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Review

# Complexes of lanthanoids with neutral π donor ligands

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**Abstract**

The synthesis, structures and reactions of lanthanoid complexes with alkenes, alkynes and arenes have been reviewed. Whilst the discussion is centred on neutral π donors, including intramolecular π-arene–lanthanoid bonding, some formal $[Sm^{III}(C_5Me_5)_2(\pi\text{-donor})^-]$ complexes, derived from $Sm(C_5Me_5)_2$ and neutral π donors, have been included, especially examples which readily dissociate into the reactants. Metal–carbon bond lengths for lanthanoid(II or III) complexes have been conveniently analysed and compared by subtraction of the appropriate lanthanoid ionic radius for the formal coordination number. Derived values in the approximate range 1.70–2.10 Å are typical, with higher values often associated with intramolecular π-arene–Ln coordination or dimerization through intermolecular π-arene–Ln bonding. Lower values, 1.40–1.70 Å, can carry implications of charge transfer, e.g. $Ln^{II} - L^0 \rightarrow Ln^{III} - (L)^{-1}$ or may be partly a geometric consequence of other bonding in the molecule. The significantly covalent arene–lanthanoid(0) complexes have stronger bonding than in Ln(II or III)–(π donor) derivatives and occupy a unique place in organolanthanoid chemistry.

*Keywords:* Lanthanoid; π donor ligands; Organolanthoid chemistry

## 1. Introduction

Organolanthanoid chemistry is dominated by complexes of charged π donor ligands, such as cyclopentadienide ($C_5H_5^-$), pentamethylcyclopentadienide-($C_5Me_5^-$) and cyclooctatetraenide($C_8H_8^{2-}$), and mixed species with charged π donors and alkyl or aryl groups are also well established [1–6], e.g. $Ln(C_5X_5)_2R$ (X = H or Me; R = alkyl, aryl, hydride or amide). There are also an increasing number of neutral or anionic complexes with alkyl or aryl groups and no π donor ligands [1–6]. These frequently have associated neutral donor ligands, often derived from the solvent, e.g. tetrahydrofuran (THF), or other anionic ligands, e.g. halide or aryloxide. There are very few homoleptic aryls or alkyls [1–6]. The abundance of organometallics declines in the series lanthanoid(III) > lanthanoid(II) > lanthanoid(0) > lanthanoid(IV) organometallics. More recently, a number of complexes with neutral π donors, e.g. olefins, alkynes and arenes, have been prepared in III, II and 0 oxidation states. These complexes not only have considerable intrinsic interest, as hard lanthanoid ions would not be expected to have a strong affinity for such ligands, but also are considered to play a role in some catalytic reactions. This review describes complexes of lanthanoids with $\eta^2$-alkene, η-alkyne and $\eta^6$-arene donors, as well as compounds with intramolecular Ln–π-arene bonds. Complexes with non-hydrocarbon neutral π donors, $H_2$, CO and $N_2$ are briefly considered.

We have also included some of the important complexes $[Sm^{III}(C_5Me_5)_2(\pi\text{-acid})^{-1}]$, because they are formed by reaction of $Sm(C_5Me_5)_2$ with neutral π donors, and because they readily dissociate into the reactants despite the change in formal oxidation state on complex formation. This ready dissociation is a property more usually associated with complexes of neutral π donors. Complexes of the type $Ln(C_{10}H_8)(THF)_n$ (Ln = Sm, Eu or Yb; $C_{10}H_8$ = naphthalene; $n = 2–4$) [7–9] were initially considered to be zero-valent lanthanoid complexes [7], but their properties (see for example [9]) differ substantially from those of authentic arenelanthanoid(0) complexes (Section 3.2). Moreover, a recent crystal structure of the formally analogous $LuCp(C_{10}H_8)(dme)$ (Cp = cyclopentadienyl; dme = 1,2-dimethoxyethane) indicates that there is $\eta^2$-(C(1), C(4)) bonding of essentially a $C_{10}H_8^{2-}$ ion to $Lu^{3+}$ [10] (see also next section). Thus the $Ln(C_{10}H_8)(THF)_n$ complexes are considered to be Ln(II) derivatives of $C_{10}H_8^{2-}$ and outside the scope of the review. That these complexes are not zero valent is also indicated by

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preparations of anthracene mono- and di-anion complexes, namely $Yb(C_{14}H_{10}^{\cdot-})_2 \cdot nMX$ (e.g. MX = LiCl, NaBr or KI) [11] and $[Na(diglyme)_2]^+[LuCp_2(C_{14}H_{10})]^-$ (diglyme = bis(2-methoxyethyl) ether) [12].

## 2. $\eta^2$-Alkene complexes of lanthanoids

The insertion of olefins into M–C, M–H and M–N bonds constitutes one of the most important steps in a variety of catalytic and stoichiometric reactions of olefins with lanthanoid organometallics, hydrides and organoamides [13–20]. In several cases, $\eta^2$-olefin–lanthanoid complex intermediates were proposed [4,17,20]. The first $\eta^2$-olefin–lanthanoid complex was isolated by Burns and Andersen [21] from the reaction

$$Yb(C_5Me_5)_2 + Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2 \longrightarrow \underset{\mathbf{1}}{(C_5Me_5)_2Yb(\mu\text{-}\eta:\eta^2\text{-}C_2H_4)Pt(PPh_3)_2} \quad (1)$$

An important factor in the formation of an isolable olefin complex (**1**) is that the Lewis basicity of the olefin is maximized by the $\pi$ donor properties of platinum(0) [21]. The complex has the further significance of being the first X-ray-characterized lanthanoid(II)–d-block transition metal heterobimetallic. In the structure (Fig. 1), there is an $\eta^2$-ethylene ligand bridging $Pt(Ph_3P)_2$ and $Yb(C_5Me_5)_2$ units with a $\langle Yb\text{–}C(C_2H_4)\rangle$ of 2.781 ± 0.006 Å and a C–Yb–C angle of 29.9(1)°. The bond parameters for the $Pt(Ph_3P)_2$ moiety in the bimetallic are almost indistinguishable from those of uncomplexed $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$, whilst the parameters for the $Yb(C_5Me_5)_2$ unit are similar to those of $Yb(C_5Me_5)_2(THF)$ ($\langle Yb\text{–}C(C_5Me_5)\rangle$, 2.67 ± 0.02 and 2.66 ± 0.01 Å respectively) [4]. This latter result indicates that **1** can be regarded as having formal seven-coordinated ytterbium [1]. Subtraction of the ionic radius (1.08 Å [22]) for seven-coordinated $Yb^{2+}$ from $\langle Yb\text{–}C(C_2H_4)\rangle$ gives 1.70 Å, compared with 1.59 Å

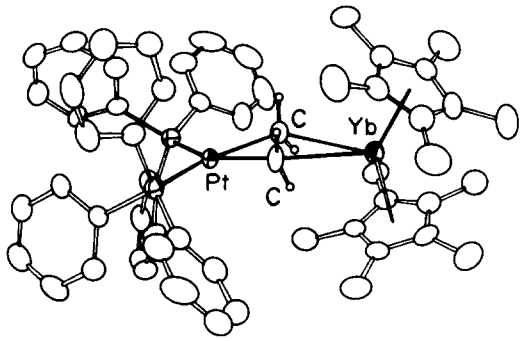



Fig. 1. $(Me_5C_5)_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)$ (**1**). (Reprinted with permission from the *Journal of the American Chemical Society.*)

for similar treatment of $\langle Yb\text{–}C(C_5Me_5)\rangle$, the latter being at the low end of the range (1.64 ± 0.04 Å [23]) for a variety of f-block cyclopentadienyls. IR spectroscopy provides no convincing evidence for olefin coordination, whilst solution NMR spectra indicate the following chemical exchange process which persists even at −70°C in $C_7D_8$:

$$\mathbf{1} \rightleftharpoons Yb(C_5Me_5)_2 + Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2 \quad (2)$$

Thus the olefin coordination to $Yb(C_5Me_5)_2$ seems to be weak with an effect on bond lengths comparable with that of THF.

The samarium complex $(C_5Me_5)_2Sm^{II}(\mu\text{-}\eta^2:\eta^5\text{-}C_5H_5)Sm^{III}(C_5Me_5)_2$ (**2**) has been prepared by the following reactions [24]:

$$2Sm(C_5Me_5)_2(THF)_2 + C_5H_6 \longrightarrow \mathbf{2} + 4THF + \tfrac{1}{2}H_2 \quad (3)$$

$$Sm(C_5Me_5)_2(C_5H_5) + Sm(C_5Me_5)_2 \longrightarrow \mathbf{2} \quad (4)$$

Whilst syntheses in toluene invariably give brown **2**, brown solutions from syntheses in hexane may either give **2** or a mixture of orange–red $Sm(C_5Me_5)_2(C_5H_5)$ and green $Sm(C_5Me_5)_2$ depending on isolation conditions. The X-ray structure (Fig. 2) indicates that the complex may be considered to involve $\eta^2$ coordination of the cyclopentadienide ring of neutral $Sm^{III}(C_5Me_5)_2\text{-}(\eta^5\text{-}C_5H_5)$ to a $Sm^{II}(C_5Me_5)_2$ group, i.e. $Sm^{II}(C_5\text{-}$

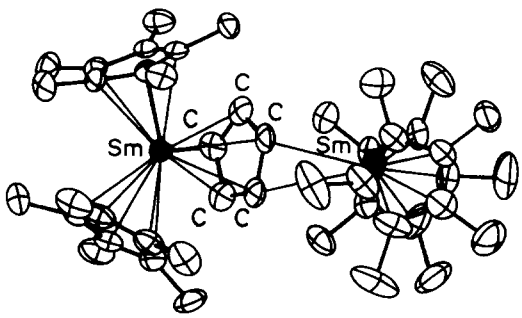



Fig. 2. $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$ (**2**). (Reprinted with permission from the *Journal of the American Chemical Society.*)

[1] The formal coordination numbers used in this review are based on the number of electron pairs avialable on the ligand. Thus the essentially ionic cyclopentadienylanthanoids are considered to contain $\eta^5$-Cp ligands, a six-electron donor, which formally occupies three coordination sites. Similarly neutral $\eta^6$-arenes are six-electron donors and occupy three coordination positions and $\eta^2$-alkenes and $\eta^2$-alkynes one coordination position (and this is justified from bond distances). In more complex cases, e.g. where there is electron transfer to alkynes or alkenes, the coordination number model is discussed with the example. Formal coordination numbers provide a basis for comparison of structures of rare earth complexes with different coordination numbers by subtraction of appropriate ionic radii [22] for the different coordination numbers (see for example Ref. [23]).

$Me_5)_2(\mu\text{-}\eta^2:\eta^5\text{-}C_5H_5)Sm^{III}(C_5Me_5)_2$. Thus it can be viewed as approximating an $Sm^{II}(\eta^2$-olefin) complex. In general, the structural parameters of the trivalent samarium in **2** are similar to those of $Sm(C_5Me_5)_2(C_5H_5)$. However, $\langle Sm^{III}\text{–}C(C_5H_5)\rangle$ is longer for **2** (2.80 Å) than for $Sm(C_5Me_5)_2(C_5H_5)$ [24] (2.74 Å), consistent with the bridging role of the cyclopentadienyl group in **2**. For the samarium(II) unit, $\langle Sm\text{–}C(C_5Me_5)\rangle$ (2.81 Å) is between corresponding values for eight-coordinated $Sm(C_5Me_5)_2(THF)_2$ (2.86 Å) and six-coordinated Sm $(C_5Me_5)_2$ (2.79 Å) [25], consistent with formal seven coordination. Subtraction of the ionic radius (1.22 Å) for seven-coordinated $Sm^{2+}$ [22] from $\langle Sm^{II}\text{–}C(C_5Me_5)\rangle$ gives 1.59 Å, which corresponds to the value derived from $\langle Yb^{II}\text{–}C(C_5Me_5)\rangle$ of **1**. $\eta^2$-Binding of the $C_5H_5$ group to Sm(II) is indicated by $Sm^{II}$–C distances of 2.986(8) and 3.180(9) Å compared with 3.78 Å or more for the other three ring carbon atoms [24]. Subtraction of the seven-coordinated $Sm^{2+}$ ionic radius gives 1.77 and 1.96 Å. Comparison with the corresponding value (1.70 Å) for **1** suggests that $\eta^2$-binding of $C_5H_5$ in **2** is weaker than $\eta^2$ attachment of $(C_2H_4)Pt(PPh_3)_2$ in **1**. The magnetic moment of **2** [24] is consistent with that expected for a class I mixed-valence system. In solution, the NMR spectrum of **2** shows time-averaged signals.

Another complex that can be considered to contain a pseudo-Ln–($\eta^2$-olefin) linkage is $[(\eta^5\text{-Cp})V^0(\mu\text{-}\eta^6:\eta^2\text{-}C_{10}H_8)Yb^{II}(\mu\text{-}\eta^5:\eta^5\text{-Cp})(THF)]_n$ (**3**) [26]. This has been obtained by two routes:

$$nYb(C_{10}H_8)(THF)_2 + nVCp_2 \longrightarrow \mathbf{3} + nTHF$$

$$nYbI_2(THF)_2 + nK[VCp(C_{10}H_8] + nKCp \longrightarrow \mathbf{3} + 2nKI + nTHF$$

There is a polymeric chain $\{[Yb^{II}(\mu\text{-}\eta^5:\eta^5\text{-Cp})]^+\}_n$ (Fig. 3(a)) and to each ytterbium is additionally coordinated a THF molecule and the neutral naphthalene ligand of a $[V^0(\eta^5\text{-Cp})(\eta^6\text{-}C_{10}H_8)]^-$ ion through two adjacent carbon atoms (Yb–C, 2.63(1) and 2.87(1) Å) (Fig. 3(b)) [26]. Both V and Yb are bonded to the same ring of the naphthalene ligand (Fig. 3). Subtraction of the ionic radius for eight-coordinated $Yb^{2+}$ (1.14 Å [22]) from the Yb–$C(C_{10}H_8)$ distances gives 1.49 and 1.73 Å. The former is much shorter than corresponding values for **1** and **2**, whilst the latter is comparable with values for **1**. The Yb–$C(7)(C_{10}H_8)$ contact (3.01(1) Å) gives a value of 1.87 Å, which could also (see **2**) be considered bonding, but its proximity can be clearly viewed as a fortuitous consequence of formation of the $\eta^2\text{-}C_{10}H_8$–Yb linkage.

In $LuCp(C_{10}H_8)(dme)$ [10], the strong $\sigma$ bonding of the naphthalenide dianion through C(1) and C(4) is accompanied by a significant Lu($\eta^2$-olefin) interaction through C(2) and C(3). Subtraction of the ionic radius for eight-coordinated $Lu^{3+}$ [22] from Lu–C(2) (2.579(8)

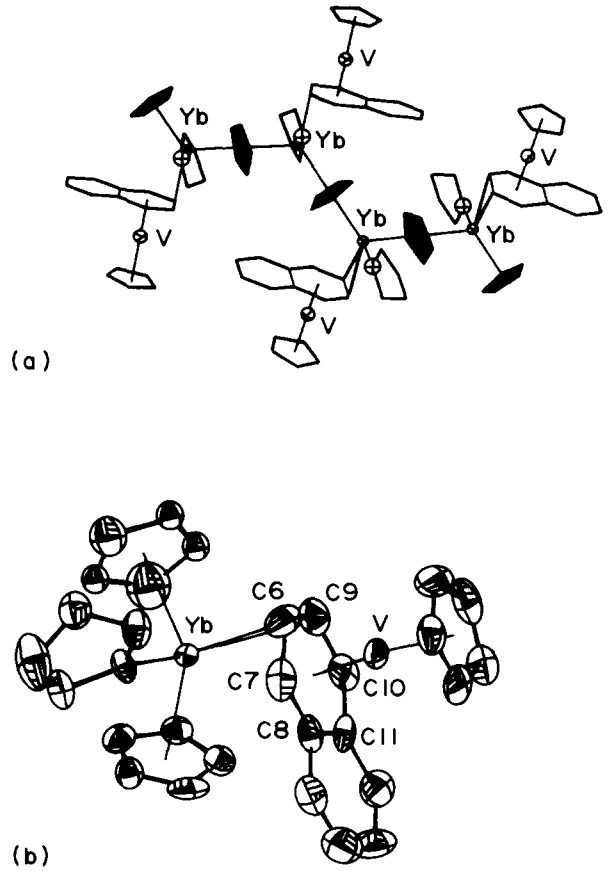
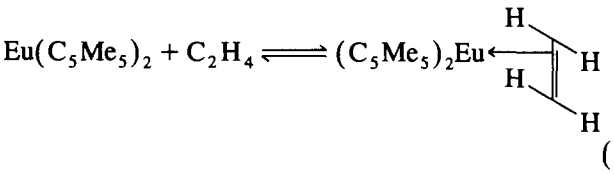



Fig. 3. The molecular structure of $[(\eta^5\text{-Cp})V(\mu\text{-}\eta^6:\eta^2\text{-}C_{10}H_8)Yb(\mu\text{-}\eta^5:\eta^5\text{-Cp(THF)}]_n$ (**3**) (a) showing the $\{[Yb(\mu\text{-}\eta^5:\eta^5\text{-Cp})]^+\}_n$ zigzag chain and (b) showing the Yb coordination environment. (Reprinted with permission from *Inorganica Chimica Acta.*)

Å) and Lu–C(3) (2.562(8) Å) [10] gives 1.60 and 1.58 Å respectively. However, this close proximity is at least in part a consequence of the strong $\sigma$ attachment of C(1) and C(4) and must be affected by the overall charge of the ligand (see for example **5** in Fig. 4 below).

Although no organolanthanoid–ethylene complex has been isolated, interaction between the olefin and $Eu(C_5Me_5)_2$ has been detected by $^1H$ NMR spectroscopy [27]. Addition of incremental amounts of $Eu(C_5Me_5)_2$ to a solution of ethylene in $C_6D_{12}$ at constant $[C_2H_4]$ causes downfield displacement and broadening of the ethylene resonance. This behaviour is in accordance with complexation of the $\pi$ system of the ethylene

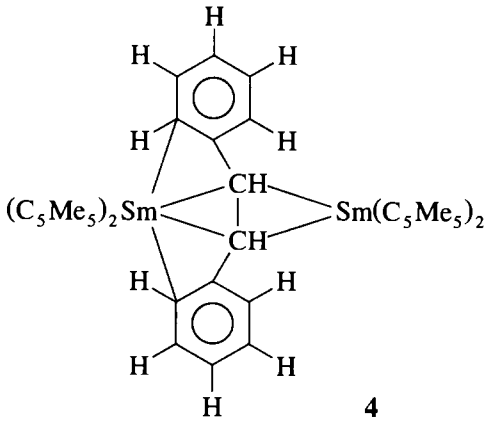



(5)

and delocalization through the ligand framework of polarization-derived carbon-centred unpaired spin den-

sity [27]. Europium(0) complexes $Eu(C_2H_4)_n$ have been prepared by codeposition of Eu atoms with ethylene at 12 K, either neat or doped with Ar or Xe [28]. Both $Eu(C_2H_4)$ and species with $n > 1$ were characterized by visible and IR spectroscopy.

Bonding in **1** and $(C_5Me_5)_2Eu(C_2H_4)$ can be viewed as weak, essentially ionic interactions between the lanthanoid Lewis acid and $\pi$ electron density of the olefins. However, stronger and more complex bonding results in complexes formed by reaction of $Sm(C_5Me_5)_2$ with *cis*-stilbene and styrene [29]. In $C_6D_6$, $Sm(C_5Me_5)_2$-$(THF)_2$ causes isomerization of *cis*-stilbene into *trans*-stilbene but with no intermediate complex detected. With use of unsolvated $Sm(C_5Me_5)_2$, complex formation is detectable by $^1H$ NMR spectroscopy. From reaction of *cis*-stilbene with $Sm(C_5Me_5)_2$ in hexane, the complex $[Sm(C_5Me_5)_2]_2(\mu\text{-}\eta^2:\eta^4\text{-PhCHCHPh})$ (**4**) was isolated. Although satisfactory bond distances and angles could not be obtained by X-ray crystallography, the connectivity of the atoms was established.




**4**

The magnetic moment of (**4**) is intermediate between those expected for Sm(II) and Sm(III) complexes [29].

From reaction of $Sm(C_5Me_5)_2$ with styrene, the complex $[Sm(C_5Me_5)_2]_2(\mu\text{-}\eta^2:\eta^4\text{-}CH_2CHPh)$ (**5**) was isolated and the structure (Fig. 4) established by X-ray crystallography. The overall geometry is similar to that of $[Sm(C_5Me_5)_2]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$ (below) with $\eta^2$ coordination of the olefinic double bond on both sides to an $Sm(C_5Me_5)_2$ moiety, and near coplanarity of the two samarium atoms and the two olefinic carbons [29]. In addition, the *ipso* and one *ortho* carbon atom of the phenyl ring are bonded to one samarium atom. The magnetic moment of **5**, $^{13}C$ NMR data and the lengthened C–C(alkene) distance (1.468(22 Å)) from those (1.28–1.368(6) Å) of free styrenes indicate that each samarium is in the +3 oxidation state and that considerable electron density has been transferred from the initially +2 samarium atoms to the styrene double bond. Thus, the complex may be formally regarded as $\{[Sm^{III}(C_5Me_5)_2]^+\}_2[PhCHCH_2]^{2-}$ by contrast with **1–3** and $(C_5Me_5)_2Eu(C_2H_4)$ where no significant charge transfer occurs. The Sm–C(alkene) distances

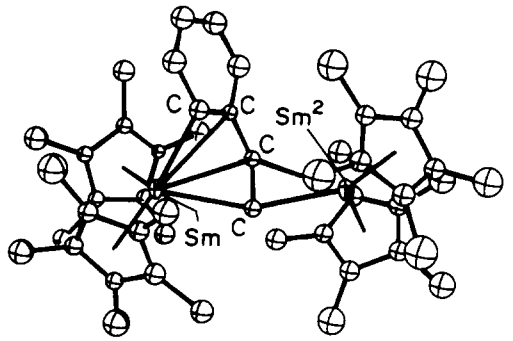



Fig. 4. $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2:\eta^4\text{-}CH_2CHPh)$ (**5**). (Reprinted with permission from the *Journal of the American Chemical Society*.)

(Sm(1)–C, 2.537(15) and 2.647(15) Å; Sm(2)–C, 2.674(15) and 2.732(15) Å) unusually are shorter than the corresponding Sm–C($C_5Me_5$) distances, and the shortest approaches the range 2.484(14)–2.511(8) Å for Sm–C(hydrocarbyl) of eight-coordinated $Sm(C_5Me_5)_2$-R(THF) complexes. Subtraction of the ionic radius for eight-coordinated $Sm^{3+}$ (1.08 Å [22]) from the Sm(1)–alkene distances gives 1.46 and 1.57 Å, much shorter than corresponding values for **1** and **2**, and consistent with a bonding model in which $PhCH^-$–$CH_2^-$ acts as ligand to trivalent Sm(1) [2]. Sm(2), with additional bonding contacts to two aromatic carbon atoms (Sm(2)–C(aryl), 2.850(16) and 2.772(17) Å), can be regarded as ten-coordinated if the aromatic carbon atoms are individually bonded or nine coordinated if the interaction is viewed as one of double-bond $\pi$ density with samarium. With the ten-coordinated model preferred by Evans et al. [29], subtraction of an ionic radius for ten-coordinated $Sm^{3+}$ (1.17 Å, interpolated from Shannon's [22] data), from Sm(2)–C(alkene) gives 1.50 and 1.56 Å, comparable with values for Sm(1) above. (Values for the nine-coordinated model (1.54 and 1.60 Å) are little different.) A similar subtraction for the Sm–C(aryl) bonds gives 1.68 and 1.60 Å, which compare with 1.70 Å for **1** where the olefin is viewed as occupying one coordination site. A nine-coordinated model would give values of 1.72 and 1.64 Å. On this basis, attachment of the aromatic ring could be viewed as a $\pi$ interaction occupying one coordinate site. Despite the occurrence of redox on formation of **5**, the complex is readily decomposed on addition of THF [29]:

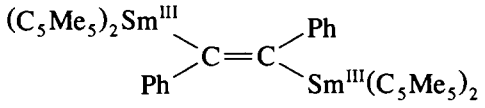
$$\mathbf{5} + 4THF \longrightarrow 2Sm(C_5Me_5)_2(THF)_2 + PhCH{=}CH_2 \quad (6)$$

[2] However, one value derived from Yb–C($C_{10}H_8$) of **3** is 1.49 Å and the metal is in the +2 oxidation state. Nevertheless, the average value for **5** (1.52 Å) is significantly less than the average (1.61) Å for **3**.

The ready occurrence of reaction (6), which would be expected for a $Sm^{II}$–olefin complex, is a reason for inclusion of **5** in this review.

## 3. $\eta^2$-Alkyne complexes

Following observations that lanthanoid metal atoms react with alkynes [30,31], the complex $[(C_5Me_5)_2Sm]_2$-(PhCCPh) (**6**) was generated from reaction of $Sm(C_5Me_5)_2(THF)_2$ with diphenylacetylene [32]. Although a crystal structure could not be obtained, a samarium (III) enediyl structure was favoured by spectroscopic data and *trans* stereochemistry preferred on consideration of steric factors.




**6**

Subsequently, two lanthanoid-$\eta$-alkyne complexes have been characterized crystallographically, namely $Yb(C_5Me_5)_2(\eta^2\text{-MeC}{\equiv}\text{CMe})$ (**7**) [33] and $[Sm(C_5Me_5)_2]_2(\mu\text{-}\eta^2:\eta^2\text{-PhC}_4\text{Ph})$ (**8**) [34]. There are striking differences between these structures.

Complex **7** was isolated with a quantitative yield from the following reaction in pentane:

$$Yb(C_5Me_5)_2 + MeC{\equiv}CMe \longrightarrow \mathbf{7} \quad (7)$$

Vibrational spectra of solid **7** and solution NMR spectra indicate that the alkyne is only weakly perturbed on coordination to ytterbium. The X-ray structure (Fig. 5) indicates that the bond parameters for coordinated 2-butyne do not differ significantly from those of the free ligand, whilst the geometry of the $Yb(C_5Me_5)_2$ moiety is very similar to that in $Yb(C_5Me_5)_2(THF)$ [4]. Thus **7** can be viewed formally as a seven-coordinated Yb(II) complex. Subtraction of the ionic radius for seven-coordinated $Yb^{2+}$ [22] from the average Yb–C (alkyne) distance ($2.850 \pm 0.010$ Å) gives 1.77 Å, somewhat longer than the value for **1** and much longer than the value (1.58 Å) derived from $\langle Yb\text{–}C(C_5Me_5)\rangle$. Bonding of the alkyne to ytterbium thus appears weaker than that of the alkene $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ in **1**.

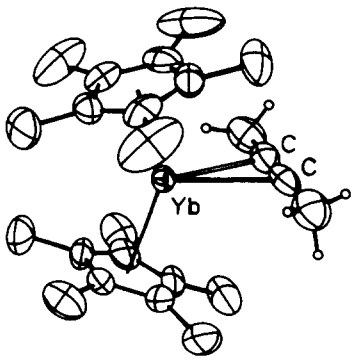



Fig. 5. $(Me_5C_5)_2Yb(\eta^2\text{-MeC}{\equiv}\text{CMe})$ (**7**). (Reprinted with permission from the *Journal of the American Chemical Society.*)

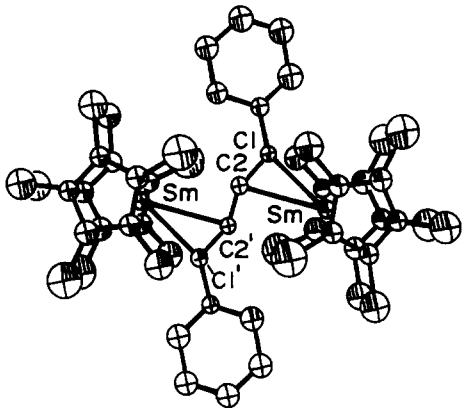



Fig. 6. $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}C_4Ph_2)]$ (**8**). (Reprinted with permission from the *Journal of the Chemical Society, Chemical Communications.*)

The complex $[Sm(C_5Me_5)_2]_2(\mu\text{-}\eta^2:\eta^2\text{-PhC}_4\text{Ph})$ (**8**) was initially prepared by the following reaction in THF [34]:

$$Sm(C_5Me_5)_2(THF)_2 + PhC{\equiv}C\text{–}C{\equiv}CPh \longrightarrow \mathbf{8} \quad (8)$$

Physicochemical data and the X-ray crystal structure of **8** in the **8** · 2PhMe solvate (Fig. 6) are indicative of an arrangement involving Sm(III) and a butatriene dianion. The ligand bridges two $Sm^{III}(C_5Me_5)_2$ units, which are in a *trans* arrangement, with each original alkyne unit $\eta^2$ bond to one samarium. The former C≡C bonds are lengthened to 1.33(2) Å, whilst C(2)–C(2′) is shortened from 1.37–1.38 Å in free diyne ligands to 1.29(2) Å. This is consistent with change transfer from Sm(II) to the diyne, and delocalization of electrons over the four-carbon chain of the coordinated ligand. Coordination is quite asymmetrical with an Sm–C(1) distance of 2.48(1) Å and an Sm–C(2) distance of 2.76(1) Å. The former is in the range 2.484(14)–2.511(8) Å for Sm–C(hydrocarbyl) of eight-coordinated $Sm(C_5Me_5)_2R(THF)$ complexes [29], whilst the latter is near the longest Sm–C(alkene) distance for the ten-coordinated samarium of $[Sm(C_5Me_5)_2]_2(\mu\text{-}\eta^2:\eta^4\text{-PhCHCH}_2)$ (**5**). Subtraction of the ionic radius for eight-coordinated $Sm^{3+}$ [22] from Sm–C(1) and Sm–C(2) gives 1.40 and 1.68 Å respectively. The first is the smallest value associated with attachment of an initially neutral $\pi$-bonding ligand, whilst the second is close to the value for the $\eta^2$-bonded $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ ligand of **1** (see above).

Besides the simple synthesis by reaction (8), **8** has also been obtained by a variety of alkyne and alkynyl coupling reactions [35]:

$$2Sm(C_5Me_5)_2(CH(SiMe_3)_2) + 2PhC{\equiv}CH \longrightarrow \mathbf{8} + 2H_2C(SiMe_3)_2 \quad (9)$$

$$[Sm(C_5Me_5)_2H]_2 + 2PhC{\equiv}CH \longrightarrow \mathbf{8} + 2H_2 \quad (10)$$

$$2Sm(C_5Me_5)_2 + 2PhC{\equiv}CH \longrightarrow \mathbf{8} + H_2 \quad (11)$$

$$2[Sm(C_5Me_5)_2(C{\equiv}CPh)(THF)] \xrightarrow[\text{benzene}]{120^\circ C} \mathbf{8} + 2THF \quad (12)$$

Single crystals of **8** · 2PhMe obtained from the product of reaction (9) [35] were crystallographically different from those from reaction (8) [34] in the orientation of a toluene molecule. From reaction (12), single crystals of **8** · 2PhH were obtained, and had a structure similar to that of **8** · 2PhMe other than the difference in the lattice solvent [35]. The product of reaction (9) was originally proposed to be $[Sm(C_5Me_5)_2(\mu\text{-}C{\equiv}CPh)]_2$ [36].

A range of complexes with structures similar to **8** have been prepared owing to interest in the C–C coupling reactions (9)–(12) [37–39]. Thus the thermolabile compounds $[Ln(C_5Me_5)_2(C{\equiv}CR)]_n$ (Ln = La or Ce; R = Me) (Ln = Ce; R = $^t$Bu) obtained by the reaction

$$n[Ln(C_5Me_5)_2(CH(SiMe_3)_2)] + nRC{\equiv}CH \longrightarrow [Ln(C_5Me_5)_2(C{\equiv}CR)]_n + nCH_2(SiMe_3)_2 \quad (13)$$

rearrange in hydrocarbon solvents to give analogous $[(Ln(C_5Me_5)_2(\mu\text{-}\eta^2:\eta^2\text{-}RC_4R)]$ complexes [37]:

$$2[Ln(C_5Me_5)_2(C{\equiv}CR)]_n \longrightarrow n[(Ln(C_5Me_5)_2)_2(\mu\text{-}\eta^2:\eta^2\text{-}RC_4R)] \quad (14)$$

The complexes with Ln = Ce, R = Me or $^t$Bu, have been shown by X-ray crystallography to have structures similar to **8**.

In a parallel study, $[La(C_5Me_5)_2(CH(SiMe_3)_2)]$ was converted by phenylacetylene in toluene into $[(La(C_5Me_5)_2)_2(\mu\text{-}\eta^2:\eta^2\text{-}PhC_4Ph)]$ in a reaction similar to (9), and the resulting single crystals of $[(La(C_5Me_5)_2)_2(\mu\text{-}\eta^2:\eta^2\text{-}PhC_4Ph)]$ · 2PhMe were shown to be isostructural with **8** · 2PhMe [38]. With the bulkier tert-butylacetylene, $[La(C_5Me_5)_2(C{\equiv}C^tBu)]_2$ was obtained by reaction (13) (Ln = La; R = $^t$Bu; $n = 2$) and was quantitatively converted in toluene at 50 or 60°C into $[(La(C_5Me_5)_2)_2(\mu\text{-}\eta^2:\eta^2\text{-}^tBuC_4{}^tBu)]$ (reaction (14); Ln = La; R = $^t$Bu; $n = 2$) [38], the structure of which was also established by X-ray crystallography.

In an amplification and elaboration of the synthetic routes (10)–(12) to **8**, the complexes $[(Sm(C_5Me_5)_2)_2\text{-}(\mu\text{-}\eta^2:\eta^2\text{-}RC_4R)]$ (R = $Ph(CH_2)_2$ or $^iPr(CH_2)_2$) were prepared by the following reaction, and their structures determined by X-ray studies [39]:

$$2Sm(C_5Me_5)_2 + 2RC{\equiv}CH \longrightarrow [(Sm(C_5Me_5)_2)_2(\mu\text{-}\eta^2:\eta^2\text{-}RC_4R)] + H_2 \quad (15)$$

By contrast with reaction (10), $[Sm(C_5Me_5)_2H]_2$ reacted with the bulkier $^t$BuC≡CH to yield $[Sm(C_5Me_5)_2(C{\equiv}C^tBu)]_2$ and the unexpected

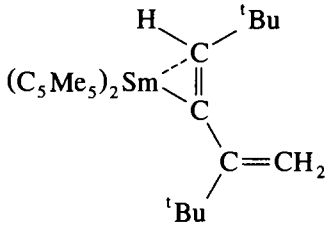
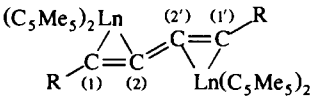



Table 1
Structural data for $[(Ln(C_5Me_5)_2)_2(\mu\text{-}\eta^2:\eta^2\text{-}RC_4R)]$ complexes




**(9)**

| Bond angle (°) or distance (Å) in **9** | L = Sm, R = Ph [a] | L = Sm, R = Ph [b] | L = Sm, R = $Ph(CH_2)_2$ [c] | L = Ce, R = Me [d] | L = Ce, R = $^t$Bu [e] | L = La, R = PH [f] | L = La, R = $^t$Bu [g] |
|---|---|---|---|---|---|---|---|
| C(1)–C(2)–C(2′) | 154(1) | 146.9(10) | 152.2(8) | 147(1)<br>146.5(9) | 154.7(5) | 148.6(13) | 153.7(3) |
| Ln–C(1) | 2.48(1) | 2.505(9) | 2.483(7) | 2.55(1)<br>2.53(1) | 2.607(4) | 2.557(10) | 2.642(3) |
| Ln–C(2) | 2.76(1) | 2.807(8) | 2.689(6) | 2.789(9)<br>2.779(9) | 2.748(4) | 2.823(9) | 2.761(3) |
| Ln–C(2′) | 3.03(1) | 2.963(9) | 2.909(6) | 2.89(1)<br>2.909(9) | 2.940(4) | 2.950(11) | 2.912(3) |
| C(1)–C(2) | 1.33(2) | 1.363(17) | 1.286(11) | 1.29(1)<br>1.31(1) | 1.312(5) | 1.36(2) | 1.310(4) |
| C(2)–C(2′) | 1.29(2) | 1.298(19) | 1.353(17) | 1.33(1) | 1.324(8) | 1.26(2) | 1.338(4) |

[a] **8** 2PhMe [34,35,39]. [b] **8** 2PhH [35,39]. [c] [39]. [d] Non-centrosymmetric complex [37]. [e] [37]. [f] [38]. [g] [38].

[39]. In addition $[Ln(C_5Me_5)_2(C{\equiv}CPh)(THF)]$ (Ln = Ce or Nd) complexes obtained by the reaction

$$[Ln(C_5Me_5)_2(N(SiMe_3)_2)] + PhC{\equiv}CH \xrightarrow{THF} [Ln(C_5Me_5)_2(C{\equiv}CPh)(THF)] + NH(SiMe_3)_2 \quad (16)$$

were converted in toluene at 125°C into $[(Ln(C_5Me_5)_2)_2(\mu\text{-}\eta^2:\eta^2\text{-}PhC_4Ph)]$ (Ln = Ce or Nd) in reactions similar to (12). X-ray crystallography showed the products to be isostructural with **8** [39]. Formation of these complexes for elements (La, Ce or Nd) without an accessible +2 oxidation state [37–39] unequivocally demonstrates that they are Ln(III) complexes of butatriene dianions rather than Ln(II) complexes of neutral diacetylenes (cf. **7**). This conclusion is in any case also evident from the detailed geometry and physical properties of **8** [34].

Details of five recent structures of $[(Ln(C_5Me_5)_2)_2(\mu\text{-}\eta^2:\eta^2\text{-}RC_4R)]$ complexes [37–39], **8** · 2PhMe [34,35,39] and **8** · 2PhH [35,39] are given in Table 1. Bond distances indicate clearly that the strongest bonding is to the terminal carbon atom C(1) of **9**. Subtraction of eight-coordinated $Ln^{3+}$ ionic radii [22] from Ln–C(1) lengths gives 1.40–1.48 Å compared with 1.60–1.73 Å for the adjacent Ln–C(2) bonds of **9**. The complexes with Ln = La or Ce and R = $^t$Bu have the nearest to symmetric binding of C(1) and C(2), as they have the longest Ln–C(1) distances and the shortest Ln–C(2). These effects may result from the bulk of the tert-butyl groups, which displace Ln away from C(1) towards C(2). It has been suggested [37] or inferred [38,39] that the triene dianions may be $\eta^3$ bonded to each metal with C(2) and C(2′) of **9** bound to each Ln atom. Subtraction of eight-coordinated $Ln^{3+}$ ionic radii from Ln–C(2′) gives 1.75–1.95 Å, values which could indicate bonding (cf. 1.70–1.96 Å for **1**, **2** and **7**). However, the close approach of C(2′) may simply be a consequence of attachment of C(2). Clearly, the structures are subject to subtle influences as can be seen by the minor differences between **8** · 2PhMe and **8** · 2PhH (Table 1). In addition, the largest C(1)–C(2)–C(2′) angles are associated with both the smallest and the two largest Ln–C(1) distances. There is alternation of C–C lengths for Ln = La, R = Ph, slightly longer terminal C–C bonds for two other complexes, and nearly equal C–C bonds or slightly longer C(2)–C(2′) bonds for the other four. These variations are not easily rationalized.

## 4. $\eta^6$-Arene complexes of lanthanoids

At present, three types of complex in which a lanthanoid metal is $\pi$ bonded to a six-membered aromatic ring, have been prepared, namely mono(arene), bis(arene) and intramolecular $\pi$-bonded compounds.

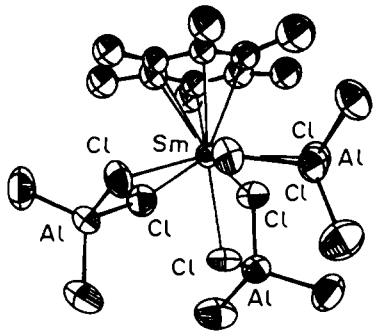



Fig. 7. $Sm(\eta^6\text{-}C_6Me_6)(AlCl_4)_3$ (**10**). (Reprinted with permission from the *Journal of the American Chemical Society*.)

### 4.1. Mono(arene) complexes

All complexes published so far have the composition $Ln(\eta^6\text{-arene})(AlCl_4)_n$ ($n$ = 2 or 3). Two synthetic methods have been used for the complexes and differ in the presence or absence of aluminium powder as a reagent. The former is the Fischer–Hafner method under reducing Friedel–Crafts conditions, whilst the latter is the so-called direct method. The first $\eta^6$-arene complex $Sm(\eta^6\text{-}C_6Me_6)(AlCl_4)_3$ (**10**) [40,41] was obtained by the reaction

$$SmCl_3 + 3AlCl_3 + C_6Me_6 \xrightarrow[\text{PhMe, reflux}]{Al} \mathbf{10} \quad (17)$$

Only a low yield of yellow **10** as **10** · $(PhMe)_{1.5}$ could be obtained, and observation of red solutions and deposition of red tar accompanying the reaction suggest concomitant formation of a Sm(II) species [40]. The X-ray crystal structure (Fig. 7) reveals formally nine-coordinated samarium with an $\eta^6\text{-}C_6Me_6$ ligand and three chelating $AlCl_4^-$ ligands. There is a distorted pentagonal bipyramidal arrangement of the centroid of the aromatic ring and the six chlorine atoms, with the centroid and one chlorine atom in the apical positions. Subtraction of the ionic radius for nine coordinate $Sm^{3+}$ [22] from ⟨Sm–C⟩ (2.89 Å) gives 1.76 Å (range, 1.69–1.82 Å). The range lies within values 1.70–1.96 Å derived from Ln–C(alkene or alkyne) of **1**, **2** and **7**, which have simple dipolar interactions between the lanthanoid metal and the $\pi$ electron density.

Subsequently, a homologous series of lanthanoid(III) $\eta^6$-arene complexes has been prepared by a similar method:

$$LnCl_3 + 3AlCl_3 + ArH \xrightarrow{Al} Ln(\eta^6\text{-}ArH)(AlCl_4)_3 \quad \mathbf{11\text{–}15} \quad (18)$$

namely $Ln(\eta^6\text{-}C_6H_6)(AlCl_4)_3$ (Ln = La, Nd (**11**) or Sm (**12**)) [42], $Ln(\eta^6\text{-}MeC_6H_5)(AlCl_4)_3$ (Ln = Nd (**13**) [43]

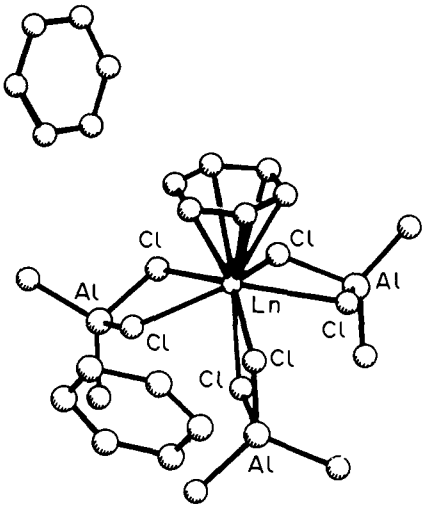



Fig. 8. $[Ln(\eta^6\text{-}C_6H_6)(AlCl_4)_3 \cdot C_6H_6$ (Ln = Nd (**11**) or Sm (**12**)). (Reprinted with permission from the *Journal of Organometallic Chemistry*.)

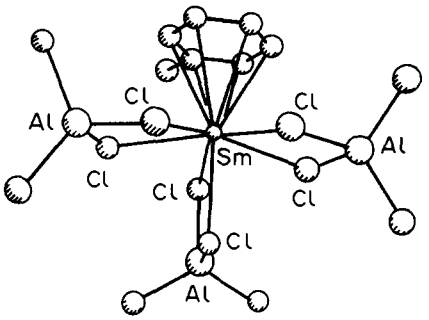



Fig. 9. $Sm(\eta^6\text{-}CH_3C_6H_5)(AlCl_4)_3$ (**14**). (Reprinted with permission from *Youji Huaxue*.)

or Sm (**14**) [44]), and $Sm(\eta^6\text{-}1,3\text{-}Me_2C_6H_4)(AlCl_4)_3$ (**15**) [45]. A number of crystal structures have been determined, e.g. for **11** and **12** (Fig. 8) [42], **13** [43], **14** (Fig. 9) [44] and **15** (Fig. 10) [45], showing that the complexes have similar structures with coordination geometries analogous to that of **10** [40,41]. Some important bond distances are summarized in Table 2. Subtraction of ionic radii for nine-coordinated $Ln^{3+}$ [22] from ⟨Ln–C⟩ (Table 2) gives 1.76–1.78 Å, essentially the same as for **10**.

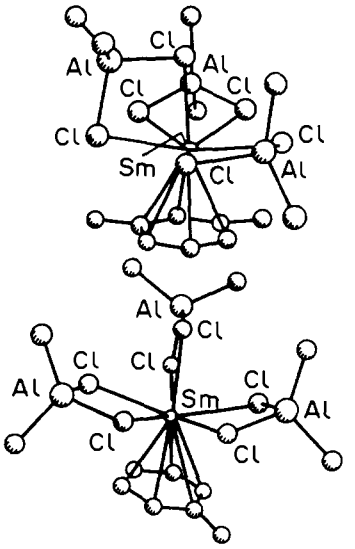



Fig. 10. $Sm(\eta^6\text{-}m\text{-}(CH_3)_2C_6H_4)(AlCl_4)_3$ (**15**). (Reprinted with permission from the *Journal of Organometallic Chemistry*.)

Since the oxidation state of the lanthanoid is unchanged in the syntheses of **10–15** by reactions (17) and (18), the presence of the reductant aluminium metal should not be necessary, especially since the lanthanoid is in the stable +3 oxidation state in these complexes. Direct syntheses

$$LnCl_3 + 3AlCl_3 + ArH \longrightarrow Ln(\eta^6\text{-}ArH)(AlCl_4)_3 \quad (19)$$

without the need for the reducing agent have recently been developed [46]. Thus reaction of $LnCl_3$, $AlCl_3$ and hexamethylbenzene in the mole ratio of 1:3:1.2 in toluene gives $Ln(\eta\text{-}C_6Me_6)(AlCl_4)_3$ (Ln = Nd, Sm, Gd or Yb). The ytterbium complex was characterized by X-ray crystallography [46]. The analogous Nd, Pr and

Table 2
Some structural parameters for $Ln(\eta^6\text{-arene})(AlCl_4)_n$ ($n$ = 2 or 3)

| Complex | Ionic radius [a] (Å) | ⟨Ln–C⟩ (Å) | ⟨Ln–C⟩ minus ionic radius (Å) | ⟨Ln–Cl⟩ (Å) | Reference |
|---|---|---|---|---|---|
| $Sm(\eta^6\text{-}C_6Me_6)(AlCl_4)_3$ (**10**) | 1.13 | 2.89 | 1.76 | 2.85 | [41] |
| $Nd(\eta^6\text{-}C_6H_6)(AlCl_4)_3$ (**11**) | 1.16 | 2.93 | 1.77 | 2.85 | [42] |
| $Sm(\eta^6\text{-}C_6H_6)(AlCl_4)_3$ (**12**) | 1.13 | 2.91 | 1.78 | 2.83 | [42] |
| $Nd(\eta^6\text{-}MeC_6H_5)(AlCl_4)_3$ (**13**) | 1.16 | 2.93 | 1.77 | 2.86 | [43] |
| $Sm(\eta^6\text{-}MeC_6H_5)(AlCl_4)_3$ (**14**) | 1.13 | 2.91 | 1.78 | 2.84 | [44] |
| $Sm(\eta^6\text{-}1,3\text{-}Me_2C_6H_4)(AlCl_4)_3$ (**15**) | 1.13 | 2.90 | 1.77 | 2.83 | [45] |
| $[Eu(\eta^6\text{-}C_6Me_6)(AlCl_4)_2]_4$ (**16**) | 1.30 | 3.00 | 1.70 | 3.04 | [52] |

[a] For nine coordination [22].

Er complexes with toluene, xylene or mesitylene can also be prepared by the direct method [43]. The electronic structure and coordination activation of the bonds of **11** have been studied by the INDO method. It is evident from the calculations that 5d orbitals play an important role in binding of arenes by lanthanoids, whereas the f orbital contribution is only 0.01%. Coordination of $NdCl_3$ to $AlCl_3$ (or $AlCl_4^-$ to $Nd^{3+}$) through six $\mu_2$-Cl ligands may reduce the Lewis acidity of neodymium, the charge difference between Nd and Cl, and the polarity of the Nd–Cl bonds. These factors increase the solubility of $NdCl_3$ in benzene and the stability of the $\eta^6$-$C_6H_6$ complex **11** [47]. The catalytic behaviour of some of the arene complexes has been studied. In the presence of a trialkylaluminium compound, $Nd(\eta^6\text{-}C_6H_6)(AlCl_4)_3$ (**11**) in hexane or toluene catalyses the polymerization of isoprene (cf. no effect for $NdCl_3 \cdot AlCl_3$) [48] or butadiene [49], and the copolymerization of isoprene and butadiene [50] to form *cis*-1,4 polymers. The activity depends remarkably on the nature of the $AlR_3$ reagent (Table 3), with optimal effects for $Al(^tBu)_3$ or $Al(^iBu_2)_2H$. Complexes **11** and the La analogue catalyse the alkylation of benzene with 1-hexene to give the two isomers, 1-phenylhexane and 2-phenylhexane in the ratio 28 : 72, whereas lanthanoid trichlorides are inactive under the same conditions [51].

A polynuclear $\eta^6$-arene complex of europium(II) has been synthesized by the direct method [52]. The reaction of $EuCl_3$, $AlCl_3$ and $C_6Me_6$ (mole ratio, 1 : 1 : 1.2) in toluene at 60°C gives green crystals of $[Eu(\eta^6\text{-}C_6Me_6)(AlCl_4)_2]_4$ (**16**), which were crystallized from toluene. This surprising synthesis in the absence of an obvious added reducing agent is not fully understood, but detection of durene and pentamethylbenzene following the reaction indicates involvement of hexamethylbenzene in the redox reaction. In addition, **16** crystallized as **16** · $Me_4C_6H_2$. The crystal structure (Fig. 11(a)) [52] shows a cyclotetrameric structure containing four $Eu(\eta^6\text{-}C_6Me_6)(AlCl_4)_2$ units. Europium is formally nine coordinated (Fig. 11(b)) with $\eta^6$-hexamethylbenzene and three bidentate $AlCl_4^-$ ligands and there is a distorted pentagonal bipyramidal array of six chlorine atoms and the centroid of the arene. Each europium has one terminal $\eta^2$-$AlCl_4^-$ group and two $\mu$-$\eta^2$ : $\eta^2$-$AlCl_4^-$ groups with the latter linking the four $Eu(\eta^6\text{-}C_6Me_6)(\eta^2\text{-}AlCl_4)$ units. The solvent fragment was modelled as $C_6Me_4H_2$ with the methyl groups disordered over all six positions. In Table 2, the average Eu–C and Eu–Cl distances are compared with those of **10–15**. Subtraction of the ionic radius (1.30 Å) for nine-coordinated $Eu^{2+}$ [22] from ⟨Eu–C⟩ gives 1.70 Å for Eu(1) and 1.71 Å for Eu(2) comparable with values (1.76–1.78 Å) for the $\eta^6$-arene–$Ln^{III}$ complexes and the same as the value for $\eta^2$-olefin–$Ln^{II}$ bonding in **1**. Similar subtractions for ⟨Eu–Cl⟩ of **16** gives 1.74 Å comparable with 1.69–1.72 Å for ⟨Ln–Cl⟩ of **10–15**. Thus the bondings in trivalent

Table 3
Influence of various alkylaluminiums on polymerization of isoprene in hexane [48]

| $AlR_3$ | Amount of catalyst used (mol Nd g isoprene)$^{-1}$ | Conversion (%) | Microstructure | |
|---|---|---|---|---|
| | | | *cis*-1,4 | 3,4 |
| $Al(^iBu)_3$ | $1.85\times10^{-5}$ | 52.5 | — | — |
| | $3.70\times10^{-5}$ | 71.5 | 93.8 | 6.2 |
| | $5.60\times10^{-5}$ | 84.6 | 92.6 | 7.4 |
| $Al(^iBu)_2H$ | $5.60\times10^{-5}$ | 46.5 | 93.1 | 6.9 |
| | $7.20\times10^{-5}$ | 48.5 | — | — |
| | $9.00\times10^{-5}$ | 63.1 | 92.7 | 7.3 |
| $AlEt_3$ | $5.60\times10^{-5}$ | 0 | | |
| | $1.20\times10^{-4}$ | 0 | | |

[M] = 10 g/100 ml; [Al]/[Nd] = 30 (mole ratio); 50°C; 6 h.

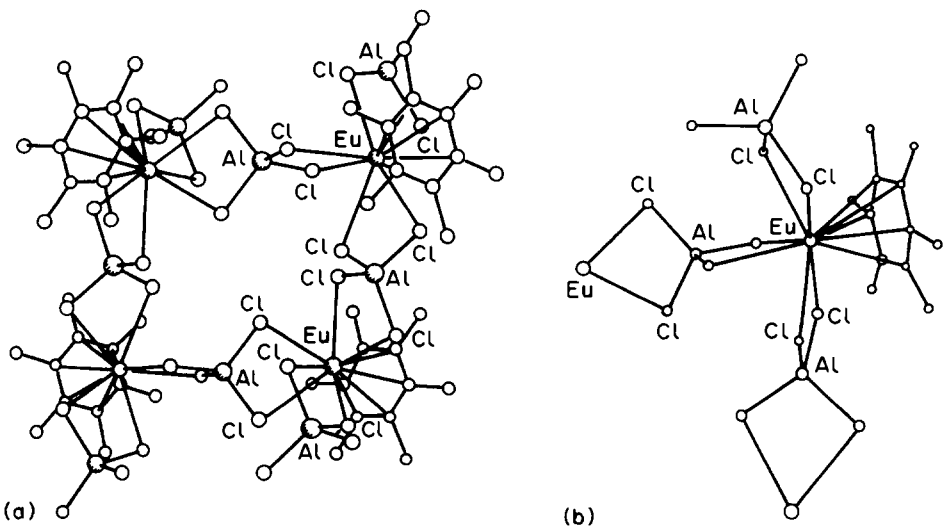



Fig. 11. $[Eu(C_6Me_6)(AlCl_4)_2]_4$ (**16**): (a) the tetrameric unit; (b) the Eu environment. ((*a*) Reprinted with permission from *Journal of the Chemical Society, Chemical Communications*.)

and divalent $\eta^6$-arene complexes are comparable and there are similarities to the $\eta^2$-alkene and $\eta^2$-alkyne binding of $(C_5Me_5)_2Yb(\mu\text{-}\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ (**1**) and $Yb(C_5Me_5)_2(\eta^2\text{-}MeC{\equiv}CMe)$ (**7**). The Mössbauer spectrum of the complex at 88 K gives isomer shifts of $-10.9$ mm $s^{-1}$, typical of ionic europium(II) [52b]. An approximate calculation of the electric field gradient at the Eu nucleus suggests that the Eu–Cl bonds may have some covalent character.

### 4.2. Bis(arene) complexes

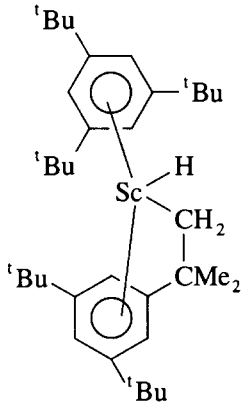
The synthesis of bis($\eta^6$-arene)lanthanoid(0) complexes [53–57] and their scandium(0) analogues [57,58] was the most unexpected and is arguably the most exciting development so far in the area of lanthanoid complexes with neutral $\pi$ donors. All isolable lanthanoid complexes with significant stability have the composition $Ln(1,3,5\text{-}^tBu_3C_6H_3)_2$ and have been prepared by cocondensation of lanthanoid atoms with 1,3,5-tri-tert-butylbenzene at 77 K [53,54,57]:

$$Ln + 2\ 1,3,5\text{-}^tBu_3C_6H_3 \longrightarrow Ln(\eta^6\text{-}1,3,5\text{-}^tBu_3C_6H_3)_2 \quad (20)$$

Stable complexes have been isolated for Ln = Y, Nd, Gd (**17**), Tb, Dy, Ho, Er and Lu. The praseodymium complex is thermally unstable above 40°C, leading to decomposition on attempted removal of free ligand by sublimation [54]. Samarium and lanthanum derivatives are even less stable, whilst Ce, Eu, Tm and Yb complexes are unisolable. Analogous complexes between yttrium and toluene or mesitylene decompose on warming from 77 to 120 K whilst $Y(1,3,5\text{-}^iPr_3C_6H_3)_2$ decomposes above 270 K [53,55].

Zero-valent scandium complexes $ScL_2$ with a range of bulky ligands, namely 1,3,5-tri-tert-butylbenzene, 1,4-di-tert-butylbenzene, 1,3,5,-tri-tert-butyl-4-methylbenzene, trindan and 2,4,6-tri-tert-butylpyridine, have been prepared [57,58]. All have good thermal stability, i.e. decomposition above 100°C. In addition, complexes with mesitylene, pentamethylbenzene and hexamethylbenzene have been detected in solution [57]. They have lower thermal stabilities than derivatives with tert-butylarenes and decompose above −30°C, above 0°C and above 40°C respectively. Thus there is a good correlation between the size of the arenes and the thermal stability of $ScL_2$ complexes, and greater stability with smaller arenes, e.g. mesitylene, than for yttrium (see above).

A second product was detected in the synthesis of $Sc(1,3,5\text{-}^tBu_3C_6H_3)_2$ and was identified by electron spin resonance (ESR) spectroscopy as a cyclometallated scandium(II) bis($\pi$-arene) complex (**18**) [58].




**18**

This compound could not be separated from $Sc(1,3,5\text{-}^tBu_3C_6H_3)_2$, which was more thermally stable. It is unusual both as a Sc(II) complex and also as a rare earth(II)–bis($\eta^6$-arene) complex and arises from scandium-induced C–H activation [58].

X-ray crystal structures have been carried out for Ln = Gd (**17**) (Fig. 12) [53] and Ho [54], although no details are yet available for the latter. Differences in bond lengths are as expected for the difference between the sizes of Gd and Ho [57]. Preliminary X-ray data indicate that the yttrium complex is isostructural with **17**. In the latter [53], gadolinium lies on a centre of symmetry and is coordinated by two eclipsed, essentially planar tri-tert-butylbenzene ligands. The tert-butyl groups are bent out of the ligand plane by 6–10°, presumably to reduce steric interactions. Two of the methyl groups of each tert-butyl substituent lie between the arene planes, and the protective screen of 12 methyl groups contributes to the kinetic stability [53]. Moreover, the instability at the beginning of the lanthanoid series (for La, Ce and Pr), which is unexpected on electronic considerations (see below) [54], has been attributed to insufficient ligand bulk to provide kinetic stability with the three largest lanthanoid elements.

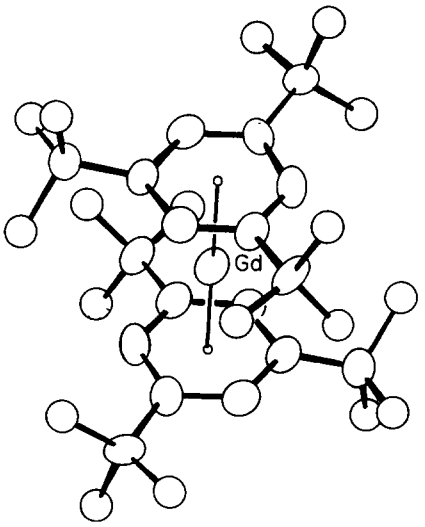



Fig. 12. $[Gd(\eta\text{-}^tBu_3C_6H_3)_2]$ (**17**). (Reprinted with permission from the *Journal of the Chemical Society, Chemical Communications.*)

The Gd–C distances average 2.630 and range from 2.585(4) to 2.660(4) Å and are markedly shorter than those of the mono(arene)–lanthanoid(II or III) complexes (Table 2) even with due allowance for differences between the oxidation states, coordination numbers and lanthanoid sizes. However, they are consistent (allowing for metal atom size) with those of bis(arene)chromium(0) or molybdenum(0) complexes [53]. Accordingly, bis(arene)lanthanoid(0) complexes are considered to have significant covalent binding between the arene ligand and the zero-valent metals [54,57].

A summary of the properties of these novel tri-tert-butylbenzene complexes is given in Table 4. The ESR spectrum and magnetic moment of the prototypical yttrium complex are as expected for a 15-electron bis(arene) complex with a $^2E(e_{2g}^3)$ ground state [55]. Accordingly, it has been proposed that a $d^1s^2$ configuration in the ground state or readily accessible is necessary for formation of a stable bis(arene)lanthanoid(0) complex. Indeed, no complexes can be isolated for Ln = Sm, Eu, Tm or Yb, which have the largest $f^ns^2 \rightarrow f^{n-1}d^1s^2$ promotion energies (Table 4). This does not account for the instability at the beginning of the lanthanoid series (Table 4), since La, Pr and Ce have very favourable promotion energies; hence an explanation based on inadequate steric stabilisation for the larger elements has been given [54]. Certainly the general stability of several heavier lanthanoid complexes and the neodymium complex, and the high stability of the gadolinium complex are consistent with promotion energies (Table 4).

The magnetic moments for $Ln(\eta^6\text{-}1,3,5\text{-}^tBu_3C_6H_3)_2$ complexes frequently diverge significantly from the values for the free atoms (Table 4), indicating considerable perturbation of the atomic f shell on binding of the lanthanoids to the arenes. Comparison of the experimental moments with those predicted on the basis of three limiting case models (two of which gave identical predictions) showed that the observed values generally fell between the two sets of calculated moments (Table 4). However, the degree of agreement with simple models was sufficient to support a bond model in which three lanthanoid valence electrons are involved in bonding to the arene ring whilst the rest remain in the f shell [54]. The molecular orbital bonding diagram for $Cr(\eta^6\text{-}C_6H_6)_2$ can be adapted to provide a satisfactory account of bonding in $Ln(\eta^6\text{-}^tBu_3C_6H_3)_2$ complexes [57].

Metal–ligand bond disruption energies have been determined for a number of $Ln(\eta^6\text{-}1,3,5\text{-}^tBu_3C_6H_3)_2$

Table 4
Properties of $Ln(\eta^6\text{-}1,3,5\text{-}^tBu_3C_6H_3)_3(LnL_3)$ complexes

| Lanthanoid (atom ground state) | Atom [a] $\mu$ ($\mu_B$) | Complex [a] $\mu/(\mu_B)$ Observed | Calculated | Calculated | Complex colour [a] | $\lambda_{max}$ [a] (nm) | $D$(Ln-L)[b] (kcal mol$^{-1}$) | Stability [a] | $E/10^3$ (cm$^{-1}$) ($f^ns^2 \rightarrow f^{n-1}d^1s^2$) [c] |
|---|---|---|---|---|---|---|---|---|---|
| $Sc(d^1s^2)$ | | 1.91 | 1.73 | 1.73 | Orange–green | 495 | | > 120°C | |
| $Y(d^1s^2)$ | | 1.74 | 1.73 | 1.73 | Purple | 529 | 72(2) | Stable | |
| $La(d^1s^2)$ | | | | | Green | 637 | | Decomposition > 0°C | −15 |
| $Ce(f^1d^1s^2)$ | | | | | — | — | | Unisolable | −5 |
| $Pr(f^3s^2)$ | | | | | Purple | 541 | | Decomposition > 40°C | 4 |
| $Nd(f^4s^2)$ | | 1.57 [d] | | | Blue | 544 | | Stable | 7 |
| | 2.68 | | 4.01 | 2.68 | | | | | |
| | | 5.3 [e] | | | | | | | |
| $Sm(f^6s^2)$ | | | | | Green | 691 | | Decomposition > −30°C | 15 |
| $Eu(f^7s^2)$ | | | | | — | — | | Unisolable | 25 |
| $Gd(f^7d^1s^2)$ | 6.51 | 8.75 | 8.12 | 8.94 | Purple | 542 | 68(2) | Stable | −11 |
| $Tb(f^9s^2)$ | 10.64 | 10.69 | 9.87 | 10.74 | Purple | 540 | | Stable | 0 |
| $Dy(f^{10}s^2)$ | 10.61 | 11.20 | 10.79 | 11.67 | Purple | 556 | 47(2) | Stable | 7.5 |
| $Ho(f^{11}s^2)$ | 9.58 | 10.10 | 10.75 | 11.63 | Deep pink | 507 | 56(2) | Stable | 8 |
| $Er(f^{12}s^2)$ | | 11.00 [f] | | | Red | 499 | 57(2) | Stable | 7.5 |
| | 7.56 | | 9.74 | 10.61 | | | | | |
| | | 9.7 [e] | | | | | | | |
| $Tm(f^{13}s^2)$ | | | | | — | — | | Unisolable | 13 |
| $Yb(f^{14}s^2)$ | | | | | — | — | | Unisolable | 23 |
| $Lu(f^{14}d^1s^2)$ | | 1.69 | 1.73 | 1.73 | Red–green | 495 | | Stable | |

[a] From Ref. [54]. [b] From Ref. [59]; metal–ligand bond disruption energies measured at 25°C. [c] Taken from Fig. 1 of Ref. [54]. [d] Below 20 K. [e] Alive 200 K. [f] Below 125 K.

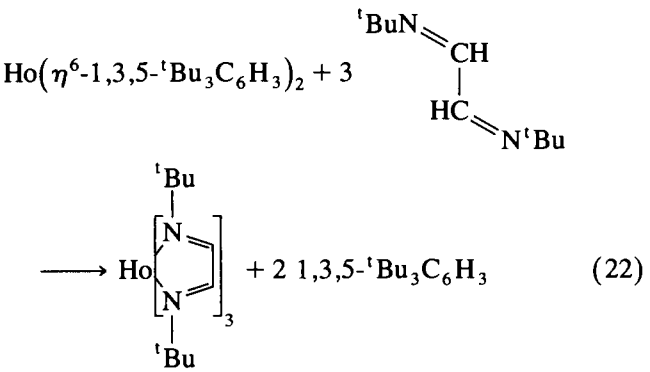
complexes (Table 4) [59]. They indicate that Ln–ligand bonding is strong, up to 30 kcal $mol^{-1}$ stronger than that of $Cr(\eta^6\text{-}C_6H_6)_2$. Further, the results offer support to the correlation of stability with $f^n s^2 \rightarrow f^{n-1}d^1s^2$ promotion energies, in that the largest $D$(Ln–L) energies are observed for the stable Y and Gd complexes, which have $d^1s^2$ and $f^7d^1s^2$ ground states respectively, whilst the Ho, Dy and Er complexes, which have significant promotion energies, have lower stabilities. Of particular interest is that the reaction of bulk lanthanoid metals with 1,3,5-tri-tert-butylbenzene is calculated to be exothermic by contrast with the situation for Group 6 elements [59].

The thermally stable $Ln(\eta^6,1,3,5\text{-}^tBu_3C_6H_3)_2$ complexes sublime with partial decomposition at 100°C ($10^{-4}$ mbar) and have been patented for use as metal–organic chemical vapour deposition feedstocks [56]. Appreciable volatility, allowing purification by sublimation, has also been observed for the scandium analogue [58].

A number of reactions of bis(arene)lanthanoid(0) complexes have been studied [57]. Thus $Y(\eta^6\text{-}1,3,5\text{-}^tBu_3C_6H_3)_2$ is oxidized by protic reagents such as 2,4,6-tri-tert-butylphenol or hexamethyldisilazane (HL) to give the yttrium(III) tris(aryloxide) or tris(bis(trimethylsilyl)amide):

$$Y(\eta^6\text{-}1,3,5\text{-}^tBu_3C_6H_3)_2 + 3HL \longrightarrow YL_3 + \tfrac{3}{2}H_2 + 2\ 1,3,5\text{-}^tBu_3C_6H_3 \qquad (21)$$

Thermal displacement of the arenes by phosphines or carbon monoxide has failed. However, photoinduced substitution by 1,4-di-tert-butyldiazabutadiene has been achieved:



The $Ln(\eta^6\text{-}1,3,6\text{-}^tBu_3C_6H_3)_2$ complexes are very active catalysts for homogeneous polymerization of ethylene in hydrocarbons. The highest polymerization rates were observed for the earlier lanthanoids and there is evidence for a $Y(\eta^6\text{-}1,3,5\text{-}^tBu_3C_6H_3)_2(C_2H_4)$ intermediate when the yttrium complex is used.

There has also been a study of interaction of Sc atoms with hydrocarbon matrices [60], by cocondensation of Sc with adamantane, cyclohexane, deuterocyclohexane, benzene, deuterobenzene and cyclohexene at 77 K. The paramagnetic products formed by the first three hydrocarbons were considered to have weak Sc...H bonding on the basis of ESR measurements, whilst benzene was considered to give $Sc(\eta^6\text{-}C_6H_6)_n$ ($n = 1$ or 2) and $Sc(\eta^2\text{-}C_6H_6)_n$. The latter had a similar spectrum to the product of reaction with cyclohexene [60]. Very recently complex formation on reactions of $Sc^+$, $Y^+$ and $Ln^+$ with 1,3,5-tri-tert-butylbenzene in the gas phase have been investigated by Fourier transform–ion cyclotron resonance mass spectrometry [61]. Complexes of the type $Ln(1,3,5\text{-}^tBu_3C_6H_3)_2^+$ were detected for Ln = Sm, Eu, Tm or Yb, but in other cases the metal ions activate C–H and C–C bonds and react with the $^tBu$ groups. In this case the ability to form complexes is the inverse of that between Sc, Y and Ln metal atoms and 1,3,5-tri-tert-butylbenzene (see above).

### *4.3. Complexes with intramolecular π-arene–lanthanoid bonding*

The first example of a complex with an intramolecular chelate Ln–π-arene interaction was $Yb(Odpp)_3$ ($Odpp^- = 2,6$-diphenylphenolate) (**19**) [62]. The complex was obtained by redox transmetallation–ligand exchange at room temperature followed by drying under vacuum or on sublimation to remove coordinated THF:

$$2Yb + 3Hg(C_6F_5)_2 + 6HOdpp \xrightarrow{THF} 2\ \mathbf{19} + 3Hg + 6C_6F_5H \qquad (23)$$

Other successful syntheses are as follows:

$$2Yb + 3Hg(C{\equiv}CPh)_2 + 6HOdpp \xrightarrow{THF} 2\ \mathbf{19} + 3Hg + 6PhC{\equiv}CH \qquad (24)$$

$$Yb(C_5H_5)_3 + 3HOdpp \xrightarrow{THF} \mathbf{19} + 3C_5H_6 \qquad (25)$$

Single crystals obtained by sublimation gave the structure shown in Fig. 13. There is a shallow trigonal pyramidal arrangement of phenolate oxygen atoms (⟨Yb–O⟩, 2.065A Å; ⟨O–Yb–O⟩, 117.5) with Yb 0.33 Å above the $O_3$ plane (Fig. 13(a)). The arrangement of ligands gives a pseudotwofold axis along Yb–O(1) (Fig. 13(b)) with pendant phenyl groups C(141)–C(146) and C(81)–C(86) above and below the ligating plane. Ytterbium is displaced from the $O_3$ plane towards the former phenyl group giving six Yb–C contacts of 2.814(4)–3.148(6) Å, and the phenyl group is inclined towards Yb with the ring plane angled at 172.7° to the *ipso* C–C bond and at only 12.9° to the $O_3$ plane. There is also a close approach of one carbon atom of the C(81)–C(86) ring with Yb–C(82) 2.882(5) Å. It is considered that the phenyl ring C(141)–C(146) is $\eta^6$–π bonded to ytterbium and that C(82) forms an $\eta^1$–π interaction with the metal [62]. Thus there is overall seven coordination with a pseudotrigonal bipyramidal arrangement of three phenolate oxygen atoms, C(82) and centroid of the C(141)–

C(146) ring about ytterbium. Further evidence for enhanced coordination beyond three is provided by ⟨Yb–O⟩ (2.065 Å) which is similar to ⟨Yb–(Odpp)⟩ (2.078 Å) of five-coordinated $Yb(Odpp)_3(THF)_2$ [62]. Moreover, subtraction of an extrapolated (from Shannon's [22] data) ionic radius for three-coordinated ytterbium from ⟨Yb–O⟩ of **19** gives 1.38 Å which is significantly longer than 1.28 Å obtained by subtraction of an extrapolated radius for $Y^{3+}$ from ⟨Yb–O⟩ of three-coordinated $Y(OC_6H_3{}^tBu_2\text{-}2.6)_3$ [63]. Subtraction of the ionic radius for seven-coordinated $Yb^{3+}$ from ⟨Yb–C⟩ (2.979 Å) of the C(141)–C(146) ring gives 2.05 Å, which is somewhat longer than the range 1.69–1.96 Å for $\eta^2$-alkene–lanthanoid, $\eta^2$-alkyne–lanthanoid and $\eta^6$-arene–lanthanoid(II or III) bonding without substantial charge transfer (Sections 1, 2 and 3.1). For the individual Yb–C interactions, the range is 1.89–2.22 Å. Similar treatment of Yb–C(82) gives 1.96 Å. It should be noted that even the longest of the Yb–C $\pi$ interactions (3.148(6) Å) is well within the sum (3.7 Å) of the metallic radius (pseudo van der Waals radius) of ytterbium (1.94 Å [64]) and the van der Waals radius (1.73 Å) of an aromatic ring [65].

Subsequently, $\eta^1$-$\pi$-arene–Ln interactions, similar to

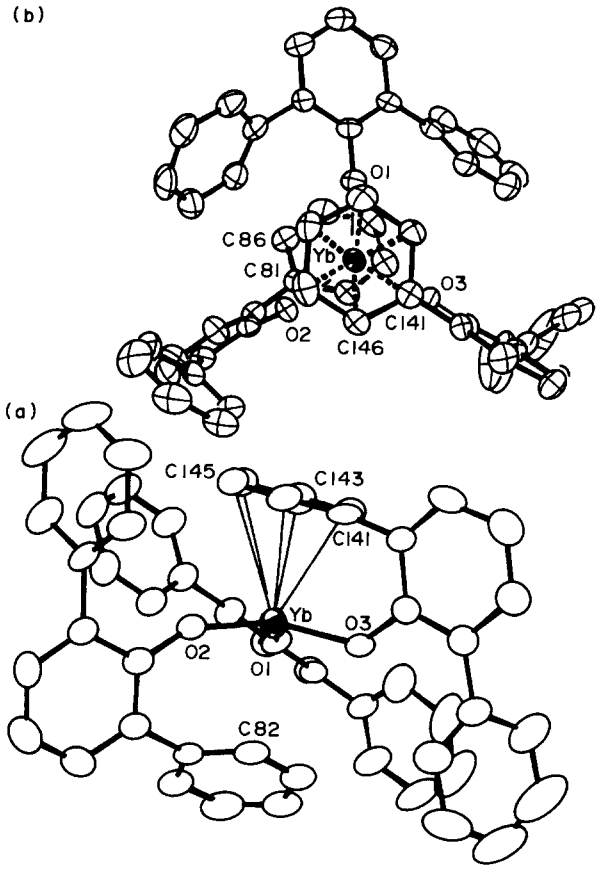



Fig. 13. $Yb(Odpp)_3$ (**19**) (a) showing the coordination sphere and (b) showing the pseudotwofold axis along Yb–O(1). (Reprinted with permission from the *Australian Journal of Chemistry*.)

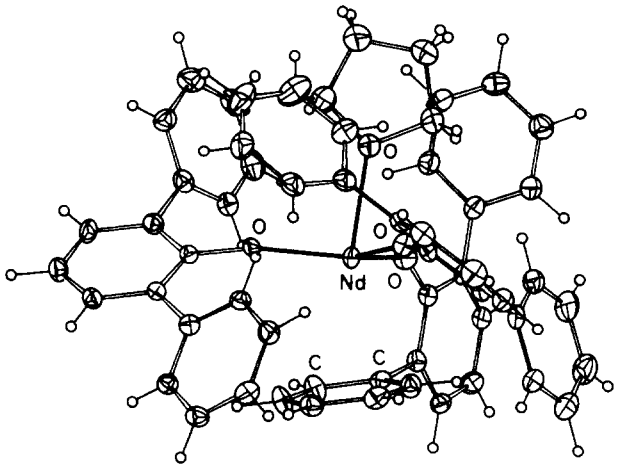



Fig. 14. $Nd(Odpp)_3(THF)$ (**23**). (Reprinted with permission from the *Australian Journal of Chemistry*.)

that for Yb–C(82) of **19**, have been observed for other compounds [66,67]. Thus the X-ray structure of $La(CH(SiMe_3)_2)(1,1'\text{-}(2\text{-}OC_6H_2{}^tBu\text{-}3,5)_2)(THF)_3$ (**20**) ($1,1'\text{-}(2\text{-}OC_6H_2{}^tBu\text{-}3,5)_2$ is the 3,3′,5,5′-tetra-tert-butylbiphenyl-2,2′-diolate ligand) shows a 3.096(13) Å weak bond between La and an *ipso* carbon atom of one phenolate group [66]. Subtraction of the ionic radius for coordinated $La^{3+}$ [22] from this bond length gives 2.00 Å in good agreement with values for **19**. Similarly, the structure of $[Ce(OSiPh_3)_3]_2$ (**21**) has an *ipso* carbon atom of one triphenylsiloxide ligand on each cerium in a basal position of a $CeO_4C$ square pyramidal arrangement with a Ce–C distance of 2.982(9) Å [67]. Subtraction of an extrapolated ionic radius for five-coordinated $Ce^{3+}$ from this value gives 2.03 Å, consistent with intramolecular chelate $\pi$ bonding. On the contrary, in intramolecular Y...C the approach of 3.47 Å in the structure of the bimetallic $YCu(OSiPh_3)_4(PMe_2Ph)$ is considered non-bonding [68]. An appropriate subtraction from this distance gives 2.63 Å, which is well beyond values considered indicative of $\pi$ bonding in **19–21**.

In further studies of 2,6-diphenylphenolatolanthanoid complexes, intramolecular $\pi$-arene coordination has been established in $Nd(Odpp)_3$ (**22**) and $Nd(Odpp)_3$-(THF) (**23**) [69]. The former was prepared by sublimation of $Nd(Odpp)_3(thf)_2$, which was synthesized by a reaction analogous to (23), whilst the latter was obtained by crystallization of $Nd(Odpp)_3(THF)_2$ from toluene. X-ray crystallography showed, perhaps surprisingly [3], that **22** is isostructural with $Yb(Odpp)_3$ (**19**). For the $\eta^6$-phenyl ligand, ⟨Nd–C⟩ is 3.046 Å (range,

[3] Complexes of Nd, a light lanthanoid, are more usually isostructural with the corresponding La complexes than with Yb derivatives. In this case $La(Odpp)_3$ (see below) has a structure different from the isostructural $Ln(Odpp)_3$ (Ln = Nd or Yb).

2.946(6)–3.158(9) Å), and Nd–C of the $\eta^1$-bonded group is 2.964(7) Å. Subtraction of an interpolated ionic radius (data [22]) from these distances gives 2.01 Å (range, 1.91–2.12 Å) and 1.92 Å respectively, values which are generally marginally lower than those for **19**.

In the structure of $Nd(Odpp)_3(THF)$ (**23**) (Fig. 14), the coordination sphere comprises a triangular array of phenolate oxygen atoms ($\Sigma$O–Nd–O, 358.7°), a more distant THF oxygen atom and an intramolecular $\pi$-bonded phenyl, giving overall pseudotrigonal bipyramidal stereochemistry [69]. The C(Ph)–Nd distances fall into two groups: (i) 3.094(5), 3.144(5) and 3.101(5) Å; (ii) 3.300(5), 3.427(5) and 3.377(5) Å. Only the first three are considered sufficiently close for $\pi$ bonding, and the resulting $\eta^3$ attachment gives a coordination number of five. Subtraction of an extrapolated ionic radius (data [22]) for five-coordinated $Nd^{3+}$ from ⟨Nd–C⟩ of the shorter Nd–C contacts gives 2.16 Å, which is at the limit for $\pi$ bonding. Similar treatment of the longer ⟨Nd...C⟩ gives 2.45 Å. (For $\eta^6$ bonding and seven coordination, the subtraction values are 2.04 and 2.33 Å.) Neodymium is displaced 0.149(1) Å from the $O_3$ plane away from the THF oxygen atom and towards the capping phenyl group, providing further evidence for coordination. The phenyl plane is at 175.0(3)° to the *ipso* C–C bond, and is near parallel to the $O_3$ plane (interplanar angle, 14.9(1)°). Thus, addition of the THF molecule to **22** leads to displacement of the $\eta^1$-bonded phenyl to allow THF coordination, and the stronger bonding of the THF oxygen atom in **23** than of the $\eta^1$-Ph in **22** leads to $\eta^3$-Ph bonding *trans* to THF by contrast with $\eta^6$-bonding *trans* to the $\eta^1$-Ph. There is an interesting contrast between the structure of $Nd(Odpp)_3(THF)$ (**23**) [69] and $Yb(OC_6H_2{}^tBu_3\text{-}2,4,6)_3(THF)$ [70]. In the latter, Yb is displaced from the phenolate $O_3$ plane towards THF and away from a blocking $^t$Bu *trans* to THF whereas, in **23**, Nd is displaced away from THF towards the capping phenyl.

Another interesting example of intramolecular chelate $\pi$ bonding has been recently observed in $La(Odpp)_3$ (**24**) [71]. By contrast with $Yb(Odpp)_3$ (**19**) (Fig. 13), **24** has a sandwich of intramolecular chelate $\pi$-bonded rings, with one ring $\eta^6$ bonded and one $\eta^3$ bonded. In **19**, the $\eta^1$-bonded ring is turned away from the ytterbium atom making an angle of 30.1° with the $O_3$ ligating plane compared with 12.9° for the $\eta^6$-bound ring. In **24**, the $\eta^6$- and $\eta^3$-phenyl bound rings are at 13.4(2)° and 14.2(2)° respectively to the $O_3$ plane. This appears to be the first sandwich compound with intramolecular phenyl $\pi$ bonding.

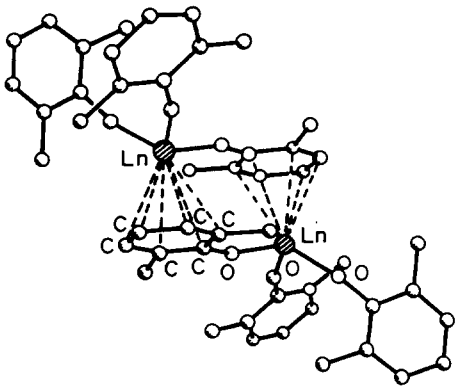



Fig. 15. The X-ray structure of $[Ln(OC_6H_3{}^iPr_2\text{-}2,6)_2(\mu\text{-}(OC_6H_3{}^iPr_2\text{-}2,6)\text{-}O:\eta^6)]_2$ Ln = Nd (**25**) or Sm (**26**). (Reprinted with permission from *Inorganic Chemistry*.)

The novel scandium(II) $\pi$-arene complex **18** [58] has one intramolecular $\pi$-arene–Sc bond (Section 3.2).

### 4.4. Complexes with intermolecular $\pi$-arene lanthanoid bonding

The complexes $Ln_2(OC_6H_3{}^iPr_2\text{-}2,6)_6$ (Ln = Nd (**25**), Sm (**26**) or Er (**27**)), recently prepared by the following reaction in toluene, provide unexpected examples of intermolecular $\pi$-arene coordination [72]:

$$2Ln(N(SiMe_3)_2)_3 + 6\ 2,6\text{-}{}^iPr_2C_6H_3OH \longrightarrow \underset{\mathbf{25-27}}{Ln_2(OC_6H_3{}^iPr_2\text{-}2,6)_6} + 6HN(SiMe_3)_2. \quad (26)$$

X-ray structures of **25** and **26** (Fig. 15) show a dimeric structure held together by $\eta^6$-arene–Ln bonds involving one unique aryloxide ligand of each $Ln(OC_6H_3{}^iPr_2\text{-}2,6)_3$ unit. This results in formal six coordination for the lanthanoid elements. Even with O$\pi$ bridging rather than the more usual oxygen bridging in lanthanoid alkoxides and aryloxides [73], average Ln–O distances for the bridging ligands (2.211 Å (**25**) and 2.198 Å (**26**)) are longer than those (2.122 Å (**25**) and 2.101 (**26**) Å) for the terminal ligands [72]. Average Ln–C distances are 3.035 Å for **25** and 2.986 and 3.016 Å for the two independent molecules of **26**. IR spectra and $^1$H and $^{13}$C NMR spectra provide strong evidence for retention of the dimeric structures in solution. Subtraction of ionic radii for six-coordinated $Ln^{3+}$ [22] from ⟨Ln–C⟩ gives 2.00, 2.00 and 2.03 Å respectively. These are higher than values derived from ⟨Ln–C⟩ of Ln($\eta^6$-arene)$(AlCl_4)_n$ ($n = 2$ or 3) complexes, i.e. 1.70–1.80 Å (Table 2), and within the range 1.90–2.16 Å derived from complexes considered to have intramolecular Ln–$\pi$-arene interactions (Section 3.3). Indeed, since there can be no doubt about the intermolecular $\pi$-arene–Ln coordination of **25–27**, their bond lengths provide support for interpretation of similar distances in monomeric species as intramolecular $\pi$-arene–Ln coordination.

## 5. $\eta^2$-(Non-hydrocarbon ligand)–lanthanoid complexes

It is possible to envisage molecules such as dihydrogen or dinitrogen forming $\eta^2$-bonded complexes with

lanthanoids analogous to those with olefins (Section 1). These can be regarded as pseudo-$\eta^2$-$\pi$-bonded complexes. Such complexes with hydrogen are often invoked as intermediates in lanthanoid-centred hydrogenolysis reactions (see for example Refs. [17–74]).

It has been found that incremental addition of $Eu(C_5Me_5)_2$ to a solution of $H_2$ in $C_6D_{12}$ at constant $[H_2]$ results in upfield displacement (cf. $C_2H_4$, Section 1) and pronounced broadening of the hydrogen resonance [27]. This has been interpreted in terms of reversible formation of the dihydrogen complex **28**:

$$Eu(C_5Me_5)_2 + H_2 \rightleftharpoons (C_5Me_5)_2Eu \longleftarrow \begin{matrix} H \\ | \\ H \end{matrix} \quad (27)$$

**28**

Addition of THF causes the hydrogen resonance to shift towards the free hydrogen resonance in accordance with the displacement

$$\mathbf{28} + THF \longrightarrow Eu(C_5Me_5)_2(THF) + H_2 \quad (28)$$

Slow crystallization of $Sm(C_5Me_5)_2$ from toluene under dinitrogen over 4 weeks gives a quantitative yield of $[Sm(C_5Me_5)_2]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$ (**29**) [75]:

$$2Sm(C_5Me_5)_2 + N_2 \xrightleftharpoons{\text{toluene}} \mathbf{29} \quad (29)$$

The reaction is readily reversible with evolution of dinitrogen occurring on dissolution in toluene [75]. The structure (Fig. 16) provided the first example of side-on ($\eta^2$) coordination by nitrogen. There is a $C_2$ axis along the Sm...Sm vector for a plane containing the $N_2$ unit and the samarium atoms. Both the Sm–N distances (2.347(6) and 2.368(6) Å) and the Sm–C($C_5Me_5$) distances (2.685(6)–2.768(6) Å) are typical of eight-coordinated samarium(III) complexes. These distances and the NMR data indicate Sm(III) and a $(N_2)^{2-}$ ligand. However, the N–N distance is similar to that of free nitrogen, and this together with the ready dissociation is as expected for a complex with $N_2$ $\pi$ bonded to Sm(II). This ambivalence of properties is of great interest, especially in view of the remarkably facile Sm(III) → Sm(II) reduction that occurs on dissociation.

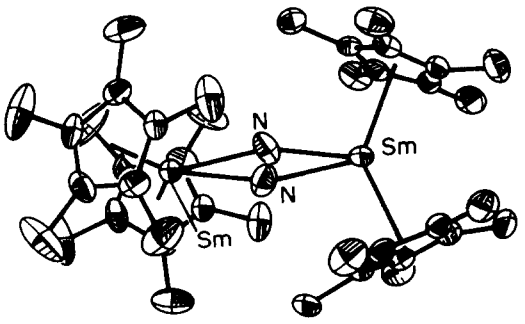



Fig. 16. $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$ (**29**). (Reprinted with permission from the *Journal of the American Chemical Society*.)

At first sight, the complex $[Sm(C_5Me_5)_2]_2(\mu\text{-}\eta^2:\eta^2\text{-}NHNH)$ obtained from reaction of hydrazine with either $Sm(C_5Me_5)_2$ or $[Sm(C_5Me_5)_2H]_2$ under conditions of strict stoichiometric control [76] might be considered an $\eta^2$-$\pi$ complex of HN=NH. However, all X-ray data point to formulation as a Sm(III) complex of $(NHNH)^{2-}$ [76]. Ready reversion into $Sm(C_5Me_5)_2$ has not been observed, by contrast with **29** [75].

Matrix isolation studies have provided evidence of lanthanoid(0) complexes with CO, namely $Ln(CO)_n$ (Ln = Pr, Nd, Eu, Gd or Yb; $n$ = 1–6) [77]. Because decomposition occurred above 20 K, there appears little prospect of development of these species. However, their detection raises the possibility of Ln–CO intermediates in reactions.

## 6. Conclusions

The advances in the chemistry of organolanthanoids with neutral $\pi$ donors have demonstrated that organolanthanoid chemistry is no longer a limited ionic chemistry. Significant covalence has been introduced with the novel lanthanoid(0)–$\eta^6$-arene complexes. It is now evident that a much wider variety of ligands and reagents can be used in organolanthanoid chemistry with correct choice of oxidation state and coordination environment. Since this area is a relatively young branch of organometallic chemistry, much remains to be explored in this field, especially complexation of organolanthanoids with olefins, CO, $H_2$ and subsequent reaction chemistry. As general knowledge of organolanthanoids increases, considerable development of their chemistry with neutral $\pi$-donor ligands should result. With catalytic activity demonstrated for representative complexes, there are prospects of applications for these compounds. A particularly interesting feature has been the contrasting behaviour of $Yb(C_5Me_5)_2$ and $Sm(C_5Me_5)_2$. The first gives Yb(II)–$\pi$ complexes with alkenes and alkynes, whilst the more strongly reducing samarium compound usually induces electron transfer. However, $Sm(C_5Me_5)_2$ can give a normal $\pi$-alkene complex, e.g. **2**, or the resulting Sm(III) complex can show dissociation lability typical of a Sm(II)–$\pi$ complex, e.g. **5** and **29**.

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