available to the former. Thus, in many instances ligand redistributions are observed eventually leading to stable $M^+[(C_8H_8)_2Ln]^-$ (M = alkali metal) species and unidentified byproducts.[636,644] A prominent example of such a reaction has already been mentioned (see section II.A.2) which interestingly led to the formation of an unexpected complex $(C_5Me_5)_3Sm$.[201] It is therefore not surprising that air-sensitive $(C_8H_8)Lu(CH_2SiMe_3)(THF)_2$ decomposes in toluene (eq 214).[636] Nevertheless, two well-characterized types of cyclooctatetraenyllanthanide compounds with a Ln−C σ-bond could be prepared following the synthetic routes outlined in eqs 215 and 216.

$$\underset{\mathbf{102r}}{[(C_8H_8)LuCl(THF)_2]_2} + 2LiCH_2SiMe_3 \xrightarrow[-2LiCl]{THF} 2(C_8H_8)Lu(CH_2SiMe_3)(THF)_2 \quad (214)$$

$$\underset{\mathbf{102}}{1/2\,[(C_8H_8)LnCl(THF)_2]_2} + 2\ LiCH(SiMe_3)_2 \xrightarrow[-LiCl]{toluene\ /\ THF}$$

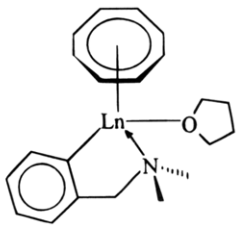


(215)

103

Ln = Y (**103b**), Sm (**103h**), Lu (**103r**)[610]

$$\underset{\mathbf{102}}{1/2\,[(C_8H_8)LnCl(THF)_2]_2} + LiC_6H_4CH_2NMe_2 \xrightarrow[-LiCl]{THF}$$



(216)

104

Ln = Er (**104o**),[644] Lu (**104r**)[636,641,644]

Table 44. Spectroscopic and Other Data of Cyclooctatetraenyllanthanide Complexes Containing Lanthanide to Element Group 14 Bonds

compound	Ln		color, characterization, etc.
$(C_8H_8)LnCH_2SiMe_3$	Lu		complex with 2THF: white, IR, NMR[636]
$(THF)_2Li(C_8H_8)Ln[CH(SiMe_3)_2]_2$	Y	**103b**	colorless, NMR[610]
	Sm	**103h**	red, NMR, X-ray[610]
	Lu	**103r**	colorless, NMR[610]
$(C_8H_8)LnC_6H_4$-2-CH_2NMe_2	Er	**104o**	complex with THF: IR[644]
	Lu	**104r**	complex with THF: beige,[636] X-ray,[644] NMR, IR[636,641,644]
$(C_8H_8)LnC{\equiv}C^tBu$	Lu		complex with 0−1THF: cream, NMR, IR[644]

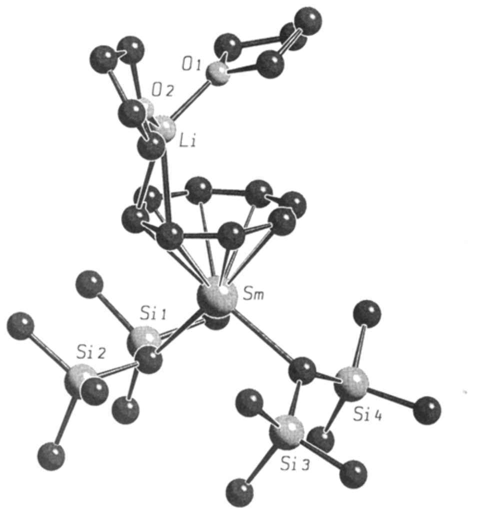


Figure 168. Structure of $(THF)_2Li(\mu\text{-}\eta^2{:}\eta^8\text{-}C_8H_8)Sm[CH(SiMe_3)_2]_2$ (**103h**) in the crystal.[610]

The kinetic stability of **103** (**b**, **h**, and **r**) and the good solubility in nonpolar solvents is attributable to the frequently emphasized favorable properties of $CH(SiMe_3)_2^-$ ligands. Nevertheless the compounds are still very sensitive toward oxidation and they are thermally unstable. However, **103h** was characterized by proton and carbon NMR spectroscopy as well as by X-ray crystallography. The molecule is depicted in Figure 168. As expected the carbon atoms of the $(C_8H_8)^{2-}$ ring are bonded to Sm^{3+} at nearly equal distances in an η^8-fashion. The centroid of the $(C_8H_8)^{2-}$ ring and two carbon atoms of the $CH(SiMe_3)_2^-$ ligands define a planar triangle. Whereas the two alkyl ligands show no unusual features it is interesting to note that the Li^+ cation is coordinated to two carbon atoms of the $(C_8H_8)^{2-}$ ring. Two additional bonds to two THF oxygen atoms provide Li^+ with a four coordinate environment. The latter result was not determined by the spectroscopic data, as the molecule is fluxional.[610]

The chelating ligand $o\text{-}C_6H_4CH_2NMe_2^-$ has often proven useful in the synthesis of complexes that need to become sterically saturated. The X-ray structure analysis[644] of **104r** is in accord with this expectation since the dimethylamino group serves as a hard Lewis base and coordinates to Lu^{3+}. Although the corresponding erbium compound is also isolable, the synthesis of species with middle and early lanthanide ions are reported to be unsuccessful. Again the most important byproduct was $[Li(THF)_4][(C_8H_8)_2Ln]$. Reaction of **104r** with excess of the terminal alkyne 3,3-dimethyl-1-butyne in THF allowed the isolation of $(C_8H_8)Lu(C{\equiv}C^tBu)(THF)_x$ ($x = 0{-}1$) in 75% yield.[644]

Known cyclooctatetraenyl complexes of the rare earth elements which contain at least one rare earth to element group 14 bond are summarized in Table 44.

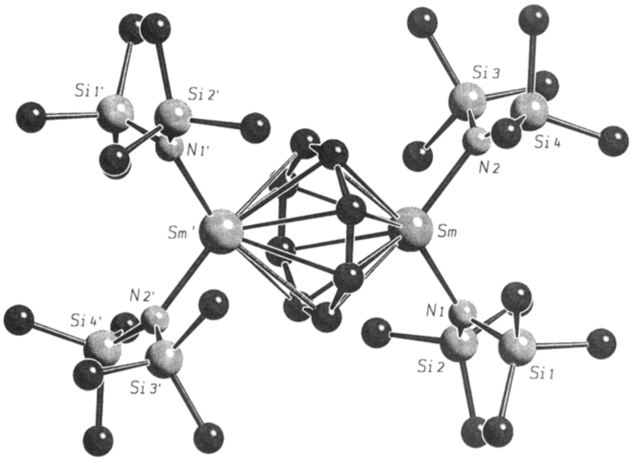


Figure 169. Structure of $\{Sm[N(SiMe_3)_2]_2\}_2(\mu\text{-}C_8H_8)$ in the crystal.[617]

When $CH(SiMe_3)_2^-$ is replaced by its isolobal analogue $N(SiMe_3)_2^-$ neutral pnictogenide complexes of the type $(C_8H_8)Ln[N(SiMe_3)_2](THF)$ (eq 217) and $\{Ln[N(SiMe_3)_2]_2\}_2(\mu\text{-}C_8H_8)$ (eq 218), depending on the size of the lanthanide ion, can be isolated:[617]

$$\underset{\mathbf{102}}{{}^1/_2[(C_8H_8)LnCl(THF)_2]_2} + NaN(SiMe_3)_2 \xrightarrow[-NaCl]{\text{toluene}} (C_8H_8)Ln[N(SiMe_3)_2](THF) \quad (217)$$

Ln = Y, Gd, Er, Lu

$$\underset{\mathbf{102h}}{3[(C_8H_8)SmCl(THF)_2]_2} + 8NaN(SiMe_3)_2 \xrightarrow{\text{toluene}} 2\{Sm[N(SiMe_3)_2]_2\}_2(\mu\text{-}C_8H_8) + 2[Na(THF)_x][Sm(C_8H_8)_2] + 6NaCl \quad (218)$$

Whereas $(C_8H_8)Lu[N(SiMe_3)_2](THF)$ consists of monomeric molecules, as expected, $\{Sm[N(SiMe_3)_2]_2\}_2(\mu\text{-}C_8H_8)$ (Figure 169) is made up of two centrosymmetrically arranged $Sm[N(SiMe_3)_2]_2^+$ units which are η^8 bonded to opposite sites of the $(C_8H_8)^{2-}$ ring.[617] Thus, the structure of the latter complex is that of a perfect inverse sandwich. Probably due to the mutual repulsion of the positively charged Sm ions the averaged Sm−C distance of 283.1(2) pm is 14.3 pm longer than in comparable half-sandwich compounds such as $[Li(THF)_2]\{(C_8H_8)Sm[CH(SiMe_3)_2]_2\}$[610] ($d$ = 268.8(5) pm). By contrast, the Sm−N bonds are as short as 228.1(2) pm, which is comparable to the values found in homoleptic tris[bis(trimethylsilyl))amide lanthanide complexes such as $Ln[N(SiMe_3)_2]_3$ (Ln = Eu, d(Eu−N) = 225.9(9) pm;[645] Nd, d(Nd−N) = 229(2) pm[647]).

Table 45. Spectroscopic and Other Data of Cyclooctatetraenyllanthanide Pnicogenides

compound	Ln	color, characterization, etc.
$(C_8H_8)LnN(SiMe_3)_2$	Y	complex with THF: colorless, NMR, MS, melt./dec.[617]
	Gd	complex with THF: colorless, MS, melt./dec.[617]
	Er	complex with THF: pink, MS, melt./dec.[617]
	Lu	complex with THF: colorless, X-ray, NMR, MS, melt./dec.[617]
$\{Ln[N(SiMe_3)_2]_2\}_2(\mu\text{-}C_8H_8)$	Sm	orange, X-ray, NMR, melt./dec.[617]
$(C_8H_8)Ln[HB(N_2C_3H_3)_3]$	Y	colorless, NMR, MS, IR, melt./dec.[646b]
	Ce	pink red, NMR, MS, melt./dec.[646a]
	Pr	yellow orange, NMR, MS, melt./dec.[646a]
	Nd	green, NMR, MS, melt./dec.[646a]
	Sm	dark red, NMR, MS, melt./dec.[646a]
$(C_8H_8)Ln[HB(N_2C_3HMe_2\text{-}3,5)_3]$	Y	colorless, NMR, MS, IR, melt./dec.[646b]
	Ce	pink, NMR, MS, melt./dec.[646a]
	Pr	yellow, NMR, MS, melt./dec.[646a]
	Nd	green, NMR, MS, melt./dec.[646a]
	Sm	violet, NMR, MS, melt./dec.[646a]
$(C_8H_8)Ln[Ph_2P(NSiMe_3)_2]$	Y	complex with THF: colorless, NMR, MS, IR, melt./dec.[646b]
	Ce	complex with THF: green brown, NMR, MS, IR, melt./dec.[646a,756]
	Pr	complex with THF: orange yellow, NMR, MS, IR, melt./dec.[646a,756]
	Nd	complex with THF: green, X-ray, IR, NMR, MS, melt./dec.[646a,756]
	Sm	complex with THF: red, NMR, MS, IR, melt./dec.[646a]
$(C_8H_8)Ln[PhC(NSiMe_3)_2]$	Y	complex with THF: colorless, NMR, MS, Raman, melt./dec.[756]
	Ce	complex with THF: orange, NMR, MS, IR, melt./dec.[756]
	Pr	complex with THF: yellow, NMR, MS, IR, melt./dec.[756]
	Nd	complex with THF: blue green, NMR, MS, I, melt./dec.[756]
	Sm	complex with THF: red, NMR, MS, melt./dec.[756]
	Tm	complex with THF: yellow, X-ray, MS, Raman, melt./dec.[756]
	Lu	complex with THF: colorless, NMR, MS, Raman, melt./dec.[756]
$(C_8H_8)Ln[MeOC_6H_4C(NSiMe_3)_2]$	Y	complex with THF: colorless, NMR, MS, IR, Raman, melt./dec.[646b,756]
	Ce	complex with THF: brown, NMR, MS, IR, melt./dec.[646a,756]
	Pr	complex with THF: yellow, NMR, IR, MS, melt./dec.[646a,756]
	Nd	complex with THF: green, NMR, MS, IR, melt./dec.[646a,756]
	Sm	complex with THF: orange, NMR, IR, MS, melt./dec.[646a,756]
$(C_8H_8)Ln[MeOC_6H_4C(NSiMe_3)_2]$	Tm	complex with THF: yellow, MS, melt./dec.[756]
	Lu	complex with THF: colorless, X-ray, NMR, Raman, MS, melt./dec.[756]
$(C_8H_8)Ln[F_3CC_6H_4C(NSiMe_3)_2]$	Y	complex with THF: colorless, NMR, MS, IR, Raman, melt./dec.[646b,756]
	Tm	complex with THF: yellow, MS, Raman, melt./dec.[756]
	Lu	complex with THF: colorless, NMR, Raman, MS, melt./dec.[756]

Very recently, it has been reported that similarly stable monomeric half-sandwich species with Ln to nitrogen bonds can be prepared by using pyrazol-1-yl ligands such as hydrotris(pyrazolyl)borate and hydrotris(3,5-dimethylpyrazolyl)borate, or chelating ligands like $[Ph_2P(NSiMe_3)_2]^-$, and $[4\text{-}XC_6H_4C(NSiMe_3)_2]^-$, with X = H, MeO, and CF_3.[646,756]

Spectroscopic and other data of cyclooctatetraenyllanthanide pnictogenides are given in Table 45.

Monomeric aryloxy and siloxy complexes are available by reacting stoichiometric amounts of $[(C_8H_8)LnCl(THF)_2]_2$ (**102**) with the appropriate alkali salts in toluene or THF according to eq 219:[587]

$$\underset{\textbf{102}}{{}^1/_2[(C_8H_8)LnCl(THF)_2]_2} + NaOR \rightarrow (C_8H_8)LnOR(THF) + NaCl \quad (219)$$

Ln = Y, Lu: R = C^tBu_3, $SiPh_3$

These complexes have been characterized by ^1H- and ^{13}C-NMR and mass spectrometry which gives evidence for monomeric structures. Dimeric species with bridging aryloxy ligands (OPh and $OC_6H_3Me_2$-2,6, respectively) may be prepared in a manner similar to that described above (Ln = Y, Lu). The dimeric nature of $[(C_8H_8)Y(\mu\text{-}OPh)(THF)]_2$ was confirmed by X-ray structure analysis (Figure 170).[587]

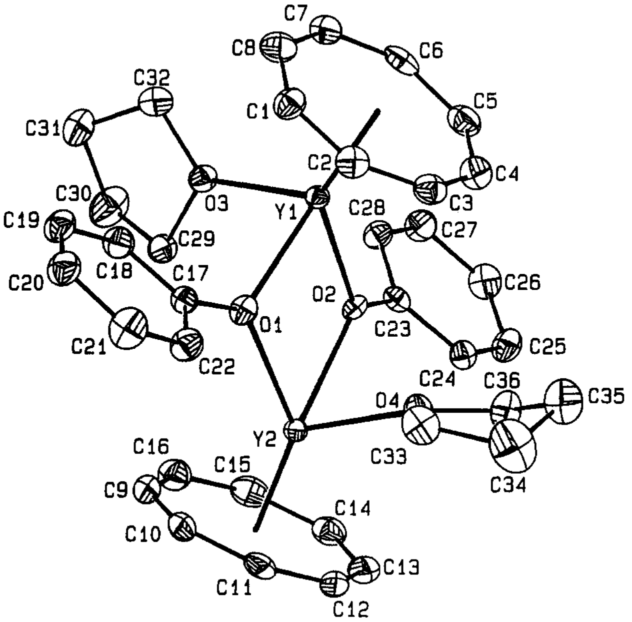


Figure 170. Structure of $[(C_8H_8)Y(\mu\text{-}OPh)(THF)]_2$ in the crystal.[587]

Already in 1977 synthesis of the cerium isopropoxide $(C_8H_8)Ce(\mu\text{-}O^iPr)_2AlEt_2$ and its acetonitrile adduct had been accomplished by reduction of the cerium(IV) compound $Ce(O^iPr)_4(LB)$ (LB = ^iPrOH or py) by $AlEt_3$ in the presence of cyclooctatetraene.[648] Cyclooctatetraenyl complexes with lanthanide to oxygen bonds (Ln = Pr, Sm) are also available using the anionic tripod ligand system $\{(C_5H_5)Co[P(O)(OEt)_2]_3\}^-$.[646a]

Very recently, Edelmann et al.[642b,646b] reported the synthesis and full characterization of new starting

Table 46. Spectroscopic and Other Data of Cyclooctatetraenyllanthanide Chalcogenides

compound	Ln	color, characterization, etc.
$(C_8H_8)Ln(\mu\text{-}O^iPr)_2AlEt_2$	Ce	yellow, NMR, IR, melt./dec.; complex with acetonitrile: yellow, NMR[648]
$(C_8H_8)LnOC^tBu_3$	Y	complex with THF: colorless, NMR, MS, melt./dec.[587]
	Lu	complex with THF: white, NMR, MS, melt./dec.[587]
$(C_8H_8)LnO(CH_2)_3CH{=}CH_2$	Dy	complex with THF: dimer, yellow, X-ray, IR[757]
$(C_8H_8)LnOPh$	Y	complex with THF: colorless, X-ray, NMR, MS, melt./dec.[587]
	Lu	complex with THF: colorless, NMR, MS, melt./dec.[587]
$(C_8H_8)LnOC_6H_3Me_2\text{-}2,6$	Y	complex with THF: colorless, NMR, MS, melt./dec.[587]
	Lu	complex with THF: colorless, NMR, MS, melt./dec.[587]
$(C_8H_8)LnOSiPh_3$	Y	complex with THF: colorless, NMR, MS, melt./dec.[587]
	Lu	complex with THF: colorless, NMR, MS, melt./dec.[587]
$(C_8H_8)LnO_2S(O)CF_3$	Y	complex with 2THF: light yellow, NMR, IR, melt./dec.[646b]
	Ce	complex with 2THF: yellow, NMR, IR, melt./dec.[642b]
	Pr	complex with 2THF: yellow, NMR, IR, melt./dec.[642b]
	Nd	complex with 2THF: green, X-ray, NMR, IR, melt./dec.[642b]
	Sm	complex with 2THF: violet, NMR, IR, melt./dec.[642b]
$(C_8H_8)Ln\{(C_5H_5)Co[P(O)(OEt)_2]_3\}$	Pr	beige, NMR, MS, melt./dec.[646a]
	Sm	orange, NMR, MS, melt./dec.[646a]
$(C_8H_8)LnSPh$	Sm	complex with 2THF: dimer, blue purple, X-ray, NMR, melt./dec.[649,755]
$(C_8H_8)LnSC_6H_2Me_3\text{-}2,4,6$	Sm	complex with 2THF:dimer, purple, NMR, melt./dec.[649,755]
$(C_8H_8)LnSC_6H_2{}^iPr_3\text{-}2,4,6$	Sm	complex with 1THF: dimer, purple, X-ray, NMR, melt./dec.[649,755]
$(C_8H_8)LnSePh$	Sm	complex with 2THF: dimer, purple, X-ray, NMR, melt./dec.[649,755]

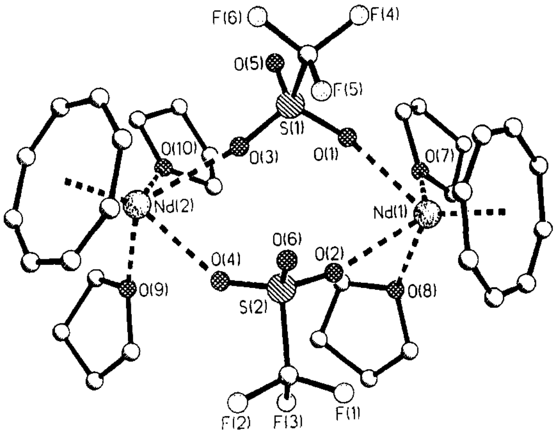


Figure 171. Structure of $\{(C_8H_8)Nd[\mu\text{-}\eta^2\text{-}O_2S(O)CF_3](THF)_2\}_2$ in the crystal.[642b] (Reprinted from ref 642b. Copyright 1994 Elsevier Sequoia.)

materials in COT–lanthanide chemistry; dimeric cyclooctatetraenyllanthanide triflates of the type $\{(C_8H_8)Ln[\mu,\eta^2\text{-}O_2S(O)CF_3](THF)_2\}_2$. The triflates are superior to the cyclooctatetraenyllanthanide chloride starting materials **102**, since they are more soluble. Equimolar reaction of appropriate lanthanide triflates $Ln(OSO_2CF_3)_3$ with $K_2(C_8H_8)$ in THF proceeds smoothly to give $\{(C_8H_8)Ln[\mu\text{-}\eta^2\text{-}O_2S(O)CF_3](THF)_2\}_2$ (Ln = Ce, Pr, Nd (Figure 171), Sm,[642b] Y[646b]) in good yields.

A very simple and convenient synthetic route affording cyclooctatetraenyllanthanide thiolates and selenolates has been introduced by Mashima et al.[649,755] Direct treatment of metallic samarium with cyclooctatetraene, diaryl disulfide or diaryl diselenide, and a catalytic amount of iodine yields new dimeric COT complexes bearing Ln–S and Ln–Se bonds, respectively, as outlined in eq 220:

$$2Sm + 2C_8H_8 + REER \xrightarrow[I_2]{THF} [(C_8H_8)Sm(\mu\text{-}ER)(THF)_n]_2 \quad (220)$$

$n = 2$: ER = SPh, $SC_6H_2Me_3$-2,4,6, and SePh

$n = 1$: ER = $SC_6H_2{}^iPr_3$-2,4,6

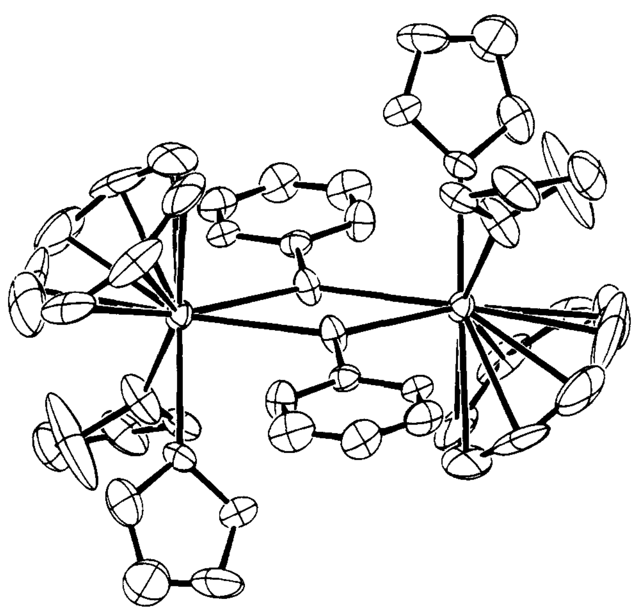


Figure 172. Structure of $[(C_8H_8)Sm(\mu\text{-}SPh)(THF)_2]_2$ in the crystal.[649] (Reprinted from ref 649. Copyright 1993 Chemical Society of London.)

The solid-state structure of binuclear thiolate-bridged $[(C_8H_8)Sm(\mu\text{-}SC_6H_2{}^iPr_3\text{-}2,4,6)(THF)]_2$ resembles the phenoxyyttrium derivative, $[(C_8H_8)Y(\mu\text{-}OPh)(THF)]_2$[587] (*vide supra*). However, the corresponding thiolate (and selenolate) dimers which contain less bulky phenyl groups, instead of the sterically very demanding 2,4,6-triisopropyl phenyl ligand, need two molecules of tetrahydrofuran to satisfy the coordination sphere of each Sm^{3+}, as can be seen in Figure 172.[649]

A survey of cyclooctatetraenyl rare earth chalcogenide compounds is given in Table 46.

D. Cyclooctatetraenyl Rare Earth Complexes with Substituted Cyclooctatetraenyl Ligands

Some progress has been made recently in synthesis of cyclooctatetraenyllanthanide complexes that have substituents on the ring. The substituents are alkyl groups such as ^nBu, ^tBu, or two trimethylsilyl groups in 1,4-position (see Table 47).

The chloride $[(^nBuC_8H_7)LuCl(THF)_2]$[437] and the amide $Li[(^nBuC_8H_7)Lu\{NMe(CH_2)_2NMe_2\}_2]$[437] exhibit

Table 47. Spectroscopic and Other Data of Cyclooctatetraenyllanthanide Complexes Containing Substituted Cyclooctatetraenyl Ligands

compound	Ln	color, characterization, etc.
$[K(diglyme)][({}^tBuC_8H_7)_2Ln]$	Yb	blue[634a]
$Li[\{(Me_3Si)_2C_8H_6\}_2Ln]$	Ce	green, reactions[683]
$[(C_5H_5)_2Co][\{(Me_3Si)_2C_8H_6\}_2Ln]$	Ce	green, NMR, MS, IR, melt./dec.[683]
$(C_4H_9C_8H_7)LnCl$	Lu	complex with THF: reactions[437]
$\{[1,4\text{-}(Me_3Si)_2C_8H_6]Ln(\mu\text{-}Cl)\}_2(\mu\text{-}THF)$	Sc	yellow, X-ray, NMR[643]
$\{[1,4\text{-}(Me_3Si)_2C_8H_6]Ln(\mu\text{-}Cl)\}_2(THF)_2$	Y	white, NMR[643]
$Li[(C_4H_9C_8H_7)Ln(NMeCH_2CH_2NMe_2)_2]$	Lu	colorless, NMR[437]

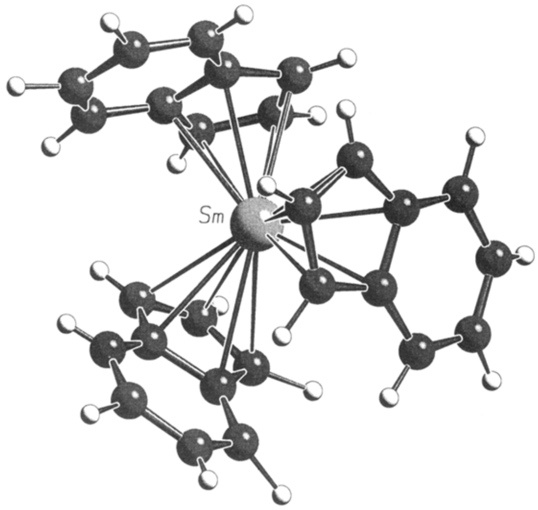


Figure 173. Structure of $(C_9H_7)_3Sm$ (**105h**) in the crystal.[650]

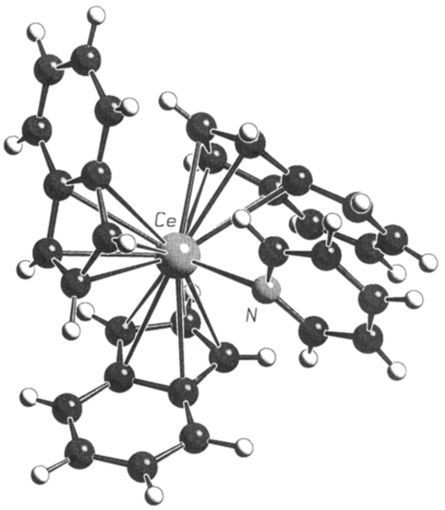


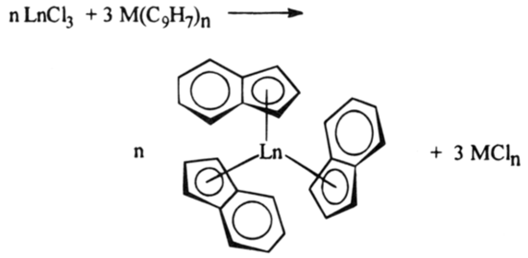
Figure 174. Structure of $(C_9H_7)_3Ce(py)$ in the crystal.[656]

no unusual features. The complexes [K(diglyme)]-[$({}^tBuC_8H_7)_2Yb$][634a] (see section III.A) and $[\{1,4\text{-}(Me_3Si)_2C_8H_6\}Ln(\mu\text{-}Cl)]_2(THF)_n$ (Ln = Sc (n = 1), Y (n = 2))[643] are also as expected, although the latter scandium species possesses a semibridging THF ligand (see section III.B, Figure 166).

IV. Indenyl Rare Earth Compounds

A. Triindenyl, Indenyl-Cyclopentadienyl, and Indenyl–Cyclooctatetraenyl Rare Earth Complexes

Triindenyllanthanide complexes can be prepared by reaction of stoichiometric amounts of $Mg(C_9H_7)_2$[650] or KC_9H_7[651] and the appropriate lanthanide trichloride, suspended in benzene or THF, as outlined in eq 221:



(221)

105

M = K (n = 1): Ln = Sc (**105a**), Y (**105b**), Ce (**105d**), Pr (**105e**), Nd (**105f**)[651]
M = Mg (n = 2): Ln = Sm (**105h**)[650]

The complexes **105** are insoluble in benzene, toluene, xylene, and CCl_4 but soluble in THF. The solid-state structure of the deep-red complex **105h** (Figure 173) shows a formally nine-coordinate samarium ion which is bonded to the five-membered ring of the indenyl anions in an η^5-fashion. The absence of intermolecular contacts in solid-state contrasts with the polymeric chain structure of the tris(cyclopentadienyl)samarium parent compound **1h**,[31,32a] a result consistent with the greater steric demand of the indenyl groups.

Nevertheless, triindenyllanthanide complexes form adducts with THF,[28,107,652–655] pyridine,[656] and $OSMeC_6H_4Me$[121b] in reactions outlined in eqs 222[652,653] and 223,[656] or for example by reaction[654] of lanthanide trichlorides (Ln = Nd, Gd, Er) with 2 equiv of indenyl potassium and 1 equiv of cyclooctadienyl potassium in THF. A single-crystal X-ray structure analysis of

$$LnCl_3 + 3NaC_9H_7 \xrightarrow{THF} (C_9H_7)_3Ln(THF) + 3NaCl \quad (222)$$

Ln = La, Sm, Gd, Tb, Dy, Yb

$$Ce(O^iPr)_4(py) \xrightarrow{AlEt_3/indene} (C_9H_7)_3Ce(py) \quad (223)$$

the isolated product, $(C_9H_7)_3Ce(py)$, is depicted in Figure 174. The yellow crystalline triindenylcerium pyridine complex has a distorted pseudo-tetrahedral coordination geometry.[656] Actually, a halide ion can also serve as Lewis base, eventually bridging two metal ions as in $[Na(THF)_6]\{[(C_9H_7)_3Nd]_2(\mu\text{-}Cl)\}$.[657,658]

For a survey of triindenyl compounds of the rare earth elements see Table 48.

Mixed π-complexes (see also Table 49) of the general formula $(C_9H_7)Ln(C_5H_5)_2(THF)$ are quite well-known and are accessible by reaction of bis-

Table 48. Spectroscopic and Other Data of Triindenyllanthanide Complexes

compound	Ln		color, characterization, etc.
$(C_9H_7)_3Ln$	Sc	**105a**	scarlet[651]
	Y	**105b**	light brown[651]
	La	**105c**	complex with THF: pale tan,[653] magn. d.[652]
	Ce	**105d**	violet;[651] complex with py: yellow, X-ray[656]
	Pr	**105e**	yellow;[651] complex with THF: UV;[107] with $OSMeC_6H_4Me$: NMR, UV[121b]
	Nd	**105f**	dark brown;[651] complex with THF: green, X-ray, IR;[654] with 2THF: bond energy[655]
	Sm	**105h**	reddish, X-ray;[650] complex with THF: red,[28,653] NMR,[28,652,653] IR,[28] melt./dec.,[653] magn. d.[652,653]
	Gd	**105k**	complex with THF: yellow, X-ray, IR,[654] pale green,[653] magn. d.[652,653]
	Tb	**105l**	complex with THF: pale yellow,[653] magn. d.[652,653]
	Dy	**105m**	complex with THF: pale tan,[653] magn. d.[652,653]
	Er	**105o**	complex with THF: pink, IR[654]
	Yb	**105q**	complex with THF: dark green,[653] magn. d.[652,653]
$[Na(THF)_6]\{[(C_9H_7)_3Ln]_2(\mu\text{-}Cl)\}$	Nd		green, MS, IR,[658] X-ray[657,658]

Table 49. Spectroscopic and Other Data of Indenylcyclopentadienyllanthanide and Indenylcyclooctatetraenyllanthanide Complexes

compound	Ln		color, characterization, etc.
$(C_9H_7)Ln(C_5H_5)_2$	Sm	**106h**	complex with THF: yellow orange, MS, IR, melt./dec.[246]
	Dy	**106m**	complex with THF: pale yellow, MS, IR, melt./dec.[246]
	Er	**106o**	complex with THF: pink, MS, IR, melt./dec.[246]
	Ho	**106n**	complex with THF: yellow, MS, IR, melt./dec.[246]
	Yb	**106q**	complex with THF: deep green, MS, IR, melt./dec.[246]
$(C_9H_7)Ln(C_8H_8)$	Pr		complex with 2THF: X-ray[622]
	Nd		complex with 2THF[622]

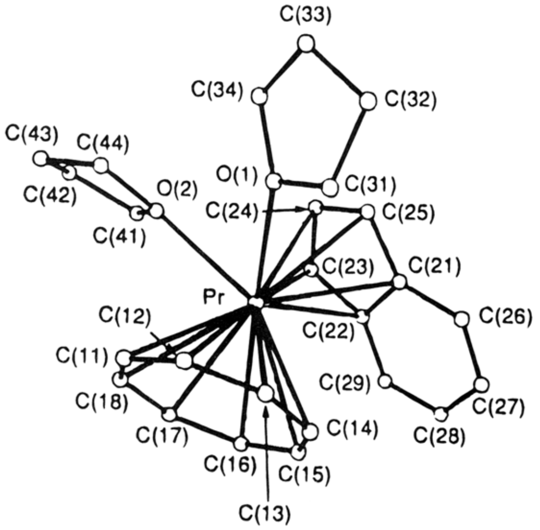


Figure 175. Structure of $(C_9H_7)Pr(C_8H_8)(THF)_2$ in the crystal.[622] (Reprinted from ref 622. Copyright 1991 Chemical Society of London.)

(cyclopentadienyl)lanthanide halides **21** with indenyl sodium, given in equation 224:[246]

$$\underset{\mathbf{21}}{(C_5H_5)_2LnCl(THF)} + NaC_9H_7 \xrightarrow{THF} \underset{\mathbf{106}}{(C_9H_7)Ln(C_5H_5)_2(THF)} + NaCl \quad (224)$$

Ln = Sm (**106h**), Dy (**106m**), Ho (**106n**), Er (**106o**), Yb (**106q**)

While no X-ray structural data are available for **106,** X-ray quality single crystals of the mixed indenyl−cyclooctatetraenyl complex $(C_9H_7)Pr(C_8H_8)(THF)_2$ have been prepared and investigated (Figure 175). $(C_9H_7)Ln(C_8H_8)(THF)_2$ (Ln = Pr, Nd) is formed in the equimolar reaction of $LnCl_3$, KC_9H_7 and $K_2(C_8H_8)$ in THF.[622]

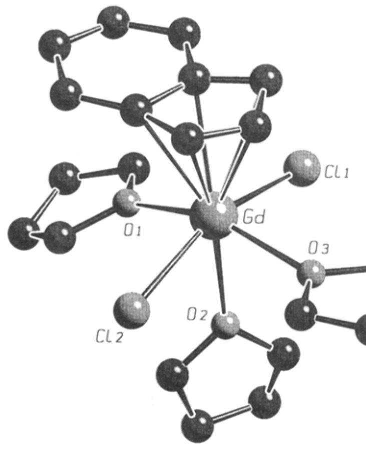


Figure 176. Structure of $(C_9H_7)GdCl_2(THF)_3$ (**107k**) in the crystal.[659]

B. Indenyl Rare Earth Complexes with Rare Earth to Element Group 14, 15, 16, or 17 Bonds

There are reports on monoindenyllanthanide dichlorides **107** which were poorly characterized.[655] Very recently, however, the first crystal structure of $(C_9H_7)GdCl_2(THF)_3$ (**107k**) was published.[659] The solid-state structure of **107k** (Figure 176) shows a formally eight-coordinate Gd^{3+} ion located in a center of a distorted trigonal bipyramid. The indenyl ligand coordinates to the gadolinium ion via the five-membered ring in an η^5 fashion at normal bond distances. Thus the complex strongly resembles that of monocyclopentadienyllanthanide dichloride species $(C_5H_5)LnCl_2(THF)_3$ (**89**) whose crystal structures have been determined (Ln = Nd,[145,553] Er,[555] and Yb[261,364]). Also proven by X-ray crystallography is the existence of the already discussed chloro-bridged neodymium species $[Na(THF)_6]\{[(C_9H_7)_3Nd]_2(\mu\text{-}Cl)\}$.[657,658]

Only a few indenyl chalcogenide complexes of the rare earth elements are known. Besides $(C_9H_7)_2PrOCHMeEt$,[121b] a series of diindenyllanthanide aryl-

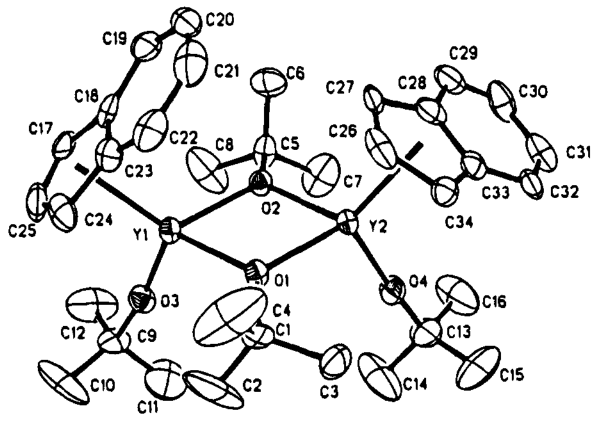


Figure 177. Structure of $[(C_9H_7)Y(\mu\text{-}O^tBu)(O^tBu)]_2$ in the crystal.[581] (Reprinted from ref 581. Copyright 1993 American Chemical Society.)

oxides have been published:[660] Reactions of triindenyl compounds **105f** and **105h** with 8-hydroxyquinoline or *o*-aminophenol afford the appropriate mono- and diindenyllanthanide chelates. Evans et al.[581] succeeded in obtaining the X-ray crystallographic characterization of dimeric $[(C_9H_7)Y(\mu\text{-}O^tBu)(O^tBu)]_2$, prepared according to eq 225:

$$YCl_3(THF)_x + 2NaO^tBu + KC_9H_7 \xrightarrow[-2NaCl,\ -KCl]{} {}^1/_2[(C_9H_7)Y(\mu\text{-}O^tBu)(O^tBu)]_2 \quad (225)$$

As can be seen from Figure 177, the monoindenyl yttrium alkoxide has a structure that is similar to the related complexes with the π-ligands cyclopentadienyl, pentamethylcyclopentadienyl, and trimethylsilylcyclopentadienyl, respectively, instead of the indenyl ring system.[581]

The sole known indenyl complex containing direct nitrogen to lanthanide bonds has been provided by Arnold et al.[590] This work takes advantage of the sterically very demanding character of the porphyrin dianion to stabilize the monoindenyllanthanide unit.

With the exception of a monoindenyl rare earth THF adduct,[595] which involves the chelating 1,2,3,4-tetraphenylbutadienyl dianion, no organolanthanides bearing both, the indenyl system and a lanthanide to carbon bond are as yet known; no bonds to silicon are known either.

Table 50 gives spectroscopic and other important data of indenyl rare earth halides, pnictogenides, chalcogenides, or indenyl complexes with rare earth to element group 14 bonds.

C. Indenyl Rare Earth Complexes with Substituted Indenyl Rings

Similar to the synthesis of triindenyllanthanide complexes, reactions of stoichiometric quantities of permethylindenyl potassium and $LnCl_3$ yield tris-, bis-, or mono(heptamethylindenyl)lanthanide species as outlined in eq 226:[661]

$$LnCl_3 + nKC_9Me_7 \xrightarrow[\text{room temperature, 2 days}]{THF} (C_9Me_7)_nLnCl_{3-n}(THF)_x + nKCl \quad (226)$$

$n = 3$: Ln = Nd ($x = 5$), Er ($x = 3$)

$n = 2$: Ln = La ($x = 1$), Nd ($x = 1$), Er ($x = 0$)

$n = 1$: Ln = La ($x = 1$), Nd ($x = 0$), Er ($x = 0.5$)

Equimolar addition of 1,3-diphenyl-2-methylindenyl lithium to a suspension of the cerium aryloxide $Ce(OC_6H_3{}^tBu_2\text{-}2,6)_3$ in toluene results in the fomation

Table 50. Spectroscopic and Other Data of Indenyllanthanide Complexes Containing Lanthanide to Element Group 14, 15, 16, or 17 Bonds

compound	Ln		color, characterization, etc.
$(C_9H_7)LnCl_2$	Pr	**107e**	yellowish green; complex with 2THF: yellowish red; with THF, HCl: yellowish green[655]
	Nd	**107f**	light red; complex with THF: light red, bond energy; with 2THF: light purple, IR; with HCl: light purple; with THF, HCl: light purple, IR; with 2THF, HCl: light purple[655]
	Sm	**107h**	complex with THF: light yellow, IR; with 2THF: light yellow; with 3THF: light yellow; with 2THF, HCl: light yellow[655]
	Gd	**107k**	light yellow;[655] with 3THF (+THF): yellowish,[655,659] X-ray, IR[659]
$(C_9H_7)_2LnOCHMeEt$	Pr		NMR, UV[121b]
$(C_9H_7)_2LnOC_6H_4NH_2$	Nd		IR, melt./dec.[660]
	Sm		IR, melt./dec.[660]
$(C_9H_7)_2LnOC_9H_6N$	Nd		IR, melt./dec.[660]
	Sm		IR, melt./dec.[660]
$[(C_9H_7)Ln(\mu\text{-}O^tBu)(O^tBu)]_2$	Y		X-ray, NMR, IR[581]
$(C_9H_7)Ln(OC_6H_4NH_2)_2$	Sm		IR, melt./dec.[660]
$(C_9H_7)Ln(OC_9H_6N)_2$	Nd		IR, melt./dec.[660]
	Sm		IR, melt./dec.[660]
$(C_9H_7)Ln(OEP)$	Sc		X-ray, NMR, IR, UV, melt./dec.[590]
$(C_9H_7)Ln(\eta^2\text{-}C_4Ph_4)$	Nd		complex with THF: IR[595]

Table 51. Spectroscopic and Other Data of Indenyllanthanide Complexes Containing Substituted Indenyl Rings

compound	Ln	color, characterization, etc.
$(C_9Me_7)_3Ln$	Nd	complex with 5THF: IR, UV[661]
	Er	complex with 3THF: IR, UV[661]
$(C_9Me_7)_2LnCl$	Nd	complex with THF: IR, UV[661]
	Er	IR, UV[661]
$(C_9Me_7)LnCl_2$	La	complex with THF: NMR, IR, UV[661]
	Nd	IR, UV[661]
	Er	complex with 0.5THF: IR, UV[661]
$(1,3\text{-}Ph_2C_9H_4Me\text{-}2)Ln(OC_6H_3{}^tBu_2\text{-}2,6)_2$	Ce	orange, NMR, IR[586]

Table 52. Spectroscopic and Other Data of Fluorenyllanthanide Complexes

compound	Ln		color, characterization, etc.
$(C_{13}H_9)_3Ln$	Sc	**108a**	brown, IR[651]
	Y	**108b**	colorless, IR[651]
	La	**108c**	light yellow, IR[651]
	Ce	**108d**	pale yellow, IR,[651,662] IR, melt./dec.[662]
	Pr	**108e**	green, IR[651]
	Nd	**108f**	yellow, IR[651]
	Sm	**108h**	yellow, IR[651]
	Gd	**108k**	colorless, IR[651]
	Dy	**108m**	colorless, IR[651]
$(C_{13}H_9)_2Ln(\mu\text{-}Cl)_2Li(THF)_2$	La		light brown[663,664]
	Nd		brown, IR[664]
	Sm		yellow,[663,664] IR[664]
	Ho		red brown,[663,664] IR[664]
	Lu		dark red, NMR, IR[664]

of orange $(1,3\text{-}Ph_2C_9H_4Me\text{-}2)Ce(OC_6H_3{}^tBu_2\text{-}2,6)_2$ which is soluble in aromatics but poorly soluble in aliphatic hydrocarbons.[586]

Spectroscopic and other data of indenyl rare earth complexes containing substituted indenyl ligands are summarized in Table 51.

V. Fluorenyl Rare Earth Compounds

Three equivalents of fluorenyl potassium $(KC_{13}H_9)$[651] or sodium $(NaC_{13}H_9)$[662] react with $LnCl_3$ to yield trifluorenyllanthanide complexes **108** according to eq 227. Characterization of these sensitive materials

$$LnCl_3 + 3MC_{13}H_9 \xrightarrow{THF} \underset{\textbf{108}}{(C_{13}H_9)_3Ln} + 3MCl \quad (227)$$

M = K:[651] Ln = Sc (**108a**), Y (**108b**), La (**108c**), Ce (**108d**), Pr (**108e**), Nd (**108f**), Sm (**108h**), Gd (**108k**), Dy (**108m**)

M = Na:[662] Ln = Ce (**108d**)

108, which precipitate from a THF solution after addition of petroleum ether, was achieved only by elemental analysis and infrared spectroscopy.

When 2 (or even 3) equiv of fluorenyl lithium $LiC_{13}H_9$ are allowed to react with 1 equiv of $LnCl_3$, difluorenyllanthanide chlorides presumably stabilized by coordination to LiCl $(C_{13}H_9)_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ (Ln = La, Nd, Sm, Ho, Lu) form.[663,664]

In fact, all of the preceding fluorenyllanthanides are poorly characterized. None of them has been investigated by an X-ray diffraction study. The data that are available are given in Table 52.

VI. Organometallic Rare Earth Compounds with Other Aromatic π-Ligands

The major part of the research on organometallic rare earth π-complexes has focused upon the very popular aromatic anionic ligand systems cyclopentadienyl $C_5H_5^-$, pentamethylcyclopentadienyl $C_5Me_5^-$, cyclooctatetraenyl $C_8H_8^{2-}$, indenyl $C_9H_7^-$, and fluorenyl $C_{13}H_9^-$. However, several organolanthanides have been obtained which contain neutral arenes. In 1986 Cotton et al.[665] succeeded in the preparation of the first arene complex with a rare earth element. Reaction of $SmCl_3$ with $AlCl_3$ and hexamethylbenzene in refluxing toluene in the presence of aluminum foil gives yellow plates of $(C_6Me_6)Sm[(\mu\text{-}Cl)_2AlCl_2]_3$ (**109h**) which crystallize from a blood red solution (indicative of Sm(II) species) in a total yield of 14% within two days (eq 228). The latter Sm(III) complex **109h** is found by X-ray crystallography to form a distorted pentagonal bipyramidal coordination polyhedron with the η^6-arene in an apical position (Figure 178).[665,666] Recently the Nd, Gd, and Yb derivative have been described and characterized as well.[759]

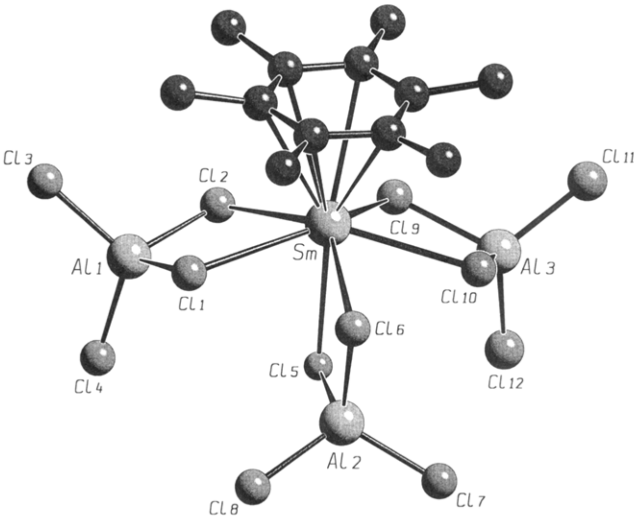
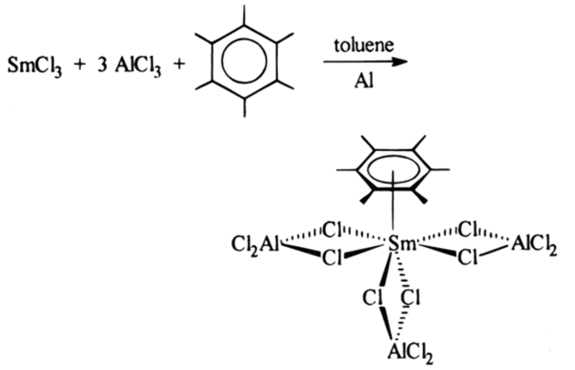


Figure 178. Structure of $(C_6Me_6)Sm[(\mu\text{-}Cl)_2AlCl_2]_3$ (**109h**) in the crystal.[665,666]



(228)

109h

Later on, it was shown that less substituted arenes such as *m*-xylene[667] or even benzene[668] also yield

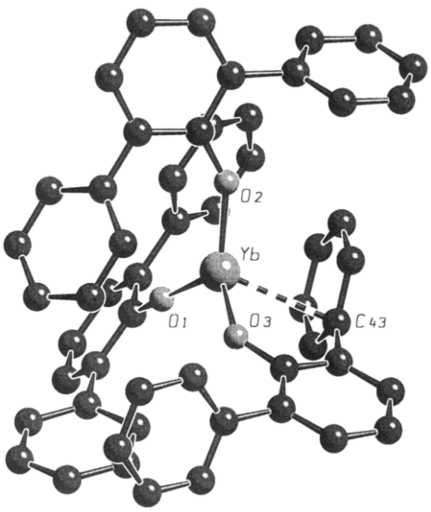
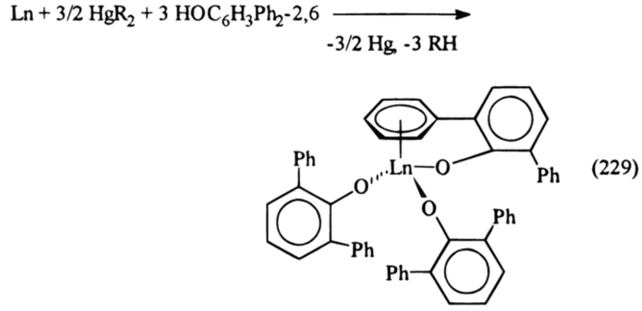


Figure 179. Structure of (π-2-Ph,6-PhC_6H_3O)Yb(OC_6H_3-Ph_2-2,6)$_2$ (**110q**) in the crystal.[94]

isolable analogoues of the type (1,3-$Me_2C_6H_4$)Sm[(μ-Cl)$_2$AlCl_2]$_3$ or (C_6H_6)Ln[(μ-Cl)$_2$AlCl_2]$_3$ (Ln = La, Nd, Sm).

An unusual intramolecular chelate with a Yb−π-arene interaction is reported to exist for the homoleptic ytterbium(III) aryloxide complex (π-2-Ph,6-PhC_6H_3O)Yb($OC_6H_3Ph_2$-2,6)$_2$ (**110q**) (Figure 179). The stereochemistry of corresponding homoleptic species **110** with other rare earth elements (Ln = Nd (**110f**), Sm (**110h**), Er (**110o**), Lu (**110r**)) are suggested to be similar to those for Ln = Yb (**110q**).[94] Complexes **110** are available by using two different synthetic approaches. Reactions between the rare earth metal, bis(pentafluorophenyl)mercury, and 2,6-diphenylphenol in THF affords the aryloxides **110**. Treatment of ytterbium metal with bis(phenylethynyl)mercury and 2,6-diphenylphenol yields **110q** (eq 229). Protolysis of tris(cyclopentadienyl)lanthanides with 3 equiv of 2,6-diphenylphenol in THF provides another access to the tris(2,6-diphenylphenoxo)lanthanides **110f** and **110q**.[94]



(229)

110

R = C_6F_5: Ln = Nd (**110f**), Sm (**110h**), Er (**110o**), Yb (**110q**), Lu (**110r**)
R = PhCC: Ln = Yb (**110q**)

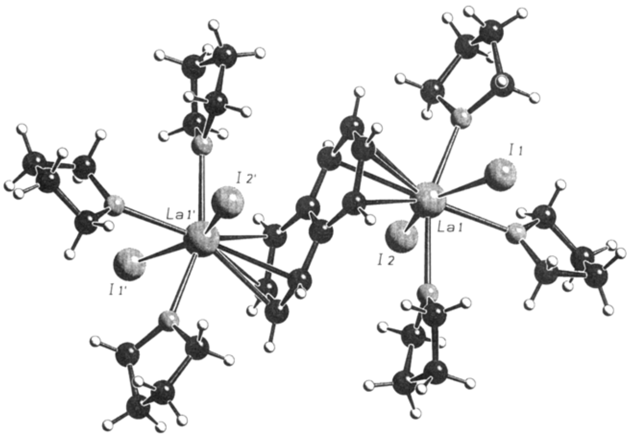


Figure 180. Structure of (μ-η^4:η^4-$C_{10}H_8$)[LaI_2(THF)$_3$]$_2$ in the crystal.[673]

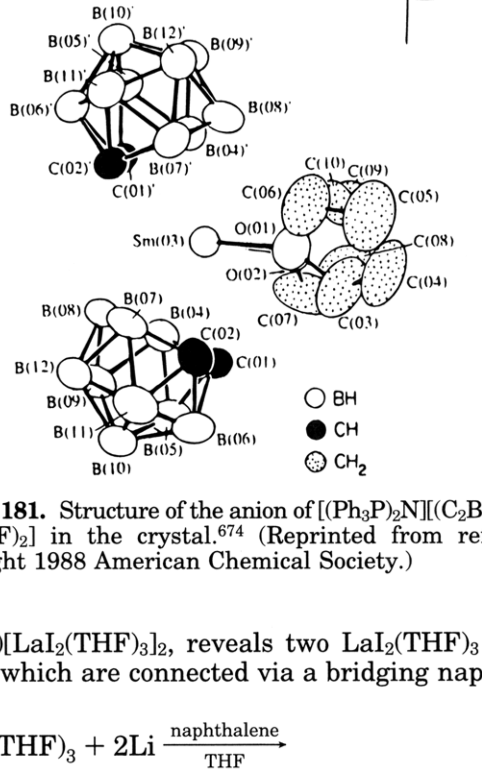


Figure 181. Structure of the anion of [(Ph_3P)$_2$N][($C_2B_9H_{11}$)$_2$-Sm(THF)$_2$] in the crystal.[674] (Reprinted from ref 674. Copyright 1988 American Chemical Society.)

Further organolanthanides with neutral π-ligands such as arenes or naphthalene are only known for zerovalent or divalent lanthanides (see, for example refs 669−672.) Recently, however, rare earth triiodides have been shown to react with equimolar amounts of lithium and excess naphthalene (formation of 2Li^+ and [$C_{10}H_8$]$^{2-}$) in THF according to eq 230. The X-ray structure analysis of the product, ($C_{10}H_8$)[LaI_2(THF)$_3$]$_2$, reveals two LaI_2(THF)$_3$ fragments which are connected via a bridging naphthalene dianion ($C_{10}H_8$)$^{2-}$ in μ-η^4:η^4 fashion (Figure 180).[673] A similar structure was found for (μ-η^4:η^4-PhCH=CHCH=CHPh)[LaI_2(THF)$_3$]$_2$ by X-ray crystallography.[760]

$$2\mathrm{LaI_3(THF)_3} + 2\mathrm{Li} \xrightarrow[\mathrm{THF}]{\text{naphthalene}} (\mu\text{-}\eta^4{:}\eta^4\text{-}\mathrm{C_{10}H_8})[\mathrm{LaI_2(THF)_3}]_2 + 2\mathrm{LiCl} \quad (230)$$

Relying on the isolobal analogy between $C_5H_5^-$ and the dicarbollide dianion [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ three anionic homoleptic lanthanacarboranes were synthesized. The samarium THF adduct [(Ph_3P)$_2$N][(η^5-$C_2B_9H_{11}$)$_2$Sm(THF)$_2$] has been subjected to a single-crystal X-ray diffraction study, and is seen in Figure 181.[674] The anions of the gadolinium complexes, Na[($C_2B_9H_{11}$)$_2$Gd](THF) and [Bu_4N][($C_2B_9H_{11}$)$_2$Gd](THF), have only been investigated by elemental analysis, ^{11}B-NMR and EPR.[675]

Important data of organometallic rare earth compounds containing other π-ligands than cyclopentadienyl, cyclooctatetraenyl, indenyl, or fluorenyl derivatives are summarized in Table 53.

Table 53. Spectroscopic and Other Data of Organolanthanides with Other Aromatic π-Ligands

compound	Ln		color, characterization, etc.
$(C_6H_6)Ln[(\mu\text{-}Cl)_2AlCl_2]_3$	La		synthesis[668]
	Nd		X-ray[668]
	Sm		X-ray, IR[668]
$(C_6Me_6)Ln[(\mu\text{-}Cl)_2AlCl_2]_3$	Nd	**109f**	blue, MS, IR, melt./dec.[759]
	Sm	**109h**	yellow,[665,759] X-ray,[665,666] MS, IR, melt./dec.[759]
	Gd	**109k**	yellow, MS, IR, melt./dec.[759]
	Yb	**109q**	blue, X-ray, MS, IR, melt./dec.[759]
$(1,3\text{-}Me_2C_6H_4)Ln[(\mu\text{-}Cl)_2AlCl_2]_3$	Sm		yellow, X-ray, IR[667]
$(\pi\text{-}2\text{-}Ph,6\text{-}PhC_6H_3O)Ln(OC_6H_3Ph_2\text{-}2,6)_2$	Nd	**110f**	blue, MS[94]
	Er	**110o**	pink, MS, IR, UV–vis[94]
	Yb	**110q**	orange, X-ray, MS, IR, UV–vis[94]
	Lu	**110r**	white, MS, IR[94]
$(\mu\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8)[LnI_2(THF)_3]_2$	La		blue, X-ray, IR, vis, melt./dec.[673]
$(PhCH{=}CHCH{=}CHPh)[LnI_2(THF)3]2$	La		red, X-ray, melt./dec.[760]
$[(Ph_3P)_2N][(C_2B_9H_{11})_2Ln]$	Sm		complex with 2THF: greenish yellow, X-ray, NMR, IR[674]
$Na[(C_2B_9H_{11})_2Ln]$	Gd		complex with THF: NMR, EPR[675]
$[Bu_4N][(C_2B_9H_{11})_2Ln]$	Gd		complex with THF: NMR, EPR[675]

VII. Conclusions and Outlook

It has been 40 years since organolanthanide chemistry began with the synthesis of the tris(cyclopentadienyl)lanthanide complexes $Ln(C_5H_5)_3$ by Wilkinson and Birmingham.[12a] Since then cyclopentadienyl complexes containing the unsubstituted cyclopentadienyl ligand and later on an increasing number with simple and not so simple substituted cyclopentadienyls have been the subject of numerous organometallic studies concerning all the rare earth metals (with exception of the radioactive promethium). Eventually, most of the gaps have been filled at least for the simple compounds. This has been made possible by improved synthetic routes and by the rapid determination of crystal structures, an important advance particularly for paramagnetic compounds.

After the pioneering work was done, more and more types of organolanthanide compounds were prepared using ligands such as cyclooctatetraenyl[613] and allyl complexes,[676] alkyl and aryl compounds and ions like LnR_3,[677] $[LnR_4]^-$,[678] and $[LnR_6]^{3-}$,[679] π-arene complexes,[665] carborane derivatives,[680] phosphinomethanide complexes,[761–763] carbene complexes,[753,764–766] and even the first lanthanide inclusion compound of the fullerenes showed up with a lanthanum atom presumably trapped on the inside of the carbon cage of C_{60},[681] followed by metallofullerenes containg Sc,[767] Y,[767,768] La,[767,769] Ce,[770] as well as radioactive ^{159}Gd and ^{161}Tb.[771] Most of this work exhibited a fascinating diversity in structure and reactivity. In addition a great deal of interest has focused on complexes of samarium, europium, and ytterbium in the oxidation state Ln^{2+},[682] certain Ce^{4+} species,[683] and organometallic compounds of zerovalent lanthanides,[2q] none of which were mentioned in this article.

However, there are still some synthetic challenges that remain within this area of chemistry since the last review by one of the authors appeared 10 years ago:[2k] No definite carbonyl and olefin complexes (with one exception)[684] of the lanthanide metals have been made; furthermore, there is only one compound in literature containing a lanthanide to transition metal bond proved by an X-ray crystal structure analysis,[146c] and not a single organometallic compound with a lanthanide to lanthanide bond is known. The synthetic routes to these compounds are by no means obvious and the door is open to creative synthetic chemists.

Organolanthanides are useful reagents in stoichiometric organic synthesis[10] and they promise to find important applications in MOCVD to make thin films for semiconductors, superconductors, and as doping materials for optoelectronic devices[685] or in catalysis e.g. ref 686. The cyclopentadienyl complexes of the lanthanides with bulky cyclopentadienyl or indenyl or bridged cyclopentadienyl ligands have created the new area of enantioselective hydrogenation, alkylation, and hydroamination.[726,735] Perhaps the most exciting development is their use in manufacturing isotactic polyolefins even without a cocatalyst.[686] Since so much is known about what can be made and what chemical and physical properties can be expected, the next decade of studies on organolanthanide compounds will surely exploit these properties for academic and idustrial utility.

VIII. List of Abbreviations

Ln	lanthanide metal, rare earth metal
M	metal
E	main group element
LB	Lewis base
R	organic ligand
Me	methyl, CH_3
Et	ethyl, C_2H_5
Pr	propyl, C_3H_7
Bu	butyl, C_4H_9
Ph	phenyl, C_6H_5
Ar	aryl
triflate	trifluoromethanesulfonate, $O_3SCF_3^-$
acac	acetylacetonate, $OCMeCHCMeCO^-$
menth	mentholate
OEP	octaethylporpyrin dianion
C_5H_5 = Cp	cyclopentadienyl (usually η^5)
Cp_g	centroid of a cyclopentadienyl group
C_5Me_5	pentamethylcyclopentadienyl (usually η^5)
RC_5H_4	monosubstituted cyclopentadienyl (usually η^5)
RC_5Me_4	monosubstituted pentamethylcyclopentadienyl (usually η^5)
C_6H_6	benzene (usually η^6)
C_6R_6	peralkylated arene (usually η^6)
$Me_2C_6H_4$	dimethylbenzene (usually η^6) = xylene
C_7H_{11}	2,4-dimethylpentadienyl
C_8H_8 = COT	cyclooctatetraenyl (usually η^8)
C_9H_7	indenyl (usually η^5)
$C_{13}H_9$	fluorenyl (usually η^5)
n, i, s, t, c	normal, iso, secundary, tertiary, cyclo
o-, m-, p-	ortho-, meta-, para-

η^n	hapticity (n = number of atoms participating in a bond)
μ_n	bridging (n = number of atoms bridged; $\mu \equiv \mu_2$)
S	solvent
THF	tetrahydrofuran
THF-d_8	deuterated tetrahydrofuran (C_4D_8O)
Et_2O	diethyl ether
DME	dimethoxyethane
DMSO	dimethyl sulfoxide
DMF	dimethylformamide
PhMe	toluene
py	pyridine
bipy	bipyridine
phen	1,10-phenanthroline
tmed	*N,N,N′,N′*-tetramethylethylenediamine
diglyme	diethylene glycol dimethyl ether
tetraglyme	tetraethylene glycol dimethyl ether
D-deriv.	deuterated derivatives
X-ray	single-crystal X-ray structure analysis
powder diffr.	powder diffractometry
diff.	electron diffraction
NMR	nuclear magnetic resonance
UV	ultraviolet spectroscopy
vis	visible spectroscopy
PE	photoelectron spectroscopy
XPS	X-ray photoelectron spectroscopy
ESCA	electron spectroscopy for chemical analysis
ESR	electron spin resonance
EPR	electron paramagnetic resonance
IR	infrared spectroscopy
Raman	Raman spectroscopy
Mößb.	Mössbauer spectroscopy
CD	circular dichroism
fluores.	fluorescence spectroscopy
lumines.	luminescence spectroscopy
MS	mass spectrometry
melt./dec.	melting/decomposition/(sublimation) point
v.p.	vapor pressure
dip.	dipole moment
mol. w.	molecular weight
magn. d.	magnetic data
elec. d.	electronic data
thermo. d.	thermodynamic data
cond.	conductivity
HSAB	concept of hard and soft acids and bases
MOCVD	metalorganic chemical vapor depositon
DTG	differential thermogravimetry
MNDO	modified neglect of (diatomic) differential overlap
DF	nonlocal density functional calculations
MO	molecular orbital
I	nuclear spin quantum number
n	neutron
β	β-radiation
γ	γ-radiation
r	radius
τ	torsion angle
d	distance
T	temperature
RT	room temperature
(g)	gaseous
(l)	liquid
(s)	solid

IX. Acknowledgments

The work of the authors cited in this review could not have been carried out without the dedicated efforts of a great many of co-workers whose inspiring valuable contributions are recognized in the reference section. Financial support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowlegded. In addition, we are very grateful to the Bundesminister für Bildung und Wissenschaft who supported our work by means of the Graduiertenkolleg "Synthese und Strukturaufklärung niedermolekularer Verbindungen". In particular, we thank Professor R. A. Andersen, Department of Chemistry, University of California, Berkeley, for many helpful discussions and, above all, for editing our manuscript and improving our English.

X. References

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