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Arene complexes of rare-earth metals

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Abstract. Data on syntheses, structures and reactivities of scandium, yttrium, lanthanum and lanthanide complexes with π-bonded ligands containing one or several six-membered aromatic rings are surveyed and systematised. The bibliography includes 107 references.

I. Introduction

Early investigations in the field of chemistry of organometallic compounds containing rare-earth metals were aimed at synthesising and studying compounds typical of organometallic chemistry, such as σ-alkyl(aryl), cyclopentadienyl, indenyl, fluorenyl, cyclooctadienyl, *etc*. derivatives. Complexes containing π-bonded arene ligands were studied later.[1] However, the chemistry of these compounds was extensively investigated in the last 12 years after the first benzene derivatives of lanthanides had been synthesized. The accumulated data allow some general conclusions to be drawn about the characteristic features of the synthesis, structures, the character of metal – ligand bonding and reactivity of π-arene lanthanide complexes belonging to a class of compounds unique in many respects. Particular types of π-arene lanthanide complexes were surveyed in the reviews.[2, 3] The present review is devoted to comprehensive and critical consideration of the available data on the synthesis, structures, the character of bonding, reactivity and catalytic activity of rare-earth metal complexes containing π-bonded six-membered aromatic rings, which were published before January 2000. Derivatives of stilbene, tolan and analogous compounds fall outside the scope of this review because π-electrons of multiple bonds of substituents in aromatic rings of these compounds are generally involved in Ln ligand interactions.

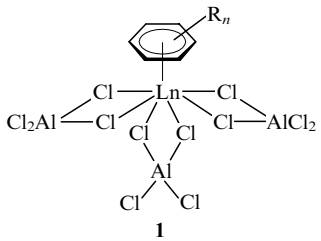
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II. Complexes of rare-earth metals with derivatives of benzene and its homologues

1. Arene chloroaluminate complexes

The chloroaluminate complex of samarium, $(C_6Me_6)Sm(AlCl_4)_3$, was the first complex of a rare-earth metal with a π-bonded arene ligand synthesised under conditions of the Friedel – Crafts reaction.[4 – 6] This procedure for the synthesis was extended to other complexes of the type **1**. The reactions were carried out with $1,3\text{-}Me_2C_6H_4$,[7] C_6H_6,[8 – 10] $Me_4C_6H_2$,[11, 12] MeC_6H_5 (see Ref. 13) and a large series of lanthanides (Y, Pr, Nd, Gd,[12] La,[8] Eu and Yb [13]). The compositions and structures of complexes of the type **1** indicate that the aromatic moiety is η^6-coordinated to the trivalent metal atom and serves as a neutral π-donor ligand. The average Ln – C distances [2.93 Å (Nd),[11] 2.90 Å (Sm),[7] 2.999 Å (Eu) [14] and 2.978 Å (Yb) [15]] are noticeably shorter than the sums 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 whole series of lanthanides).



1

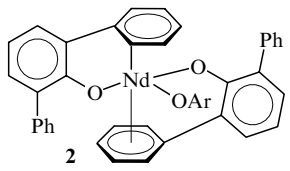
Ln = Y, Pr, Nd, Gd, La, Eu, Yb; R = H, Me; n = 0, 1, 2, 4.

The replacement of one of the bridging chlorine atoms by the alkyl group, for example, in the complexes $(C_6H_5Me)Ln.(AlCl_3Me)_3$ (Ln = Y or Nd) and $(C_6H_5Me)Nd(AlBr_3Et)_3$,[12] does not lead to a change in the character of the arene – metal bond. The divalent europium complex $(C_6Me_6)Eu(AlCl_4)_2$ has an analogous structure.[14]

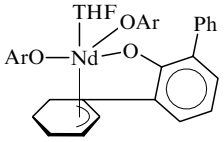
2. Arene aryloxide complexes

In aryloxides of lanthanides, there are nonvalent interactions between the metal atom and the benzene ring identical to those found in arene chloroaluminate complexes. The presence of the phenyl substituent at the *ortho* position of the aryloxy group [for

example, in the complex $Nd(OC_6H_3Ph_2\text{-}2,6)_3$ (**2**)] results in an intramolecular η^6-interaction between the lanthanide atom and one of the phenyl substituents of the phenoxy ligand. The phenyl substituent in the second phenoxy ligand is η^1-bonded to the Ln atom, whereas the third phenoxy ligand remains monodentate.[15–17] In the analogous complex $Nd(OC_6H_3Ph_2\text{-}2,6)_3(THF)$ (**3**), which differs by the presence of one THF molecule coordinated to the metal atom, only one $OC_6H_3Ph_2$-2,6 substituent serves as a chelate ligand, the multiplicity of the Ln–Ph π-bond decreasing (becoming triple).[16]



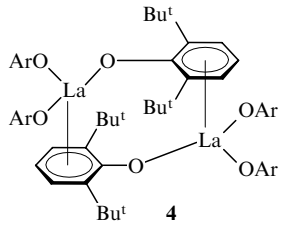
2



3

Ar = 2,6-$Ph_2C_6H_3$.

In lanthanide triphenoxides containing the *tert*-butyl substituents at positions 2 and 6, the metal atom is η^6-bonded to the phenoxide ligand to form the dimers $(2,6\text{-}Bu^t_2C_6H_3O)_2Ln(\mu\text{-}2,6\text{-}Bu^t_2C_6H_3O)_2Ln(OC_6H_3Bu^t_2\text{-}2,6)_2$ (**4**).[18,19]



4

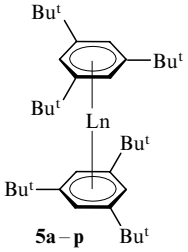
Ar = 2,6-$Bu^t_2C_6H_3$.

The Ln–Arn contacts (Arn is arene) are retained upon dissolution of complexes of the type **4** in nonsolvating solvents. However, π-bonds are cleaved in THF or upon addition of ammonia and the coordination site of the η^6-arene ligand in the resulting complexes is occupied by solvent molecules, which is indicative of low strength of the Ln–Arn bond. The Ln–C bond lengths in these fragments (the average distances are 2.986–3.061 Å) are virtually identical to the corresponding values in arene chloroaluminate complexes.

3. Bisarene complexes

Co-condensation of benzene and neodymium vapours on a surface cooled to −196 °C afforded a binuclear complex with composition $Nd_2(C_6H_6)_3$,[20] which was isolated as black insoluble crystals. The magnetic moment (3.42 μ_B) corresponds to the Nd(III) cation (3.68 μ_B[21]) 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 bisarene complexes of rare-earth metals of the $(1,3,5\text{-}Bu^t_3C_6H_3)_2Ln$ type (**5**) analogous to the well-known bisarene complexes of *d* transition metals were prepared by cocondensation of 1,3,5-tri-*tert*-butylbenzene and metal vapours at 75 K.[22–25] The structures and magnetic moments of the complexes **5** confirm the η^6-character of the bond between the neutral aromatic ring and the formally zero-valent metal atom.

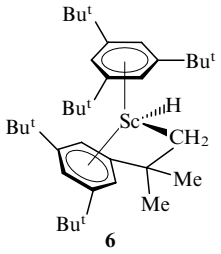


5a–p

Ln = Gd (**a**), Y (**b**), Ho (**c**), Nd (**d**), Tb (**e**), Dy (**f**), Er (**g**), Lu (**h**), Ce (**i**), Eu (**j**), Yb (**l**), La (**m**), Pr (**n**), Sm (**o**), Sc (**p**).

In gadolinium complex **5a** characterised 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). 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[26]). The yttrium (**5b**) and holmium (**5c**) complexes were found to have analogous structures.[3,22]

The stability of the compounds **5** depends on the nature of lanthanide. Thus the Yb, Nd, Gd, Tb, Dy, Ho, Er and Lu complexes are stable (some of them can be sublimed *in vacuo* without decomposition), whereas the Ce, Eu, Tm and Yb complexes do not form stable products. Derivatives of La, Pr and Sm are intermediate in stability. In the synthesis of the scandium complex, the formation of the expected sandwich $(1,3,5\text{-}Bu^t_3C_6H_3)_2Sc$ (**5p**) was accompanied by the formation of the complex $(\eta^6\text{-}Bu^t_3C_6H_3)[\eta^6,\eta^1\text{-}Bu^t_2(CMe_2CH_2)C_6H_3]ScH$ (**6**) containing Sc(II) due to the insertion of Sc at the C–H bond of the methyl group of the substituent.[27]



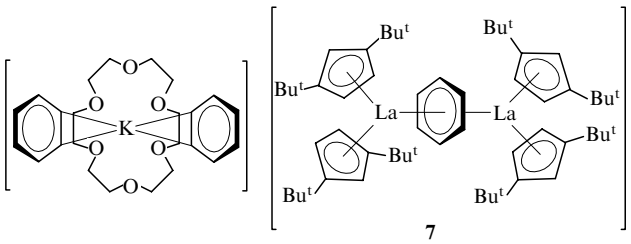
6

Since a strong arene–lanthanide π-bond can be formed if the metal atom adopts the d^1s^2 configuration, the difference in thermal stability of the complexes **5** was attributed to the difference in energy of promotion of $f^ns^2–f^{n-1}d^1s^2$ transitions for different lanthanides. Thermodynamic studies[25] confirmed the high stability of Ln–Arn bonds in bisarene complexes. Thus the enthalpies of cleavage of these bonds in the Yb, Gd, Dy, Ho and Er complexes are 72, 68, 47, 56 and 57 kcal mol^{-1}, respectively.[25]

The stability of bisarene complexes increases as the number and size of substituents in the aromatic ring increase as was exemplified by scandium derivatives.[3] Calculations by molecular mechanics[28] for $(C_6H_6)_2Gd$ and $(1,3,5\text{-}Bu^t_3C_6H_3)_2Ln$ (**5**) [Ln = Gd (**a**), Y (**b**) or Yb (**l**)] confirmed that the benzene complex is substantially less stable than the complexes **5a**,**b**,**l** containing the *tert*-butyl groups in the benzene ring. Quantum-chemical calculations[29,30] demonstrated that the metal atoms are bound to the benzene ligands primarily through back donation from the occupied $d_{\pm2}$ orbitals of the metal atom to the unoccupied π-orbitals of the benzene ligands.

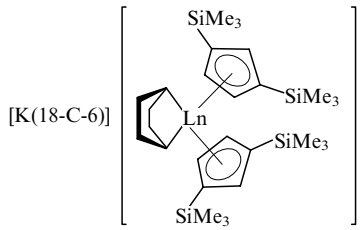
4. Complexes with benzene radical anions and dianions

Reduction of the cyclopentadienyl complex of lanthanum containing two *tert*-butyl substituents in the cyclopentadienyl rings, *viz.*, Cp^{tt}_3La, where $Cp^{tt} = \eta^5\text{-}C_5H_3Bu^t_2\text{-}1,3$, with an excess of potassium in benzene in the presence of 18-crown-6 (18-C-6) afforded a dark-red product. Subsequent heating of the latter in benzene at 70 °C gave rise to the dark-green ate-complex $[K(18\text{-}C\text{-}6)(\eta^2\text{-}C_6H_6)_2][(Cp^{tt}_2La)_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)]$ (**7**).[31] X-Ray diffraction analysis demonstrated that the bridging six-membered ring in the anionic moiety of the complex **7** is planar and the C–C bond lengths in this ring are almost identical. All La–C(benzene) bond lengths vary over a narrow range (2.75–2.79 Å). Based on these data, the structure of a salt containing two Cp^{tt}_2La(II) units η^6-bonded to the benzene anion was assigned to the complex **7**.



7

An analogous reaction of potassium with the complexes Cp^{ts}_3Ln [$Cp^{ts} = C_5H_3(SiMe_3)_2$-1,3; Ln = La, Ce, Pr or Nd] also afforded dark-red ionic complexes [K(18-C-6)][$Cp^{ts}_2Ln(C_6H_6)$] (**8a–d**). However, the cations in these complexes do not contain coordinated benzene molecules and the C_6H_6 ligand in the anionic moiety exists as the dianion of cyclohexa-1,4-diene η^6-bonded to the Cp^{ts}_2Ln unit with the trivalent Ln atom.[32,33] In the complex **8a**, two short La–C(cyclohexadiene) distances are 2.617 and 2.652 Å. In analogous complexes of cerium and neodymium **8b**,**c**, the corresponding bond lengths are 2.588 and 2.612 Å (Ce) and 2.555 and 2.572 Å (Nd).



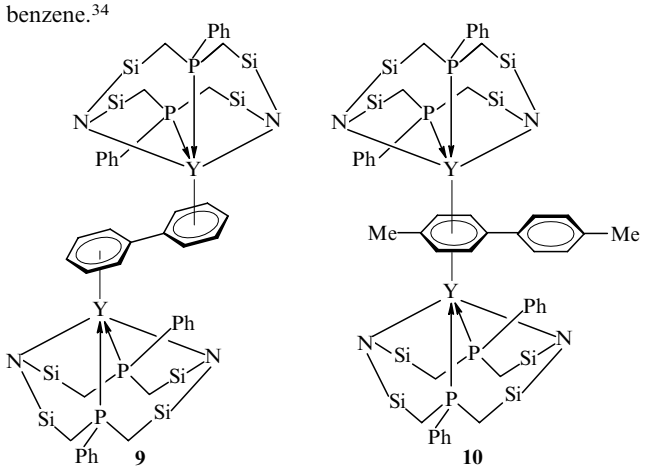
8a–d

Ln = La (**a**), C (**b**), Nd (**c**), Pr (**d**).

ESR studies demonstrated[33] that reduction of Cp^{ts}_3La with potassium in benzene in the presence of 18-C-6 afforded at least four metal-centred free-radical species. The authors believed that the latter are La(II) derivatives. In this stage, the reaction mixture was dark-blue-violet in colour, which then changed to dark-red.

5. Biphenyl complexes

Treatment of the yttrium(III) chloride complex with composition LYCl, where L = 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)$_2$(μ-PhPh) (**9**)† containing the biphenyl dianion as the bridging ligand.[34] The complex **9** was also prepared by the reaction of the σ-alkyl complex $LYCH_2SiMe_3$ {L = PhP[$CH_2(SiMe_2)N(SiMe_2)CH_2]_2$PPh} with benzene.[34]

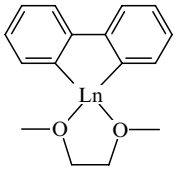


9 **10**

In the complex **9**, both rings in the biphenyl ligand remain virtually planar and the Y–C distances vary over a narrow range (2.675–2.738 Å), which are evidence of η^6-interaction. These distances (the average distance is 2.723 Å) are close to the Y–C bond lengths in the complex $Cp_3Y(THF)$ (the average distance is 2.71 Å)[35] and are somewhat larger than those in the complexes $[Cp_2YCl]_2$ (2.60 Å)[36] and $(C_5Me_5)_2YCl(THF)$ (2.659 Å).[37]

The reaction of LYCl with 3-MeC_6H_4Li also resulted in the formation of a C–C bond. According to the data of ^{1}H NMR and UV spectroscopy, the dark-blue reaction product is structurally similar to the complex **9**. However, 4-MeC_6Me_4Li under the same conditions gave the dark-brown compound ({PhP[CH_2. .$(SiMe_2)N(SiMe_2)CH_2]_2$PPh}Y)$_2$(μ-MePhPhMe) (**10**) in which both YL fragments are bound to the same ring of the $[MeC_6H_4C_6H_4Me]^{2-}$ anion.[34] The average Y–C distances in the fragments of **10** (2.676 and 2.699 Å) are somewhat shorter than the corresponding bond lengths in the complex **9**. ^{1}H NMR spectral studies of the complex **10** demonstrated that slow (within the NMR time scale) migration of one of the YL groups from one benzene ring to another occurs in solution. It was assumed[34] that such behaviour in solutions is also typical of other complexes with bridging Ar–Ar ligands.

Samarium and ytterbium powders activated with diiodoethane reacted with biphenylene at room temperature to form dark-coloured solutions.[38] Attempts to isolate reaction products in the individual state failed. However, their reactions with oxygen (giving rise to 1,1′-biphenyl-2,2′-diol), deuteromethanol (yielding a mixture of biphenyl and dideuterobiphenyl) and Me_2SiCl_2 (forming a mixture of biphenyl and 1,1-dimethylsilafluorene) were carried out. These results testify that the reactions of lanthanides with biphenylene lead to the cleavage of the four-membered ring giving rise to the lanthanide σ-complexes with biphenyl (**11**). It was suggested[38] 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 the complex **11**.



11

Apparently, an analogous product was formed in the reaction of octamethylbiphenylenedilithium with SmI_2.[38]

III. Complexes with naphthalene derivatives

It was found that reduction of anhydrous ytterbium diiodide with two equivalents of lithium naphthalenide in THF or dimethoxyethane (DME) afforded insoluble black pyrophoric powders with composition $(C_{10}H_8)Yb(THF)_3$ or $(C_{10}H_8)Yb(DME)$.[39–44] Based on the facts that the resulting compounds are diamagnetic [Yb(0) is diamagnetic] and their reactivities are surprisingly high (even for organolanthanides), it was originally conceived that these products are complexes of zero-valent ytterbium π-bonded to the neutral naphthalene ring. However, additional data on tetrahydrofuran complex **12** obtained more recently demonstrated that these compounds in fact contain the naphthalene dianion and the Yb^{2+} cation.

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

12

Analogous naphthalene complexes with samarium and europium[43,45–48] as well as 1-methylnaphthalene complex with ytterbium[40,48] were synthesised. The naphthalene complexes of samarium, europium and ytterbium, like alkali metal naphthalenides, are powerful reducing agents. However, the former complexes in contrast to naphthalenides do not react with naphthalene [the reactions could form radical-anionic derivatives of the type $(C_{10}H_8^{-\bullet})_2Ln(THF)_x$].

† Hereinafter, the methyl groups at the silicon atoms are omitted.

The reactions of equimolar amounts of LnI_2 (Ln = Eu or Yb) and sodium naphthalenide resulted in the replacement of only one iodide anion and afforded binuclear derivatives **13** containing the bridging naphthalene dianion rather than radical-anionic complexes $(C_{10}H_8^{-\bullet})LnI(THF)_x$.[49,50]

$$LnI_2 + C_{10}H_8Na \xrightarrow{DME} [ILn(DME)_2]_2(\mu\text{-}C_{10}H_8)$$
13

Ln = Eu, Yb.

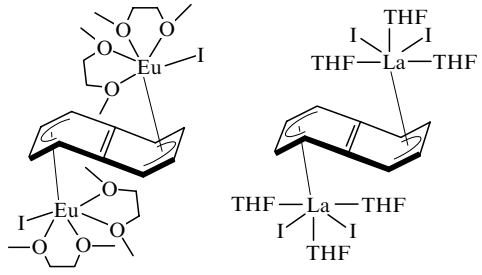
The $Ln(\mu\text{-}C_{10}H_8)Ln$ moiety containing the naphthalene bridging dianion (complex **14**) was also formed in the reaction of sodium naphthalenide with lanthanum iodide.[49] Analogous complexes were obtained for Ce, Pr, Nd and Gd.[50]

$$LaI_3 + C_{10}H_8Na \xrightarrow{THF} I_2La(THF)_3(\mu\text{-}C_{10}H_8)LaI_2(THF)_3$$
14

The stability of complexes of the type **14** decreases on going from light to heavy lanthanides. From Tb and onwards, attempts to isolate such complexes failed even at low temperature. The neodymium derivative **15** was synthesised by oxidation of divalent neodymium iodide with naphthalene in a solution in THF.[51]

$$NdI_2(THF)_5 + C_{10}H_8 \xrightarrow{THF} I_2Nd(THF)_3(\mu\text{-}C_{10}H_8)NdI_2(THF)_3$$
15

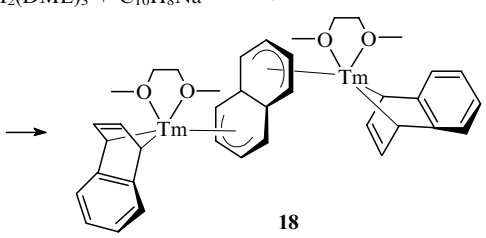
The naphthalene complexes of europium and lanthanum, *viz*., $[I_2Eu(DME)_2]_2(\mu\text{-}C_{10}H_8)$ (**16**) and $[I_2La(THF)_3]_2(\mu\text{-}C_{10}H_8)$ (**17**), respectively, were studied by X-ray diffraction analysis.[49] In these complexes, the metal atoms are located on the opposite sides of the plane of the bridging naphthalene ligand and are η^4-bonded to different rings. The naphthalene moiety is nonplanar and the dihedral angles between the rings are 5.8° and 15.2° in the complexes **16** and **17**, respectively. The shortest La–C and Eu–C distances are in the ranges of 2.782–2.808 and 2.815–2.858 Å, respectively.



16 **17**

With the aim of preparing halogen-free naphthalene complexes of lanthanides, the reactions of triiodides LnI_3 with a threefold excess of $C_{10}H_8Na$ were carried out.[43,52] After removal of the solvent, solid black or dark-brown amorphous substances were obtained from the resulting dark-brown solutions. Attempts to isolate individual products from these substances failed. The individual compound $[C_{10}H_8Tm(DME))]_2(\mu\text{-}C_{10}H_8)$ (**18**) was obtained only for thulium starting from the salt $TmI_2(DME)_3$.[53]

$$TmI_2(DME)_3 + C_{10}H_8Na \xrightarrow{DME}$$



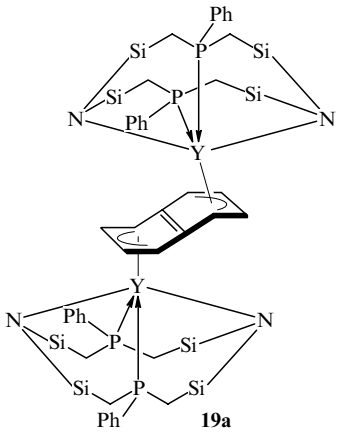
18

It is worthy of note that thulium was oxidised in the course of the reaction to the trivalent state in spite of the fact that $C_{10}H_8Na$ is a strong reducing agent. The trivalent state of thulium was confirmed by magnetic measurements and by the fact that the colour of the reaction mixture changed from green to red-brown. The compound **18** has the structure of a triple-decker sandwich. According to the valence balance, all three naphthalene groups in the complex exist as dianions. The central binuclear unit with the $\eta^4:\eta^4$-bonded bridging naphthalene ligand is structurally similar to those in the iodine-containing complexes **16** and **17**.

The lengths of the short Tm–C(bridging $C_{10}H_8$) bonds are in the range of 2.59–2.62 Å. The folding angle of the rings along the C(1)–C(4) line is 19.28°. Based on 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 (taking account of the difference in the ionic radii and coordination numbers of the metal atoms) to the Ln–C σ-bonds in the complexes $[Li(THF)_3].\{[(Me_3Si)_2CH]_3YbCl\}$ (the average distance is 2.375 Å),[54] $Cp^*CeCH(SiMe_3)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$, 2.535 Å)[55] and $Cp^*NdCH(SiMe_3)_2$ (2.517 Å)[56]

It was assumed[46,57] that black insoluble finely dispersed products formed upon reduction of $SmBr_3$ and $YbBr_3$ with sodium naphthalenide are metallic lanthanides. However, there are strong grounds to believe that these reactions, like the analogous reactions with iodides, afforded naphthalene complexes of lanthanides. Apparently, the results of reduction of $NdCl_3$ with lithium naphthalenide were also misinterpreted.[58] Reinvestigation[59] of reduction of $NdCl_3$ with insufficient lithium in THF in the presence of naphthalene demonstrated that the reaction performed under these conditions gave 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 has been reported previously.[60]

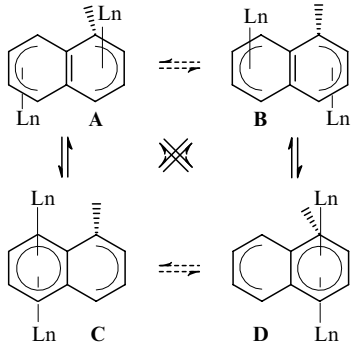
Binuclear complexes of the general formula $(\{PhP[CH_2.(SiMe_2)N(SiMe_2)CH_2]_2PPh\}Ln)_2Arn$ (**19a–d**) [Arn = $C_{10}H_8$, Ln = Y (**a**) or Lu (**b**); Arn = $C_{10}H_7Me$, Ln = Y (**c**) or Lu (**d**)] containing the Ln(μ-Arn)Ln group were prepared by the reactions of a mixture of potassium-intercalated graphite (KC_8) and naphthalene or 1-methylnaphthalene with the complex $(\{PhP[CH_2.(SiMe_2)N(SiMe_2)CH_2]_2PPh\}YCl)_2$ (**9**) or its lutetium analogue.[61] X-Ray diffraction analysis demonstrated that the fragments containing the phosphorus ligand bound to Y in the compound **19a**, like those in the complex $[I_2La(THF)_3)]_2(\mu\text{-}C_{10}H_8)$ (**17**), are located on the opposite sides of the bridging naphthalene ligand η^4-bonded to the Y atoms. 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 the 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 similar structure.



19a

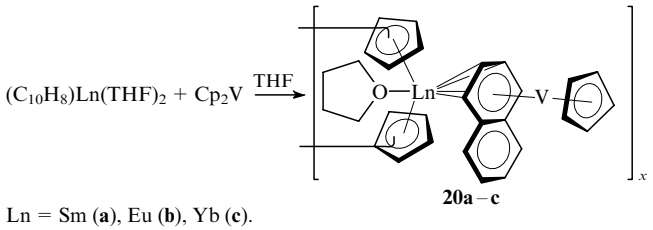
The $^{31}P\{^1H\}$ NMR spectra of all the four compounds are similar (the spectrum of the yttrium derivative has a doublet at

δ 21, $^1J_{YP}$ = 60 Hz), which is indicative of the equivalence of the phosphorus ligands. Based on this fact, it was suggested [61] that intramolecular migration of the {PhP[CH_2($SiMe_2$)N.($SiMe_2$)CH_2]$_2$PPh}Ln moieties between the naphthalene rings (structures **A**–**D**) occurs in solution. Apparently, the moieties migrate independently and, as a consequence, **A** is converted into **B** through the intermediates **C** and **D**.



R = H, Me; Ln = Y, Lu.

The lanthanide complexes [CpLn(THF)(μ-η^4 : η^6-$C_{10}H_8$)VCp]$_x$ (**20a**–**c**) containing the bridging naphthalene ligand were prepared by the reactions of naphthaleneytterbium, -europium or -samarium with vanadocene.[62, 63]

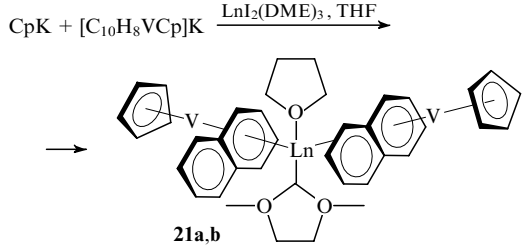


20a–**c**

Ln = Sm (**a**), Eu (**b**), Yb (**c**).

According to the data of ESR spectroscopy and magnetic measurements, the bridging naphthalene ligand in the complexes **20a**–**c** is neutral and the negative charge is located at the vanadium atom as a result of which the latter becomes formally zero-valent. 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.

Analogous lanthanide–vanadium complexes [CpV(μ-η^6 : η^6-$C_{10}H_8$)]$_2$Ln(THF)(DME) (**21**) were synthesised in THF by the reactions of samarium or europium diiodides with cyclopentadienylnaphthalenevanadium anions prepared *in situ*.[63] The reactions in hexane gave rise to monomeric complexes in which the rare-earth atom is coordinated to two CpV($C_{10}H_8$) units.

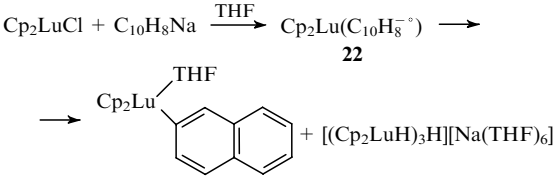


21a,b

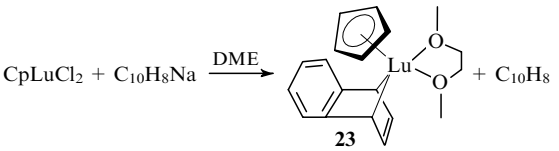
Ln = Sm (a), Eu (b).

The naphthalene ligands in the complexes **20** and **21** are planar. The Ln–C(naphthalene) bond lengths in the complex **20b** [Eu–C(α), 2.828 and 2.869 Å; Eu–C(β), 3.037 and 3.098 Å] are indicative of η^4-interaction in the CpLn($C_{10}H_8$)VCp moieties. In the quadruple-decker compound **21b**, the Eu–C bond lengths are in the range of 2.872–3.084 Å, *i.e.*, η^6-coordination occurs in the ($C_{10}H_8$)Eu($C_{10}H_8$) moieties.

The reaction of lithium naphthalenide with Cp_2LuCl proceeded through another pathway. In this case, the resulting (apparently, unstable) radical-anionic intermediate $Cp_2Lu(C_{10}H_8^{-\bullet})$ (**22**) underwent rapid conversions involving metallation of naphthalene and formation of hydride and naphthyl derivatives.[64]



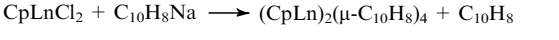
Reduction of $CpLuCl_2$ with sodium naphthalenide afforded the mononuclear complex (η^5-C_5H_5)Lu($C_{10}H_8$)(DME) (**23**).[65]



The molecular geometry of the complex is indicative of the σ-character of the bond between the lutetium atom and the naphthalene ligand whose coordinated ring loses aromaticity.

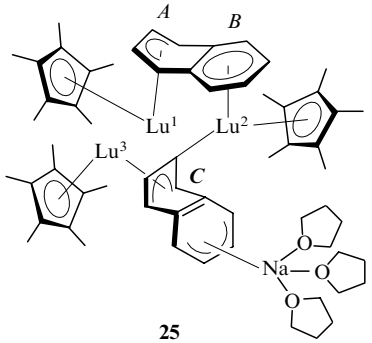
The Lu–C(α) bond lengths (2.406 and 2.397 Å) are comparable with the Lu–C σ-bond lengths in the complexes Cp_2LuBu^t(THF) (2.47 Å) [66] and $Cp_2LuCH_2SiMe_3$(THF) (2.376 Å).[67] The Lu–C(β) bond lengths (2.579 and 2.562 Å) are close to the Lu–C(Cp) bond lengths (2.65 Å), which suggests the presence of 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 the coordinated ring is 31.5°.[68] Therefore, the bond between the naphthalene ligand and the metal atom in this case may be characterised as $2\eta^1 : \eta^2(2\sigma,\pi)$ interaction.[64, 65, 68] Analogous Y, Gd, Er and Tm complexes were also prepared.[69]

In the reactions with $C_{10}H_8Na$ performed under comparable conditions, lanthanide derivatives characterised by lower potentials of Ln(II)/Ln(III) transitions (such as Sm and Yb) were reduced to form the binuclear Ln(II) complexes containing the bridging naphthalene group, *viz*., (CpLn)$_2$(μ-$C_{10}H_8$)$_4$ (**24**).[69]



Ln = Sm, Yb.

The reaction with the use of the pentamethylcyclopentadienyl derivative of lutetium, Cp^*LuCl_2, as the starting compound yielded the diamagnetic ate-cluster {[(Cp^*Lu)$_3$($C_{10}H_8$)($C_{10}H_7$)].[Na(THF)$_3$]}$^{2+}$ (**25**) whose trinuclear cation contains the naphthalene dianion and the naphthyl group with a charge of -3.[70]



25

The naphthalene dianion, which is not coordinated to 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. As in the complex **23**, the Lu–C

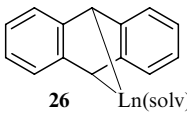
bond lengths of this fragment in **25** [Lu–C(α), 2.58 and 2.60 Å; Lu–C(β), 2.67 and 2.77 Å] and the folding angle along the C(α)–C(α) line (the dihedral angle is 172.5°) correspond to $2\eta^1:\eta^2$-interaction. The *B* ring remains planar and is η^6-bonded to the Lu(2) atom (the Lu–C bond lengths 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 dihedral angle along the C(α) line is 142.5°. The Lu(3)–C(α,β) distances are 2.44, 2.47, 2.54, and 2.59 Å, respectively. The naphthyl ring *C* is σ-bonded to the Lu(2) atom. The short Lu(1)–ring *C* (2.81 Å) and Lu(3)–ring *A* (2.72 Å) distances are, apparently, indicative of some degree of bonding in these fragments. It is not inconceivable that the anionic cluster contains a bridging proton bound to the Lu(1) and Lu(2) atoms. However, the presence of this proton has not been unambiguously established.

It was reported[71] that thin films of cerium and europium readily reacted with naphthalene in diethyl or dipropyl ethers at room temperature to form colourless solutions. Based on the spectral characteristics, it was concluded that pale-brown substances obtained after removal of the solvent and excess naphthalene are bis(naphthalene) π-complexes of zero-valent lanthanide of the bis(naphthalene)chromium type. However, this conclusion is in contradiction with the following facts: the products are pale in colour, which is untypical of neutral and charged arene complexes; under these conditions, naphthalene does not react with other lanthanides (Pr, Nd, Gd, Tb, Dy, Ho or Er); the reaction does not proceed in THF; the reaction with anthracene proceeds more slowly than that with naphthalene.

The reaction of acenaphthylene with permethylsamarocene readily proceeded in benzene giving rise to a dark-blue compound. According to the data of NMR and IR spectroscopy and elemental analysis, the compound can be described by the chemical formula $(Cp^*_2Sm)_2(C_{12}H_8)$.[72] The structure of the product was not established.

IV. Complexes with anthracene

Anthracene which possesses the higher electron affinity than naphthalene forms complexes with lanthanides in the direct reactions with ytterbium, samarium and cerium activated with diiodoethane.[73–75] Attempts to isolate these complexes in an individual state failed. However, structure **26** was assigned to the resulting complexes by reasoning from the products of reactions with MeOD, MeI and Me_3SiCl.



26

A film of metallic ytterbium prepared by concentrating a solution of the metal in liquid ammonia also reacted with anthracene in the presence of LiCl, NaBr, LiI, KI or Bu^n_4NI.[76] The authors believed that the reactions gave rise to complexes containing the anthracene radical anion with composition $Yb(C_{14}H_{10}^{-\bullet})_2\cdot n$MX. However, attempts to identify the reaction products were also unsuccessful. After washing of the substance with benzene, a violet powder containing the anthracene dianion, ytterbium and NaI in a ratio of 1 : 1 : 6 was obtained.

Anthracene complexes were prepared by the reactions of anthracene with naphthaleneytterbium in THF in the presence of alkali metal halides or by the reaction of YbI_2 with $C_{14}H_{10}Na$.[40,77] These complexes were isolated as black insoluble powders, which are similar in properties to naphthalene analogues. ESR spectral studies of these compounds and their hydrolysis products suggested the existence of an equilibrium between the radical-anionic (**A**) and dianionic (**B**) forms, with the latter predominating:

$$(C_{10}H_8)Yb(THF)_3 + C_{14}H_{10} + LiX \rightleftharpoons$$

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

or

$$Yb + C_{14}H_{10} \overset{MX}{\rightleftharpoons} \underset{\mathbf{A}}{(C_{14}H_{10}^{-\bullet})_2Yb\cdot n MX} \overset{C_{14}H_{10}}{\rightleftharpoons}$$

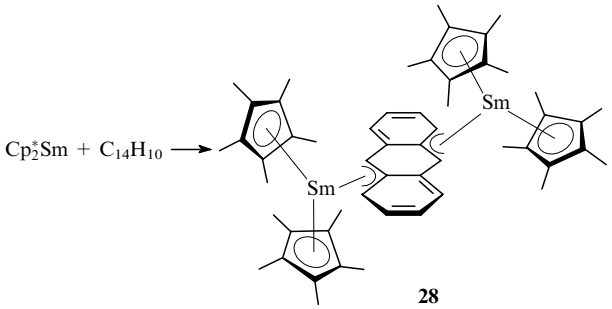
$$\rightleftharpoons \underset{\mathbf{B}}{(C_{14}H_{10}^{2-})Yb} + n\,MX.$$

Since the resulting complexes are poorly soluble, their high-quality crystals were not prepared and the structures could not be established by X-ray diffraction analysis. However, analogous investigations were successfully performed by the use of cyclopentadienyllanthanide derivatives. It appeared that rare-earth metals form two types of anthracene complexes through addition at either an edge or a plane; however, the arene ligand in both cases carries a negative charge −2.

The reaction of CpLuCl with the dianion or two radical anions of anthracene gave rise to heterobimetallic ate-complex **27** containing the anthracene dianion.[78]

$$\left.\begin{array}{l} CpLuCl + (C_{14}H_{10}^{-\bullet})Na^+ \\ CpLuCl + [C_{14}H_{10}^{2-}]Na_2^+ \end{array}\right\} \xrightarrow{THF} \underset{\mathbf{27}}{CpLu(C_{14}H_{10}^{2-})Na^+}$$

Neutral complexes of samarium $(Cp^*_2Sm)_2(\mu\text{-}\eta^3:\eta^3\text{-}C_{14}H_{10})$ (**28**) and lanthanum $(Cp^*_2La)_2(\mu\text{-}\eta^3:\eta^3\text{-}C_{14}H_{10})\cdot 2PhMe$ (**29**) with the anthracene dianion were prepared by oxidative addition of decamethylsamarocene to anthracene[72] or by metathesis of the lanthanum potassium complex with disodium anthracene.[79]



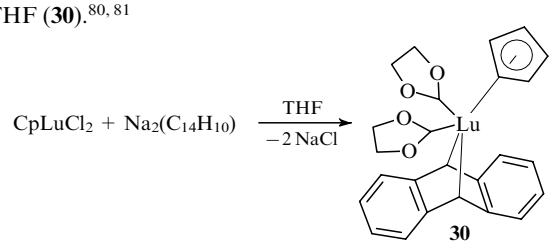
28

$$Cp^*_2La(Cl)K(DME)_2 + Na_2C_{14}H_{10} \xrightarrow{PhMe}$$

$$\longrightarrow \underset{\mathbf{29}}{(Cp^*_2La)_2(\mu\text{-}\eta^3:\eta^3\text{-}C_{14}H_{10})\cdot 2\,PhMe}$$

Both products are structurally similar. The planar anthracene dianion is $\eta^3:\eta^3$-bonded to two Cp^*_2Ln units located on the opposite sides of its plane. Apparently, the product of the reaction of Cp^*_2Sm with 9-methylanthracene, *viz.*, $(Cp^*_2Sm)_2C_{15}H_{12}$, has an analogous structure.[72]

The reaction of $C_{14}H_{10}^{2-}$ with $CpLuCl_2$ afforded a complex with different composition and structure, *viz.*, $CpLu(C_{14}H_{10}^{2-})\cdot 2THF$ (**30**).[80,81]



30

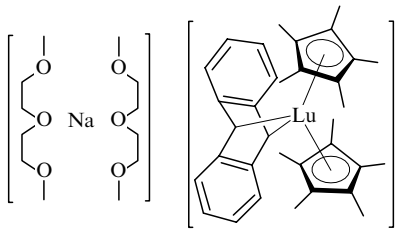
In the complex **30**, the character of the bond between the Lu atom and the arene ligand is analogous to that observed in the complex **23**, *i.e.*, it can be interpreted as σ,σ-interaction although

the Lu–C(9,10) distances (2.44 and 2.45 Å, respectively) are somewhat longer than the analogous contacts in the naphthalene derivative **23**, but are substantially shorter than those in the binulcear anthracene compound (2.683, 2.850 and 2.882 Å). The folding angle of the anthracene molecule along the C(9)–C(10) line is 38.7° (29.9° for the second symmetrically independent molecule in the crystal).

The complex **30** containing the anthracene dianion was also synthesised by the reaction of $CpLuCl_2$ with the anthracene radical anion. In this case, free anthracene was detected in the reaction mixture.[80,81]

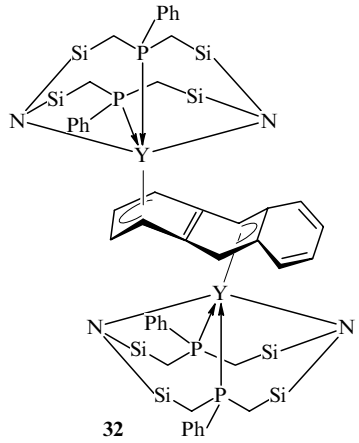
$$CpLuCl_2 + [C_{14}H_{10}^{-}]Na^{+} \xrightarrow[-NaCl]{THF} \underset{\mathbf{30}}{CpLu[C_{14}H_{10}^{2-}]\cdot 2THF} + C_{14}H_{10}$$

Unlike the lanthanum and samarium complexes, lutetium dicyclopentadienyl chloride gave the ate-complex $[CpLu(C_{14}H_{10}^{2-})].[Na^{+}(THF)]$ in the reactions both with $C_{14}H_{10}^{-\cdot}$ and $C_{14}H_{10}^{2-}$.[81] The replacement of coordinated THF by diglyme afforded complex **31**. The authors managed to grow perfect crystals of **31** and to establish its structure by X-ray diffraction analysis.[81] It appeared that the character of the bond between anthracene and the lanthanide atom in this compound is similar to that in the complexes $CpLu(C_{10}H_8)(DME)$ (**23**) and $CpLu(C_{14}H_{10}^{2-})$ (**30**). The arene ligand is folded along the C(9)–C(10) line (the dihedral angle is 40.1°). The shortest distances between the anthracene ligand and the lutetium atom [Lu–C(9,10) are 2.473 and 2.482 Å, respectively] are only 0.03 Å larger than the corresponding distances in the complex **30**.



31

The reaction of the aminophosphine yttrium complex **9** with anthracene in the presence of KC_8 yielded the binuclear complex $(\{PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh\}Y)_2(\mu\text{-}C_{14}H_{10})$ (**32**). The latter, like the anthracene derivatives **30** and **31**, contains the $C_{14}H_{10}^{2-}$ dianion.[61] The metal atoms in the compound **32** are located on the opposite sides of the aromatic ligand and are η^4-bonded to the central ring and one terminal ring.



32

The coordinated rings are folded along the C(1)–C(4) and C(9)–C(10) 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 **19a**. Based on the data of ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, it was assumed[61] that in solution the metal-containing moieties in the complex **32**, as those in the naphthalene derivative **19a**, migrate along the arene plane. It is significant that intermolecular migration of the $\{PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh\}Ln$ moieties in the anthracene complexes or in mixtures of anthracene and naphthalene analogues does not occur. This is evidence that the complexes do not dissociate in solution in spite of the ionic character of the Ln–Arn bond.

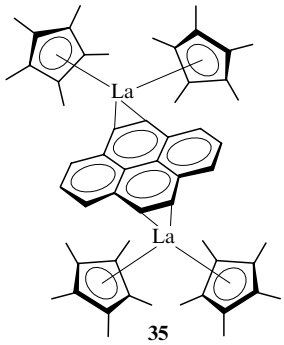
V. Pyrene and benzoanthracene derivatives

Pyrene can form three types of complexes with rare-earth metals.[82] The reaction of $Cp^*_2La(\mu\text{-}Cl)_2K(THF)_2$ (**33**) with the pyrene dianion in THF afforded red crystals with composition $[Cp^*_2La(THF)_2](C_{16}H_{11})$ (**34**) in low yield. The ^1H NMR spectrum of **34** has nine signals with equal intensities and one double-intensity signal (at δ 4.12). The authors believed[82] that these signals are indicative of the presence of the hydropyrene anion $C_{16}H_{11}$, which was, apparently, formed as a result of detachment of protons from the solvent.

$$\underset{\mathbf{33}}{Cp^*_2La(\mu\text{-}Cl)_2K(THF)_2} + C_{16}H_{11}^{2-} \xrightarrow{THF} \underset{\mathbf{34}}{[Cp^*_2La(THF)_2](C_{16}H_{11})}$$

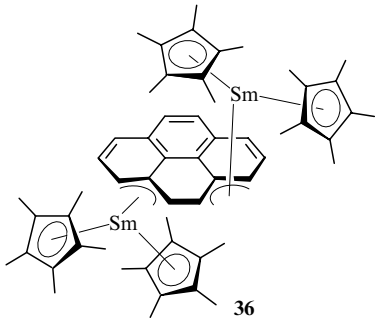
It was assumed[82] that the $[Cp^*_2La(THF)_2]^+$ cation does not form a strong bond with the aromatic anion, *i.e.*, the complex in solution exists as a solvent-separated ion pair.

The reaction of the ate-complex **33** with pyrene and potassium in toluene taken in a ratio of 2:2:1 gave rise to black-green crystals. The NMR spectrum of these crystals corresponds to the binuclear complex $(Cp^*_2La)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_{16}H_{10})$ (**35**). It was suggested[82] that the Cp^*_2La units in **35**, like those in the anthracene derivatives **29**, are located on the opposite side of the plane of the aromatic ligand and are bound to the opposite rings.



35

The samarium analogue $(Cp^*_2Sm)_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{16}H_{10})$ (**36**), which was prepared by the reaction of free pyrene with Cp^*_2Sm, differs in structure (according to the X-ray diffraction data) from **35**.[72] Both metallocene moieties in **36** 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.

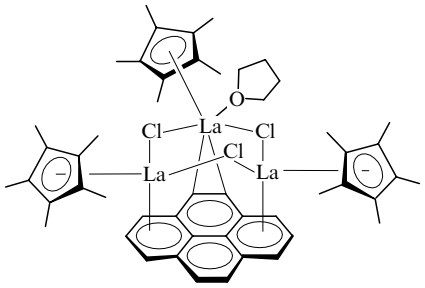


36

The angles between the samarium atoms and the plane of the polycyclic ligand are 117° and 120°. The Sm–C distances are in the range of 2.660–2.806 Å, which is somewhat larger than the

corresponding distances in the allylic complexes $Cp^*_2Sm(\eta^3\text{-}CH_2CHCHR)$ (2.551 – 2.643 Å),[83] but are substantially shorter than the Sm – C bonds in the arene chloroaluminate compounds $[ArnSm(AlCl_4)_3]$ (2.89 – 2.91 Å).[5, 7, 11]

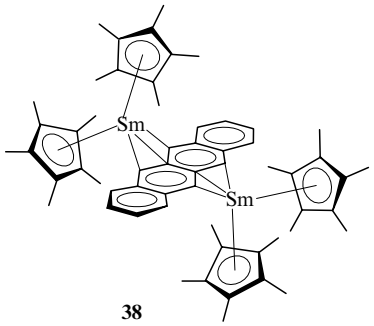
In the reaction with the use of the reagent ratio Cp^*_2Sm : pyrene : THF = 3 : 3 : 1 or in the reaction of pyrene and potassium with the monocyclopentadienyl complex $Cp^*LaCl(\mu\text{-}Cl)_2 \cdot Li(THF)_2$, pyrene was reduced to the trianion yielding the red-violet trinuclear complex $(Cp^*LaCl)_2[Cp^*LaCl(THF)](C_{16}H_{10})$ (**37**).[82] According to the X-ray diffraction data, 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 moiety containing an additional coordinated THF molecule forms only two short La – C(pyrene) contacts.



37

The lengths of the La – C bonds with the participation of the η^6-coordinated rings are in the range of 2.766 – 3.072 Å and the lengths of the La – C bonds with the participation of the η^2-coordinated rings are 2.823 and 2.841 Å, which are 0.1 Å larger than the corresponding contacts in the naphthalene complex $[I_2La(THF)_3]_2(\mu\text{-}C_{10}H_8)$ (**14**).

2,3-Benzoanthracene, like pyrene, readily reacts with Cp^*_2Sm to give green crystals of the complex $(Cp^*_2Sm)_2(\mu\text{-}\eta^3 : \eta^3\text{-}C_{18}H_{12})$ (**38**),[72] which is structurally similar to the pyrene complex **36**. Two Cp^*_2Sm fragments are coordinated at the edge of the arene ligand and are located on the opposite sides of its plane. The distance from the Sm atoms to this plane is 2.063 Å. Both metal atoms are bound to the same central ring. The Sm – C(Arn) bond lengths (2.688 – 2.828 Å) are similar to those in the pyrene analogue **36**.



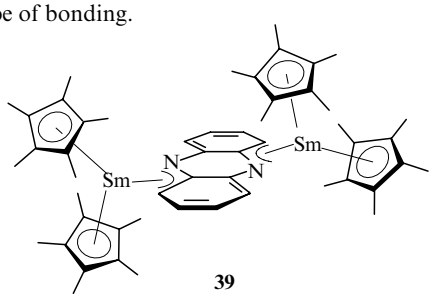
38

Interestingly, all permethylsamarocene complexes with arenes, unlike other arenelanthanides, are readily decomposed upon dissolution in THF to form $Cp^*_2Sm(THF)_2$ and the corresponding polycyclic hydrocarbon.[72] This lability of the Sm – Arn bond may be evidence for its nonvalent character, *i.e.*, the formation of these derivatives is not accompanied by redox processes and the coordination complexes $[Cp^*_2Sm(II)]_2(Arn^0)$ 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) in the course of the reaction and, consequently, the arene ligand in the complexes exists as the dianion. The Sm – Cp* distances in these complexes and their electronic spectra also correspond to trivalent samarium. The characteristic feature of the permethylsamarocene complexes with arenes is the allylic type of bonding between the arene ligand and the Cp^*_2Sm unit.[72]

VI. Complexes with heterocyclic aromatic ligands

The great 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.[1] In these complexes, the ligands can be either neutral or charged (–1 or –2). The charges are localised primarily on heteroatoms. However, examples of compounds similar in nature to typical bisarene complexes are also available. One of them, *viz.*, $(2,4,6\text{-}Bu^t_3C_5H_2N)_2Sc$, was prepared under conditions of the cryogenic synthesis.[3] It was suggested that this compound contains the formally zero-valent scandium atom and the neutral *tert*-butyl-substituted pyridine ligands. The molecule was represented as a planar-parallel sandwich.

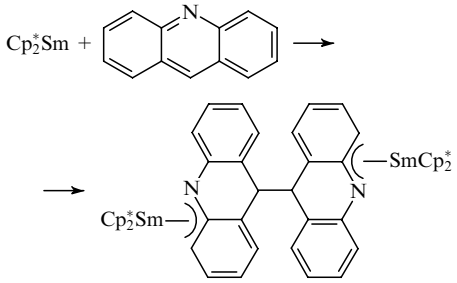
The reaction of Cp^*_2Sm with phenazine, like that with anthracene, afforded the binuclear complex $(Cp^*_2Sm)_2(\mu\text{-}\eta^3 : \eta^3\text{-}C_{12}H_8N_2)$ (**39**) in which the samarocene fragments are in the transoid orientation with respect to the $[C_{12}H_8N_2]^{2-}$ dianion.[72] The presence of three short contacts between the samarium atoms and the phenazine ligand are indicative of the allylic type of bonding.



39

The Sm – N bond length (2.360 Å) is slightly larger than the Sm – N σ-bond length in the complex $Cp^*_2SmN(SiMe_3)_2$ (2.306 Å),[84] which is evidence for substantial localisation of the charge on the nitrogen atoms, as in the complexes of the $Cp_3Ln(py)$ [1] and $Ln(bipy)_4$ types (bipy is 2,2′-bipyridyl).[85]

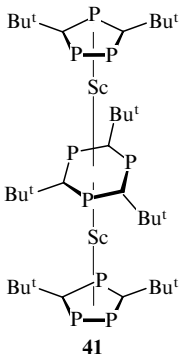
The reaction of permethylsamarocene with acridine was accompanied by dimerisation of the latter to form a C – C bond.[73]



40

The character of the metal – arene bond in the complex **40** is analogous to that in the phenazine derivative, *i.e.*, corresponds to η^3-interaction, with the Sm – N component predominating.

Arene lanthanide complexes of an unusual type were prepared by cocondensation of vapours of scandium and *tert*-butylphosphoalkyne $Bu^tC \equiv P$ at 77 K.[86] The reaction was accompanied by cyclisation of the phosphoalkyne giving rise to two products, *viz.*, dark-violet scandocene $(\eta^5\text{-}Bu^t_3C_3P_2)_2Sc$ containing divalent scandium and the green triple-decker complex $[(\eta^5\text{-}Bu^t_2C_2P_3)Sc]_2.(\mu\text{-}\eta^6 : \eta^6\text{-}Bu^t_3C_3P_3)$ (**41**) containing formally monovalent scandium. The valence states of the scandium atoms in both complexes were unambiguously established by UV and ESR spectroscopy and magnetic measurements. The structure of the triple-decker complex was confirmed by X-ray diffraction analysis.[87] The central six-membered ring in the complex **41** is located on a crystallographic mirror plane. All P – C bond lengths in this ring have closely similar values (1.793 – 1.807 Å).



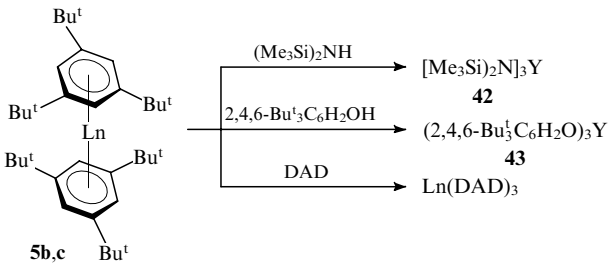
41

It is worthy of note the distance from Sc to the central ring in the compound **41** is noticeably shorter (1.787 Å) than the analogous distance in the bisarene complex $(Bu^t_3C_6MeH_2)_2Sc$ (1.983 Å).[87] In spite of the valence state +1 untypical of scandium, the compound **41** is quite stable and can be even sublimed *in vacuo* at 250 °C. The magnetic moment (3.98 μ_B) of **41** is somewhat smaller than the value calculated for four unpaired electrons, which was attributed to the presence of an orbital contribution.[87]

VII. Reactivity of arene lanthanide complexes

The chemical properties of complexes of rare-earth metals with π-bonded arene ligands were studied primarily using naphthalene derivatives as examples. For compounds with other aromatic hydrocarbons, only the most common characteristics are known. All arene lanthanide complexes exist as dark-coloured solids, which are readily oxidised in air (often with ignition). It was found that bisarene complexes of formally zero-valent Sc, Y, Nd, Gd, Tb, Dy, Ho, Er and Lu are thermally stable under an inert atmosphere or *in vacuo*. Some of them can even be sublimed with insignificant decomposition at 100 °C (at 10^{-4} mm Hg). These complexes are readily soluble in aromatic and aliphatic hydrocarbons. Complexes with arene dianions are virtually insoluble.

The yttrium complex $(1,3,5\text{-}Bu^t_3C_6H_3)_2Y$ (**5b**) readily reacted with phenol, $2,4,6\text{-}Bu^t_3C_6H_2OH$ and hexamethyldisilazane to form tri(aryloxide) (**42**) and yttrium tris(trimethylsilyl)amide (**43**) in good yields. The reaction of the holmium complex **5c** with bi-*tert*-butyl-1,3-diazabuta-1,3-diene (DAD) also resulted in complete replacement of the arene ligands.[3]



Ln = Y (**b**), Ho (**c**); DAD = $Bu^tN{=}CHCH{=}NBu^t$.

All $(Arn)_2Ln$ complexes are efficient catalysts of ethylene polymerisation.

Naphthalene lanthanide complexes of all types exhibit very high reactivities with respect to many inorganic, organic and organometallic compounds. Essentially in all cases, these complexes act as strong reducing agents comparable in reducing ability to alkali metal naphthalenides. The reactions were carried out in THF or DME at room or lower temperature. Generally, the yields of the products many of which were characterised by X-ray diffraction studies are higher than 60%–70%. Hence, these reactions may be recommended as preparative (often the only possible) procedures for the synthesis of organolanthanide compounds. The important advantage 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 the complexes $(C_{10}H_8)Ln(THF)_x$ are listed in Table 1.

The compounds $(C_{10}H_8)Ln(THF)_x$ also exhibit high reactivity in catalytic processes. Thus the complex $(C_{10}H_8)Yb(THF)_3$ catalyses hydrogenation of hex-1-ene, stilbene, isoprene and piperylene at room temperature under atmospheric pressure of H_2 yielding the corresponding hydrocarbons.[41] Tolan was hydrogenated to form *trans*-stilbene and diphenylethane. In the presence of 1%–5% of $(C_{10}H_8)Yb(THF)_3$, styrene, methyl methacrylate, ethyl acrylate, isoprene and piperylene formed polymers at room temperature.[48] The conversion reached 100% in several hours. 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. Naphthaleneytterbium catalyses polymerisation of epoxides and their reactions with CO_2. In the latter case, a mixture of monomeric and polymeric alkyl carbonates was obtained.[48] It is interesting to note that naphthalene complexes of 'trivalent' lanthanides, which were not isolated in the individual state, appeared to be efficient catalysts of polymerisation of conjugated dienes.[43] The reactions of the latter [like that of $(C_{10}H_8Tm)_2(C_{10}H_8)$] with cyclopentadiene afforded the corresponding Cp_3Ln in 15%–60% yield depending on the metal.[52, 53]

It was found [58] 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 as has been suggested in Ref. 58) readily reacted with ketones and aldehydes to yield the corresponding diols or ethylene derivatives as a results of coupling of the substrate.

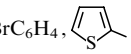
Generally, mixed-ligand complexes containing naphthalene as well as the iodine atom, the cyclopentadienyl substituent or the double-decker $CpV(C_{10}H_8)$ moiety bound to the rare-earth element react analogously to compounds of the $(C_{10}H_8)Ln(THF)_3$ type, *i.e*., the attack occurs primarily on the $(C_{10}H_8)Ln$ group. 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 most typical reactions are given in Table 2.

The chemical properties of anthracene lanthanide complexes are analogous to 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). Triphenylmethane did not enter into the reaction at all.[76] Deuterolysis of the complexes $(C_{14}H_{10})Ln(THF)_x$ (Ln = Sm or Yb) gave rise to 9,10-dideutero-9,10-dihydroanthracene,[48, 74] 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%). It is noteworthy that attempts to alkylate naphthalene in the reactions of naphthaleneytterbium with different alkyl halides have not met with success. In all cases, only unsubstituted naphthalene was obtained. ‡

For anthracene mixed-ligand complexes of lanthanides, only the reaction of $CpLu(C_{14}H_{10})(THF)_2$ with iron pentacarbonyl giving rise to the heterobimetallic product with composition $[CpLu(THF)]Fe(CO)_4$ was reported.[106]

‡ Unpublished data of the author of the present review.

Table 1. Reactions of the naphthalene complexes $(C_{10}H_8)Ln(B)_x$ (Ln = Sm, Eu or Yb; B = THF or DME, x = 2 or 3).

Substrate	Products	Ref.
O_2	$Ln_2O_3 + C_{10}H_8$	48
H_2	$LnH_2 + C_{10}H_8$	88, 89
H_2O	$C_{10}H_{10} + Ln(OH)_3$	48
Bu^tOH	$(Bu^tO)_2Ln + C_{10}H_8$	see [a]
R_2NH [R = Et, $N(SiMe_3)_2$]	$(R_2N)_2Ln + C_{10}H_8 + C_{10}H_{10} + H_2$	48
CpH	$Cp_2Ln + C_{10}H_8 + H_2$	48
IndH[b]	Ind_2Yb	see [a]
FluH[c]	Flu_2Yb	see [a]
$CpCH_2CH_2OH$	$[(\eta^5\text{-Cp})CH_2CH_2(\eta^1\text{-O})]Yb(B) + C_{10}H_8 + H_2$	90
$CpCH_2CH(Me)OH$	$[(\eta^5\text{-Cp})CH_2CH(Me)(\eta^1\text{-O})]Yb(THF) + C_{10}H_8 + H_2$	90
$CpCH_2CH(CH_2OBu)CH_2OH$	$[(\eta^5\text{-Cp})CH_2CH(CH_2OBu)CH_2(\eta^1\text{-O})]Yb(THF) + C_{10}H_8 + H_2$	90
$CpSiMe_2NHBu^t$	$[(\eta^5\text{-Cp})SiMe_2(\eta^1\text{-NBu}^t)]Yb(THF) + C_{10}H_8 + H_2$	90
$C_5Me_4HSiMe_2OSiMe_2OH$	$\{[(\eta^5\text{-Cp})Si(Me_2)OSi(Me_2)(\eta^1\text{-O})]Yb(THF)\}_2 + C_{10}H_8 + H_2$	91
$HC\equiv CH$	$LnC_2(THF)_x + C_{10}H_8 + H_2$	45
$PhC\equiv CH$ [d]	$(PhCH=CHCH=CHPh)Ln(DME)_2 + C_{10}H_8$	92
Ph_2Hg [e]	$Ph_2Yb(THF)(\mu\text{-Ph})_3Yb(THF)_3 + Ph_3Yb + Hg + C_{10}H_8$	93
Ph_3GeH [e]	$(Ph_3Ge)_2Yb(THF)_4 + C_{10}H_8$ $(Ph_3Ge)_2Eu(DME)_3 + C_{10}H_8$	88, 94
Ph_4Sn [e]	$Ph_3SnYb(THF)(\mu\text{-Ph})_3Yb(THF)_3 + (Ph_3Sn)_2Yb(THF)_4 + C_{10}H_8$	95, 96
Ph_6Sn_2 (see [e])	$(Ph_3Sn)_2Yb(THF)_4 + C_{10}H_8$	96
Cp_2V[d]	$CpVC_{10}H_8VCp$ $[CpLn(THF)C_{10}H_8VCp]_n$	62, 63, 97
Cp_2Ni [e]	Cp_2Yb	97
Cp_2Co [e]	Cp_2Yb	97
Cp_2Cr [e]	$Cp_2Yb + (C_{10}H_8)_2Cr$	97
DAD[e]	$Yb(DAD)_3 + C_{10}H_8$	98
bipy[e, f]	$[Yb(\mu_2\text{-bipy})(THF)_3]_3$	99
PhN=NPh[e]	$[Yb_4(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}Ph_2N_2)_4(\mu_3\text{-PhN})_2(THF)_4]$	39
see [f]	$[Sm_4(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}Ph_2N_2)_4(\mu_3\text{-PhN})_2(THF)_6]$	47
$PhC\equiv CPh$ [h]	$[CpLu(DME)]_2[1,1\text{-}\mu\text{-}4,4\text{-}\mu\text{-PhCC(Ph)=(Ph)CCPh}] + C_{10}H_8$	100
S_8 (see [f])	$SmS(THF) + C_{10}H_8$	101
RX (R = Ph, C_6F_5, X = Br, I)	RLnX (Sm, Yb)	46
RX (R = Ph, 4-BrC_6H_4, , X = Br)	RLnX (Sm, Yb)	57
Ph_2CO (H^+)	$(Ph_2COH)_2$	48
PhCHO (H^+)	$(PhCHOH)_2$	48
(H^+)	$HOCH_2(CH_2)_2CH_2OH + C_{10}H_8$	48
CO_2	$C_{10}H_8(COOH)_2$	48
CO	$C_{10}H_8(COOH)_2$	48

[a] Unpublished data of the author of the present review; [b] Ind is 9-indenyl; [c] Flu is 9-fluorenyl; [d] for Eu and Yb; [e] for Yb; [f] for Sm; [g] for Lu.

Table 2. Reactions of the naphthalene mixed-ligand lanthanide complexes.

Complex	Substrate	Products	Ref.
$[LaI_2(bipy)_2(THF)_3]_2[C_{10}H_8]$	bipy	$LaI_2(bipy)_2(DME) + C_{10}H_8$	102
	bipy	$LaI_2(bipy)(DME)_2 + C_{10}H_8$	102
$[YbI(DME)_2]_2(C_{10}H_8)$	bipy	$YbI(bipy)(DME)_2$	103
$Cp^*Lu(C_{10}H_8)(DME)$	C_{60}	$Cp^*Lu(C_{60})(DME)$	104
$CpLu(C_{10}H_8)(DME)$	H_2O	$Lu(OH)_3 + C_{10}H_{10} + CpH$	65
	O_2	$Lu_2O_3 + C_{10}H_8$	65
	CpH	$Cp_3Lu + C_{10}H_{10} + C_{10}H_8 + H_2$	65
	$PhC\equiv CPh$	$[CpLu(DME)]_2(1,1\text{-}\mu\text{-}4,4\text{-}\mu\text{-PhCC(Ph)=(Ph)CCPh}] + C_{10}H_8$	99
$CpLu(C_{10}H_8)(THF)_2$	Ph_2N_2	$[CpLu(THF)]_2(Ph_2N_2)$	99
$(C_{10}H_8)[LnI(DME)_2]_2$ (see [a])	$PhC\equiv CH$	$[PhC\equiv CLnI(DME)_2]_2 + C_{10}H_8 + H_2$	95
$(C_{10}H_8)[EuI(DME)_2]_2$	Ph_3GeH	$Ph_3GeEuI(DME)_2 + C_{10}H_8 + H_2$	97
$[CpV(C_{10}H_8)YbCp(THF)]_n$	H_2O	$CpYbOH(THF)_2 + CpVC_{10}H_8$	105
	CO	$Cp_2Yb + CpVC_{10}H_8$	105
	CO_2	$Cp_2Yb + CpVC_{10}H_8$	105
	$Cr(CO)_6$	$Cp_2Yb + CpVC_{10}H_8 + Cp_2V + CpVC_{10}H_8VCp + C_{10}H_8$	105
	CpTl	$Cp_2Yb + CpVC_{10}H_8$	105
	Ph_2N_2	$[CpYb(THF)_2]_2(Ph_2N_2)_2 + CpVC_{10}H_8$	105

[a] For Eu and Yb.

VIII. Conclusion

Based on analysis of the available data, the characteristic features of complexes of rare-earth metals with π-bonded arene ligands were revealed. First, it should be noted that these compounds exist in the two major forms, *viz*., with neutral arene or with the arene dianion. Forms with arene carrying a charge −1 or −3 are untypical of these complexes. Apparently, these forms can be obtained and exist only under particular 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 § or DAD) exhibiting polyvalence.[107] The mode of bonding of lanthanide with arene ligands can vary from η^2 to η^6. The Ln atom can be coordinated both at the plane of the arene ligand and at its edge. The character of the Ln–Arn bond in complexes with neutral arene and formally zero-valent lanthanide is similar to the character of the metal–arene bond in complexes of *d* 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 neutral ligands coordinated to the Ln^{3+} cation {complexes of the $(Arn)Ln[(\mu\text{-}Cl)_2AlCl_2]_3$ or $Ln(OC_6H_3Ph_2\text{-}2,6)_3$ types}, the *d* orbitals of the metal atoms are unoccupied and interactions occur, 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 $(X_2Ln)^+$ cations and the arene dianion (naphthalene lanthanide complexes and related derivatives) 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 electron density from the π-orbitals of arene to the unoccupied orbitals of the metal atom. In spite of the high (judging from the geometric parameters of the molecules) energy of the metal–arene bond, naphthalene lanthanide complexes exhibit very high reactivity. At the same time, these complexes are readily accessible owing to which they show promise as a source of lanthanides or lanthanide-containing fragments in the synthesis of other derivatives of rare-earth metals.

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