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Synthesis, Arrangement, and Reactivity of Arene–Lanthanide Compounds

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Contents

Mikhail N. Bochkarev was born in Nizhny Novgorod (former Gorky), Russia, in 1939. He graduated from Technical University of NN in 1961 and then worked for three years in the Institute of Polymers in Dserzhinsk as a Junior Research Scientist. In 1963 he joined the group of Professor N. S. Vyazankin at the G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences. In 1967 he received his Ph.D. degree and in 1982 his Doctor of Sciences degree from the A. N. Nesmeyanov Institute of Organoelement Compounds, Moscow. In 1986 he received a title of Professor of Organometallic Chemistry. He is currently Head of Laboratory in the G. A. Razuvaev Institute of Organometallic Chemistry. Scientific interests of Bochkarev involve the coordination and organolanthanide chemistry, chemistry of dendrimer and hyperbranched polymers and polynuclear organometallics.

I. Introduction

Rare-earth complexes containing π-bonded C_6-cyclic aromatic ligands (i.e., arene complexes) are among the most exciting and challenging organometallic compounds. These complexes have attracted the interest of chemists working in the area of organolanthanide chemistry for several reasons. (i) No other organic ligand provides the variety of coordination modes with lanthanide metals as the arenes. (ii) Only the arenes permit the synthesis of zero- or monovalent group 3 metal complexes. (iii) A diverse series of derivative complexes have been prepared using procedures that take advantage of the high reactivity of arene lanthanides toward other inorganic, organic, and organometallic compounds. (iv) High activity found for the naphthalene and bis(arene) complexes in hydrogenation, polymerization, and other catalytic processes has generated great interest in arene–lanthanide catalysts. (v) Last, but not least, a particularly attractive feature of arene–lanthanides is relative availability of most of them.

This direction of organolanthanide chemistry is relatively new; the first authentic arene–lanthanide complex was reported in the mid-1980s.[1] Nevertheless, sufficient data exists on this in many respects unique class of compounds pointing to generalizations and conclusions. Specific classes of complexes have been the subject of review articles by Deacon,[2] Cloke,[3] Schumann,[4] Pampaloni,[5] and our review[6] and book.[7] In the present article we attempted to compile and analyze data on the synthesis, structure, bonding, and reactivity of π-bonded arene complexes of Sc, Y, La, and lanthanides. In some cases the dominant mode of bonding is mainly an electrostatic interaction between metal cation and the aromatic anion. However, in every case, the coordination constituent,

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playing an important role in the molecule arrangement, is noticeably manifested.

Included in this review with more normal arene complexes are the Ln−arene$^+$ cations formed in gas-phase reactions of Ln$^+$ metal cations with various hydrocarbons. These products are generally omitted in reviews on condensed-phase compounds. However, in our paper, these products provide pertinent insights into the stability, reactivity, and bonding interactions in lanthanide−arene complexes and have been included. Beyond the scope of the review are the compounds that contain bonds to alkenyl or alkynyl substituents of an aromatic ring. These include complexes with stylbene, diphenylacetylene, and styrene ligands and also complexes of fullerene, indenyl, fluorenyl, and acenaphthylenyl ligands, with the exception of molecules that have been strictly shown to contain coordination through a C_6 ring.

II. Derivatives of Benzene and Its Homologs

1. Products of Gas-Phase Reactions of Metal Ions with Hydrocarbons

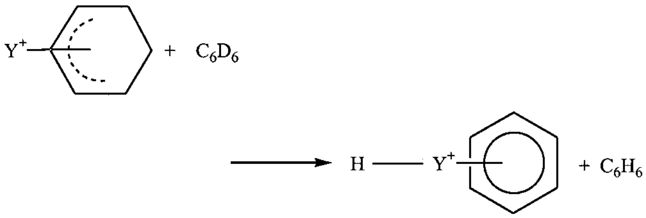
Studying the gas-phase reactions of Sc$^+$, Y$^+$, and La$^+$ ions with alkanes by Fourier transform mass spectrometry, Freiser and co-workers found that the predominant process in the case of cyclohexane is multiple dehydrogenation with formation of $LnC_6H_6^+$ species.[8] This result was reproduced in ref 9. The ions $LnC_6H_6^+$ were detected as well among the products of secondary reactions of Y$^+$ and La$^+$ with cyclopropane and cyclobutane. On the basis of collision-induced dissociation experiments with $LaC_6H_6^+$, which gave C_6H_6 as a main peak, it was assumed that $LnC_6H_6^+$ species have metal−benzene structure. Exclusively double dehydrogenation yielding $ScC_6H_6^+$ ions was observed in the reaction of Sc$^+$ with cyclohexene.[10] Secondary reaction resulted in formation of $Sc(C_6H_6)_2^+$ species. The same double dehydrogenation was found in the primary and secondary reactions of Sc$^+$ with 1-methyl-1-cyclohexene. The masses of formed products in this case corresponded to Sc$^+$−toluene and Sc$^+$−bis(toluene) cations. The bis(arene) structure of the products has been supported by CID, yielding sequential losses of C_6H_6 and, likewise, C_7H_8 fragments. To evaluate the energy of Sc$^+$−benzene bond, a series of gas-phase reactions of ligand substitution was carried out. It was found that benzene weakly substitutes proton in ScH^+ but easy displaces acetylene in $ScC_2H_2^+$. In its turn, benzene in the ions $ScC_6H_6^+$ is superseded by butadiene. From these experiments the Sc$^+$−benzene bond strength was estimated as 53 ± 5 kcal/mol.[10] Note that determined later enthalpy of metal−ligand bond disruption in condensed-phase bis(arene) lanthanide complexes turned out close to this magnitude (vide infra). Calculations of binding energy for $ScC_6H_6^+$ and $YC_6H_6^+$ carried out in C_{6v} symmetry gave somewhat lower magnitudes: 44.1 ± 5 kcal/mol for Sc and 37.5−40.8 kcal/mol for Y.[11]

Formation of metal−benzene species $LnC_6H_6^+$ was observed as well in the reactions of "bare" Ln$^+$ cations with propene,[12] cyclopropane,[12] cyclohexane,[9,12b,13] cyclohexene,[13] 1,4-cyclohexadiene,[12b,13] and benzene.[13] Toluene-containing cations $LnC_7H_8^+$ were obtained in the reactions of Sc$^+$ with methylcyclohexane[14] and Tb$^+$ with toluene.[13] In most cases the secondary reactions result in formation of bis(arene) cations $Ln(C_6H_6)_2^+$ in low yield. Reactions of Pr$^+$ with fluorobenzene and hexafluorobenzene result only in single and double defluorination of aromatic rings.[15] However, interaction of the formed PrF_2^+ with C_6H_5F leads to adduct $PrF_2(C_6H_5F)^+$. Investigation of comparative reactivity of rare-earth metals in the condensation with cycloalkanes and cycloalkenes resulting in metal−η^6-benzene ions formation has shown that it decreases in a series: $Ce^+ \geq Tb^+ \geq Gd^+ \approx Pr^+ \geq Ho^+ \geq Dy^+ \geq Lu^+ > [Sm^+, Tm^+, Eu^+, Yb^+]$.[13] Activity of La$^+$ is close to that of Ce$^+$, but Nd$^+$ and Er$^+$ react a little slower than Pr$^+$.[12b] The abundance of $LnC_6H_6^+$ cationic products for Sc$^+$, Y$^+$, La$^+$, Ce$^+$, and Gd$^+$ reaches 100%, whereas in the reactions of Sm$^+$, Tm$^+$, Eu$^+$, and Yb$^+$ with cycloalkenes, it drops down to zero. The metals of latter group form $LnC_6H_6^+$ ions in the reactions with 1,4-cyclohexadiene.[12b] Differences in reactivity are explained by diversity of the metal-ion ground-state configuration and promotion energy for excitation of 4f electrons to a valence 5d orbital.[12b,13]

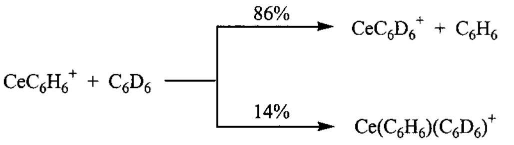
The gas-phase reactions of rare-earth metal cations with 1,3,5-tri-*tert*-butylbenzene represent particular interest because they allow one to carry out a direct comparison the reaction pathway and stability of the formed products with the data obtained in metal vapor synthesis of the same but neutral compounds (see section II.4). It was established that Sm$^+$, Eu$^+$, Tm$^+$, and Yb$^+$ afford $LnC_6H_3Bu^t{}_3^+$ in primary reactions and sandwich complex ions $Ln(C_6H_3Bu^t{}_3)_2^+$ as secondary reaction products.[16] Abundance of mono- and bis(arene) species reaches 100%. Only 13% and 2% of sandwich cations were detected in the cases of Dy$^+$ and Ho$^+$. The other metals activate C−H and C−C bonds of *tert*-butyl groups to give various organometallic ions with elimination of hydrogen, methane, and other neutrals. The reasons for differences in the reaction directions, likewise the reactions with cycloalkanes, are supposed to be the electronic configuration and 4f−5d promotion energy of Ln$^+$ cations.[16] The metals with an easily accessible d^1s^1 configuration (i.e., all the metals except Sm, Eu, Tm, and Yb) reveal the highest reactivity stimulating C−C and C−H bond activation. For Sm, Eu, Tm, and Yb the $f^ns^1 \rightarrow f^nd^1s^1$ promotion energy is too high to permit facile C−C and C−H activation; therefore, the reactions give only the adducts Ln(arene)$^+$ and Ln(arene)$_2^+$. It is interesting that in the cases of condensed-phased neutral complexes $Ln(C_6H_3Bu^t{}_3)_2$ the situation is quite the opposite: the derivatives of Y, Nd, Gd, Tb, Dy, Ho, Er, and Lu are most stable, whereas Ce, Eu, Tm, and Yb compounds cannot be isolated due to their extremely instability.

A number of ligand-mixed ions of $Ln(R)(C_6H_6)^+$ type have been obtained in the ion-molecular reactions of organometallic LnR^+ species. It was found that the reaction of allylyttrium ion $YC_3H_5^+$ with benzene yields the condensation product $Y(C_3H_5)(C_6H_6)^+$ exclusively.[17] CID of the product at 12 eV gives back $YC_3H_5^+$ and benzene supporting the allyl−

arene−yttrium structure of the ion. Similar simple benzene addition with formation of $Y(C_4H_7)(C_6H_6)^+$ was observed in the reaction of C_6H_6 with $Y(C_4H_7)^+$ generated from Y^+ and isobutene. An interesting ion $YHC_6D_6^+$ was detected when (η^5-cyclohexadienyl)yttrium ion was allowed to react with deuterated benzene.[17] CID on the product gave YH^+ (60%) and $YC_6D_6^+$ (40%) suggesting a (hydrido)(benzene)yttrium structure.



Two other benzene-containing ions were observed among the products: $Y(C_6H_5)(C_6D_6)^+$ and $Y(C_6H_7)(C_6D_6)^+$. Scandium perdeuteriobenzene adducts $Sc(C_3H_4)(C_6D_6)^+$ and $Sc(C_4H_6)(C_6D_6)^+$ were obtained in ca. 30% and 70% yields, respectively, in the reaction of $ScC_4H_8^+$ ions with C_6D_6.[18] To investigate the nature of the $CeC_6H_6^+$ species, formed as a secondary product reaction of Ce^+ with propene, it was treated with C_6D_6.[12a] The expected ligand-exchange reaction resulted in $CeC_6D_6^+$ formation as the major product at ca. 50% the theoretical collision rate. This result as well as the formation of bis(benzene) complexes $Ce(C_6H_6)(C_6D_6)^+$ and $Ce(C_6D_6)_2^+$ serves as evidence for π-bonding between benzene ligand and metal ion.



High reactivity of Sc^+ causes dehydrogenation of benzene resulting in Sc^+−benzyne ion formation which reacts further with initial C_6H_6 to form the condensation products $Sc(C_6H_4)(C_6H_6)_n^+$ ($n = 1, 2$).[14] Isolated from the mixture $Sc(C_6H_4)^+$ was studied in the reactions with alkanes and alkenes C_2−C_4. It was found that benzene-containing cations are generated in small yield in the cases of ethane, propane, *n*-butane, *n*-pentane, and *cis*- and *trans*-2-butene. In the reaction with C_4H_{10}, along with benzene derivative ethylbenzene−scandium ion $Sc(C_8H_{10})^+$ was detected in abundance 35%. Metal−toluene structure has the $ScC_7H_8^+$ species from reaction with propene. An interesting product with a mass corresponding to $Sc(C_9H_{10})^+$ ion was obtained in the reaction of $Sc(C_6H_4)^+$ with propane. The CID fragmentation patterns of it at several different energies as well as the experiment with deuterated propane suggest that the species have Sc^+−η^6-indane structure.[14]

Heterobimetallic benzene species $LaFeC_6H_6^+$ and $ScFeC_6H_6^+$ were obtained in the gas-phase reactions of binuclear cations $LaFe^+$ and $ScFe^+$ with hydrocarbons and following CID of the formed products.[19] Nothing is known about arrangement of these cluster cations, but among the CID products, besides the indicated benzene−binuclear ions, the $LaC_6H_6^+$ or $ScC_6H_6^+$ species are often observed with lack of $FeC_6H_6^+$. It suggests predominant Ln−benzene interaction in the benzene cluster ions. In support, the reaction of $ScFe^+$ with benzene affords 9% of $ScFe(C_6H_6)^+$, 16% of $Sc(C_6H_4)^+$, 73% of $Sc(C_6H_6)^+$, and only 2% of $Fe(C_6H_6)^+$ ions.[19b] Sandwich ions $Sc(C_6H_6)_2^+$ along with $ScFe(C_6H_6)_2^+$ were obtained in secondary reactions of $ScFe(C_6H_6)^+$ with cyclohexene.[19b]

2. Arene–Halogenoaluminate Complexes

The chloroaluminate complex of samarium, $(\eta^6\text{-}C_6Me_6)Sm[(\mu\text{-}Cl)_2AlCl_2)]_3$ (**1.28**) (Table 1), was the first complex of a rare-earth metal with π-bonded arene ligand. It was synthesized under the Friedel−Crafts reaction.[1,28] This method has been used later for preparation of compounds with other aromatics such as C_6H_6,[20,22,23,25] C_6H_4Me,[20,21,26,] 1,3-$C_6H_3Me_2$,[27] and $C_6H_2Me_4$.[20,21] Besides Sm, similar complexes have been obtained for Y, Pr, Nd, Sm, Gd,[20,21] La,[22] Eu,[29,30] and Yb.[24,31] When $AlBr_3$ was applied instead of $AlCl_3$, the related bromoaluminates **1.2**, **1.9**, **1.15**, **1.16**, and **1.33** were isolated.[20] In the case of AlI_3, only the complexes with Pr and Nd were obtained.[20,21] Interestingly, despite the presence in the reaction mixture of aluminum powder (a rather strong reductant), only europium is reduced in the synthesis to the divalent state.[29] Later it was shown that complexes (arene)$Ln(AlCl_4)_3$ could be synthesized directly from $LnCl_3$, $AlCl_3$, and arene without participation of aluminum powder.[20,24]

$$LnX_3 + 3AlX_3 \xrightarrow{\text{arene, }\Delta} (\eta^6\text{-arene})Ln(AlX_3)$$

$$\text{arene} = C_6H_6,\ PhMe,\ C_6H_2Me_4;\ X = Cl,\ Br,\ I$$

The disproportionation reactions between Ln(arene)$(AlX_4)_3$ and the appropriate AlR_3 were used for preparation of the compounds with alkylated aluminum fragments $AlCl_2R$ (R = Me, Et).[21] An attempt to substitute the halogen in the anions (AlX_3) with alkoxy groups was reported.[20]

The compositions and structures of the complexes indicate that the aromatic moiety is η^6-coordinated to the trivalent metal atom and serves as a neutral π-donor ligand. The arrangement of all the haloaluminates (except Eu(II) derivative) is factually the same: distorted pentagonal bipyramid with the arene in an apical position (Figure 1).

The average Ln−C distances (2.93 Å for Nd in **1.11**,[22b] 2.898 Å for Sm in **1.28**,[28] 2.999 Å for Eu in **1.30**,[29] 2.87 for Gd in **1.33**,[20] and 2.865 Å for Yb in **1.36**[24]) are noticeably shorter than the sum of the van der Waals radius of the carbon atom and the ionic radius of the corresponding metal atom but are substantially longer than the Ln−C contacts in the cyclopentadienyl derivatives (2.60−2.82 Å for the total series of lanthanides). These data correspond to a relatively weak Ln−arene bond in the arene−haloaluminates, which is confirmed by their dissociation to the starting LnX_3 and AlX_3, easily occurring in THF solution.[20] However, the compounds are quite stable thermally: most of them in the crystalline state do not decompose upon heating to 80 °C.[20]

Table 1. Data of Halogenoaluminate Complexes of $Ln(\eta^6\text{-}C_6H_6)(\eta^2\text{-}AlCl_4)_3$ Type

compound	no.	color, mp	other characteristics, ref
$Y(C_6H_5Me)(AlCl_4)_3$	**1.1**	pale yellow	IR[20]
$Y(C_6H_5Me)(AlBr_4)_3$	**1.2**	colorless	IR[20]
$Y(C_6H_5Me)(AlCl_3Me)_3$	**1.3**	colorless crystals	IR, catalysis[21]
$La(C_6H_6)(AlCl_4)_3{\cdot}(C_6H_6)$	**1.4**		IR[22]
$Pr(C_6H_6)(AlI_4)_3$	**1.5**	yellow-green	IR[20]
$Pr(C_6H_5Me)(AlI_4)_3$	**1.6**	yellow-green	IR[20]
$Pr(C_6H_2Me_4)(AlI_4)_3$	**1.7**	pale green	IR[20]
$Pr(C_6H_5Me)(AlCl_3Et)_3$	**1.8**	pale green crystals	IR, catalysis[21]
$Pr(C_6H_5Me)(AlBr_4)_3$	**1.9**	pale green	IR[20]
$Nd(C_6H_6)(AlI_4)_3$	**1.10**	light blue	IR[20]
$Nd(C_6H_6)(AlCl_4)_3{\cdot}(C_6H_6)$	**1.11**		X-ray, IR,[22] catalysis[23]
$Nd(C_6H_5Me)(AlI_4)_3$	**1.12**	yellow-brown	IR[20]
$Nd(C_6H_2Me_4)(AlI_4)_3$	**1.13**	yellow-brown	IR[20]
$Nd(C_6Me_6)(AlCl_4)_3$	**1.14**		catalysis[23]
$Nd(C_6H_5Me)(AlBr_4)_3$	**1.15**	light blue	IR[20]
$Nd(C_6H_2Me_4)(AlBr_4)_3$	**1.16**	light blue	IR[20]
$Nd(C_6H_5Me)(AlCl_3Me)_3$	**1.17**	light blue crystalline solid	IR, NMR[21]
$Nd(C_6H_5Me)(AlCl_3Et)_3$	**1.18**	light blue crystals	IR, catalysis[21]
$Nd(C_6H_5Me)(AlBr_3Et)_3$	**1.19**	light blue crystals	IR, catalysis[21]
$Nd(C_6H_5Me)(AlI_3Et)_3$	**1.20**	light blue crystals	IR, NMR[21]
$Nd(C_6H_2Me_4)(AlCl_3Me)_3$	**1.21**	light blue crystals	NMR[21]
$Nd(C_6H_2Me_4)(AlCl_3Et)_3$	**1.22**		IR[21]
$Nd(C_6Me_6)(AlCl_4)_3{\cdot}(C_6H_5Me)$	**1.23**	blue crystals, 103 °C(dec)	IR, MS[24]
$Sm(C_6H_6)(AlCl_4)_3{\cdot}(C_6H_6)$	**1.24**		X-ray, IR[22b,25]
$Sm(C_6H_5Me)(AlCl_4)_3$	**1.25**	yellow	X-ray,[26] IR[20,26]
$Sm(C_6H_5Me)(AlCl_3Me)_3$	**1.26**	yellow crystals	IR[21]
$Sm(C_6H_4Me_2{-}1,3)(AlCl_4)_3$	**1.27**	yellow, >110 °C (dec)	X-ray, IR[27]
$Sm(C_6Me_6)(AlCl_4)_3{\cdot}(C_6H_5Me)_{1.5}$	**1.28**	yellow plates	X-ray[1,28]
$Sm(C_6Me_6)(AlCl_4)_3{\cdot}(C_6H_5Me)$	**1.29**	yellow crystals, 104 °C(dec)	IR, MS[24]
$[Eu(C_6Me_6)(AlCl_4)_2]_4$	**1.30**	green crystals, >140 °C(dec)	X-ray, luminescence[29]
$[Eu(C_6Me_6)(AlCl_4)_2]_4{\cdot}(C_6H_2Me_4)$	**1.31**		X-ray, UV[30]
$Gd(C_6H_5Me)(AlCl_4)_3$	**1.32**	colorless	IR[20]
$Gd(C_6H_5Me)(AlBr_4)_3$	**1.33**	colorless	X-ray, IR[20]
$Gd(C_6H_5Me)(AlBr_3Me)_3$	**1.34**	colorless crystals	IR, catalysis[21]
$Gd(C_6Me_6)(AlCl_4)_3{\cdot}(C_6H_5Me)$	**1.35**	yellow crystals, 103 °C (dec)	IR, MS[24]
$Yb(C_6Me_6)(AlCl_4)_3{\cdot}(C_6H_5Me)$	**1.36**	deep blue crystals, 104 °C (dec)	X-ray, IR, MS[24,31]

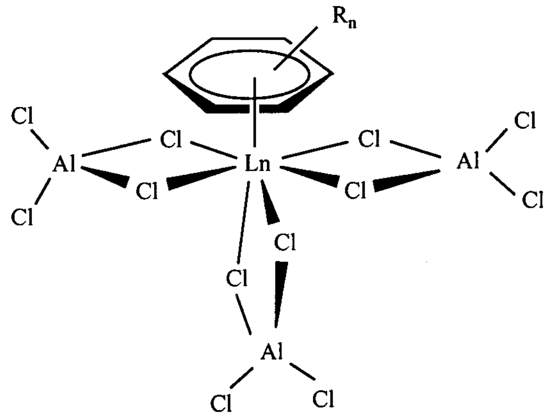


Figure 1.

The replacement of AlX_4 groups in the complexes with alkylated fragments AlX_3R, for example, in complexes **1.3**, **1.8**, and **1.18**, does not lead to a change of the character of the arene−metal bond. Europium complex **1.30** in a crystal exists as a cyclotetramer composed of four $Eu(C_6Me_6)(AlCl_4)_2$ units.[29] Each Eu atom is coordinated by three $AlCl_4$ groups and one C_6Me_6 ligand to form a distorted pentagonal bipyramid.

3. Complexes with Heterobidentate Ligands

There are two types of complexes in which the metal−ligand σ-bond is supported by π-interaction between Ln atom and pendant C_6 aromatic group: arene−aryloxides or thio analogues and terphenyl and similar derivatives (Table 2). The molecules of the compounds can be depicted as general scheme **A** for intramolecular Ln−arene complexes and **B** for dimers with intermolecular π-bonded bridges (Figure 2).

Several paths have been used for preparing the phenoxides. Probably the simplest of them is direct reaction of lanthanide metal with phenol in the presence of mercury.[32,33,38] The synthesis is conducted in a sealed tube at 200 °C; the yield of solvated free products reaches 80−90%. A no less efficient method is the substitution of R in complexes LnR_3 by the more acidic phenoxy group.

$$LnR_3 + 3ArOH \rightarrow Ln(OAr)_3 + 3RH$$

$$Ln = Nd, Sm, Er, Yb, Lu;\ R = Cp, CCPh, C_6F_5;$$
$$Ar = 2,6\text{-}Ph_2C_6H_3;^{37}\ Ln = Nd, Sm, Er;$$
$$R = N(SiMe_3)_2;\ Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3{}^{35}$$

The reactions with phenyl acetylene and pentafluorophenyl derivatives usually are realized in a one-pot reaction from HgR_2, lanthanide metal, and phenol without isolation of intermediate LnR_3.

$$3HgR_2 + 2Ln + 6HOC_6H_3Ph_2 \rightarrow 2Ln(OC_6H_3Ph_2)_3 + 3Hg + 6RH$$

Table 2. Data of Complexes with Heterobidentate Ligands

compound	no.	color, mp	other characteristics, ref
π-arene−aryloxides and −arylsulfides			
$Sc(OC_6H_3Ph_2\text{-}2,6)_3$	**2.1**	colorless. >220 °C	X-ray, NMR, IR, MS[32]
$Y(OC_6H_3Ph_2\text{-}2,6)_3$	**2.2**	colorless	X-ray, MS[33]
$La_2(OC_6H_3\text{-i-}Pr_2\text{-}2,6)_6$	**2.3**	colorless	X-ray, NMR, IR[34]
$La(OC_6H_3Ph_2\text{-}2,6)_3$	**2.4**	colorless	X-ray[33]
$Ce(OC_6H_3Ph_2\text{-}2,6)_3$	**2.5**	yellow-greenish	X-ray, MS[33]
$Pr(OC_6H_3Ph_2\text{-}2,6)_3$	**2.6**	pale green	X-ray, UV/Vis, MS[33]
$Nd_2(OC_6H_3\text{-i-}Pr_2\text{-}2,6)_6$	**2.7**	pale blue	X-ray, NMR, IR[35]
$Nd(OC_6H_3Ph_2\text{-}2,6)_3$	**2.8**	blue	X-ray,[36] MS[37]
$Nd(OC_6H_3Ph_2\text{-}2,6)_3(THF)$	**2.9**		X-ray, IR, MS, Vis[36]
$[Sm(OC_6H_3\text{-i-}Pr_2\text{-}2,6)_3]_2$	**2.10**	deep yellow	X-ray, NMR, IR[35]
$Eu_2(OC_6H_3Ph_2\text{-}2,6)_4\cdot(PhMe)$	**2.11**	yellow	X-ray, IR, MS[38]
$Eu[SC_6H_3(C_6H_2\text{-i-}Pr_3\text{-}2,4,6)_2\text{-}2,6]_2\,(THF)_{0.5}$	**2.12**	orange, 289−292 °C	X-ray, IR, MS[39]
$Gd(OC_6H_3Ph_2\text{-}2,6)_3$	**2.13**	colorless	MS[33]
$Ho(OC_6H_3Ph_2\text{-}2,6)_3$	**2.14**	pink	MS[33]
$Er_2(OC_6H_3\text{-i-}Pr_2\text{-}2,6)_6$	**2.15**	pink	NMR, IR[35]
$Er(OC_6H_3Ph_2\text{-}2,6)_3$	**2.16**	pink	IR, UV/Vis, MS[33,37]
$Yb[SC_6H_3(C_6H_2\text{-i-}Pr_3\text{-}2,4,6)_2\text{-}2,6]_2\cdot(C_6H_6)_{0.5}$	**2.17**	purple, 263−265 °C	X-ray, NMR, IR, UV/Vis, MS[39]
$Yb(OC_6H_3Ph_2\text{-}2,6)_3$	**2.18**	orange-yellow	X-ray, IR, UV/Vis, MS[37]
$Yb_2(OC_6H_3Ph_2\text{-}2,6)_4\cdot(PhMe)_{1.5}$	**2.19**	dark red	X-ray, MNR, IR, MS[38]
$\{[Yb(OC_6H_3Ph_2\text{-}2,6)_4][Yb_2(OC_6H_3Ph_2\text{-}2,6)_3]\}\cdot(toluene)$	**2.20**	red-orange	X-ray, NMR, IR,[38]
$Lu(OC_6H_3Ph_2\text{-}2,6)_3$	**2.21**	white	X-ray,[33] IR, MS[37]
terphenyl and related derivatives			
$(2,6\text{-}Mes_2C_6H_3)SmCp_2$	**2.22**	orange-yellowish, >155 °C(dec)	NMR, MS[40]
$(2,6\text{-}Ph_2C_6H_3)_2Eu(THF)_2$	**2.23**	orange	X-ray[41]
$(2,6\text{-}Ph_2C_6H_3)_2Yb(THF)_2$	**2.24**	red	X-ray, NMR[41]
$(2,6\text{-}Ph_2C_6H_3)YbI(THF)_3$	**2.25**	orange-red, 110−125 °C (dec)	X-ray, NMR[41]
$(2,6\text{-}Mes_2C_6H_3)Yb(C_5H_4Me)_2$	**2.26**	dark red, 148 °C	X-ray, MS[40]

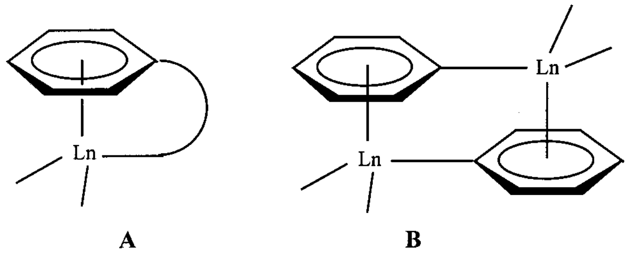


Figure 2.

Complex **2.3** with di-isopropyl-substituted phenol has been synthesized by treatment of $LaCl_3$ with sodium metal in liquid ammonia followed by addition of $2,6\text{-i-}Pr_2C_6H_3OH$.[34] All the indicated reactions (except direct method and the reaction with amides proceeding in toluene) produce complexes with solvated THF or NH_3 molecules which detain the secondary π-arene bonding. To remove these ligands, the products are sublimed[36] or refluxed in toluene.[35]

The arylthiolate complexes **2.12** and **2.17** were synthesized by protolysis of a Grignard-like compound $2\text{-}CF_3C_6H_4LnI$ with thiol $HSC_6H_3(C_6H_2\text{-i-}Pr_3\text{-}2,4,6)_2\text{-}2,6$.[39]

The *m*-terphenyl derivatives **2.23**, **2.24**, and **2.25** were isolated from the mixture of $Ln(Ar^*)I(THF)_x$, $Ln(Ar^*)_2(THF)_2$ ($Ar^* = 2,6\text{-}Ph_2C_6H_3$), and $LnI_2(THF)_x$ formed due to Schlenk-like equilibrium in the reactions of Eu or Yb metals with terphenyl iodide.[41] Treatment of Cp_3Sm or $(C_5H_4Me)_3Yb$ with aryllithium $2,6\text{-}(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3Li$ has been used for preparation of compounds **2.22** and **2.26**.[40]

It has been found that pure coordinating interactions between the metal atom and C_6 aromatic rings, identical to that observed in halogenoaluminate complexes, exist in many solvent-free aryl oxides or thiolates. The presence of the phenyl substituents at the ortho position of the aryloxy group (for example, in complexes **2.5**, **2.6**, **2.8**, and **2.21**) results in an intramolecular η^6-interaction between the lanthanide atom and one of the phenyl substituents of the phenoxy ligand. The phenyl substituent of the second phenoxy ligand is η^1-bonded to the Ln atom, whereas the third phenoxy ligand remains monodentate.[33,36,37] In the case of lanthanum analogue **2.4**, the second π-interaction is η^3-type, probably because of the larger size of La than Ce, Pr, or Nd. The smallest rare-earth metal, scandium, demonstrated $\eta^1{:}\eta^1$-bonding in complex **2.1** (Figure 3).[32]

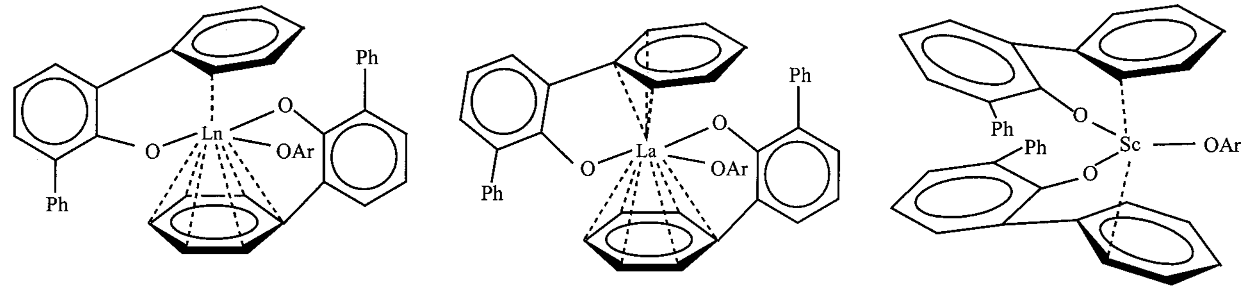
The presence of one coordinated THF molecule in compound **2.9** causes disruption of the second Ln−arene π-bond and decreases the hapticity of the first one up to three (Figure 4).[36]

The addition of methyl or *tert*-butyl substituents into the 3,5-positions of phenoxy groups, $OC_6H(Ph_2\text{-}2,6)(R_2\text{-}3,5)$, results in a complete cancel of π-interactions in the phenoxides of Sc, Sm, and Yb.[32]

The 2,6-diphenylphenoxides of Eu(II) (**2.11**) and Yb(II) (**2.19**) form the dimers with three (Eu) or two (Yb) bridged phenoxy groups.[38] One of Eu atoms in complex **2.11** has three short Eu−C contacts (3.222, 3.082, 3.240 Å) with pendant phenyl rings which can be considered as an η^1-Ph−Eu interaction, while for the second Eu atom there are three η^2-π-Ph−Eu bonds. The π-Ph−Yb interactions in **2.19** have η^3 and η^1,η^4 type (Figure 5).

In contrast, the terphenylthiolate complexes of Eu(II) **2.12** and Yb(II) **2.17** are monomeric. Two of $\text{i-}Pr_3C_6H_2$ substituents at every thiolate ligand in these compounds are oriented in such a way that a sandwich-like structure with two η^6-Ln−arene groups is realized (Figure 6).[39]

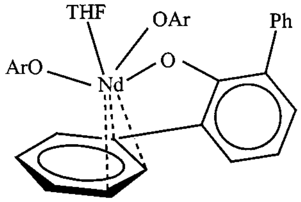
In a crystal of the mixed-valent complex **2.20** the discrete $[Yb(OC_6H_3Ph_2\text{-}2,6)_4]^+$ cations and $[Yb_2(OC_6\text{-}$



2.5, 2.6, 2.8, 2.21 **2.4** **2.1**

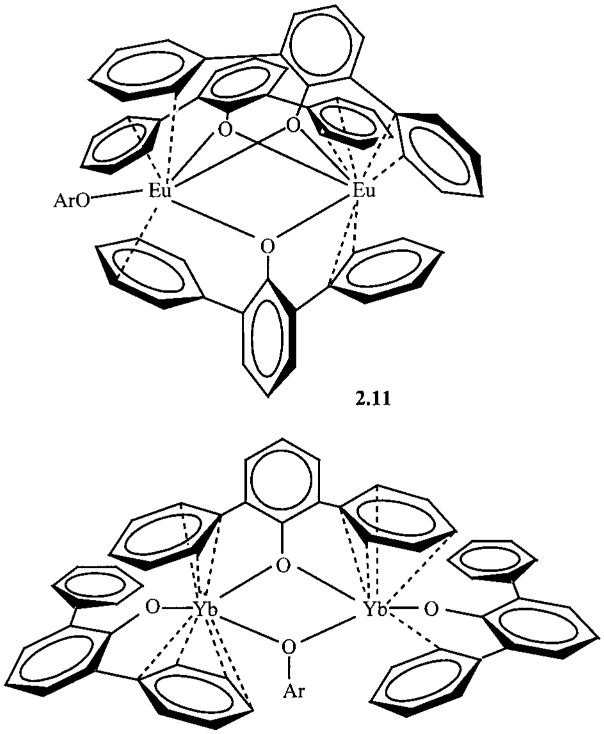
Ar =2,6,-$Ph_2C_6H_3$

Figure 3.



2.9

Figure 4.



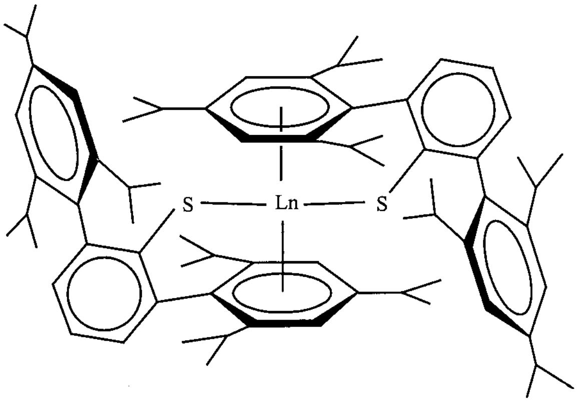
2.11

2.19

Figure 5.

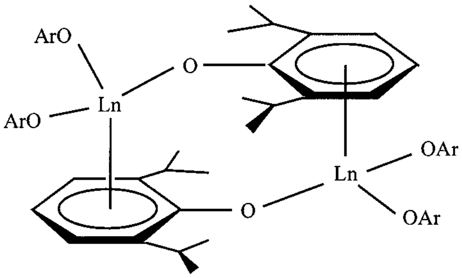
H_3Ph_2-2,6$)_3]^-$ anions have been found.[38] The anionic part does not contain π-bonding between Yb and Ph groups, but in the binuclear cation, a structure which resembles the arrangement of **2.11**, there are η^1-, η^2-, and η^6-Ph−Yb(1) interactions and η^1- and η^6-type for Yb(2).

Dimeric structures were found in lanthanide triphenoxides with isopropyl substituents in ortho positions **2.3**, **2.7**, **2.10**, and **2.15**. In these cases the bridged phenoxy groups are σ-bonded to one Ln atom by means of the O-atom and by η^6-π-bond to the second metal center (Figure 7).[34,35]



2.12, 2.17

Figure 6.



2.3, 2.7, 2.10, 2.15

Ar = 2,6-*i*-$Pr_2C_6H_3$

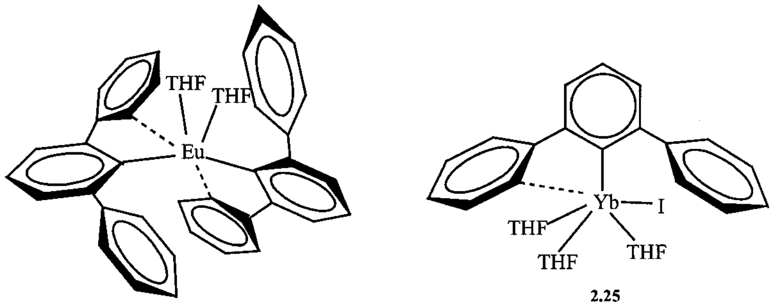
Figure 7.

Noticeably, in complexes $La_2(OCPh_3)_6$ and $Ce_2(OSiPh_3)_6$, which also have a dimeric arrangement and are suitable Ln-OE-Ph fragments, additional π-Ln−arene bonding was not observed.[42]

The intramolecular π-interactions between the Ln atom and pendant Ph groups have been found in the *m*-terphenyl derivatives **2.23**, **2.24**, and **2.25**.[41] The π-bonds in these cases have η^1-type and, judging on their lengths (Eu−C 3.218, 3.153 Å; Yb−C 3.104 Å), are weak (Figure 8).

The terphenyl groups bonded to Cp_2Sm or $(C_5H_4Me)_2Yb$ moieties in complexes **2.22** and **2.26** also reveal additional Ln−arene π-bonding. In the first compound Sm is connected to one of the pendant 2,4,6-mesityls by a η^3-bond; in the second one the Yb−Mes bond has η^1-type.[40]

The Ln−arene contacts are retained upon dissolution of the indicated complexes in nonsolvating solvents; however, π-bonds are cleaved in THF or in



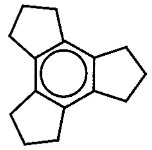
2.23 **2.25**

Figure 8.

Table 3. Data for Bis(benzene) Sandwich Complexes

compound	no.	color, mp	other characteristics, ref
$Sc(1,3,5\text{-}Me_3C_6H_3)_2$	**3.1**	dec. >−30 °C	Vis.[3]
$Sc(Me_5C_6H)_2$	**3.2**	dec. >0 °C	Vis.[3]
$Sc(1,4\text{-t-}Bu_2C_6H_4)_2$	**3.3**	dec. >100°C	Vis.[3]
$Sc(C_6Me_6)_2$	**3.4**	dec. >40 °C	Vis.[3]
$Sc(1,3,5\text{-t-}Bu_3C_6H_3)_2$	**3.5**	deep orange-green, dec >120 °C	ESR,[43,44] Vis.[3,44]
$Sc(C_{15}H_{18})_2$[a]	**3.6**	dec. >100 °C	Vis.[3]
$Sc(1,3,5\text{-}t\text{-}Bu_3\text{-}4\text{-}MeC_6H_2)_2$	**3.7**	dec. >120 °C	Vis.[3]
$Y(1,3,5\text{-}t\text{-}Bu_3C_6H_3)_2$	**3.8**	deep purple	subl., MS,[45] ESR,[46] Vis, magn.[47]
$La(1,3,5\text{-}t\text{-}Bu_3C_6H_3)_2$	**3.9**	green, dec >0 °C	Vis[47]
$Pr(1,3,5\text{-t-}Bu_3C_6H_3)_2$	**3.10**	purple, dec >40 °C	Vis[47]
$Nd(1,3,5\text{-t-}Bu_3C_6H_3)_2$	**3.11**	blue	subl., Vis, magn.[47]
$Nd_2(C_6H_6)_3$	**3.12**	black	magn., catalysis[48]
$Sm(1,3,5\text{-t-}Bu_3C_6H_3)_2$	**3.13**	green, dec >−30 °C	Vis[47]
$Gd(1,3,5\text{-t-}Bu_3C_6H_3)_2$	**3.14**	purple	X-ray, NMR,[46] Vis, magn.[47]
$Tb(1,3,5\text{-t-}Bu_3C_6H_3)_2$	**3.15**	purple	subl., Vis, magn.[47]
$Dy(1,3,5\text{-t-}Bu_3C_6H_3)_2$	**3.16**	purple	subl., Vis, magn.[47]
$Ho(1,3,5\text{-t-}Bu_3C_6H_3)_2$	**3.17**	deep pink	X-ray, subl., Vis, magn.[47]
$Er(1,3,5\text{-t-}Bu_3C_6H_3)_2$	**3.18**	red	subl., Vis, magn.[47]
$Lu(1,3,5\text{-t-}Bu_3C_6H_3)_2$	**3.19**	red-green	subl., ESR, Vis, magn.[47]

[a] $C_{15}H_{18}$ =



(trindan)

the presence of ammonia. The coordination site of the η^6-arene ligand in the resulting compounds is occupied by THF, DME, or NH_3 molecules, which is indicative of a low strength of the Ln−arene bonds. The lengths of these contacts (average Ln−C distances for trivalent lanthanides are 2.986−3.061 Å) are virtually identical to the corresponding values in arene−halogenoaluminate complexes. Analyzing the IR spectra of the lanthanide complexes with a secondary π-arene interaction, Niemeyer came to conclusion that such an interaction weakens the aromatic C=C bonds.[39]

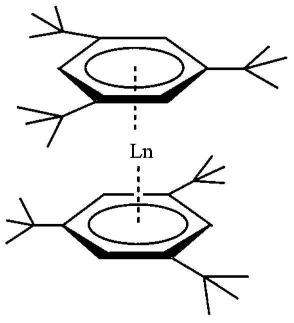
4. Bis(Benzene) Sandwich Complexes of Zerovalent Lanthanides

Co-condensation of benzene and neodymium vapors on the surface cooled to −196 °C afforded a binuclear complex with composition $Nd_2(C_6H_6)_3$ (**3.12**) (Table 3), which was isolated as black insoluble crystals.[48] The magnetic moment (3.42 μ_B) corresponds to the Nd(III) cation (3.68 μ_B[49]) and the dianionic form of all three benzene ligands. The complex was not studied by X-ray diffraction analysis, but it is reasonable to suppose that its structure is similar to that of the thulium naphthalene analogue $[(C_{10}H_8)Tm(DME)]_2(\mu\text{-}C_{10}H_8)$ considered below.

Sandwich bis(arene) complexes of rare-earth metals $(1,3,5\text{-t-}Bu_3C_6H_3)_2Ln$ (**3.5**, **3.8**−**3.11**, **3.13**−**3.19**) analogous to the well-known bis(arene) complexes of d-transition metals were prepared by co-condensation of 1,3,5-tri(*tert*-butyl)benzene and metal vapors at 75 K.[44−47] The structures and magnetic moments of the complexes confirm the η^6-character of the bond between the neutral aromatic ring and the formally zerovalent metal atom (Figure 9).

In gadolinium complex **3.14,** characterized by X-ray diffraction analysis, the Gd−C distances are in the range of 2.585−2.660 Å (the average distance is 2.630 Å).[46] These distances are virtually identical to the Ln−C bond lengths in cyclopentadienyl complexes of the Cp_2GdBr type (2.635, 2.639, and 2.630 Å[50]). The holmium complex **3.17** was found to have the same structure with average Ho−C contacts 2.630 Å.[47]

The stability of the indicated compounds depends on the nature of the lanthanide. Thus, the Sc, Y, Nd, Gd, Tb, Dy, Ho, Er, and Lu complexes are stable (some of them can be sublimed in a vacuum without decomposition), whereas the Ce, Eu, Tm, and Yb



3.5, 3.8 - 3.11, 3.13 - 3.19

Figure 9.

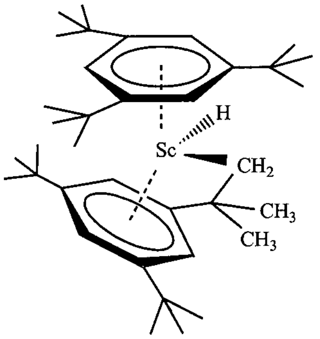
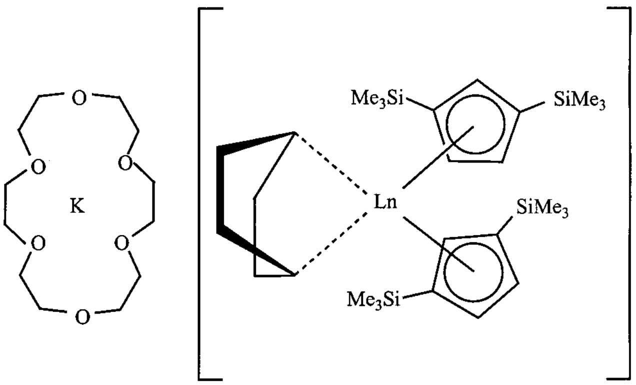


Figure 10.

complexes do not form stable products. Derivatives of La, Pr, and Sm are intermediate in stability. In the reaction of Sc with tri-*tert*-butylbenzene, besides the expected sandwich **3.5,** the product of insertion of Sc at the C−H bond of butyl groups has been found. It was suggested on the basis of an ESR spectrum that this product is the unprecedented 17-electron Sc(II) complex Sc(η^6-t-$Bu_3C_6H_3$)[(η^6,η^1-t-$Bu)_2(CMe_2CH_2)C_6H_3$]H (Figure 10).[44]

The difference in the thermal stability of the complexes with the same ligands but different metals is explained, as in the considered above ionic species Ln−arene$^+$, by the difference in the promotion energy of $f^ns^2 \rightarrow f^{n-1}d^1s^2$ for different lanthanides. Thermodynamic studies confirmed the rather high stability of the Ln−arene bond for some rare-earth metals. Thus, the enthalpy of cleavage of these bonds in complexes $Ln(Bu_3C_6H_3)_2$ was found to be 72, 68, 47, 56, 57, and 62 kcal mol^{-1} for the derivatives of Y, Gd, Dy, Ho, Er, and Lu, respectively[51] (cp. 53 ± 5 kcal mol^{-1} for $Sc(C_6H_6)^+$ [10]).

The stability of bis(arene) complexes increases as the number and size of substituents in the aromatic ring increase, as exemplified by scandium derivatives.[3] Calculation by molecular mechanics[52] for $Gd(C_6H_6)_2$ and complexes **3.8**, **3.14**, and their Yb analogue confirmed that the benzene derivatives are substantially less stable than the complexes with *tert*-butyl-substituted ligands. This is consistent with the



4.2, 4.3, 4.5

Figure 11.

experimental data on deposition of vaporized scandium on the surface on benzene or C_6D_6 at 77 K.[43] The products, $Sc(C_6H_6)_2$ or $Sc(C_6D_6)_2$, detected in the resulting matrices by ESR spectroscopy are characterized by very low stability. Quantum-chemical calculations[53,54] demonstrated that the metal atoms in the Ln(arene)$_2$ complexes are bound to the benzene rings primarily through back-donation from the occupied $d_{\pm 2}$ orbitals of the metal atom to the unoccupied π-orbitals of the benzene ligands.

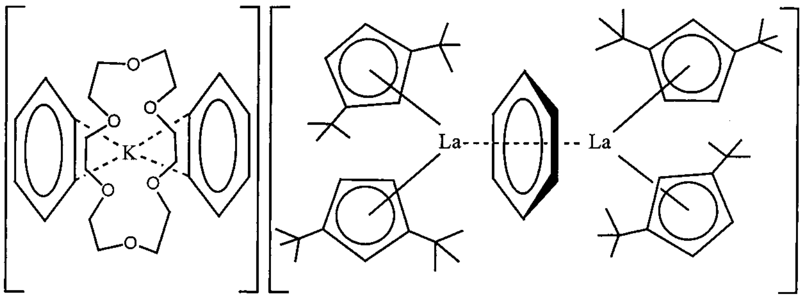
5. Complexes with Anionic Benzene Ligand

Studying the reduction of lanthanum, cerium, and neodymium cyclopentadienyl complexes of $Cp^{\#}_3Ln$ type, where $Cp^{\#}$ is C_5H_3-t-Bu_2-1,3 or $C_5H_3(SiMe_3)_2$-1,3, by lithium or sodium metal Lappert and coworkers found that the reactions in DME medium result in formation of $Cp^{\#}_2LnOMe$ products.[55,56] The color transitions and ESR monitoring of the reactions suggested the generation of unstable and highly reactive divalent intermediates of $LnCp^{\#}_2$ and $[K(DME)_x][LnCp^{\#}_3]$ type. When the reduction of $Ln[C_5H_3(SiMe_3)_2]_3$ (Ln = La, Ce, Pr, Nd) by an excess of potassium was carried out in benzene in the presence crown ether, the dark red ionic complexes **4.2**−**4.5** (Table 4) were obtained.[58,59] Most of them have been characterized by X-ray diffraction analysis, which revealed that the C_6H_6 moiety bonded to the Ln[η^5-$C_5H_3(SiMe_3)_2]_2$ fragment in the anionic part of the molecule has a boat conformation with two short Ln−C contacts: 2.617, 2.652 Å (La), 2.588, 2.612 Å (Ce), and 2.55, 2.572 Å (Nd) (Figure 11).

The structure of the anions indicates that the C_6H_6-Ln_2 fragments should be considered as cyclohexadiene-1,4 (rather than benzene) η^2-bonded to two $LnCp^{\#}_2$ parts in which the lanthanide is trivalent. ESR control of the reaction with $La[C_5H_3(SiMe_3)_2]_2$ has shown that in the intermediate stage at least four metal-centered free-radical species appear, which the

Table 4. Data for Complexes with Anionic C_6H_6 Ligands

compound	no.	color	other characteristics, ref
$[K([18]\text{-crown-6})(C_6H_6)_2]$ $\{[La\{C_5H_3\text{-t-}Bu_2\text{-1,3}\}_2]_2C_6H_6\}$	**4.1**	dark green	X-ray[57]
$[K([18]\text{-crown-6})]$ $[La\{C_5H_3(SiMe_3)_2\text{-1,3}\}_2C_6H_6]$	**4.2**	red	X-ray, NMR, IR, UV/Vis[58,59]
$[K([18]\text{-crown-6})]$ $[Ce\{C_5H_3(SiMe_3)_2\text{-1,3}\}_2C_6H_6]$	**4.3**	dark red	X-ray, NMR, IR, UV/Vis[58,59]
$[K([18]\text{-crown-6})]$ $[Pr\{C_5H_3(SiMe_3)_2\text{-1,3}\}_2C_6H_6]$	**4.4**	dark red-brown	NMR, IR, UV/Vis[58]
$[K([18]\text{-crown-6})]$ $[Nd\{C_5H_3(SiMe_3)_2\text{-1,3}\}_2C_6H_6]$	**4.5**	dark red	X-ray, NMR, IR, UV/Vis[58]



4.1

Figure 12.

Table 5. Data for Biphenyl and Miscellaneous Complexes

compound	no.	color, mp	other characteristics, ref
($\{PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh\}Y)_2(\mu\text{-}PhPh)$	**5.1**	deep blue	X-ray, NMR[61]
($\{PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh\}Y)_2(\mu\text{-}MeC_6H_4C_6H_4Me)$	**5.2**	dark brown	X-ray, NMR[61]
$Nd[N(C_6F_5)_2]_3(PhMe)$	**5.3**	purple	X-ray, NMR, IR[62]
$Sm(\eta^6\text{-}Me_3SiC_{13}H_8\text{-}AlMe_3)_2$	**5.4**	dark red	X-ray, NMR, MS[63]
$Sm(\eta^6\text{-}Me_3SiC_{13}H_8\text{-}AlEt_3)_2$	**5.5**	dark red	X-ray, NMR, MS[63]
$Sm[(\eta^6\text{-}Me_3SiC_{13}H_8\text{-}Al(C_3H_7)_3]_2$	**5.6**		NMR[63]
$Sm(\eta^6\text{-}Me_3SiC_{13}H_8\text{-}AlBu_3)_2$	**5.7**		NMR[63]
$Sm(\eta^6\text{-}Me_3SiC_{13}H_8\text{-}BEt_3)_2$	**5.8**		NMR[63]
$Yb(\eta^5\text{-}Me_3SiC_{13}H_8\text{-}AlMe_3)(\eta^6\text{-}Me_3SiC_{13}H_8\text{-}AlMe_3)$	**5.9**	red	X-ray, NMR, MS[63]
$Yb(\eta^6\text{-i-}PrC_9H_6\text{-}AlMe_3)_2$	**5.10**	red	NMR, MS[63]

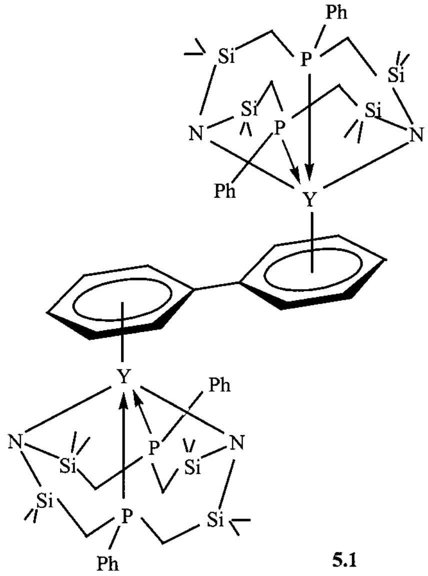
authors believe are the derivatives of La(II).[58] In this stage the reaction mixture has a dark blue-violet color, which then changes to dark-red.

Treatment of the cyclopentadienyl complex of lanthanum containing *tert*-butyl substituents in the cyclopentadienyl rings, $La(C_5H_3\text{-t-}Bu_2\text{-}1,3)_3$, with a 1.5 mol excess of potassium in benzene in the presence of [18]crown-6 at ambient temperature initially affords a dark red solution which gradually becomes dark green. In 1 week the dark green extremely air- and light-sensitive crystals of **4.1** were isolated from the obtained mixture.[57] The X-ray structure analysis demonstrated that the product to be also an ate complex with $[K([18]crown\text{-}6)(C_6H_6)_2]^+$ cation and $\{[La(C_5H_3\text{-t-}Bu_2)_2]_2C_6H_6\}^-$ anion, but in this case the bridging C_6H_6 is planar and bonded to both La atoms in an η^6-fashion. All La−C(benzene) contacts vary in a narrow range 2.75−2.79 Å, which is comparable with La−C distances in the terminal LaCp groups of $LaCp_3$.[60] On the basis of these data, the structure of a salt containing two $Cp^{\#}_2La(II)$ units π-bonded to the benzene anion was assigned to the complex (Figure 12).

Reduction of $La[C_5H_3(SiMe_3)_2]_2$ under the same conditions also leads to a dark green solid containing La(II), according to ESR, NMR, UV/Vis, and mass spectra.[57] However, its structure analysis was not done because of lack of good crystals.

6. Biphenyl Complexes

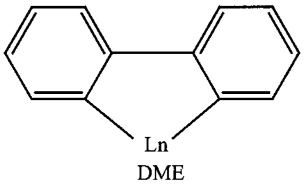
Treatment of the yttrium(III) chloride complex $(LY)_2(\mu\text{-}Cl)_2$, where L is a phosphorus−nitrogen−silicon macrocycle $PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2$-PPh, with phenyllithium gave rise to the dark blue binuclear product ($\{PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2$-$PPh\}Y)_2(\mu\text{-}PhPh)$ (**5.1**) (Table 5) containing the biphenyl dianion as the bridging ligand, which means the reaction is accompanied by coupling of phenyl groups.[61] The same compound was slowly formed when $(LY)_2(\mu\text{-}Cl)_2$ reacted with $LiCH_2SiMe_3$ in benzene solution. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy revealed that the initially formed σ-alkyl complex $LYCH_2SiMe_3$ undergoes intermolecular σ-bond metathesis with the benzene solvent. The new resonances of aryl groups with a great upfield shift (5.10(2H), 4.46(2H), and 4.18 ppm (1H)) observed in the reaction mixture indicated the appearance of a π-type Y−arene interaction (Figure 13).[61]



5.1

Figure 13.

In complex **5.1** the Y atoms are bonded to opposite sides of different rings in the biphenyl ligand, which remains virtually planar. The Y−C distances lay in a narrow range (2.675−2.738 Å), evidence of η^6-interaction. These distances (average 2.723 Å) are close to the Y−C bond lengths in complexes Cp_3Y-(THF) (the average distance is 2.71 Å[64]) and $(C_5Me_5)_2$-YCl(THF) (2.659 Å[65]).



A

Figure 14.

The reaction of LYCl with 3-MeC_6H_4Li also resulted in the formation of a C−C bond. According to the data of ^1H NMR and UV spectroscopy, the dark blue reaction product is structurally similar to complex **5.1**. However, 4-MeC_6H_4Li under the same conditions gave the dark brown compound ({$PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh$}$Y)_2(\mu$-$MeC_6H_4C_6H_4Me$) (**5.2**) in which both YL fragments are bonded to the same ring of the $[MeC_6H_4C_6H_4Me]^{2-}$ anion.[61] The average Y−C contacts in the fragment $Y(MeC_6H_4C_6H_4Me)Y$ (2.676 and 2.699 Å) are somewhat shorter than the corresponding bond lengths in complex **5.1**. ^1H NMR spectral studies of complex **5.2** demonstrated that slow (within the NMR time scale) migration of one of the YL groups from one MeC_6H_4 ring to another occurs in solution. It was assumed that such behavior in solution is also typical of other complexes with bridging Ar−Ar ligands.

Samarium and ytterbium powders activated with diiodoethane react with biphenylene at room temperature to form dark colored solutions.[66] Attempts to isolate reaction products in the crystalline state failed. However, the reactions of their solutions with oxygen (giving rise to 1,1′-biphenyl-2,2′-diol), deuteriomethanol (yielding a mixture of biphenyl and dideuteriobiphenyl), and Me_2SiCl_2 (forming a mixture of biphenyl and 1,1-dimethylsilafluorene) were carried out. These results testify that in the reactions of lanthanides with biphenylene the metal atom inserts into one of two $C_6H_4{=}C_6H_4$ bonds to give the lanthanide biphenydiyl complexes **A** containing metallocycle (Figure 14).

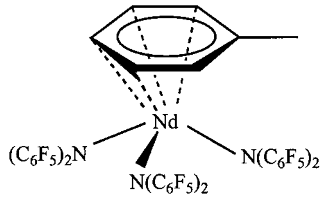
It was suggested[66] that the first stage involved reduction of biphenylene to form the ionic intermediates $C_{12}H_8{}^{2-}Ln^{2+}$, which abstracted hydrogen from the solvent to form biphenyl and complex **A**.

Apparently an analogous product was formed in the reaction of octamethylbiphenylenedilithium with SmI_2.[66]

7. Miscellaneous π-Complexes with C_6-Aromatic Compounds

An unusual complex of neodymium with π-bonded toluene $(PhMe)Nd[N(C_6F_5)_2]_3$ (**5.3**) was obtained in good yield by the reaction of $Nd[N(SiMe_3)_2]_3$ with bis(pentafluorophenyl)amine in toluene solution.[62] The X-ray diffraction analysis of this compound, isolated as purple air-sensitive crystals, revealed that its molecule has a distorted three-legged piano-stool geometry (Figure 15).

The toluene ligand is bound to the Nd center in a rather asymmetrical manner: four Nd−C contacts are short (2.982, 2.98, 3.103, and 3.167 Å) but the remaining two are long (3.313 and 3.324 Å), which is typical for η^4-type interactions. The average length of the short contacts (3.058 Å) is slightly larger than the Nd−C distances in chloroaluminate complex $(\eta$-$C_6H_6)Nd(AlCl_4)_3$ (average 2.93 Å[22b]), presumably indicative of a weaker bonding in the **5.3**.



5.3

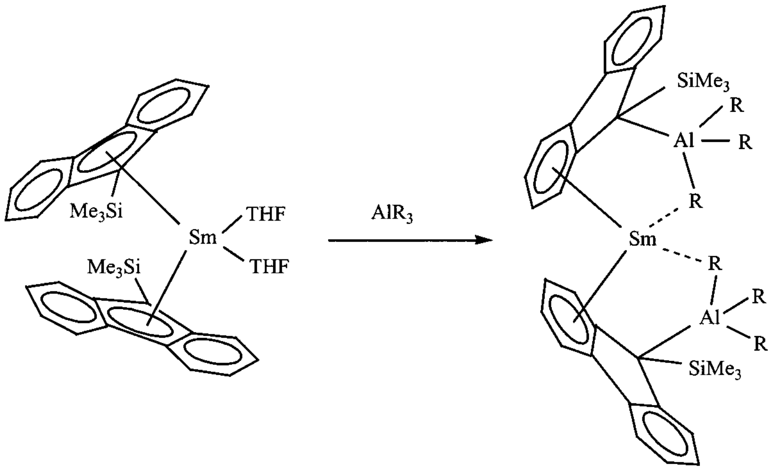
Figure 15.

Indenyl and fluorenyl complexes of rare-earth metals fall into a group of well-studied organolanthanides.[4,6] In all compounds, an exclusively η^5-type of bonding between the metal atom and the C_5-ring of the ligand was observed. However, recently it has been found that these ligands under certain conditions can coordinate to lanthanide in an η^6-fashion by the C_6-rings.[63] Such a transformation was realized by addition of excess of Me_3Al or Et_3Al to a toluene solution of bis(fluorenyl)samarium containing Me_3Si substituents in the 1-position of fluorenyl ligands. After recrystallization from a toluene/hexane mixture, the dark red crystals of composition $(Me_3SiC_{13}H_8{-}AlR_3)_2Sm$ (**5.4**, **5.5**) were isolated in 57% and 25% yields, respectively. The X-ray study of the products revealed that in both complexes the Sm atom is η^6-coordinated to the benzene rings of the fluorene ligands. One of alkyl substituents at Al serves as an agostic group (Figure 16).

The distances Sm−C_5-ring(centroid) (3.59 Å) and Sm−C_6-ring(centroid) (3.41−3.66 Å) in the initial η^5-version differ from those in **5.4** and **5.5**: Sm−C_5(centroid) 3.56−3.59 Å, Sm−C_6(centroid) 2.74−2.77 and 5.08−5.15 Å, which confirms the η^6-coordination of the fluorene ligand in the obtained Sm−Al complexes. Such a confirmation has been obtained as well from ^1H NMR spectra of the compounds, which allowed the determination that the η^6-complexes can convert to η^6-species by the successive addition of excess THF. The products **5.6**, **5.7**, and **5.8**, which were obtained in the reactions of $(Me_3SiC_{13}H_8)_2Sm$ with $Al(C_3H_7)_3$, $AlBu_3$, and BEt_3 could not be isolated in crystalline form, but they are nearly identical with those of **5.5**, suggesting the same type of bonding.

In the case of Yb analogue, the addition of Me_3Al to η^5-complex $(Me_3SiC_{13}H_8)_2Yb$ leads to formation of a product **5.9** in which one $Me_3SiC_{13}H_8$ ligand is η^5-bonded to Yb but the second one has η^6-coordination. The experiments with i-Pr-substituted indenyl complex of ytterbium, $(\eta^5$-i-$PrC_8H_6)_2Yb(THF)_2$, suggested that the similar $\eta^5{-}\eta^6$-rearrangements can occur with indenyl derivatives (**5.10**).[63]

Note that the nature of binding in these unusual η^6-fluorenyl heterobimetallic derivatives remains unclear because no reasonable scheme, including Al(III), Sm(II), and −1 or −2 charged fluorene, satisfies the observed compositions and structures of the complexes.



5.4, 5.5

Figure 16.

Table 6. Data for Completely Reduced Naphthalene Complexes

compound	no.	color, mp	other characteristics, ref
$(C_{10}H_8)_2Ce(OEt_2)$	**6.1**	pale brown	UV[69]
$(C_{10}H_8)Sm(THF)_3$	**6.2**	black	IR, magn.[67]
$(C_{10}H_8)Eu(THF)_3$	**6.3**	black	IR, magn.[67]
$(C_{10}H_8)Eu(DME)$	**6.4**		synthesis[68]
$(C_{10}H_8)Eu(DME)_2$	**6.5**		synthesis[70]
$(C_{10}H_8)_2Eu(OEt_2)$	**6.6**	pale brown	UV[69]
$[(C_{10}H_8)Tm(DME)]_2(\mu\text{-}C_{10}H_8)$	**6.7**	black, >100 °C(dec)	X-ray, magn.[71]
$(C_{10}H_8)Yb(THF)_3$	**6.8**	black	IR, magn.[67]
$(C_{10}H_8)Yb(DME)$	**6.9**	black	synthesis[68]
$(C_{10}H_8)Yb_2(THF)_3(NaCl)_3$	**6.10**	black	IR,[72a] synthesis[72b]
$(2\text{-}MeC_{10}H_7)Yb(THF)x$ $(x = 2, 3)$	**6.11**	black	synthesis[67a,72b]

III. Naphthalene Derivatives

1. Completely Reduced Complexes

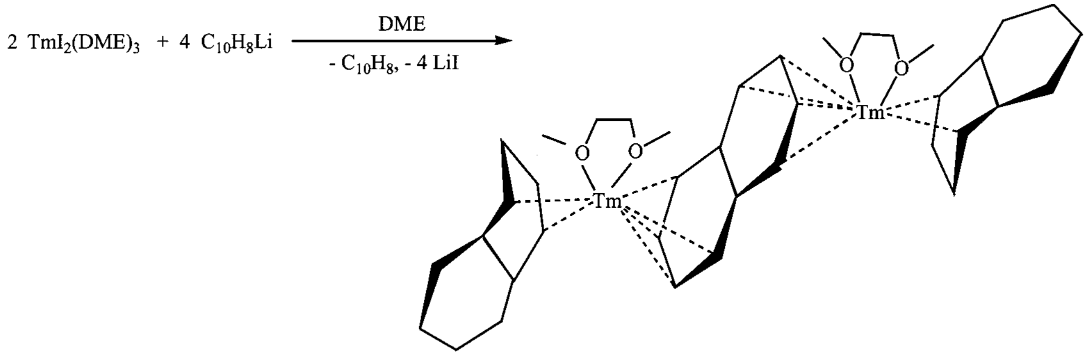
It was found that the reduction of anhydrous ytterbium diiodide with 2 equiv of lithium naphthalenide in THF or DME afforded insoluble black pyrophoric powders with composition $(C_{10}H_8)Yb(THF)_3$ (**6.8**) or $(C_{10}H_8)Yb(DME)$ (**6.9**)[67,68] (Table 6). The number of coordinated THF molecules can be reduced to 2 by drying the complex in a vacuum at 60 °C.

$$YbI_2 + 2C_{10}H_8Li \xrightarrow{THF} (C_{10}H_8)Yb(THF)_3$$

When $YbCl_3$ was reduced by $C_{10}H_8Na$, the formed product was comprised of three molecules of NaCl and an increased amount of Yb, probably due to the presence of admixture of $[YbCl_2{\cdot}NaCl]$,[72] but the chemical and magnetic properties of the substances were the same. On the basis of the fact that the resulting compounds are diamagnetic (Yb(0) with configuration f^{14} is diamagnetic) and on their reactivity, which is surprisingly high (even for organolanthanides), it was originally assumed that these products are complexes of zerovalent ytterbium π-bonded to the neutral naphthalene ring. However, additional data obtained later demonstrated that these compounds in fact contain the naphthalene dianion and Yb^{2+} cation.

Analogous naphthalene complexes with samarium (**6.2**) and europium (**6.3**–**6.5**)[67,68,70] as well as 1-methylnaphthalene complex with ytterbium (**6.11**)[67,72b] were synthesized. The naphthalene compounds of Sm, Eu, and Yb, likewise alkali-metal naphthalenides, are powerful reducing agents. Nevertheless, the former complexes, in contrast to $C_{10}H_8Li_2$ or $C_{10}H_8Na_2$, do not react with naphthalene (the reaction could form radical–anionic derivatives of the type $(C_{10}H_8^{-\bullet})_2Ln(THF)_x$). The salts LnI_3 or $LnCl_3$ of all other rare-earth metals, besides Sm, Eu, and Yb, in the reactions with naphthalenelithium in a ratio 1:3 in THF give black or black-brown solutions from which no products of definite composition could be isolated.[73,74] However, hydrolysis of these solutions (affords dihydronaphthalene), reactions with CpH (yields Cp_3Ln), and magnetic measurements indicate the presence of $C_{10}H_8Ln$ groups. Halogen-free naphthalene complex of trivalent lanthanide, $[(C_{10}H_8)Tm(DME)]_2(\mu\text{-}C_{10}H_8)$ (**6.7**), was obtained only when $TmI_2(DME)_3$ was used as an initial reagent (Figure 17).[71]

It is worth noting that thulium in the reaction was oxidized to the trivalent state, although $C_{10}H_8Li$ is a strong reducer. The oxidation degree of thulium was confirmed by magnetic measurements and by the fact that the color of the reaction mixture changed from green to red-brown. The pathway of the reaction remained unclear. Compound **6.7** has the structure of a triple-decker sandwich. According to the charge balance, all three naphthalene groups in the complex exist as dianions. The central binuclear unit $Tm(\mu\text{-}C_{10}H_8)Tm$ is arranged in such a way that thulium atoms are located on the opposite sides of the plane



6.7

Figure 17.

Table 7. Ligand-Mixed Naphthalene–Halide and Similar Complexes

compound	no.	color, mp	other characteristics, ref
$(LY)_2(C_{10}H_8)^a$	**7.1**	dark blue	X-ray, NMR[78]
$(LY)_2(1\text{-}MeC_{10}H_7)^a$	**7.2**	dark blue	NMR[78]
$(C_{10}H_8)[LaI_2(THF)_3]_2$	**7.3**	blue, 80–100 °C (dec)	X-ray, IR, UV/Vis[79]
$(C_{10}H_8)[CeI_2(THF)_3]_2$	**7.4**	dark blue, >100 °C (dec)	IR, magn.[80]
$(C_{10}H_8)[PrI_2(THF)_3]_2$	**7.5**	dark blue, >100 °C (dec)	IR, magn.[80]
$(C_{10}H_8)[NdI_2(THF)_3]_2$	**7.6**	dark blue, >100 °C (dec)	IR, magn.[80]
$[NdCl_2(THF)_2LiCl]_n(C_{10}H_8)$ $n = 4-7$	**7.7**	brownish-black	magn.[81]
$(C_{10}H_8)[EuI(THF)_4]_2$	**7.8**	red-brown	IR, UV/Vis, magn.[79]
$(C_{10}H_8)[EuI(DME)_2]_2$	**7.9**	dark red	X-ray, IR[79]
$(C_{10}H_8)[GdI_2(THF)_3]_2$	**7.10**	dark blue, >100 °C (dec)	IR, magn.[80]
$(C_{10}H_8)DyI(DME)_2$	**7.11**	light gray	X-ray, IR[82]
$(C_{10}H_8)[YbI(DME)_2]_2$	**7.12**	dark violet, >100 °C	IR, magn.[80]
$(LLu)_2(C_{10}H_8)^a$	**7.13**	dark purple	NMR[78]
$(LLu)_2(1\text{-}MeC_{10}H_8)^a$	**7.14**	dark purple	NMR[78]

[a] $L = PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh$.

of the bridging naphthalene ligand and are η^4-bonded to different rings. The naphthalene moiety is nonplanar with dihedral angles at bent lines C(1)–C(4) and C(5)–C(8) of 19.28°. The lengths of the short Tm–C(bridging $C_{10}H_8$) contacts are in the range of 2.59–2.62 Å. On the basis of the shortest Tm–C distances to the terminal naphthalene moieties (2.41 and 2.42 Å) for C(α) and 2.54 and 2.54 Å for C(β)), both types of interactions can be considered as η^4 and η^2. However, the dihedral angle (26.22°) and the redistribution of the C–C bond lengths in the coordinated rings correspond to cyclohexa-1,4-diene. The absolute values of the shortest Tm–C distances are identical (accounting for the difference in the ionic radii and coordination numbers of the metal atoms) to the Ln–C σ-bonds in complexes $[Li(THF)_4]\{[(Me_3Si)_2CH]_3YbCl\}$ (the average distance is 2.375 Å[75]), $Cp^*CeCH(SiMe_3)_2$ (2.535 Å[76]), and $Cp^*NdCH(SiMe_3)_2$ (2.517 Å[77]).

2. Ligand-Mixed Naphthalene Iodides and Amides

The reactions of equimolar amounts of LnI_2 (Ln = Eu or Yb) and lithium naphthalenide resulted in the replacement of only one iodide anion and led to binuclear derivatives of $[ILn(DME)_2]_2(\mu\text{-}C_{10}H_8)$ type (Table 7) containing the bridging naphthalene dianion rather than radical–anionic complexes $(C_{10}H_8{}^{-\bullet})LnI$.[79,80]

$$2LnI_2 + 2C_{10}H_8Li \xrightarrow{DME} [ILn(DME)_2]_2(\mu\text{-}C_{10}H_8)$$

7.9, **7.12**

Ln = Eu, Yb

The $Ln((\mu\text{-}C_{10}H_8)Ln$ moiety containing the naphthalene bridging dianion (complex **7.3**) was also formed in the reaction of lanthanum iodide with lithium and naphthalene.[79] Analogous complexes were obtained for Ce, Pr, Nd, and Gd.[80]

$$2LaI_3(THF)_3 + 2Li + C_{10}H_8 \xrightarrow{THF} [I_2La(THF)_3]_2(\mu\text{-}C_{10}H_8)$$

7.3

The neodymium derivative **7.6** was synthesized as well by oxidation of neodymium(II) iodide with naphthalene in THF.[83]

$$NdI_2(THF)_5 + C_{10}H_8 \xrightarrow{THF} I_2Nd(THF)_3(\mu\text{-}C_{10}H_8)NdI_2(THF)_3$$

7.6

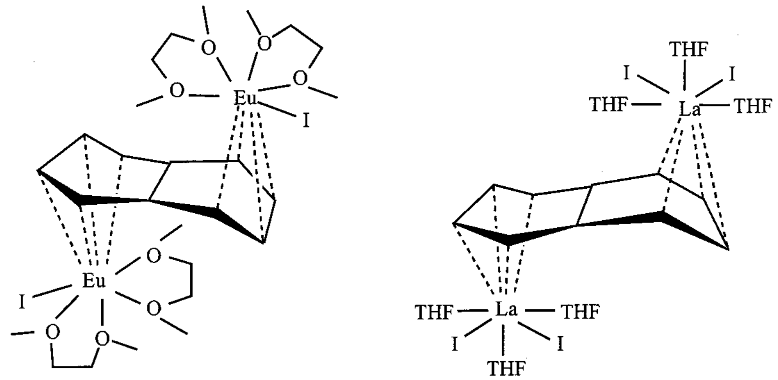
Interestingly, the similar reaction between DyI_2 and naphthalene in DME medium at −45 °C led to another type of complex **7.11**, in which the $DyI(DME)_2$ fragment is η^2-bonded to naphthalene.[82]

$$DyI_2 + C_{10}H_8 \xrightarrow{DME} (C_{10}H_8)DyI(DME)_2$$

7.11

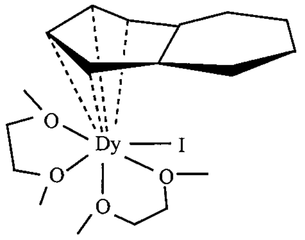
It was found that the stability of complexes of this type decreases on going from light to heavy lanthanides. Beginning with Tb, attempts to isolate such products failed even at low temperature.

The complexes of europium, $[IEu(DME)_2]_2(C_{10}H_8)$ (**7.9**),[79] lanthanum, $[I_2La(THF)_3]_2(C_{10}H_8)$ (**7.3**),[79] and



7.9 7.3

Figure 18.



7.11

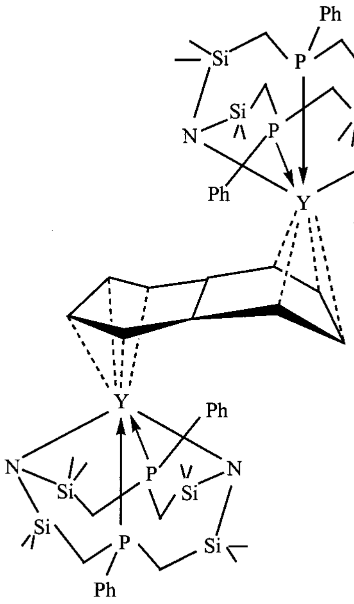
Figure 19.

dysprosium, $(C_{10}H_8)DyI(DME)_2$ (**7.11**),[82] were studied by X-ray diffraction analysis. In the first two the central binuclear units with the η^4:η^4-bonded bridging naphthalene ligands are structurally similar to that in the thulium complex **6.7**. The dihedral angles along C_1-C_4 and C_5-C_8 in **7.9** and **7.3** are 5.8° and 15.2°, and the shortest La−C and Eu−C distances are in the ranges of 2.782−2.808 and 2.815−2.858 Å, respectively (Figure 18).

A set of Dy−C distances (2.510, 2.599, 2.605, 2.486, 2.992, and 3.002 Å) in complex **7.11** suggested also η^4-interaction rather than η^6 (Figure 19).

It was assumed that black insoluble powders formed upon reduction of $SmBr_3$ and $YbBr_3$ with sodium naphthalenide are finely dispersed lanthanide metals.[84] However, the reported properties and reactivity of these products as well as the similarity of the synthesis with the reduction of iodides indicate that in reality the obtained powders are naphthalene complexes of lanthanides. Apparently the results of reduction of $NdCl_3$ with a lack of lithium and naphthalene were also misinterpreted.[85] Reinvestigation[81] of this synthesis with thorough reproduction of the published procedure demonstrated that the reaction gives rise to a mixture of naphthalene complexes with composition $[NdCl_2(THF)_2LiCl]_n(C_{10}H_8)$ (n = 4−7) rather than divalent neodymium chloride $NdCl_2(THF)_2$ as reported previously.[85]

Binuclear complexes of the general formula $(\{PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh\}Ln)_2(arene)$ (arene = $C_{10}H_8$, Ln = Y (**7.1**), Lu (**7.13**); arene = $C_{10}H_7Me$, Ln = Y (**7.2**), Lu (**7.14**) containing a Ln(μ-arene)Ln group were prepared by reaction of a mixture of potassium-intercalated graphite (KC_8) and naphthalene or 1-methylnaphthalene with the complex $[(\{PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh\}Y)_2(\mu-Cl)_2]$ or its lutetium analogue.[78] The X-ray diffraction analysis of



7.1

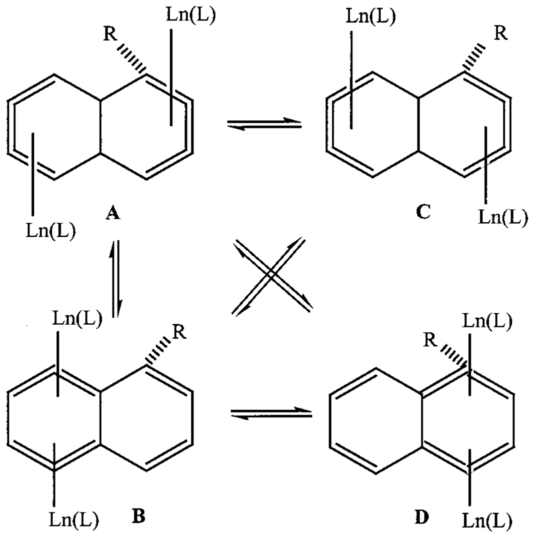
Figure 20.

7.1 revealed that the amido−yttrium units are located on opposite faces of the bridging naphthalene ligand and the metal atoms are η^4-bonded to different rings similar to the arrangement observed in $[I_2La(THF)_3]_2(\mu-C_{10}H_8)$ (**7.3**). The shortest Y−C(1,2,3,4)-(naphthalene) distances are 2.696, 2.684, 2.686, and 2,652 Å, respectively. The rings in naphthalene ligand are folded along the C(1)−C(4) and C(5)−C(8) lines. According to the preliminary data, the lutetium analogue has a resembling structure.

The $^{31}P\{^1H\}$ NMR spectra of all four compounds with polycyclic phospho−amido ligands are similar (the spectrum of the yttrium derivative **7.2** has a doublet at 21, $^1J_{YP}$ = 60 Hz), which is indicative of the equivalence of the phosphorus ligands. These data suggested that intramolecular migration of the $\{PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh\}Ln$ moieties between the naphthalene rings (forms **A**−**D**) occurs in solutions. Apparently the moieties migrate independently, stimulating the presence in a solution of all four possible isomers (Figures 20 and 21).[78]

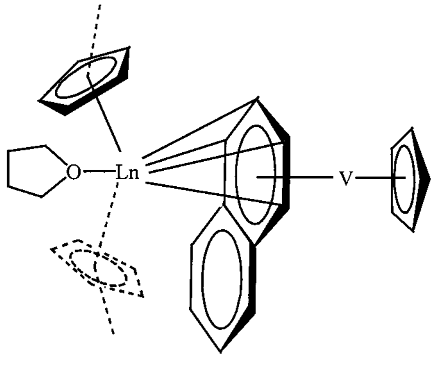
3. Heterobimetallic Compounds

The heterobimetallic compounds of lanthanides $[CpLn(THF)(\mu-\eta^4:\eta^6-C_{10}H_8)VCp]_n$ (Table 8) containing



R = PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh, R = H, Me

Figure 21.



Ln = Sm (**8.1**), Eu (**8.2**), Yb (**8.3**)

Figure 22.

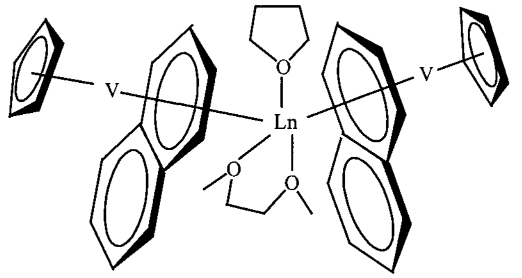
the bridging naphthalene ligand were prepared by the reaction of vanadocene with excess of naphthaleneytterbium or −europium[70,86]

$$(C_{10}H_8)Ln(THF)_2 + Cp_2V \xrightarrow{THF} [CpLn(THF)(\mu\text{-}C_{10}H_8)VCp]_x$$

8.2, **8.3**

$$Ln = Eu, Yb$$

According to the data of ESR spectroscopy and magnetic measurements, in these cases the bridging naphthalene ligand is neutral and the negative charge is localized at the vanadium atom, transforming it into formally zerovalent. Compounds of this type can be considered as dicyclopentadienyl complexes of lanthanides in which one of the cyclopentadienyl anions is coordinated to the metal atom through the neutral (C$_{10}$H$_8$)V group (Figure 22). Note, the same reactions with an equimolar amount of reagents lead to the products of metathesis, Cp$_2$Yb and CpV(μ-C$_{10}$H$_8$)VCp.[87]



8.4, **8.5**

Figure 23.

The analogous vanadium−lanthanide complexes have been obtained by reactions of samarium or europium diiodides with cyclopentadienylnaphthalenevanadium anions, [CpV(C$_{10}$H$_8$)]$^-$, prepared in situ.[70]

$$LnI_2(DME)_3 + CpK + K[(C_{10}H_8)VCp] \xrightarrow{THF} [CpLn(THF)(\mu\text{-}C_{10}H_8)VCp]_x +$$

8.1, **8.2**

$$[CpV(\mu\text{-}C_{10}H_8)]_2Ln(THF)(DME)$$

8.4, **8.5**

$$Ln = Sm, Eu$$

When the reactions were carried out in DME with a subsequent change of the solvent with a THF/hexane mixture, the monomeric complexes **8.4** and **8.5**, in which the Ln atom is coordinated by two CpVC$_{10}$H$_8$ units, were isolated (Figure 23).[70]

In all complexes with Ln(μ-C$_{10}$H$_8$)V fragments the bridging naphthalene is planar. The Eu−C(naphthalene) distances in **8.2** (2.828, 2.869, 3.037, 3.098, 3.308, and 3.344 Å) display an η^4-type of Eu−arene bond. In the quadruple-decker compound **8.5**, all six Eu−C(naphthalene) contacts lay in the rather narrow range of 2.872−3.084 Å, indicative of η^6-coordination in the (C$_{10}$H$_8$)Eu(C$_{10}$H$_8$) moiety. It should be noted that ESR spectra of **8.5** (g_{eff} = 2.65, $g_{\parallel}$ = 1.60, and $g_{\perp}$ = 3.19) differ from that of vanadium d^5, radical−anion of naphthalene, and the spectrum of Eu(II). A possible explanation for the observed spectra would be the presence of Eu(0) atoms, which agrees with the geometry of the complex, but this supposition needs additional proof.[70]

4. Ligand-Mixed Naphthalene−Cyclopentadienyl Complexes

The reaction of sodium naphthalenide with Cp$_2$LuCl proceeds through another pathway. In this case the resulting (apparently unstable) radical−anionic

Table 8. Data on Hetrobimetallic Complexes with Bridging Naphthalene

compound	no.	color, mp	other characteristics, ref
[(CpV(C$_{10}$H$_8$)SmCp(THF)]$_n$(THF)$_{n/2}$	**8.1**	black	IR, magn.[70]
[(CpV(C$_{10}$H$_8$)EuCp(THF)]$_n$(THF)$_{n/2}$	**8.2**	black	X-ray, IR, magn.[70]
[(CpV(C$_{10}$H$_8$)YbCp(THF)]$_n$	**8.3**	black, 180−190 °C (dec)	X-ray, ESR, IR, magn.[86]
[CpV(C$_{10}$H$_8$)]$_2$Sm(THF)(DME)	**8.4**	dark, 110−115 °C (dec)	IR[70]
[CpV(C$_{10}$H$_8$)]$_2$Eu(THF)(DME)	**8.5**	dark, 113−116 °C (dec)	X-ray, ESR, IR, magn.[70]

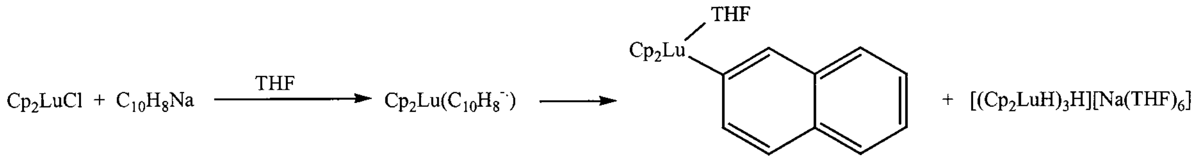
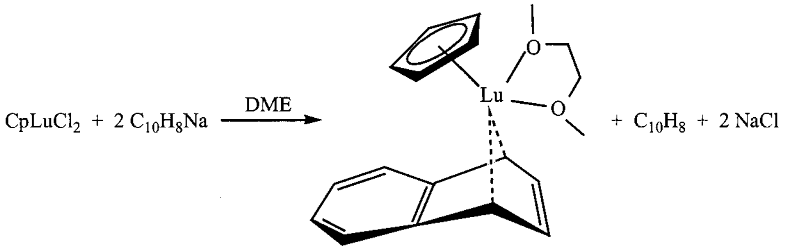


Figure 24.

Table 9. Data on Ligand-Mixed Cyclopentadienyl–Naphthalene Complexes

compound	no.	color, mp	other characteristics, ref
$CpYC_{10}H_8(DME)$	**9.1**	119 °C (dec)	X-ray, magn.[88,90]
$(CpSm)_2C_{10}H_8(THF)_4$	**9.2**	100 °C (dec)	magn.[90]
$CpGdC_{10}H_8(DME)$	**9.3**	116 °C (dec)	magn.[90]
$CpErC_{10}H_8(DME)$	**9.4**	122 °C (dec)	magn.[90]
$CpTmC_{10}H_8(DME)$	**9.5**	116 °C (dec)	magn.[90]
$(CpYb)_2C_{10}H_8(THF)_4$	**9.6**	100 °C (dec)	magn.[90]
$CpLuC_{10}H_8(THF)_2$	**9.7**	black	synthesis[89]
$CpLuC_{10}H_8(DME)$	**9.8**	black, 120 °C (dec)	X-ray[89]
$Cp^*LuC_{10}H_8(DME)$	**9.9**	black, 153–154 °C	IR[91]
$\{[Cp^*Lu)_3(C_{10}H_8)(C_{10}H_7)(H)][Na(THF)_3]\}_2C_{10}H_8$	**9.10**	black, 153–154 °C	X-ray, IR[91]



9.8

Figure 25.

intermediate $[Cp_2Lu^+(C_{10}H_8^{-\bullet})]$ underwent rapid transformations involving metalation of naphthalene and formation of hydride and naphthyl derivatives (Figure 24).[88]

Reduction of $CpLuCl_2$ with sodium naphthalenide yields the naphthalene–lutetium complex $CpLu(C_{10}H_8)(DME)$ (**9.8**) or $CpLu(C_{10}H_8)(THF)_2$ (**9.7**) depending on the used solvent.[89] Compounds of this type are compiled in Table 9 (Figure 25).

The molecular geometry of complex **9.8** is indicative of the σ-character of the bond between the lutetium atom and the naphthalene ligand whose coordinated ring loses aromaticity. The Lu–C(α) bond lengths (2.406 and 2.397 Å) are comparable with the Lu–C σ-bond lengths in complexes Cp_2Lu-t-Bu(THF) (2.47 Å)[92] and $Cp_2LuCH_2SiMe_3(THF)$ (2.376 Å).[93] The Lu–C(β) bond lengths (2.579 and 2.562 Å) are close to the Lu–C(Cp) bond lengths (2.65 Å), which suggests the presence of an additional π-interaction of the lutetium atom with the double bond (1.36 Å) between the C(β) atoms of the coordinated ring. The folding angle in this ring is 31.5°. Thus, the Lu–naphthalene bonding in **9.8** may be characterized as a $2\eta^1:\eta^2$ $(2\sigma,\pi)$ interaction.[89]

Analogous complexes were prepared by the same way for Y (**9.1**), Gd (**9.3**), Er (**9.4**), and Tm (**9.5**).[88]

In the reactions of $C_{10}H_8Li$ with cyclopentadienyl chlorides of Sm(III) and Yb(III) (which have lower potentials for the Ln(III)/Ln(II) transition), reduction of lanthanides occurs leading to binuclear complexes of Ln(II) with bridging naphthalene group $(CpLn)_2(\mu\text{-}C_{10}H_8)(THF)_4$ (**9.2** and **9.6**).[90]

$$2CpLnCl_2 + 4C_{10}H_8Li \xrightarrow{THF} [CpLn(THF)_2]_2(C_{10}H_8) + 3C_{10}H_8 + 4LiCl$$

$$Ln = Sm\ (\mathbf{9.2}),\ Yb\ (\mathbf{9.6})$$

When the pentamethylcyclopentadienyl derivative of lutetium, $Cp^*LuCl_2{\cdot}NaCl$, was used as the initial reagent in the reaction with $C_{10}H_8Na$, an unusual diamagnetic cluster of ate-type $\{[(C_5Me_5)Lu)_3(C_{10}H_8)(C_{10}H_7)(H)][Na(THF)_3]\}_2C_{10}H_8$ (**9.10**) was isolated in low yield.[91] An X-ray analysis revealed that the 3+ nuclear cation of the complex contains three Cp*Lu moieties, solvated sodium cation, naphthalene dianion, and a naphthyl group bearing a −3 charge (Figure 26).

The naphthalene dianion, which is not involved in the coordination of the metal atoms, represents the anionic moiety of the complex. The ring **A** of one of the naphthalene ligands in the cationic moiety is η^4-bonded to the Lu(1) atom. The Lu–C bond lengths in this fragment (Lu–C(α), 2.58 and 2.60 Å; Lu–C(β), 2.67 and 2.77 Å) and bend shape of the coordinated ring (the dihedral angle at C(α)-C(α) line is 17.4°) correspond to a $2\eta^1:\eta^2$-interaction similar to the arrangement of the same fragment in **9.8**. The **B** ring remains planar and is η^6-bound to the Lu(2) atom (the Lu–C contacts are in the range of 2.61–2.88 Å). The $2\eta^1:\eta^2$-interaction is most pronounced in the Lu(3)–$C_{10}H_7$ group. In this case the bent angle along the C(α)-C(α) line is 37.5°. The Lu(3)–C(α,β) distances are 2.44, 2.47, 2.54, and 2.59 Å, respectively. The ring **C** of the naphthyl group is σ-bonded as well to the Lu(2) atom (2.36 Å). The short Lu–ring **C** (2.81 Å) and Lu(3)–ring **A** (2.72 Å) contacts apparently

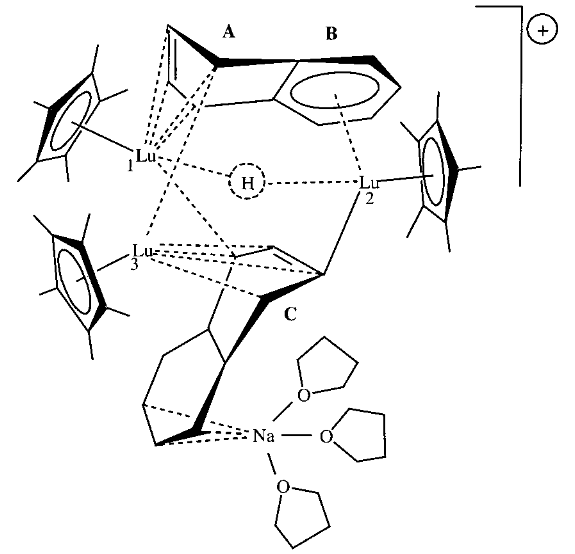


Figure 26.

indicate some bonding in these fragments. The geometry of this cation and the charge balance suggest the existence of a proton between Lu(1) and Lu(2) atoms bonded to one or both of them. However, the presence of this proton has not been unambiguously established.

It was reported that thin films of cerium and europium readily react with naphthalene in diethyl or dipropyl ethers at room temperature to form colorless solutions.[69] On the basis of the spectral characteristics the authors concluded that pale-brown substances isolated after removal of the solvent and excess naphthalene are bis(naphthalene) π-complexes of zerovalent lanthanides of the bis(naphthalene)chromium type. However, some data quoted in this publication contradict such a conclusion. For instance, the products are pale in color, which is not typical of neutral and charged arene–lanthanide complexes; under the same conditions naphthalene does not react with other lanthanides (Pr, Nd, Gd, Tb, Dy, Ho or Er); the reactions do not proceed in THF; the reactions of Ce or Eu with anthracene (stronger oxidant than naphthalene) proceed more slowly than with naphthalene.

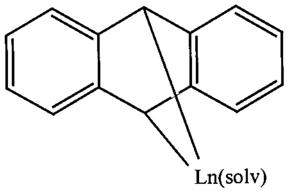


Figure 27.

5. η^6-Acenaphthylene Compound

The reaction of acenaphthylene with permethylsamarocene readily proceeds in benzene, resulting in a dark blue product. The data from NMR and IR spectroscopy and analysis for C, H, and metal of the compound correspond to the formula $(Cp^*_2Sm)_2(C_{12}H_8)$.[94] The structure of the complex was not established. The acenaphthylene–lanthanum complex of composition $[I_2La(THF)_3]_2(C_{12}H_8)\cdot(THF)_4$ has been obtained by the reaction of acenaphthylene with $[I_2La(THF)_3]_2(C_{10}H_8)$ (**7.3**).[95] In this case an X-ray analysis was carried out but the structure was not solved completely because of the structural peculiarities. Nevertheless, the obtained data allow one to conclude that in the molecule of the complex two $LaI_2(THF)_3$ cations are bonded to a dianion of acenaphthylene in such a way that one La atom is coordinated to the C_5 ring but the second one is linked to the C_6 ring.

IV. Complexes with Anthracene

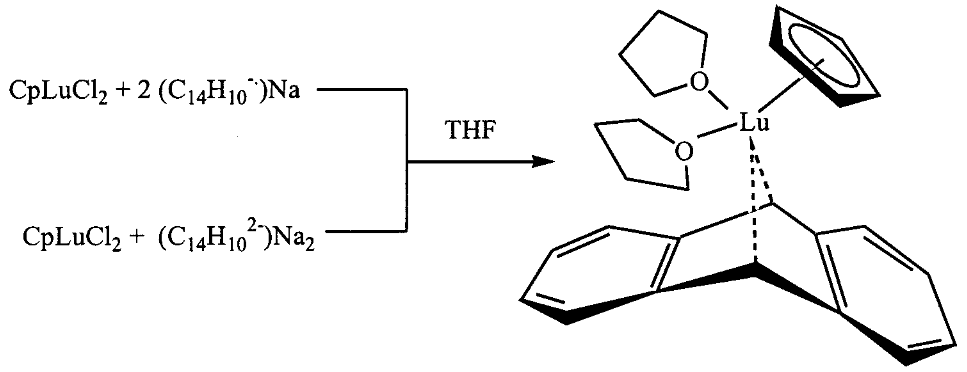
Anthracene, possessing a higher electron affinity than that of naphthalene, can be involved in direct reaction with ytterbium, samarium, and cerium activated with diiodoethane.[96] The products **10.3**, **10.4**, and **10.9** (Table 10) were not isolated from the blue suspension that formed, but their reactions with MeOD, MeI, and Me_3SiCl which gave the corresponding 9,10-substituted 9,10-dihydroanthracenes suggested that the blue solutions contain anthracene–lanthanide complexes of the type shown in Figure 27.

A film of ytterbium metal prepared by evaporation of NH_3 from the solution of Yb in liquid ammonia also reacts with anthracene in the presence of LiCl, NaBr, LiI, KI, or Bu_4NI.[100] The authors believe that the

Table 10. Data on Anthracene–Lanthanide Complexes

compound	no.	color, mp	other characteristics, ref
$(LY)_2(C_{14}H_{10})^a$	**10.1**	dark blue	X-ray, NMR[78]
$(Cp^*_2La)_2(C_{14}H_{10})(PhMe)_2$	**10.2**	black-green	X-ray, NMR[97]
$Sm[C_{14}H_8(C_6H_{13})_2{-}1,8]$	**10.3**	blue solution in DME	synthesis, reactions[96a]
$Sm(C_{14}H_{10})(DME)_x$	**10.4**	blue-violet	synthesis, reactions[96b]
$(Cp^*_2Sm)_2(C_{14}H_{10})$	**10.5**	green	X-ray[94]
$(Cp^*_2Sm)_2(9\text{-}MeC_{14}H_9)$	**10.6**	dark red	NMR[94]
$[NdI_2(THF)_3]_2(C_{14}H_{10})$	**10.7**	blue-violet, 80–90 °C (dec)	IR[98]
$TmI(C_{14}H_{10})(DME)_2$	**10.8**	red, >90 (dec)	X-ray, IR[99]
$Yb(C_{14}H_{10})(DME)_x$	**10.9**	blue-violet	synthesis, reactions[96b]
$Yb(C_{14}H_{10})\cdot 6\ NaI$	**10.10**	violet	UV/Vis[100]
$Yb_2(C_{14}H_{10})(THF)_x(LiCl)_2$ ($X = 2-3$)	**10.11**	black	synthesis[72b]
$Yb_2(C_{14}H_{10})(THF)_x(NaCl)_3$ ($X = 2-3$)	**10.12**	black	synthesis, reactions[72b]
$CpLu(C_{14}H_{10})(THF)_2$	**10.13**	red-orange	X-ray, NMR[101]
$[Cp_2Lu(C_{14}H_{10})][Na(THF)]$	**10.14**	orange-red	UV/Vis[102]
$[Cp_2Lu(C_{14}H_{10})][Na(diglyme)_2]$	**10.15**	orange-red	X-ray[102a]
$(LLu)_2(C_{14}H_{10})^a$	**10.16**	dark purple	NMR[78]

[a] $L = PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh$.



10.13

Figure 28.

reactions yield complexes containing the anthracene radical–anion of composition $Yb(C_{14}H_{10}^{-\bullet})_2\cdot(MX)_n$. However, attempts to identify the reaction products were unsuccessful. After washing of the substances with benzene, a violet powder containing the anthracene dianion, ytterbium, and MI in a ratio of 1:1:6 was obtained.

It was found that anthracene complexes **10.11** and **10.12** are formed in the reactions of $C_{14}H_{10}$ with naphthaleneytterbium in THF in the presence of alkali-metal halides or by the reaction of YbI_2 with sodium anthracenide.[72b,103] The anthraceneytterbium complex **10.10** containing six molecules of NaI was obtained in the reaction of ytterbium metal with anthracene in DME in the presence of NaI.[100] All these complexes were isolated as dark colored almost black insoluble powders, properties which are similar to those of naphthalene analogues. Investigation of the compounds by means of ESR spectroscopy and study of hydrolysis products suggested the existence of the equilibrium between the radical–anionic (**A**) and dianionic (**B**) forms with predominance of the latter.

$$\mathrm{Yb(C_{10}H_8(THF)_3 + C_{14}H_{10} + LiX \rightleftharpoons YbX(C_{10}H_8) + (C_{14}H_{10}{}^{-\bullet})Li^+ \rightleftharpoons [C_{10}H_8)Yb(X)(C_{14}H_{10}{}^{-\bullet})]Li^+}$$

or

$$\mathrm{Yb + C_{14}H_{10} + LiX \xrightleftharpoons{MX} \underset{\mathbf{A}}{Yb(C_{14}H_{10}{}^{-\bullet})_2\cdot \mathit{n}MX} \xrightleftharpoons{C_{14}H_{10}} \underset{\mathbf{B}}{Yb(C_{14}H_{10}{}^{2-})} + \mathit{n}MX}$$

Because of the extremely low solubility the complexes were not isolated as good crystals and their structures were not determined by X-ray analysis. However, such an investigation has been performed with cyclopentadienyllanthanide derivatives. It appeared that rare-earth metals form two types of complexes with anthracene: through addition to an edge or coordination to a plane, but in both cases the arene ligand bears a charge of −2.

The reactions of cyclopentadienyllutetium dichloride with dianion or 2 equiv of radical–anion of anthracene result in the formation of the same neutral complex $CpLuC_{14}H_{10}(THF)_2$ (**10.13**) with a dianion of anthracene (Figure 28).[101,102a]

It was assumed that the lutetium radical ionic complex $CpLu(C_{14}H_{10}^{-\bullet})_2$ is generated in the initial stage of the first reaction.[102a] The intermediate quickly transforms into **10.13**, eliminating free anthracene, which was detected in the reaction mixture.

The character of bonding between the Lu atom and arene ligand is similar to that observed in the naphthalene complex **9.7**, i.e., it can be interpreted as a *σ,σ*-interaction although the Lu–C(9,10) distances (2.44 and 2.45 Å) are somewhat longer than the analogous contacts in the naphthalene derivative. The bend angles of the anthracene molecule along the C(9)–C(10) axes is 38.7° (29.9° for the second symmetrically independent molecule in the crystal).

Neutral complexes of samarium **10.5** and neodymium **10.7** with anthracene dianion were prepared by oxidation addition of decamethylsamarocene[94] or iodide of Nd(II)[98] to anthracene.

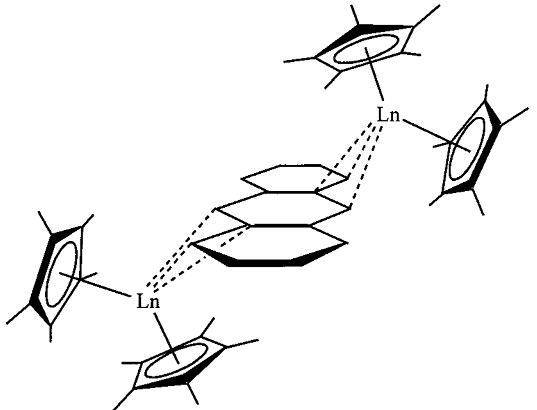
$$\mathrm{Cp^*{}_2Sm + C_{14}H_{10} \xrightarrow{PhMe} \underset{\mathbf{10.5}}{[Cp^*{}_2Sm]_2[\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{14}H_{10}]}}$$

$$\mathrm{NdI_2 + C_{14}H_{10} \xrightarrow{THF,\ -20\ ^\circ C} \underset{\mathbf{10.7}}{[NdI_2(THF)_3]_2(\mu\text{-}C_{14}H_{10})}}$$

In the case of 9-methylanthracene, the product **10.6** has the same Sm:arene ratio but its arrangement is not quite clear. The similar lanthanum compound **10.2** has been synthesized by metathesis of the lanthanum–potassium complex with disodium anthracene.[97]

$$\mathrm{2Cp^*{}_2La(Cl)K(DME)_2 + Na_2(C_{14}H_{10}) \xrightarrow{PhMe} \underset{\mathbf{10.2}}{[Cp^*{}_2La]_2[\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{14}H_{10}]\cdot 2C_6H_5CH_3}}$$

Both products **10.2** and **10.5** are structurally related. The two crystallographically equivalent $Cp^*{}_2Ln$ units are located on either side of the nearly planar $C_{14}H_{10}$ moiety. The closest Sm–C(9,10) contacts (2.595 Å) are only slightly longer than the Sm–C *σ*-bonds in $Cp^*{}_2SmMe(THF)$[104] (2.484 Å) and $Cp^*{}_2SmPh(THF)$[105] (2.511 Å). The two other short contacts are noticeably longer (2.791 and 2.840 Å) but also fall in the range of bonding distances (Figure 29).



10.2, 10.5

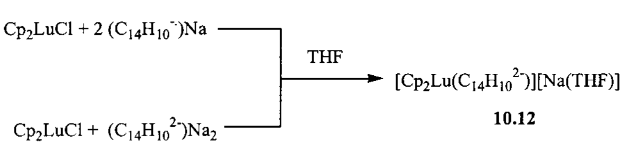
Figure 29.

An interesting peculiarity of complex **10.5** was found: dissolved in THF, this compound regenerates anthracene and forms $Cp^*_2Sm(THF)_2$, indicative of easy reversibility of the Sm(III)/Sm(II) transition in this complex.

Another arrangement has complex **10.8** obtained by the reaction of thulium diiodide with lithium anthracide (Figure 30).[99]

In this case the $Tm-C_{14}H_{10}$ unit is organized like the Ln−arene fragments in **7.11**, **9.1**, **9.8**, **10.13**, and **10.15**, i.e., the coordinated ring has a bent shape (dihedral angle along C_9-C_{10} line is 37.8°) and two short contacts to the Tm atom 2.479 and 2.471 Å which are very close to Tm−C(terminal naphthalene) bond lengths (2.41, 2.42 Å) in triple-decker complex **6.7** and comparable with those in **7.11** (2.510 and 2.486 Å) and **9.8** (2.44 and 2.45 Å) regarding the differences in the ionic radii of Tm, Dy, and Lu. The magnetic moment of **10.8** (6.6 μ_B) confirmed the divalent state of thulium and consequently the −2 charge on the anthracene ligand.

In contrast to $CpLuCl_2$, dicyclopentadienyllutetium chloride in reactions with dianion or radical−anion of anthracene in THF affords the ate complex $\{[Cp_2Lu(C_{14}H_{10})][Na(THF)]$ (**10.14**), isolated as a red-orange oil.[102a,b] However, the change of coordinated THF with diglyme (complex **10.15**) allowed the preparation of this compound in crystalline form and determination of its structure.[102a] It was found that the molecule consists of isolated cation $[Na(diglyme)]^+$ and anion $[Cp_2Lu(C_{14}H_{10})]^-$ in which the Lu atom has two short contacts with the anthracene ligand (Lu−C(9,10), 2.473 and 2.482 Å), indicative of a σ,σ-character of bonding. Overall, the arrangement of Lu−anthracene fragments is similar to that in complex **10.13**. The dihedral angle along the C(9)−C(10) axis is 40.1° (Figure 31).



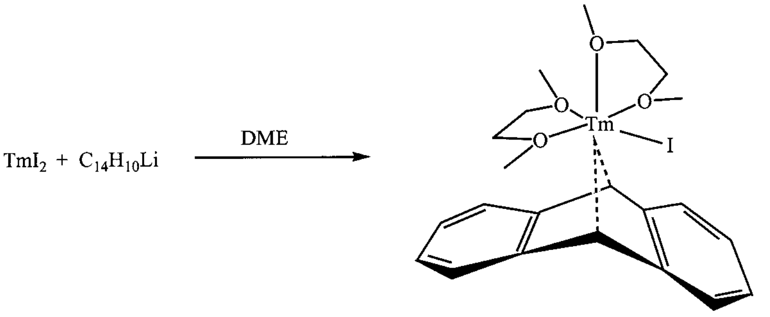
10.12

The reaction of yttrium or lutetium chlorides $(LLn)_2(\mu\text{-}Cl)_2$, where L is $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$, with anthracene in the presence of KC_8 yields the binuclear complexes $(LLn)_2(\mu\text{-}C_{14}H_{10})$ (**10.1**, **10.16**) containing anthracene dianion.[78] The ^1H NMR and $^{31}P\{^1H\}$ NMR spectra of complex **10.1** suggested symmetrical arrangement of it: each LY moiety is bonded to opposite faces of the middle ring of anthracene or coordinates to different outside rings. However, X-ray analysis revealed that one of the Y atoms is η^4-bound to the middle ring but the second one is linked by the same fashion to the outside ring (Figure 32).

The coordinated rings are slightly bent along C(1)−C(4) and C(9) −C(4) lines. The shortest Y−C distances (the average values are 2.694 and 2.751 Å) are virtually identical to the corresponding distances in the naphthalene analogue **7.1**. To explain the difference in NMR and X-ray data, a fluxional process (an intramolecular migration of LY units along the top and the bottom of the polycyclic ligand) similar to that assumed for the naphthalene complexes was suggested. It is significant that intermolecular migration of LLn moieties in the anthracene or naphthalene complexes or in the mixture of these derivatives does not occur. This indicates that the complexes do not dissociate in solution despite the ionic character of the Ln−arene bond.

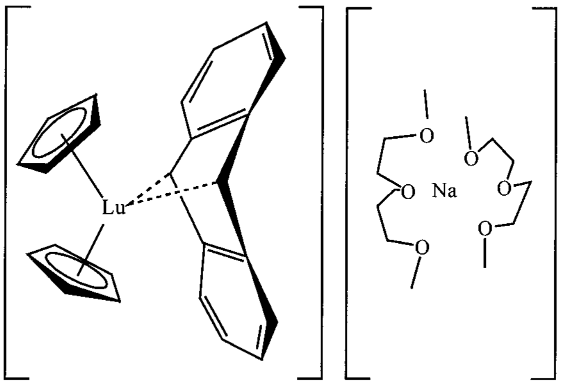
V. Derivatives of Pyrene and Benzanthracene

Pyrene can form three types of complexes with rare-earth metals (Table 11): with hydropyrene, pyrene^{2-}, and pyrene^{3-}. The reaction of $Cp^*_2La(\mu\text{-}Cl)_2K(THF)_2$ with the pyrene dianion in THF affords red crystals of composition $[Cp^*_2La(THF)_2](C_{16}H_{11})$ (**11.1**) in low yield.[106] The ^1H NMR spectrum of the product (10 signals with equal intensities and one double-intensity signal at δ 4.12, besides the signal of Cp* at δ 1.97) suggested the presence of the hydropirene anion $C_{16}H_{11}^{-}$• This unit is formed apparently as a result of detachment of proton from the solvent.



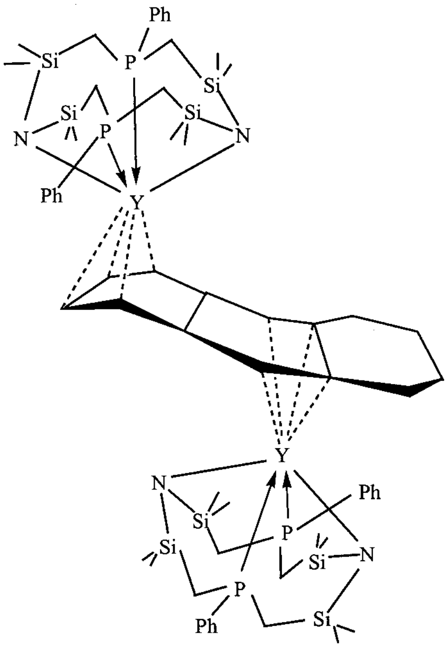
10.8

Figure 30.



10.13

Figure 31.



10.1

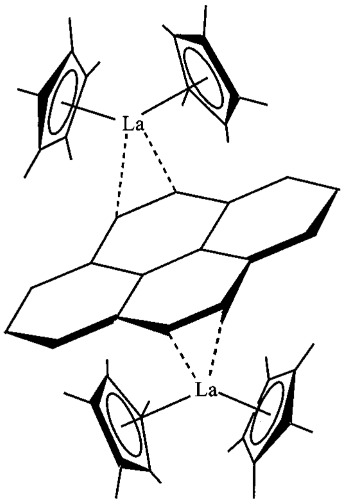
Figure 32.

$$\mathrm{Cp^*_2La(\mu\text{-}Cl)_2K(THF)_2 + (C_{16}H_{11})K_2 \xrightarrow{THF} [Cp^*_2La(THF)_2]^+(C_{16}H_{11})^-}$$

11.1

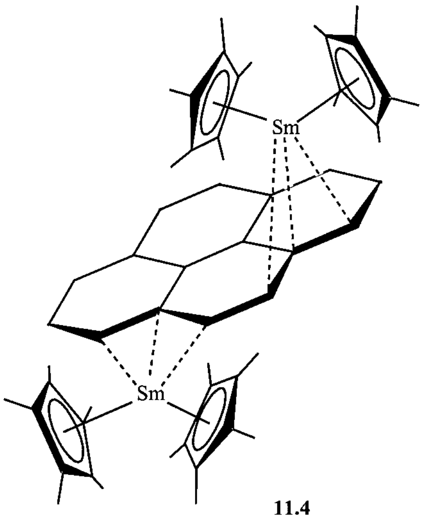
It was assumed that the $[\mathrm{Cp^*_2La(THF)_2}]^+$ cation does not coordinate to polycyclic anion, i.e., the complex in solution exists as a solvent-separated ion pair.[106]

The reaction of the ate complex $\mathrm{Cp^*_2La(\mu\text{-}Cl)_2K(THF)_2}$ with pyrene and potassium in toluene in a ratio of 2:2:1 give rises to black-green crystals.[106] The NMR spectrum of these crystals corresponds to the binuclear complex $\mathrm{(Cp^*_2La)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_{16}H_{10})}$ (**11.2**). It was suggested that the $\mathrm{Cp^*_2La}$ units in the product, as with those in the anthracene derivatives **10.2** and **10.5**, are located on the opposite side of the plane of the aromatic ligand and are bound to the opposite rings (Figure 33).



11.2

Figure 33.



11.4

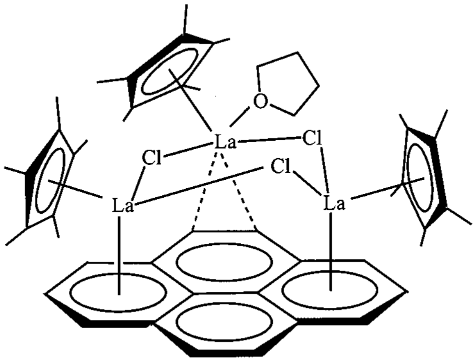
Figure 34.

According to the X-ray diffraction data, the samarium analogue $\mathrm{(Cp^*_2Sm)_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_{16}H_{10})}$ (**11.4**), prepared by the reaction of free pyrene with $\mathrm{Cp^*_2Sm}$ in toluene solution, has a different structure.[94] Both metallocene moieties in **11.4** are coordinated at the edge of pyrene and are located above and below its plane, but they form three short contacts each with the adjacent rings rather than with the opposite rings (Figure 34).

The angles between the Sm atoms and the plane of the polycyclic ligand are 117° and 120°. The bonding Sm−C distances are in the range of 2.660−2.806 Å, which are somewhat longer than the corre-

Table 11. Data on Complexes with Pyrene and Benzanthracene

compound	no.	color, mp	other characteristics, ref
$[\mathrm{Cp^*_2La(THF)_2}][\mathrm{C_{16}H_{11}}]$	**11.1**	reddish	NMR[106]
$\mathrm{(Cp^*_2La)_2(C_{16}H_{10})}$	**11.2**	black-green	NMR[106]
$[\mathrm{(Cp^*LaCl)_3(C_{16}H_{10})}]\cdot\mathrm{(THF)_2}$	**11.3**	red-violet	X-ray, NMR[106]
$\mathrm{(Cp^*_2Sm)_2(C_{16}H_{10})}$	**11.4**	dark green	X-ray, NMR, IR[94]
$\mathrm{(Cp^*_2Sm)_2(C_{18}H_{12})}$	**11.5**	green	X-ray, NMR, IR[94]



11.3

Figure 35.

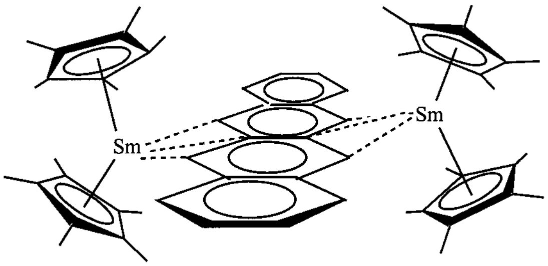
sponding distances in the allylic complexes $Cp^*_2Sm(\eta^3\text{-}CH_2CHCHR)$ (2.551−2.643 Å)[107] but are substantially shorter than the Sm−C bonds in the arene chloraluminate compounds $[(arene)Sm(AlCl_4)_3]$ (2.89−2.91 Å).[1,26,27a]

The reaction of pyrene, potassium, and $Cp^*LaCl(\mu\text{-}Cl)_2Li(THF)_2$ in a ratio 3:3:1 in toluene leads to reduction of pyrene to the trianion. The formed trinuclear complex $[(Cp^*LaCl)_3(C_{16}H_{10})](THF)$ (**11.3**) was isolated in 28% yield as red-violet crystals.[106] As established by X-ray diffraction analysis, all three Cp*LaCl moieties are located above the plane of the pyrene ligand. Two of these moieties are η^6-bonded to the arene ligand, whereas the third unit containing an additional coordinated THF molecule forms only two short La−C(pyrene) contacts (Figure 35).

The distances between La and C atoms involved in the η^6-interaction are in the range of 2.766−3.072 Å, and the lengths of the La−C bonds in the fragment with η^2-coordination are 2.823 and 2.841 Å, which are 0.1 Å longer than the corresponding contacts in the naphthalene complex $[I_2La(THF)_3]_2(\mu\text{-}C_{10}H_8)$ (**7.3**).

The 2,3-benzanthracene, like pyrene, readily reacts with Cp^*_2Sm to give green crystals of complex $(Cp^*_2Sm)_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{18}H_{12})$ (**11.5**).[94] Two Cp*Sm fragments are coordinated at the edge of the nearly planar arene ligand and are located on the opposite faces of its plane. The distance from the Sm atoms to the plane of $C_{16}H_{10}$ unit is 2.063 Å. The arrangement of Sm−arene−Sm fragment is similar to that of anthracene complex **10.5** with the difference in the mutual situation of two Cp^*_2Sm units. In compound **11.5** they are directly across from each other and are bound to the same rings. A further difference is presence in **11.5** of two close Sm−C(arene) contacts (2.688 and 2.708 Å). The Sm−C distance for the carbon atom between them is 2.828 Å (Figure 36).

As noted above, the samarium−anthracene complex **10.5** in the presence of THF easy dissociates to $Cp^*_2Sm(THF)_2$ and anthracene. Such an unusual lability is inherent in all permethylsamarocene complexes with arene ligands, unlike other arenelanthanides. Upon addition of THF to the solutions of these compounds in benzene or toluene, they decompose to form Cp^*_2Sm and the corresponding polycyclic hydrocarbon.[94] The instability of the Sm−arene bond may be evidence for its nonvalent character, i.e., the formation of these derivatives is not accompanied by redox process and the coordination complexes $\{Cp^*_2Sm(II)\}_2(arene^0)$ are formed. However, the ^1H and ^{13}C NMR spectra of the reaction products are unambiguously indicative of the change in the valence state of the metal atom (from Sm(II) to Sm(III)) and arene ligand (from $arene^0$ to $arene^{2-}$) in the course of the reactions. The Sm−Cp* distances in these complexes and their electronic spectra also correspond to trivalent samarium. This peculiarity of $(Cp^*_2Sm)_2(arene)$ complexes could be explained by the low potential of the Sm(III)/Sm(II) transition, compared with the potentials of “trivalent” lanthanides, but due to the lack of dissociation in THF solutions of naphthalenesamarium (**6.2**), −ytterbium (**6.8**), and −europium (**6.3**), those Ln(III)/Ln(II) potentials are even lower than that of Sm, which contradicts such an explanation. Another characteristic feature of the permethylsamarocene complexes with arenes is the allylic type of bonding between the arene ligand and the Cp^*_2Sm units,[94] which probably is connected with the their ability to dissociate in polar solvent.



11.5

Figure 36.

VI. Complexes with Heterocyclic Aromatic Ligands

The overwhelming majority of complexes of rare-earth metals with heterocyclic aromatic ligands are formed through coordination interaction between the lone electron pair of the heteroelement and the Ln atom.[6] In these complexes the ligands can be either neutral or charged (−1 or −2). The charges are localized primarily on heteroatoms. However, a number of compounds similar in nature to typical bis(arene) complexes are also known (Table 12).

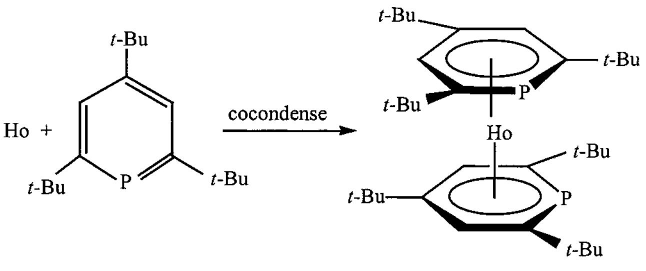
One of them, $(2,4,6\text{-}t\text{-}Bu_3C_5H_2N)_2Sc$ (**12.9**), was prepared by co-condensation of scandium vapor with 2,4,6-tri-*tert*-butylpyridine.[3] It was suggested that the compound contains the formally zerovalent scandium atom and the neutral *tert*-butyl-substituted pyridine ligands, which is confirmed by the paramagnetism of the complex. The molecule was represented as a planar-parallel sandwich.

The same nature and arrangement of the molecule was found for holmium complex **12.14** containing 2,4,6-tri-*tert*-butylphosphorine cycles. The product was obtained also by cryogenic synthesis, and its structure was determined by X-ray analysis (Figure 37).[110c]

Both C_5P rings in the molecule were found to be planar apart from the slight inclination of each phosphorus atom toward the metal. The average Ho−C distance is 2.612 Å, which is fairly equal to that of bis(benzene) complex **3.17** (2.630 Å). The

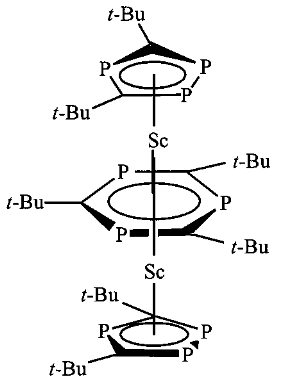
Table 12. Data on Lanthanide Complexes with Heterocyclic Aromatic Ligands

compound	no.	color, mp	other characteristics, ref
$[Sc(C_5H_5BMe)_2Cl]_2$	**12.1**	orange, 160−161 °C	X-ray, NMR[108]
$[ScCl(3,5\text{-}Me_2C_5H_3BNMe_2)_2]_2$	**12.2**	orange, 97−98 °C	X-ray, NMR[108]
$[ScCl(3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$	**12.3**	light orange-yellow, 124−125 °C	X-ray, NMR[108]
$ScPh_2(C_5H_5BPh)(THF)$	**12.4**	bright brown	X-ray, NMR, MS[109]
$ScPh(C_5H_5BPh)_2(THF)\cdot 3\ THF$	**12.5**	colorless	NMR, MS[109]
$[ScPh(C_5H_5BPh)_2]_2$	**12.6**	dark green	NMR, MS[109]
$Sc(CH_2SiMe_3)_2(C_5H_5BCH_2SiMe_3)(THF)$	**12.7**	orange oil, r.t. (dec)	NMR[109]
$Sc(CH_2SiMe_3)(C_5H_5BCH_2SiMe_3)_2(THF)$	**12.8**	orange oil, r.t. (dec)	NMR[109]
$(2,4,6\text{-t-}Bu_3C_5H_2N)_2Sc$	**12.9**	>100 °C (dec)	UV, ESR[3]
$[(t\text{-}Bu_2C_2P_3)Sc]_2(t\text{-}Bu_3C_3P_3)$	**12.10**	forest-green	X-ray, UV/Vis, MS[110a]
$[Y(C_5H_5BMe)_2Cl]_2$	**12.11**	pale yellow	X-ray, NMR, MS, powder diffraction[111]
$(Cp^*{}_2Sm)_2(C_{12}H_8N_2)$	**12.12**	dark brown	X-ray, NMR, IR[94]
$(Cp^*{}_2Sm)_2(C_{13}H_9N)_2$	**12.13**	orange	X-ray, NMR[94]
$Ho(PC_5H_2\text{-t-}Bu_3\text{-}2,4,6)_2$	**12.14**	purple, subl. 160 °C/10^{-5} mbar	X-ray, UV/Vis, magn.[110c]



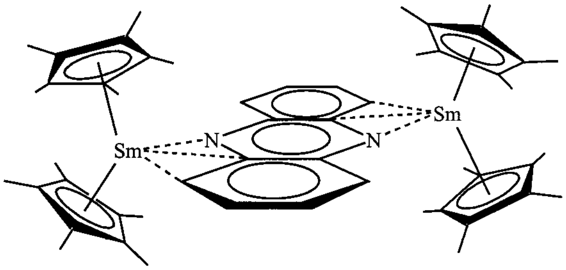
12.13

Figure 37.



12.10

Figure 38.



12.12

Figure 39.

lowered magnetic moment of **12.14** (8.9 μ_B) compared with **3.17** (10.75 μ_B) was explained by a more extensive degree of distribution of the unpaired electron density away from the metal.[110c]

Arene−lanthanide complexes with phosphorus-containing aromatic ligands were prepared as well by co-condensation of scandium vapor with 2,2-dimethylpropylidynephosphine, t-BuCP, at 77 K.[110a,b] The reaction was accompanied by cyclization of the phosphaalkyne, giving rise to two products: dark violet scandocene $(\eta^5\text{-t-}Bu_3C_3P_2)_2Sc$ containing divalent scandium and the green triple-decker complex $[(\eta^5\text{-t-}Bu_2C_2P_3)Sc]_2(\mu\text{-}\eta^6{:}\eta^6\text{-t-}Bu_3C_3P_3)$ (**12.10**) containing formally monovalent scandium. The valence state of the scandium atoms in both complexes was unambiguously established by UV and ESR spectroscopy and magnetic measurements. A structural study of the complex showed that the central triphosphabenzene ring lies on a crystallographic mirror plane and is planar with no significant variation in ring P−C bond lengths (1.793−1.807 Å), indicative of an $\eta^6{:}\eta^6$-type of bonding between the metal atom and arene ligand (Figure 38).[110a]

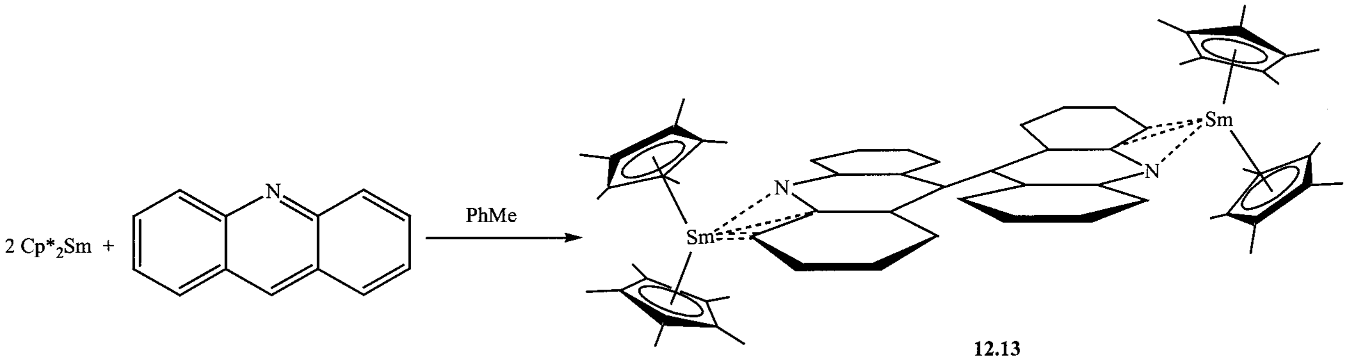
It is worth noting that the distance from Sc to the central ring (1.787 Å) in compound **12.10** is noticeably shorter than the analogous distance in the bis(arene) complex $(t\text{-}Bu_3C_6H_2Me)_2Sc$ (**3.7**), which probably is caused by different oxidation degrees of the metal in these compounds.[110a] Despite the valence state +1 not typical of scandium, compound **12.10** is quite stable and can be even sublimed in vacuo at 250 °C. The magnetic moment (3.98 μ_B) of **12.10** is somewhat smaller than the value calculated for four unpaired electrons, which was attributed to the presence of some orbital contribution.[110a]

Phenazine, like anthracene, easy oxidizes $Cp^*{}_2Sm$ to give the binuclear complex $(Cp^*{}_2Sm)(\mu\text{-}\eta^3{:}\eta^3\text{-}C_{12}H_8N_2)$ (**12.12**) in which the samarocene fragments are in the transoid orientation with respect to the $(C_{12}H_8N_2)^{2-}$ dianion.[94] The presence of three short contacts between the samarium atoms and the phenazine ligand suggests the allylic type of bonding (Figure 39).

The Sm−N bond length (2.360 Å) is slightly larger than the Sm−N σ-bond length in complex $Cp^*{}_2SmN(SiMe_3)_2$ (2.306 Å),[112] which is evidence for substantial localization of the charge on the nitrogen atoms, as in complexes of $Cp_3Ln(py)$[6] and $Ln(bipy)_4$[113] types.

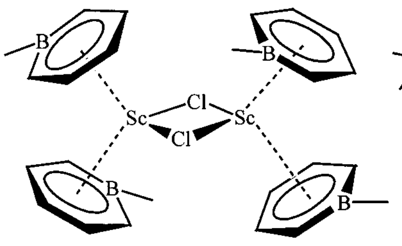
The reaction of permethylsamarocene with acridine independent of the ratio of the reagents is accompanied by dimerization of the arene via C−C bond formation.[94] The character of metal−arene bonding in the formed complex **12.13** is analogous to that in the phenazine derivative, i.e., corresponds to an η^3-interaction with the Sm−N component predominating (Figure 40).

The boratabenzene derivatives **12.1**, **12.2**, **12.3**, and **12.11** containing six-membered C_5B cycles were

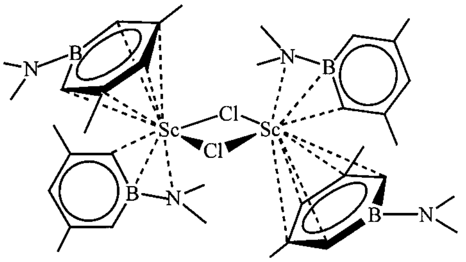


12.13

Figure 40.



12.1



12.2

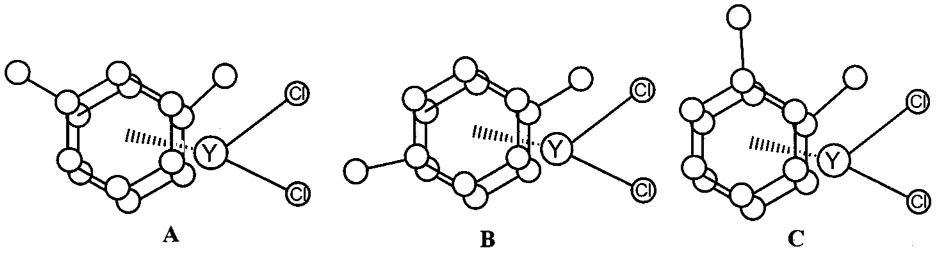


Figure 41.

synthesized by prolonged heating of scandium or yttrium trichloride with the appropriate lithium compound in toluene.[108,111]

$$\mathrm{LnCl_3 + 2\mathit{n}LiL \rightarrow [LnClL_2]_{\mathit{n}} + 2\mathit{n}LiCl}$$

$$\mathrm{L = C_5H_5BMe\ (\mathbf{12.1},\ \mathbf{12.11}),\quad Me_2C_5H_3BNMe_2\ (\mathbf{12.2}),\quad Me_2C_5H_3BN(SiMe_3)_2\ (\mathbf{12.3})}$$

An unusual pathway has been found to form ligand-mixed halide-free boratabenzene complexes **12.4**–**12.8**.[109] It was established that the reaction of neutral boratabenzene–base adduct $C_5H_5B{\cdot}PMe_3$ with an equimolar amount of triphenylscandium quantitatively affords diphenyl–boratabenzene derivatives $ScPh_2(C_5H_5BPh)(THF)$ (**12.4**).

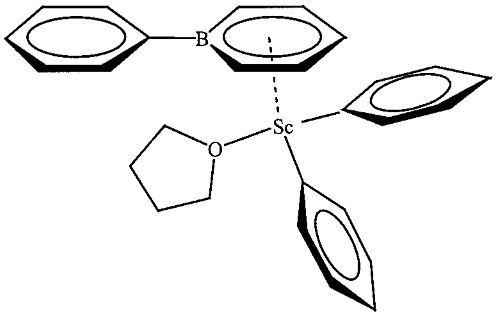
$$\mathrm{Ph_3Sc(THF)_2 + C_5H_5B{\cdot}PMe_3 \xrightarrow{PhMe} \underset{\mathbf{12.4}}{ScPh_2(C_5H_5BPh)(THF)} + PMe_3}$$

Addition of a second equivalent of boratabenzene adduct leads to formation of the bis(boratabenzene)scandium compound $ScPh(C_5H_5BPh)_2(THF)$, which in THF solution exists as adduct **12.5**. After removal of THF by repeated chlorobenzene condensation/evaporation, dimeric solvent-free product **12.6** was obtained. According to ^1H NMR data the reactions with alkylscandium complexes $(Me_3SiCH_2)_3Sc(THF)_2$ or $(PhMe_2CCH_2)_3Sc(THF)$ proceed analogously; however, because of the low stability, the formed products were not isolated in pure form. It was assumed that transformation of neutral boratabenzene to anionic ligand is a result of an intramolecular nucleophilic attack of the R group in ScR_3 on boron upon coordination of $C_5H_5BPMe_3$.[109]

On the basis of their nature, the boratabenzene complexes are closer to cyclopentadienyl derivatives than to benzene compounds. It is reflected in the structures of the products. The arrangement of a binuclear molecule of **12.1** with bridging chlorine atoms is typical for $[Cp_2LnCl]_2$ complexes: two bent sandwich units with two focally bonded ring ligands are joined by two chlorine bridges (Figure 41).

The boratabenzene rings are virtually planar. The distances Sc–C (average 2.593 Å) are somewhat longer than those in $(Cp_2ScCl)_2$ (2.46 Å)[114] and Sc–$C(C_3P_3$ ring) contacts (average 2.429 Å) in **12.10** but shorter than Sc–$C(C_2P_3$ rings) (2.714 and 2.771 Å) bonds in the same complex.[110a]

A study of yttrium complex **12.11** by means of single-crystal and powder diffraction methods allowed the existence of three conformational polymorphs with space groups $P2_1/n$, $P2_1/a$, and $Pbca$ to



12.4

Figure 42.

be established.[111] The main geometrical features of all the forms are similar to those of scandium analogue **12.1** but differ from each other by the rotation position of C_5H_5BMe ligands in the sandwiches $(C_5H_5BMe)_2Y$.

The rotation angles of the boratabenzene rings in isomers **A**, **B**, and **C** are, respectively, 91.1°, 133.1°, and 24.9°. Quantum chemical calculation and lattice energy minimization revealed that conformers **A** and **B** are noticeably more stable than the modification **C**.

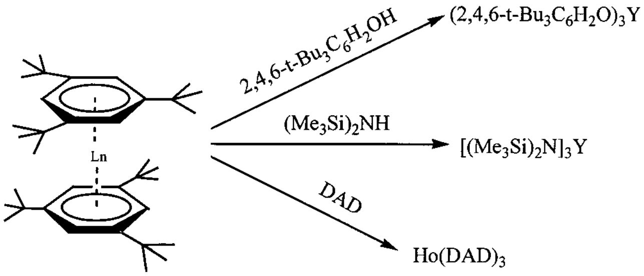
The arrangement of the molecule of **12.2** resembles the structure of **12.1**, but the bond lengths between Sc and the atoms of the ligands as well as the shapes of C_5B rings indicate another type of bonding. One of the rings in $Sc(C_5H_5BNMe_2)_2$ has a planar C_5-fragment with Sc−C distances in the range of 2.482−2.563 Å, but the boron atom in this moiety is bent away from the metal by 17.8°. The second ring is planar, but only the N, B, and C(α) atoms of this ligand are within bonding distances to Sc. Thus, the metal−arene interaction in **12.2** may be considered as η^3:η^5. However, in solution only one type of ligand is observed, indicative of easy haptotropic transformations.[108] Compound **12.3** is mononuclear, probably because essential steric hindrance stimulated by the presence of $N(SiMe_3)_2$ groups. On the basis of the Sc−C and Sc−B distances, the type of bonding is close to η^6:η^6.

In complex **12.4** the geometry of $Sc-C_5H_5B$ unit also corresponds to an η^6-fashion of bonding (Figure 42).[109] There is a slight slip-distortion of the Sc atom away from boron in a nearly planar C_5H_5B ring. The average Sc−C(arene) distance 2.569 Å is slightly shorter than that in **12.1**.

VII. Chemical Behavior of Arene–Lanthanide Compounds

1. Reactivity

The chemical properties of complexes of rare-earth metals with π-bonded arene ligands were studied for naphthalene derivatives. For compounds with other aromatic hydrocarbons, only the most common characteristics are known. All arene lanthanide complexes exist as dark-colored extremely air- and moisture-sensitive solids. Some of them are pyrophoric. As noted above, bis(arene) complexes of formally zerovalent Sc, Y, Nd, Gd, Tb, Dy, Ho, Er, and Lu are thermally stable under an inert atmosphere or in vacuo and can be even sublimed with insignificant decomposition at 100 °C (at 10^{-4} mbar).[47] These complexes are readily soluble in aromatic and aliphatic hydrocarbons, in contrast to complexes with arene dianions, which are virtually insoluble.



3.5, 3.17

Figure 43.

The yttrium complex $(1,3,5\text{-t-}Bu_3C_6H_3)_2Y$ (**3.8**) readily reacts with phenol $2,4,6\text{-t-}Bu_3C_6H_2OH$ and hexamethyldisilazene to form tri(aryloxide) and tris(trimethylsilyl)amide of yttrium in good yields. The reaction of the holmium complex **3.17** with DAD also results in complete replacement of the arene ligands (Figure 43).[3]

Naphthalene lanthanide complexes of all types exhibit very high reactivity toward inorganic, organic, and organometallic compounds. In all cases, these complexes act as strong reducing agents comparable in reducing ability with alkali-metal naphthalenides. Normally the reactions easily proceed in THF or DME at room temperature or lower. The yields of the products, many of which were characterized by X-ray diffraction studies, as a rule are higher than 60−70%. Due to these advantages as well as the availability of naphthalenelanthanides, these reactions may be recommended as preparative (often the only possible) procedures for the synthesis of other lanthanide compounds. The important benefit of these syntheses is the fact that the second product, viz., naphthalene, is unreactive and can be readily separated from the target compound. The reactions with the participation of complexes $(C_{10}H_8)Ln(B)_x$ (Ln = Sm, Eu, Yb) are listed in Table 13. Among them the reaction with $(C_6F_5)_3GeH$ needs some explanation. This complex, multistep process, including generation of $(C_6F_5)_3Ge^-$ anions, nucleophilic substitution of *p*-F atoms by this anion, formation of fluorides LnF_2, and their oxidation to LnF_3, results in formation of hyperbranched polymer $[(C_6F_5)_2(C_6F_4)Ge]_n$ containing molecules of LnF_3 in the cavities (Figure 44).[127] These molecules of fluorides trapped in dendritic matrix have a surprisingly high solubility. In contrast to “normal” lanthanide fluorides, which are insoluble even in mineral acids (except liquid HF), these salts readily dissolve in THF, DME, and aromatic solvent.

The thulium complex $[(C_{10}H_8)Tm(DME)]_2(\mu\text{-}C_{10}H_8)$ (**6.7**) was used in the reactions with phenols including crowded $2,4,6\text{-t-}Bu_3C_6H_2OH$ for preparation of tri(aryloxides).[133] The yield of desired products reached 70−90%.

Table 13. Reactions of Naphthalene Complexes $(C_{10}H_8)Ln(B)_x$ (Ln = Sm, Eu, Yb; B = THF, DME; x = 2, 3)

substrate	Ln	products	ref
O_2	Sm, Eu, Yb	$Ln_2O_3 + C_{10}H_8$	67,72a
H_2	Sm, Eu, Yb	$LnH_2(THF)_2 + C_{10}H_8$	115
H_2O	Sm, Eu, Yb	$Ln(OH)_3 + C_{10}H_{10}$	67,72a
CO	Sm, Eu, Yb	$C_{10}H_8(COOH)_2$	67,72a
CO_2	Sm, Eu, Yb	$C_{10}H_8(COOH)_2$	67,72a
S_8	Sm	$SmS(THF) + C_{10}H_8$	116
$Ph_2CO\ (H^+)$	Yb	$(Ph_2COH)_2$	67,117
$PhCO\ (H^+)$	Yb	$(PhCHOH)_2$	67,117
$C_2H_4O\ (H^+)$	Yb	$HOCH_2(CH_2)_2CH_2OH + C_{10}H_8$	67
RX (R = Ph, C_6F_5; X = Br, I)	Sm, Yb	RLnX	84a
RX (R = 4-BrC_6H_4, 4-ClC_6H_4, 4-$BrC_6H_4-C_6H_4$, 2-BrC_4H_2S; X = Cl, Br	Sm, Yb	XLnRLnX	84b,118
R_2NH (R = Et, Me_3Si)	Sm, Eu, Yb	$Ln(NR_2)_2 + C_{10}H_8 + C_{10}H_{10} + H_2$	67,72
CpH	Sm, Eu, Yb	$Cp_2Ln + C_{10}H_8 + H_2$	67,72
$C_{12}H_8$	Yb	$(\eta^5{:}\eta^5\text{-}C_{12}H_8-C_{12}H_8)Yb(THF)_2$	119
$CpCH_2CH_2OH$	Yb	$[(\eta^5\text{-}C_5H_4)CH_2CH_2(\eta^1\text{-}O)]Yb + C_{10}H_8 + H_2$	120
$CpCH_2CH(Me)OH$	Yb	$[(\eta^5\text{-}C_5H_4)CH_2CH(Me)(\eta^1\text{-}O)]Yb(THF) + C_{10}H_8 + H_2$	120
$CpCH_2CH(CH_2OBu)CH_2OH$	Yb	$[(\eta^5\text{-}C_5H_4)CH_2\text{-}\ CH(CH_2OBu)CH_2(\eta^1\text{-}O)]Yb(THF) + C_{10}H_8 + H_2$	120
$C_5Me_4HSiMe_2OSiMe_2OH$	Yb	$\{[(\eta^5\text{-}C_5Me_4)SiMe_2OSiMe_2(\eta^1\text{-}O)]Yb(THF)\}_2 + C_{10}H_8 + H_2$	121
$CpCH_2CH(OH)CH_2OBu$	Yb	$\{[(\eta^5\text{-}C_5H_4)CH_2CH(\mu^2{:}\eta^1\text{-}O)CH_2OBu]Yb\}_4$	122
$CpSiMe_2NH\text{-}t\text{-}Bu$	Yb	$[(\eta^5\text{-}C_5H_4)SiMe_2(\eta^1\text{-}N\text{-}t\text{-}Bu)]Yb(THF) + C_{10}H_8 + H_2$	120
$HC\equiv CH$	Sm, Eu, Yb	$LnC_2(THF)_x + C_{10}H_8 + H_2$	123
$PhC\equiv CH$	Eu, Yb	$(PhCH{=}CHCH{=}CHPh)Ln(DME)_2 + C_{10}H_8$	124
$C_{14}H_{10}$	Yb	$C_{14}H_{10}{}^{-\bullet} + C_{10}H_8$	72
Ph_2Hg	Yb	$Ph_2Yb(THF)(\mu\text{-}Ph)_3Yb(THF)_3 + Ph_3Yb + Hg + C_{10}H_8$	125
Ph_3Bi	Yb	$Ph_2Yb(THF)(\mu\text{-}Ph)_3Yb(THF)_3 + Ph_3Yb + Bi + C_{10}H_8$	125a
Ph_3GeH	Eu, Yb	$(Ph_3Ge)_2Ln(THF)_4$ or $(Ph_3Ge)_2Eu(DME)_3$ (in DME solution)	115b,126
$(C_6F_5)_3GeH$	Eu, Yb	$\{[(C_6F_5)_2(C_6F_4)Ge]_n\ x\ (LnF_3)_m\}$	127
Ph_4Sn	Yb	$Ph_3SnYb(THF)(\mu\text{-}Ph)_3Yb(THF)_3 + (Ph_3Sn)_2Yb(THF)_4 + C_{10}H_8$	128
Ph_6Sn_2	Yb	$(Ph_3Sn)_2Yb(THF)_4$	128b
$(Ph_3Ge)_2Hg$	Yb	$[(Ph_3Ge)_3Hg]_2Yb(THF)_2(DME)_2 + Hg + C_{10}H_8$	129
Cp_2V	Yb	$CpV(\mu\text{-}C_{10}H_8)VCp + Cp_2Yb$	87
Cp_2V(excess)	Eu, Yb	$[CpV(\mu\text{-}C_{10}H_8)LnCp(THF)]_n$	70,86
Cp_2M (M = Ni, Co)	Yb	Cp_2Yb	87
Cp_2Cr	Yb	$Cp_2Yb + (C_{10}H_8)_2Cr$	87
$PhN{=}NPh$	Yb	$[Yb_4(\mu_2\text{-}\eta^2{:}\eta^2\text{-}Ph_2N_2)_4(\mu_3\text{-}PhN)_2(THF)_4]$	130
	Sm	$[Sm_4(\mu_2\text{-}\eta^2{:}\eta^2\text{-}Ph_2N_2)_4(\mu_3\text{-}PhN)_2(THF)_6]$	131
DAD	Yb	$Yb(DAD)_3 + C_{10}H_8$	132

$$\underset{\mathbf{6.7}}{[(C_{10}H_8)Tm(DME)]_2(\mu\text{-}C_{10}H_8)} + ArOH\ (excess) \xrightarrow{DME} (ArO)_3Tm + 3\ C_{10}H_{10}$$

$$Ar = Ph,\ 2,4,6\text{-}t\text{-}Bu_3C_6H_2$$

It was found that the products of the reaction of $NdCl_3$ with $C_{10}H_8Li$ (apparently the reaction afforded naphthalene neodymium complexes rather than finely dispersed neodymium metal as suggested[134]) readily react with ketones and aldehydes to yield the corresponding diols or ethylene derivatives as a result of coupling of the substrate.[134]

Generally, mixed-ligand naphthalene complexes of rare-earth metals containing the iodine atom , the cyclopentadienyl group, or the double-decker $CpV(C_{10}H_8)$ moiety as ancillary ligands react analogously to compounds of the $(C_{10}H_8)Ln(THF)_3$ type, i.e., the attack occurs primarily onto the $C_{10}H_8-Ln$ bond. Due to the presence of the LnI or LnCp groups along with the $Ln(C_{10}H_8)$ moiety, these complexes are convenient starting compounds for the preparation of complexes of the RLnI or RLnCp types. The reactions of ligand-mixed naphthalenelanthanides are given in Table 14.

The chemical properties of anthracene lanthanide complexes mimic the properties of their naphthalene analogues. However, the activities of the former are substantially lower. Thus, the reactions of anthraceneytterbium with cyclopentadiene, fluorene, 9-*tert*-butylfluorene, tetraphenylpropene, and 9-phenylxanthene in solutions afforded the corresponding anions, i.e., the R_2Ln compounds apparently formed, but the reaction rates were low (from several days to weeks).[100] Triphenylmethane is not involved in the reaction at all. Treatment of a hexyl-substituted anthracene complex of samarium **10.3** with a stoichiometric amount of benzopinacol afforded after hydrolysis the bezophenone, benzhydrol, 9,10-dihydro-1,8-dihexylanthracene, and free 1,8-dihexylanthracene.[96a] Deuteriolysis of complexes $Ln(C_{14}H_{10})(DME)_x$ (Ln = Sm or Yb) (**10.4**, **10.9**) gives rise to 9,10-dideutero-9,10-dihydroanthracene, whereas their reactions with MeI afforded a mixture of 9,10-dimethyl-9,10-dihydroanthracene (14−20%), $MeC_{14}H_9$ (1−4%), and 9,10-dihydroanthracene (13−25%).[96b] It is noteworthy that attempts to alkylate naphthalene in the reactions of naphthaleneytterbium with different alkyl halides were filed. In all cases, only unsubstituted naphthalene was obtained.[142] The other difference between $C_{10}H_8$ and $C_{14}H_{10}$ analogues was found in the reactions with CO_2. Unexpectedly, in the case of anthracene the anthracene-2-carboxylic acid was obtained.[67]

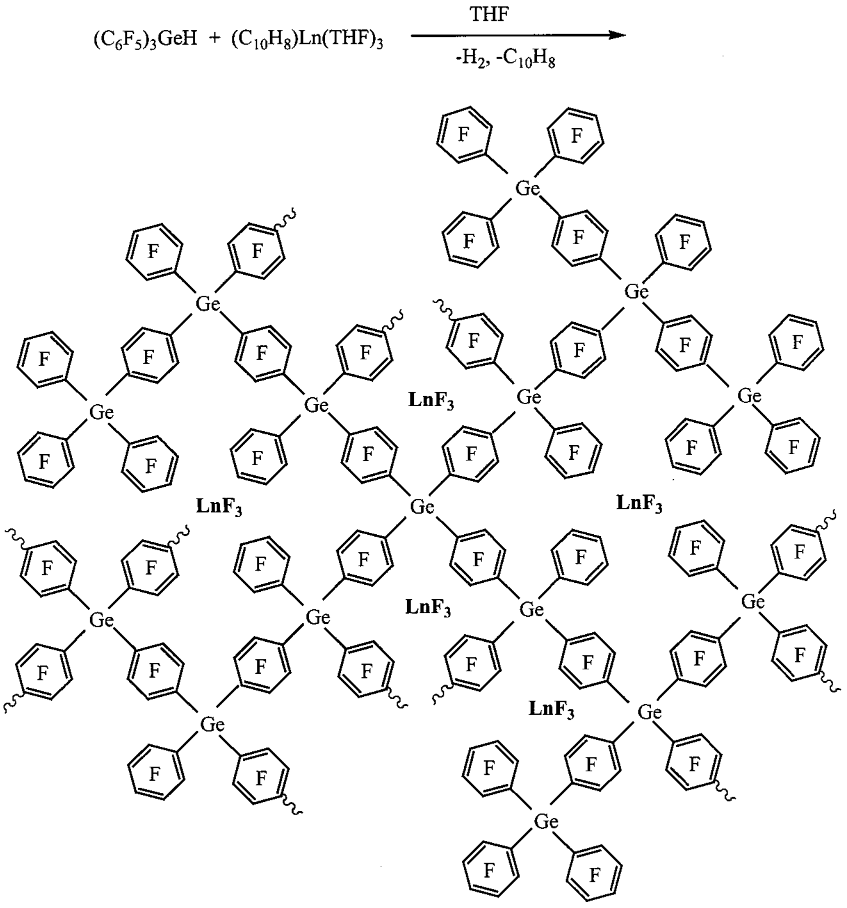


Figure 44.

Table 14. Reactions of Ligand-mixed Naphthalene Complexes

complex	substrate	products	ref
$[LaI_2(THF)_3]_2(C_{10}H_8)$ (**7.3**)	4 bipy	$LaI_2(bipy)_2(DME) + C_{10}H_8$	135
	2 bipy	$LaI_2(bipy)(DME)_2 + C_{10}H_8$	135
	$C_{12}H_8$	$[LaI_2(THF)_3]_2(\mu\text{-}\eta^5{:}\eta^6\text{-}C_{12}H_8)$	95
$[NdCl_2(THF)_2LiCl]_n(C_{10}H_8)$ ($n = 4-7$) (**7.7**)	2,4,6-t-$Bu_3C_6H_2OH$	$[\{NdCl_2(2,4,6\text{-t-}Bu_3C_6H_2O)(\mu\text{-}Cl)(THF)\}Li(THF)_2]_2$	81
$[EuI(DME)_2]_2(C_{10}H_8)$ (**7.9**)	$PhC{\equiv}CH$	$[EuI(\mu\text{-}C{\equiv}CPh)(DME)_2]_2 + C_{10}H_8 + H_2$	124
	Ph_3GeH	$Ph_3GeEuI(DME)_2 + C_{10}H_8 + H_2$	126
$DyI(C_{10}H_8)(DME)_2$ (**7.11**)	D_2O	1,4-$D_2C_{10}H_8$	82
$[YbI(DME)_2]_2(C_{10}H_8)$ (**7.12**)	bipy	$YbI(bipy)(DME) + C_{10}H_8$	136
	$PhC{\equiv}CH$	$[YbI(\mu\text{-}C{\equiv}CPh)(DME)_2]_2 + C_{10}H_8 + H_2$	124
	C_9H_8	$(C_9H_7)YbI(DME)_2 + C_{10}H_8 + H_2$	137
	$C_{13}H_{10}$	$(C_{13}H_9)_2Yb(DME) + YbI_2(DME)$	138
	$Cp^*H + C_{13}H_9K$	$(C_{13}H_9)YbCp^*(DME)$	138
$[CpV(C_{10}H_8)YbCp(THF)]_n$ (**8.3**)	H_2O	$CpYbOH(THF)_2 + CpVC_{10}H_8$	139
	CO	$Cp_2Yb + CpVC_{10}H_8$	
	CO_2	$Cp_2Yb + CpVC_{10}H_8$	
	$Cr(CO)_6$	$Cp_2Yb + CpVC_{10}H_8 + Cp_2V + CpVC_{10}H_8VCp + C_{10}H_8$	
	CpTl	$Cp_2Yb + CpVC_{10}H_8$	
	Ph_2N_2	$[CpYb(THF)]_2(Ph_2N_2)_2 + CpVC_{10}H_8$	
$CpLuC_{10}H_8(THF)_2$ (**9.7**)	Ph_2N_2	$[CpLu(THF)]_2(Ph_2N_2)_2 + C_{10}H_8$	140
$CpLuC_{10}H_8(DME)$ (**9.8**)	H_2O	$Lu(OH)_3 + C_{10}H_{10} + CpH$	89
	O_2	$Lu_2O_3 + C_{10}H_8$	89
	CpH	$Cp_3Lu + C_{10}H_8 + C_{10}H_{10} + H_2$	89
	$PhC{\equiv}CPh$	$[CpLu(DME)]_2[\mu\text{-}(Ph)C(Ph)C{=}C(Ph)C(Ph)]$	140
	C_{60}	$CpLu(C_{60})(DME) + C_{10}H_8$	141
$Cp^*LuC_{10}H_8(DME)$ (**9.9**)	C_{60}	$Cp^*Lu(C_{60})(DME)(PhMe) + C_{10}H_8$	141

For anthracene mixed-ligand complexes of lanthanides, only the reactions of $CpLu(C_{14}H_{10})(THF)_2$ (**10.13**) with iron pentacarbonyl and azobenzene were reported. In the first case the heterobimetallic product of composition $[CpLu(THF)]Fe(CO)_4$ was obtained,[143] but in the second one the binuclear complex $[CpLu(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhNNPh)$ has been isolated and structurally characterized.[144]

2. Catalytic Activity

As it is known, high catalytic activity is attributed to many lanthanide compounds (see, for instance, refs

6 and 144). The arene complexes of rare-earth metals are not an exception in this respect. Actually all compounds with π-arene−Ln groups tested as catalysts revealed high activity. Thus, the arene−chloroaluminate complexes of neodymium **1.14** and **1.17**−**1.22** in combination with AlR_3 catalyze butadiene polymerization under mild conditions to give mainly (95−99%) *cis*-1,4-polymer with a molecular weight up to 100 000.[21,23] It was found that the efficiency of the systems depends on the type of arene (C_6H_6 derivatives are most active, whereas C_6Me_6 analogues are inactive) and R groups in organoaluminum cocatalysts (the activity of $Al(i\text{-}Bu)_3$ is higher than that of $Al(i\text{-}Bu)_2H$, while $AlEt_3$, $AlEt_2Cl$, $Al(C_8H_{17})_3$ displayed no activity at all). Besides AlR_3, the magnesium compounds MgR_2 also were successfully used in these systems.[21] Interestingly, Y-based catalyst **1.3** in contrast to other rare-earth metals gave a polymer with 99.5% of 1,4-trans linkages in the system with $MgBu_2$.[21] It is worth noting the advantage of these systems in comparison with $LnCl_3$ or $Ln(OR)_3$ catalysts is their solubility in aromatic and aliphatic hydrocarbons.

The system chloroaluminate/$MgBu_2$ catalysts were tried in ethylene polymerization but revealed lower activity than well-known Ti- and Zr-based catalysts.[21] In contrast, bis(arene) complexes **3.8**−**3.11** and **3.13**−**3.19** were found to be very efficient, homogeneous catalysts for ethylene polymerization.[3] They produce polyethylene of high density and narrow mass distribution with turnover numbers in excess of 10^4. It was reported that neodymium complex $Nd_2(C_6H_6)_3$ (**3.12**) combined with $Al_2Et_3Cl_3$ polymerizes butadiene to give, like most other organolanthanides, predominantly *cis*-1,4-polymer.[48]

The η^6:η^6-indenyl complex of ytterbium $Yb(\eta^6\text{-}i\text{-}PrC_9H_6{-}AlMe_3)_2$ (**5.10**) revealed relatively high catalytic activity toward the polymerization of ethylene and ϵ-caprolactone.[63] However, it was inactive in the polymerization of methyl methacrylate and styrene.

High catalytic activity in various reactions was found for naphthalene complexes $(C_{10}H_8)Ln(THF)_3$ (**6.2**, **6.3**, and **6.8**). Thus, the ytterbium complex **6.8** catalyzes hydrogenation of hex-1-ene, stilbene, isoprene, and piperylene (but not benzene and cyclohexene) at room temperature under an atmospheric pressure of H_2 yielding the corresponding hydrocarbons.[115d] Diphenylacetylene was hydrogenated to form *trans*-stilbene and diphenylethane. In the presence of 1−5% of **6.8**, styrene, methyl methacrylate, ethyl acrylate, isoprene, and piperylene form polymers at room temperature.[67,145] The conversion reached 100% in several hours. The polymerization of styrene proceeds exothermically. Piperylene produced more than 80% of the *trans*-polymer, whereas polyisoprene was obtained as a mixture of virtually equal amounts of cis and trans forms. Complex **6.8** catalyzes the polymerization of epoxides and their reactions with CO_2 as well.[67,117] In the latter case a mixture of monomeric and polymeric alkyl carbonates was obtained. The same compound causes the copolymerization of ethylene oxide with styrene and piperilene. The yield of alternated copolymer with styrene in 4 h at 20 °C reached 92%. The yield of copolymer with piperilene was only 20% under the same conditions.[117]

The solutions formed in the reactions of halides of "trivalent" lanthanides with naphthalenelithium or −sodium, in which the presence of naphthalenelanthanide products was assumed,[73] were found to be efficient catalysts of the polymerization of conjugated dienes.[74] Interestingly, in this case the relative activity of catalysts increased on going from light to heavy lanthanides while in all other known catalytic systems the highest efficiency was observed for Nd, Pr, and Ce.

Attempts to use the isolated naphthalenelanthanide complexes in the activation of dinitrogen under ambient conditions were filed. However, the reduction of $LnCl_3$ with an excess amount of $C_{10}H_8$-Na or $C_{10}H_8Li$ in THF medium gave after hydrolysis of the formed mixture a noticeable amount of NH_3.[146] The highest yield (0.22 mol/mol $LnCl_3$) was observed for ytterbium. It was assumed that highly reactive naphthalene−lanthanide intermediates are responsible for reduction of N_2.

VIII. Conclusions

Analysis of the above data allows accentuating the characteristic features of complexes of rare-earth metals with π-bonded arene ligands. First of all, it should be noted that these compounds are quite stable and have a relatively high energy of the metal−arene bonds. The complexes exist in two main forms: with neutral arene or with the arene dianion. Forms with arene carrying a charge of −1 or −3 are not typical for these complexes. Apparently such compounds can be generated and exist only under certain conditions. It should be noted that the tendency of lanthanides to form complexes of the $[Ln]^{2+}[L]^{2-}$ type even in the presence of the free uncharged ligand is also observed in the case of other ligands (such as bipy[113] or DAD[147]) possessing the property of polyvalency. The mode of bonding of the lanthanide atom with arene ligand can vary from η^2 to η^6. The Ln atom can be coordinated both to the plane of the arene ligand and to its edge. The character of the Ln−arene bond in complexes with neutral arene and formally zerovalent lanthanide is similar to that in complexes of d-transition metals, i.e., the bond is determined by back-donation of the electron density from the occupied d_{xy} and $d_{x^2-y^2}$ orbitals of lanthanide to the unoccupied π-orbitals of arene. In compounds with a neutral ligand coordinated to the Ln^{3+} cation (complexes of the (arene)-$Ln[(\mu\text{-}Cl)_2AlCl_2]_3$ or $Ln(OC_6H_3Ph_2\text{-}2,6)_3$ type) there are no electrons on the d orbitals of the metal atoms; therefore, metal−arene interaction is formed, apparently, through donation of the electron density from the π-orbitals of the arene ligand to the unoccupied orbitals of the metal atom. The metal−arene bonds in these compounds are substantially weaker, as evidenced by the noticeably elongated Ln−C(arene) bonds. In complexes containing Ln^{2+}, $(XLn)^{2+}$, or $(X_2\text{-}Ln)^+$ cations and the arene dianion (naphthalene lanthanide and related derivatives) the bonding occurs, apparently, primarily through Coulomb interactions between the positively and negatively charged moieties of the molecule. However, the structures of the complexes and the fact that these complexes contain the shortest Ln−C(arene) bonds of all arene lanthanide complexes are indicative of the presence of the second bonding component, viz., of donation of the electron density from the π-orbitals of arene to the unoccupied orbitals of the metal atom. Despite the high (judging from the geometric parameters of the molecules) energy of the metal−arene bond, naphthalene lanthanide complexes exhibit very high reactivity. Along with their relative ability, this quality makes these derivatives a convenient source of lanthanides or lanthanide-containing fragments in the synthesis of other rare-earth metals compounds.

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X. Abbreviations

Ln	Sc, Y, La−Lu
M	Li, Na, K
CID	collision-induced dissociation
Arene	hydrocarbon containing at least one C_6 aromatic ring
Me	methyl, CH_3
Et	ethyl, C_2H_5
Bu	*n*-butyl, C_4H_9
Mes	mesityl, 2,4,6-$(CH_3)_3C_6H_2$
Cp	cyclopentadienyl, C_5H_5
Cp*	permethylated cyclopentadienyl, C_5Me_5
i-Pr	isopropyl, $CH(CH_3)_2$
Ph	phenyl, C_6H_5
Ar	aryl
magn.	magnetic data
DME	dimethoxiethane
THF	tetrahidrofurane
X-ray	X-ray structural analysis
MS	mass spectrometry
$C_{10}H_8$	naphthalene
$C_{14}H_{10}$	anthracene
Diglyme	diethylene glycol dimethyl ether, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$
$C_{16}H_{10}$	pyrene
$C_{18}H_{12}$	2,3-benzanthracene
subl.	sublimation temperature
$C_{12}H_8N_2$	phenazine
$C_{13}H_9N$	Acridine
C_5H_5BR	R-substituted boratabenzene
2,4,6-t-$Bu_3C_5H_2N$	2,4,6-tri-*tert*-butylpyridine
P_3C_3-t-Bu_3	2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene
P_3C_2-t-Bu_2	3,5-di-*tert*-butyl-1,2,4-triphosphacyclopentadienyl
Py	pyridine
Bipy	1,1′-bipyridyl
$Me_3SiC_{13}H_8$	9-Me_3Si-substituted fluorenyl
i-PrC_9H_6	1-i-Pr-substituted indenyl
$C_{10}H_{10}$	1,2- and 1,4-dihydronaphthalene
Ind	indenyl
Flu	fluorenyl
DAD	*N,N′*-di-*tert*-butyldiazabutadiene, t-BuN═CHCH═NBu-t
2,5-$Br_2C_4H_2S$	2,5-dibromthiophen
C_2H_4O	ethylene oxide
$C_{12}H_8$	acenaphthylene
C_6H_{13}	hexyl
r.t.	room temperature
C_3H_7	*n*-propyl
Δ	heating
$C_6H_2Me_4$	1,2,4,5-tetramethylbenzene
C_9H_8	indene

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