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Aspects of the lanthanide–carbon σ-bond

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Contents

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Abstract

Although the first σ-bonded organolanthanides were not fully characterized for some 20 years after the isolation of the first π-cyclopentadienyls, a wide range of these compounds is unfolding. The review discusses synthetic routes to the compounds, both with and without "supporting" polyhapto ligands and including the very recent carbenes, exploring the principles behind their isolation. Structural information is critically reviewed, with the effects of bulky ligands and the lanthanide contraction considered. © 1997 Elsevier Science S.A.

Keywords: Synthesis; Lanthanide–carbon σ-band; σ-Bonded organolanthanides

1. Introduction

1.1. Context

This review has been prompted by recent developments in the synthetic and structural chemistry of these compounds, opening perspectives for better comparisons and views of trends. It is intended to be comprehensive on homoleptic σ-bonded organometallics and selectively surveys compounds where supporting ligands, including π-bonded ligands like cyclopentadienyl, are also present, It is thus complementary (with some degree of orthogonality) to the most extensive and detailed review on π-bonded organometallics by Schumann et al. [1]. Several general reviews of organolanthanides have appeared (see, e.g., Refs. [2–7]) whilst other, more selective, reviews have recently appeared [8–12]. Structural trends for Cp^*_2Ln compounds ($Cp^* = C_5Me_5$; Ln = La–Lu, Y) have also been reviewed [13]. Catalytic work is not discussed, as it is covered in particular in Refs. [8–10], which along with Refs. 1 and 10 also give more comprehensive cover to cyclopentadienyl systems. For the purpose of the review, scandium and yttrium are classed as lanthanides.

1.2. Synthetic routes and prnciples behind the isolation of the compounds

σ-Bonded organolanthanides, like organolanthanides in general, are air- and moisture-sensitive compounds, requiring inert atmosphere techniques for successful synthesis and handling. Almost without exception (such as the recently reported $[Yb\{C(SiMe_3)_2\}_2]$ [14] which sublimes in vacuo at 95°C at 10^{-4} Torr) they are involatile and have to be purified by crystallisation from a suitable solvent.

Certain principles of successful "isolability" of σ-bonded organolanthanides are now well understood, many of which equally apply to actinides. These tend to ensure coordinative saturation and minimise decomposition pathways, such as the following:

(1) Forming adducts with Lewis bases such as THF, amines or phosphines. Thus it is possible to obtain $UMe_4(dmpe)_2$ but not UMe_4 [15], and similarly crystalline molecular THF adducts rather than amorphous unsolvated compounds as with the recent syntheses of *fac*-$[LnPh_3(THF)_3]$ [16].

(2) Obtaining an anion rather than a neutral molecule, e.g., isolation of $[Lu(2,6\text{-dimethylphenyl})_4]^-$ rather than $Lu(2,6\text{-dimethylphenyl})_3$.
(3) The effects of bulky ligands make $-CH(SiMe_3)_2$ compounds stabler than methyls, and 2,6-dimethylphenyls more stable than phenyls.
(4) Chelating ligands have also sometimes been used to ensure coordinative saturation.
(5) When compounds containing perhaps just one σ-bond are desired, the use of two bulky co-ligands such as C_5H_5 (Cp) or C_5Me_5 (Cp*) causes occupation of most of the rest of the coordination sphere, leaving little vacant space round the metal.
(6) Use of the C_5Me_5 ligand confers better hydrocarbon solubility on the organolanthanide. This may be advantageous both from the point of view of purification and that of solubility for spectroscopic measurements.

The most common synthetic route tried for σ-bonded organometallics is a metathetical route involving salt-elimination, such as

$$LnCl_3 + 3LiR \rightarrow LnR_3 + 3LiCl$$

$$LnCp_2Cl + LiR \rightarrow LnCp_2R + LiCl$$

carried out in an inert atmosphere in a non-aqueous solvent, often an ether like THF. Problems that can arise in practice include: (i) the insolubility of $LnCl_3$ in most solvents (which can be ameliorated to some extent by starting with the THF complex $LnCl_3(THF)_x$); (ii) the possibility of LiR reducing the lanthanide as occurs [17] in the reaction of $EuCl_3$ with LiMe; (iii) the solubility of LiCl, the other product in THF (or even non-polar solvents like benzene); (iv) coordination of chloride ions to the electrophilic lanthanide; (v) facile decomposition of the product.

Using small ligands may expose the metal ion and make any LnR_3 product more susceptible to attack or simply coordination by solvent (e.g., THF) as in the following reaction in THF [18].

$$LuCl_3 + 3LiCH_2SiMe_3 + 2THF \rightarrow Lu(CH_2SiMe_3)_3(THF)_2 + 3LiCl$$

The size of the ligand may affect how many groups can be coordinated to the metal, thus $YbCl_3$ reacts with excess $LiCH_2SiMe_3$ forming $[Yb\{CH_2SiMe_3\}_4]^-$, whereas with a bulkier ligand (causing crowding of the $SiMe_3$ groups) using $LiCH(SiMe_3)_2$ means that $[Yb\{CH(SiMe_3)_2\}_3Cl]^-$ is isolated [18].

Recently some chemists have started to explore the use of other alkali metal salts. Using the more soluble $KCH(SiMe_3)_2$ meant that the reaction with $LuCl_3$ forming $[Lu\{CH(SiMe_3)_2\}_3ClK(OEt_2)]$ could be carried out in Et_2O instead of THF [19]. A further possible benefit is that the alkali metal halides produced are less soluble in non-polar solvents, as in the recent synthesis [14] of $[Yb\{C(SiMe_3)_2\}_2]$ that was performed in benzene (where there was no possibility of ether coordination either).

$$YbI_2 + 2KC(SiMe_3)_3 \rightarrow [Yb\{C(SiMe_3)_2\}_2] + 2KI$$

The problems caused by the use of lanthanide chlorides are eliminated by the use of chloride-free starting materials, with alkoxides or aryloxides, pioneered by Schumann et al. in their synthesis of $Li(tmeda)_2^+\ LuBu^t_4{}^-$ from $Lu(OBu^t)_3$ and tert-butyl lithium [20].

Similarly, though reaction of $LaCl_3$ with $LiCH(SiMe_3)_2$ leads [21] to the isolation of $[La\{CH(SiMe_3)_2\}_3ClLi(pmdeta)]$ rather than $[La(\{CH(SiMe_3)_2\}_3]$, the desired product could be obtained by use of a lanthanum aryloxide starting material:

$$La(2,4,6-Bu^t_3-OC_6H_2)_3+3LiCH(SiMe_3)_2 \rightarrow La(\{CH(SiMe_3)_2\}_3$$
$$+3Li(2,4,6-Bu^t_3-OC_6H_2)$$

The use of pentane as the solvent facilitates workup as $Li(2,4,6\text{-}Bu^t_3\text{-}OC_6H_2)$ precipitates.

In an approach where an alkyl is the starting material, the organic by-product is easy to separate [22]

$$H_2oep+Ln(\{CH(SiMe_3)_2\}_3 \rightarrow Ln(oep)\{CH(SiMe_3)_2+CH_2(SiMe_3)_2$$
$$(Ln=Lu, Y)$$

Of course, if extra LiR is used an anionic species may be obtained, but this may be formed preferentially regardless of stoichiometry as has been found for compounds such as the methyls [17,20] $[\{Li(tmed)\}_3LnMe_6]$ or $[\{Li(dme)\}_3\ LnMe_6]$

Transmetallation reactions have been used for Ln(II) species most often, particularly in the synthesis

$$HgR_2+M \rightarrow Hg+LnR_2$$

of $Yb(C_6F_5)_2$ [23]. Activation of the lanthanide metal is sometimes necessary, thus $HgPh_2$ does not react with Yb metal but will react with ytterbium activated with CH_3I forming $YbPh_2$ [24]; similarly the recent synthesis of $LnPh_3(THF)_3$ catalysed by LnI_3 [16].

The stability of compounds can be affected by the alkyl or aryl grouping. Compounds with the methyl, (trimethylsilyl)methyl and neopentyl ligands, which are unable to undergo β-elimination, have been studied in particular detail, but details of such decompositions are scarce. The compounds $LnCp_2Me$ are stable dimers $[Cp_2Ln(\mu\text{-}Me_2)LnCp_2]$ but other alkyls are rare. Particular study of lutetium compounds has been made by Schumann et al. [25], who found monomers $LuCp_2R.THF$ isolable at 0°C but unstable at room temperature for Me, Pr^i, Bu^n. The *tert*-butyl $[LuCp_2CMe_3.THF]$ is stable to 70°C (similar compounds have also been isolated for Er, Yb and Y) indicating that congestion may inhibit elimination. Corresponding CH_2SiMe_3 compounds have also been isolated. For $LnCp_2R$ decomposition involves the formation of a hydride Cp_2LnH and the alkene $RCH{=}CH_2$ (The process is encouraged by hydrogenolysis) [26]. The reactivity order to hydrogenation is $Me > CH_2SiMe_3 > Bu^t$ indicating a steric origin [27].

In the reactions of $LnCl_3$ with $LiCH_2SiMe_3$ (Ln = Tb, Er, Nd) at room temperature, decomposition with elimination of hydrogen from the CH_2 moiety forming ill-defined compounds, possibly of the type $[Ln(CHSiMe_3)(CH_2SiMe_3)]$, has been reported [28]. Benzyls, which cannot β-eliminate, have not generally been isolated and indeed appear to have a high reactivity [29].

In the synthesis of cyclopentadienyls $LnCp_2R$, a facile route presents itself in the case of the methyl derivatives. The compounds $[Cp_2Ln(\mu\text{-}Me_2)AlMe_2]$ are readily made by reaction of $LiAlMe_4$ with $[LnCp_2Cl]_2$; on treatment with pyridine the bridge is cleaved

$$2[Cp_2Ln(\mu-Me_2)AlMe_2]+2py \rightarrow [Cp_2LnMe]_2+2AlMe_3py$$

but with the scandium compound the reaction takes a different course as Sc is more electrophilic than Al and $Cp_2ScMe(py)$ is the product [30].

Oxidative addition reactions converting Ln(II) to Ln(III) have been studied for some cyclopentadienyls; obviously this is restricted to those lanthanides with an accessible +2 oxidation state (Eu, Yb, Sm). Thus [31]

$$Cp_2Sm+PhCH_2X \rightarrow Cp_2SmX+Cp_2SmCH_2Ph$$

A detailed study of the reactions of $[LnCp^*_2(OEt_2)]$ with RX (R = alkyl, aryl) shows the reactions to be complicated; oxidation is not observed in the case of Eu, but for Yb and Sm after initial formation of $[LnCp^*_2R]$ with generation of R· radicals, coupling reactions take place with the formation of $[LnCp^*X_2]$ and R–R [32].

Organomercury compounds can be used as sources of organic ligands in oxidative addition [33]

$$2Cp_2Yb+R_2Hg \rightarrow 2Cp_2YbR+Hg$$

R, e.g., C_6F_5, C_6Cl_5, PhCC

and [34]

$$2Cp^*_2Sm(THF)_2+Ph_2Hg \rightarrow 2Cp^*_2SmPh(THF)+Hg$$

This reaction does not proceed with $[Cp^*_2Yb(DME)]$, possibly due to the greater stability of the +2 oxidation state for ytterbium.

Another preparative route involves reactions of hydrides, essentially a reversible reaction and not of great preparative utility [35]

$$Cp^*_2LuH+C_6H_6 \rightarrow Cp^*_2LuPh+H_2$$

$$Cp^*_2LuH+Me_4Si \rightarrow Cp^*_2LuCH_2SiMe_3+H_2$$

Some methods used for alkynyls such as metathesis with salt elimination are general; other different possibilities exist because of the greater acidity of alkynes, such as

$$YbCp_3+RC\equiv CH \rightarrow YbCp_2(C\equiv CR)+CpH \quad R=Bu^n, \text{Cy, hexyl [36]}$$

$$[(Bu^tCp)_2LnMe]_2+2HC\equiv CPh \rightarrow [(Bu^tCp)_2Ln(C\equiv CPh)]_2$$

$$+2CH_4 \ (Ln=Gd, Nd) \ [37]$$

$$LiLnBu^t_4\cdot 4THF+4HC\equiv CBu^t \rightarrow LiLn(HC\equiv CBu^t)_4$$

$+4\mathrm{Me_3CH}$ (Ln = Sm, Er, Lu) [38]

Routes beginning with a Ln(II) compound are interesting in view of the possibility of retaining the Ln(II) state or of oxidation to Ln(III). The following provide an interesting comparison of possibilities starting with rather similar Ln(II) compounds

$$[\mathrm{EuCp^*_2(OEt_2)}] + \mathrm{HC{\equiv}CPh} \rightarrow$$

$$[(\mathrm{THF})_2\mathrm{Cp^*Eu^{II}}(\mu-\mathrm{C{\equiv}CPh})_2\mathrm{Eu^{II}}(\mathrm{THF})_2\mathrm{Cp^*}]$$

$$[\mathrm{YbCp^*_2(OEt_2)}] + \mathrm{HC{\equiv}CPh} \rightarrow$$

$$[\mathrm{Cp^*_2Yb^{III}}(\mu-\mathrm{C{\equiv}CPh})_2\mathrm{Yb^{II}}(\mu-\mathrm{C{\equiv}CPh})_2\mathrm{Yb^{III}Cp^*_2}]$$

$$[(\mathrm{Bu^tCp})_2\mathrm{Sm(MeOCH_2CH_2OMe)}] + \mathrm{HC{\equiv}CPh} \rightarrow$$

$$[\{(\mathrm{Bu^tCp})_2\mathrm{Sm^{III}}(\mu-\mathrm{C{\equiv}CPh})\}_2]$$

$$\mathrm{SmCp^*_2(THF)_2} + \mathrm{HC{\equiv}CPh} \rightarrow [(\mathrm{Cp^*})_2\mathrm{Sm^{III}}(\mu-\mathrm{C{\equiv}CPh})(\mathrm{THF})] \text{ (in hexane)}$$

$$\mathrm{SmCp^*_2} + \mathrm{HC{\equiv}CPh} \rightarrow [\{(\mathrm{Cp^*})_2\mathrm{Sm}\}_2(\mu-\eta^2{:}\eta^2-\mathrm{PhC_4Ph})] \text{ (in toluene)}$$

It will be seen that the result depends on the relative stabilities of the Ln(II) and Ln(III) states, upon the coordinated ligand and steric factors [39–42].

1.3. *Structures: introductory comments*

Throughout this review, structures are compared using the ionic radii for the 6-coordinate ions given by Shannon [43], summarized in Table 1.

This review uses an approach introduced by Eigenbrot and Raymond [44] that involves a "subtracted" distance, i.e., the bond length *less* the ionic radius for the appropriate 6-coordinate metal ion. This removes the lanthanide contraction factor and gives an idea of whether a bond length is longer or shorter than might be expected, and can indicate the presence of steric effects. (It is realised that in many of the structures, the metal is *not* 6-coordinate, but these radii serve as fixed standards.)

Some justification for this approach can be found in structural data for the silylamides $[\mathrm{M^{III}\{N(SiMe_3)_2\}_3}]$. Though not organometallic compounds, they have pyramidal 3-coordinate structures similar to the alkyls $[\mathrm{Ln^{III}\{CH(SiMe_3)_2\}_3}]$. Comparing data for the 3-coordinate compounds [45] $[\mathrm{M^{III}\{N(SiMe_3)_2\}_3}]$ (M = Sc, Y, Nd, Eu, Dy, Er, Yb and U) where the M–N bond lengths are respectively

Table 1
Ionic radii (Å) for 6-coordination in lanthanide and related ions

Ion	Sc^{3+}	Y^{3+}	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	
Radius (Å)	0.745	0.901	1.132	1.010	0.990	0.983	0.970	0.958	0.947	0.938	0.923	
Ion	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}	Sm^{2+}	Eu^{2+}	Yb^{2+}	Th^{4+}	U^{3+}	U^{4+}
Radius (Å)	0.912	0.901	0.890	0.880	0.868	0.861	1.17	1.177	1.02	0.940	1.025	0.89

2.047(6), 2.224(6), 2.29(2), 2.259(8), 2.213 (6), 2.21(1), 2.16(2) and 2.320(4) Å, the figure obtained by subtracting the ionic radius of the metal from the M–N bond length for remains approximately constant, showing that the character of the bonding is essentially unchanged, and the value (Eu–N 2.448(4) Å) for the $[Eu^{II}\{N(SiMe_3)_2\}_3]^-$ ion also fits into this pattern [45]. Such extensive data is not available for any series of σ-alkyls, but suggests that the essentially ionic model of Shannon may be applied here. The correlation noted here does not appear to survive use of a less bulky amide ligand; in the 5-coordinate $[Ln\{N(SiHMe_2)_2\}_3(thf)_2]$, Y–N is 2.275 Å and Nd–N 2.353 Å [46], rather less than would be expected for 5-coordinate $[Ln\{N(SiMe_3)_2\}_3(thf)_2]$, compare Nd–N = 2.383(20) Å in 4-coordinate $[Nd\{N(SiMe_3)_2\}_3(OSiMe_3)]^-$.

In general, structures are discussed in the appropriate parts of Section 3, where it is easier to see the trends and patterns emerging for related compounds.

2. Simple homoleptic alkyls and aryls

2.1. Homoleptic aryls

Early syntheses [47] of $MEt_3 \cdot Et_2O$ (M = Sc, Y) as liquids stable at their b.p.s of 172 and 225°C and twice theoretical yields have not been repeated. Work at the time of the Manhattan project was also unsuccessful [48]. The first successful syntheses involved reaction of phenyllithium with the trichlorides of scandium, yttrium, lanthanum and praseodymium in THF, giving MPh_3 (M = Sc, Y) and $LiMPh_4$ (La, Pr) [49]. The IR spectra of the final products, insoluble after drying, showed very broad phenyl absorptions different from those of σ-phenyls such as $HgPh_2$ and suggesting that a complicated oligomerization, possibly involving both η^1- and polyhapto-phenyl-metal bonding, had occurred on removing the THF, rather analogous in some ways to what happens with the compounds $Ln(THF)_xCl_3$, a synthetically important soluble form of the halides; when first obtained from THF solution, these generally have molecular structures which polymerize on loss of THF [50]. In the absence of THF, products obtained are dispersed in the LiCl coproduct, showing "simple" phenyl IR spectra but after THF extraction and workup, again had broad IR spectra [51]. If the reaction of $EuCl_3$ and phenyllithium was conducted in benzene, a redox reaction evidently occurs with formation of $EuPh_2$. It is also possible to obtain $EuPh_2$ from the reaction between Eu and Ph_2Hg [52]. More recently, a synthesis that does not involve salt-elimination has been found to give excellent results. Extended reaction at room temperature between powdered Ln (Ln = Ho, Er, Tm, Lu) and Ph_2Hg in the presence of catalytic amounts of LnI_3 affords the σ-aryls *fac*-$LnPh_3(THF)_3$. With Eu and Yb the divalent compounds $LnPh_2(THF)_2$ are obtained [16]. The structures of the erbium and thulium compounds show them to have molecular structures with octahedral coordination of the lanthanides with bond lengths of Er–C = 2.412, 2.440, 2.442 Å and Tm–C = 2.416, 2.421, 2.425 Å. As discussed below, in comparison with $PhGdCl_2 \cdot 4THF$, these bond lengths seem slightly long, and indication of steric crowding is also given by C–Ln–C angles of 99.2–103.5° (Er) and 99.8–104.2° (Tm). Yellow $YbPh_3(THF)_3$ is a minor product of the reaction between $(C_{10}H_8)Yb(THF)_2$ and Ph_2Hg [53] along with the mixed valence $Yb_2Ph_5(THF)_4$ system. $Yb_2Ph_5(THF)_4$, which has the structure $Ph_2(THF)Yb(\mu\text{-}Ph)_3Yb(THF)_3$, has been viewed as an association of $Yb^{II}Ph_2(THF)$ and $Yb^{III}Ph_3(THF)_3$ though there is some η^2 character in some of the bridging interactions (see Fig. 1).

The terminal Yb^{III}–C distances average 2.42 Å, in keeping with the values for $[LnPh_3(THF)_3]$ (Ln = Er, Tm); though the bridging Yb–C distances are, as expected, rather longer (averaging 2.60 Å), the Yb^{III}–C distances are in two cases slightly shorter than the Yb^{II}–C distances. Thus, the triphenyls are now firmly established for the later lanthanides (Ho–Lu), and it will be interesting to see if compounds $[LnPh_3(THF)_4]$ are feasible for the lighter metals, and whether $[ScPh_3(THF)_3]$ can be isolated.

Using a deficit of reagent, monophenyls have proved isolable. Thus $LnCl_3$ and PhLi (0.5 mol) in THF give $PhLnCl_2 \cdot n$THF (Sm, Gd $n = 4$; Pr $n = 3$); the gadolinium compound has the structure shown (Fig. 2), with a Gd–C distance of 2.416(24) Å. This is is relatively short compared to the triphenyls, and suggests a possible crowding in them [54].

All the structures discussed so far have been neutral species. Historically, however, the first σ-bonded f-block organometallic to be crystallographically characterised was $[Li(THF)_4]^+$ $[Ln(2,6\text{-}Me_2C_6H_3)_4]^-$ (Ln = Lu, Yb), prepared by the reaction of $LnCl_3$ with $2,6\text{-}Me_2C_6H_3Li$ in THF. Such species could only be obtained for the smallest two lanthanides, ytterbium (lemon) and lutetium (colourless). The use of the methyls attached to the *ortho*-carbons was a deliberate attempt to introduce crowding, reduce bridging tendencies, inhibit approach between lanthanides and

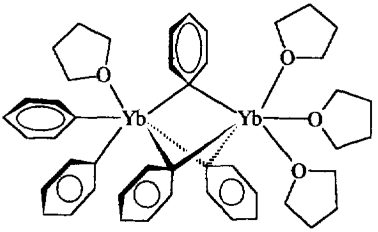


Fig. 1. The structure of $Ph_2(THF)Yb(\mu\text{-}Ph)_3Yb(THF)_3$.

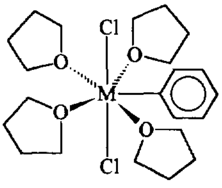


Fig. 2. The structure of $PhGdCl_2 \cdot 4THF$.

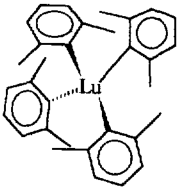


Fig. 3. The structure of the anion in $[[Li(THF)_4][Lu(C_6H_3Me_2)_4]$.

isolate simple molecular units. The structure of the anion shows lutetium in distorted tetrahedral coordination (C–Lu–C = 99.4–118.2°; Lu–C = 2.425, 2.439, 2.442, 2.501 Å); the infrared spectrum showed sharp σ-phenyl like absorption [55] (see Fig. 3).

Not only do the data in Table 2 indicate the Lu–C bond to be longer than expected, but it is also some 0.07 Å longer than the Yb–C bonds in [18] 4-coordinate $[Yb\{CH(SiMe_3)_2\}_3Cl]^-$ (Yb–C 2.372, 2.373, 2.391 Å) and 0.08 Å longer than Lu–C in 5-coordinate $Lu(OEP)\{CH(SiMe_3)_2\}$ (Lu–C = 2.374 Å) [22], indicating steric crowding. Although no such research has been reported, it is likely that suitably bulkier groups could favour isolation of 4-coordinate anionic or 3-coordinate neutral $Ln(aryl)_3$ species for lighter, larger, lanthanides. Another line of attack would additionally involve the use of Li^+-coordinating ligands like tmed that are more involatile than THF, to allow ions like $[Li(tmed)_2]^+$ to act as spacers in a structure separating $[Ln(aryl)_4]^-$ ions, inhibiting the oligomerization that otherwise tends to happen.

2.2. *Homoleptic alkyls*

Compounds with the methyl, (trimethylsilyl)methyl and neopentyl ligands, which are unable to undergo β-elimination, have been studied in particular detail.

2.2.1. *Bis(trimethylsilyl)methyls, (trimethylsilyl)methyls, and neopentyls*

The first of these to be characterized were $M(CH_2QMe_3)_3$ (M = Sc, Y; Q = C, Si), prepared by

$$MCl_3 + 3LiCH_2QMe_3 \rightarrow M(CH_2QMe_3)_3 + 3LiCl$$

isolated as colourless crystalline THF adducts $Sc(CH_2QMe_3)_3 \cdot 2$ THF and

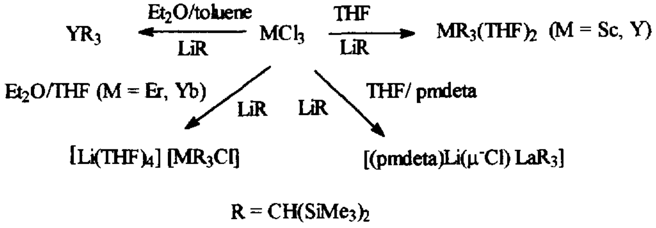
Table 2
Bond lengths in lanthanide aryls

Compound	C.N.	Ln-C (av.) (Å)	(Ln-C)-radius Ln^{3+} (Å)
$GdPhCl_2(THF)_4$	7	2.412	1.474
$ErPh_3(THF)_3$	6	2.431	1.541
$TmPh_3(THF)_3$	6	2.421	1.541
$Lu(2,6\text{-}Me_2Ph)_4^-$	4	2.452	1.591

$Y(CH_2QMe_3)_3 \cdot 2$ THF (Q = C, Si) believed to have trigonal bipyramidal structures, with axial THF ligands, from NMR evidence [56]. For lanthanides, $Ln(CH_2SiMe_3)_3 \cdot 2$ THF were isolated for Tb, Er, Tm, Yb and Lu; erbium and thulium also afforded $Ln(CH_2SiMe_3)_3 \cdot 3$ THF at low temperatures, which lost the third THF on warming to about −20°C. The bis(THF) adducts are generally stable up to their melting points around 50°C [18,28,57].

Anionic species are obtained by reaction with excess $LiCH_2SiMe_3$ in the presence of THF or tmed to solvate the lithium ion; compounds $[Li(THF)_4][Ln(CH_2SiMe_3)_4]$ (Ln = Y, Er, Tb, Yb) and $[Li(tmed)_4][Ln(CH_2SiMe_3)_4]$ (Ln = Y, Er, Yb, Lu) were obtained [18,28]. Reaction of YCl_3 with $LiCH_2SiMe_3$ and $LiOCMe_3$ gives $\{(Me_3SiCH_2)_x(Me_3CO)_{1-x}Y(\mu\text{-}OCMe_3)_4\ [Li(THF)_4](\mu_4\text{-}Cl)\}^+\ [Y(CH_2SiMe_3)_4]^-$; in the tetrahedral $[Y(CH_2SiMe_3)_4]^-$ ion, Y–C distances are in the range 2.403(8) to 2.420(9) Å, averaging 2.41(2) Å [58] (allowing for the ionic radius differences, very similar to the Yb–C distances in $[Yb\{CH(SiMe_3)_2\}_3\ Cl]^-$.

More is known about compounds of the bulkier bis(trimethylsilyl)methyl, $CH(SiMe_3)_2$ ligand [59].



Unlike $-CH_2SiMe_3$, four $-CH(SiMe_3)_2$ ligands cannot be so readily accomodated round a lanthanide ion; the inability to replace the chlorine in $[YbCl\{CH(SiMe_3)_2\}_3]^-$ recalls the inability of the isolobal $-N(SiMe_3)_2$ ligand to replace the fourth chlorine in $ThCl_4$ leading to the isolation of $[ThCl\{N(SiMe_3)_2\}_3]$ [60]. $Li[Er\{CH(SiMe_3)_2\}_4]$ could, however, be obtained by heating a solution of $[Li(THF)_4]\ [ErCl\{CH(SiMe_3)_2\}_3]$ in hexane [61]. The $[YbCl\{CH(SiMe_3)_2\}_3]^-$ ion has a distorted tetrahedral structure with Yb–C distances of 2.372(16), 2.373(24) and 2.391(20) Å and Yb–Cl = 2.486 Å, whilst lanthanum has a similar environment in $[(pmdeta)Li(\mu\text{-}Cl)La\{CH(SiMe_3)_2\}_3]$ (Fig. 4). The La–C distances (2.55(2), 2.58(2) and 2.60(2) Å) (mean value 2.57(3) Å) and C–La–C angles (average 108.8°) in the latter are, however very similar to those in the 3-coordinate pyramidal $[La\{CH(SiMe_3)_2\}_3]$ (La–C 2.515 Å; 109.9°) suggesting that the chloride bridge causes minimal distortion.

YCl_3 reacts with $LiCH(SiMe_3)_2$ in diethyl ether forming $[(Et_2O)_3Li(\mu\text{-}Cl)Y\{CH(SiMe_3)_2\}_3]$ [62] where Y–C = 2.423(12) Å, similar to those in the lanthanum and ytterbium compounds. A different, metathetic, strategy has been adopted [21] to synthesize $[Ln\{CH(SiMe_3)_2\}_3]$, involving replacement of aryloxide groups in $[Ln(OC_6H_3Bu^t_2\text{-}2,6)_3]$, thus obviating the possibility of chloride retention. $[La\{CH(SiMe_3)_2\}_3]$ and $[Sm\{CH(SiMe_3)_2\}_3]$ (Fig. 5) were both synthe-

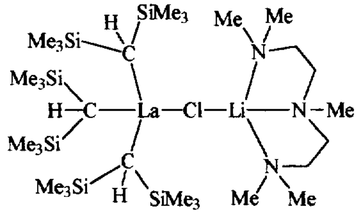


Fig. 4. The structure of $[(pmdeta)Li(\mu\text{-}Cl)La\{CH(SiMe_3)_2\}_3]$.

sized by this route

$$[Ln\{OC_6H_3Bu^t_2-2,6\}_3]+3LiCH(SiMe_3)_2 \rightarrow [Ln\{CH(SiMe_3)_2\}_3] + 3LiOC_6H_2Bu^t_2-2,6$$

They have pyramidal structures, similar to those found in the silylamides $[Ln\{N(SiMe_3)_2\}_3]$, with La–C = 2.515(9) Å and Sm–C = 2.33(2) Å; such pyramidal structures may be adopted in the solid state to minimize non-bonding interactions involving the ligands. Bond lengths can be compared with those in the analogous $[U\{CH(SiMe_3)_2\}_3]$ [63] where U–C = 2.48(2) Å; the U–C distance is 0.03 Å shorter than La–C, on ionic radius grounds a discrepancy of 0.01 Å is expected, but given the large deviations, this is not significant. The Sm–C distance is, however, some 0.1 Å less than would be anticipated, and structural data for similar compounds would be welcomed (This has been attributed [64] to agostic interactions or to the absence of other ligands capable of reducing the electron density on the lanthanide thus weakening the electrostatic metal–ligand interaction; this explanation does not address the discrepancy between the lanthanum and samarium compounds.) The lutetium and yttrium analogues have been prepared by the same route [22] and there seems to be no obvious reason that $[Sc\{CH(SiMe_3)_2\}_3]$ or any $[Ln\{CH(SiMe_3)_2\}_3]$ cannot be isolated, except for $[Eu\{CH(SiMe_3)_2\}_3]$ where redox problems may arise.

Chemically $[Ln\{CH(SiMe_3)_2\}_3]$ behave as Lewis acids, besides reacting with water, like lanthanide organometallics in general, they also are attacked by other nucleophiles such as amines and phenols forming the silylamides and aryloxides [21].

$$[Sm\{CH(SiMe_3)_2\}_3]+HOC_6H_2Bu^t_2-2,6-Me-4 \rightarrow [Sm\{OC_6H_2Bu^t_2-2,6-Me-4\}_3]$$

$$[Sm\{CH(SiMe_3)_2\}_3]+HN(SiMe_3)_2 \rightarrow [Sm\{N(SiMe_3)_2\}_3]$$

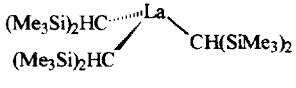


Fig. 5. The structure of $[Ln\{CH(SiMe_3)_2\}_3]$.

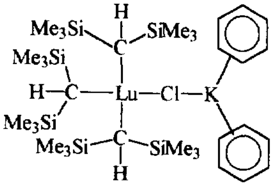


Fig. 6. The structure of $[(\eta^6\text{-}C_7H_8)_2(\mu\text{-Cl})Lu\{CH(SiMe_3)_2\}_3]$.

They undergo attack by methyllithium [65]

$$[Ln\{CH(SiMe_3)_2\}_3] + MeLi + pmdeta \rightarrow$$
$$[(pmdeta)Li(\mu-Me)Ln\{CH(SiMe_3)_2\}_3]\ (Ln = La, Sm)$$

The samarium compound has a roughly linear bridge and a long Li–CH_3 bond (2.42 Å) but a short Sm–CH_3 bond (2.33(3) Å), thus the bridge can be termed asymmetric. The Sm–C ($CH(SiMe_3)_2$) bonds (2.49(3), 2.52(3) and 2.53(3) Å) are similar in length to those in $[La\{CH(SiMe_3)_2\}_3]$.

$[Lu\{CH(SiMe_3)_2\}_3]$ displays more striking electrophilic tendencies; it (but not $La\{CH(SiMe_3)_2\}_3]$) reacts with KCl in ether, forming $[(Et_2O)K(\mu\text{-Cl})Lu\{CH(SiMe_3)_2\}_3]$ [66]; as the authors remark, it is noteworthy that solvation of the potassium and coordination of the chloride to potassium and lutetium compensate for the loss of lattice energy (The KBr analogue can be prepared similarly). The ether is removed on gentle heating in vacuo; the resulting $[K(\mu\text{-Cl})Lu\{CH(SiMe_3)_2\}_3]$ dissolves in toluene forming $[(\eta^6\text{-}C_7H_8)_2K(\mu\text{-Cl})Lu\{CH(SiMe_3)_2\}_3]$ which has a rather bent K–Cl–Lu bridge (145.9°) and Lu–Cl 2.515 A (Fig. 6). The Lu–C distances of 2.324(10), 2.349(10) and 2.357(8) Å correlate well with those in $[La\{CH(SiMe_3)_2\}_3]$, allowing for the difference in radii.

2.2.2. *Methyls*

Reaction of methyllithium with MCl_3 (M = Sc, Y, La) in THF yielded [49] products contaminated with LiCl and whose IR spectra showed the presence of THF. It is possible that these were analogous to the recently reported dimethylamides [67], products of the type $MMe_3 \cdot 3LiCl$.

Fully characterized methyls have been obtained as $M(CH_3)_6^{3-}$ anions by the action of excess (6.5 mol) of MeLi to MCl_3 in ether in the presence of 3 mol of a chelating ligand (L–L), either tetramethylethylenediamine (tmed) [20,68] or tris(1,2-dimethoxyethane) (dme) [20b], the compounds having the formulae $[Li(tmed)]_3[M(CH_3)_6]$ (M = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and $[Li(dme)]_3[M(CH_3)_6]$ (M = Y, Ce, Nd, Sm, Gd, Tb, Dy, Er, Lu) (see Fig. 7.

$$MCl_3 + 6MeLi + 3L-L \rightarrow [Li(L-L)]_3[M(CH_3)_6] + 3LiCl$$

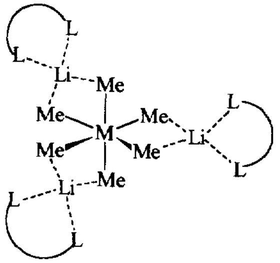


Fig. 7. The structure of $[Li(tmed)]_3[M(CH_3)_6]$.

The structures show essentially octahedral coordination of the metals with bond angles near 90° (see Table 3).

The $Ln–CH_3$ bonds are lengthened by formation of electron-deficient 3-centred $Li\cdots CH_3\cdots Ln$ bonds. The lengthening can be estimated by comparing the Lu–C bonds with those [22] in $[Lu(OEP)\{CH(SiMe_3)_2\}]$ where Lu–C = 2.374 Å indicating a lengthening of some 0.15 Å. Similarly, in the compound $[\{Li(tmed)^+\}_3ThMe_7]$ one methyl is bonded only to thorium [69], with $Th–CH_3 = 2.571(9)$; the other six methyls are all also bound in a bridging fashion to $Li(tmed)^+$ as well as to thorium, with $Th–CH_3$ distances of 2.655-2.765 Å (average 2.701 Å). Here, again, the effect of the bridge is to lengthen the metal–carbon bond by an average of 0.13 Å. A dimeric species [20b] $[\{Li_2(teed)(Et_2O)_2\}_2Lu_2(CH_3)_{10}]$ was also isolated (teed = tetraethylethylenediamine) (Fig. 8).

Another recent approach to lanthanide methyls has relied on the reaction of main-group methyls, Lewis acids, with lanthanide alkoxides [70] and amides [67], a process of the type implicated in the lanthanide-catalyzed polymerization of conjugated dienes.

$$Ln(OBu^t)_3 + 3AlMe_3 \rightarrow [Ln\{(\mu-OBu^t)(\mu-Me)AlMe_2\}_3] \text{ (Fig 9:A)}$$

$$(Ln = Pr, Nd, Y)$$

$$NdCl_3 + 3LiNMe_2 \rightarrow [Nd(NMe_2)_3(LiCl)_3] + 3MMe_3 \rightarrow [Nd(NMe_2)_3(MMe_3)_3]$$

$$(M = Al, Ga)$$

The amide products do not have the anticipated symmetrical structure, instead one MMe_3 group does not form a μ-methyl bridge (Fig. 9: B). Reaction with excess MMe_3 gives heterometallic peralkyls $[Ln\{(\mu-Me)_2MMe_2\}_3]$ (Fig. 9: C, D, E); a

Table 3
Ln–C bond lengths in the $[Ln(CH_3)_6]^{3-}$ ions

Lanthanide	Ln–C (av.) (Å)	(Ln–C)-radius Ln^{3+} (Å)
Ho	2.563(18)	1.664
Er	2.57(2)	1.68
Lu	2.53(2)	1.669

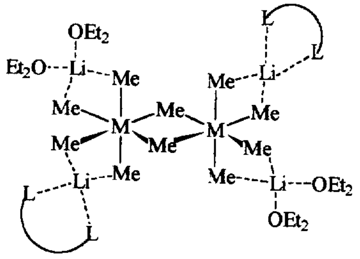


Fig. 8. The structure of $[\{Li_2(teed)(Et_2O)_2\}_2Lu_2(CH_3)_{10}]$.

partially-exchanged product has been fully characterized [67]. The heterometallic peralkyls (M=Al) form inclusion compounds where Al_2Me_6 molecules are trapped in channels between the $[Ln\{(\mu\text{-}Me)_2AlMe_2\}_3]$ molecules [71] (see Table 4).

The data show similar Ln–C distances in $[Nd\{(\mu\text{-}Me)_2GaMe_2\}_3]$, $[Nd\{(\mu\text{-}Me)_2AlMe_2\}_3]$ and $[Y\{(\mu\text{-}Me)_2AlMe_2\}_3]$ (Fig. 10: compounds C–E) allowing for ionic radii differences. These compare closely with those in the methylate ions $LnMe_6^{3-}$ which similarly are in a bridging situation. This is not the case in $[La\{(\mu\text{-}Me)(\mu\text{-}NMe_2)GaMe_2\}_2\ \{(\mu\text{-}Me)GaMe_2\}]$ (Fig. 9(F)), whilst the Ln–C distances in those bridges in $[Nd\{(\mu\text{-}OBu^t)(\mu\text{-}Me)AlMe_2\}_3]$ (Fig. 9: compound A); $[Nd\{(\mu\text{-}Me)(\mu\text{-}NMe_2)GaMe_2\}_2\{(\mu\text{-}NMe_2)GaMe_2\}]$ (Fig. 9: B), and $[La\{(\mu\text{-}Me)\text{-}(\mu\text{-}NMe_2)GaMe_2\}_2\ \{(\mu\text{-}Me)GaMe_2\}]$ (Fig. 9: F) which involve mixed methyl/amide or methyl/alkoxide bridges are also strikingly long.

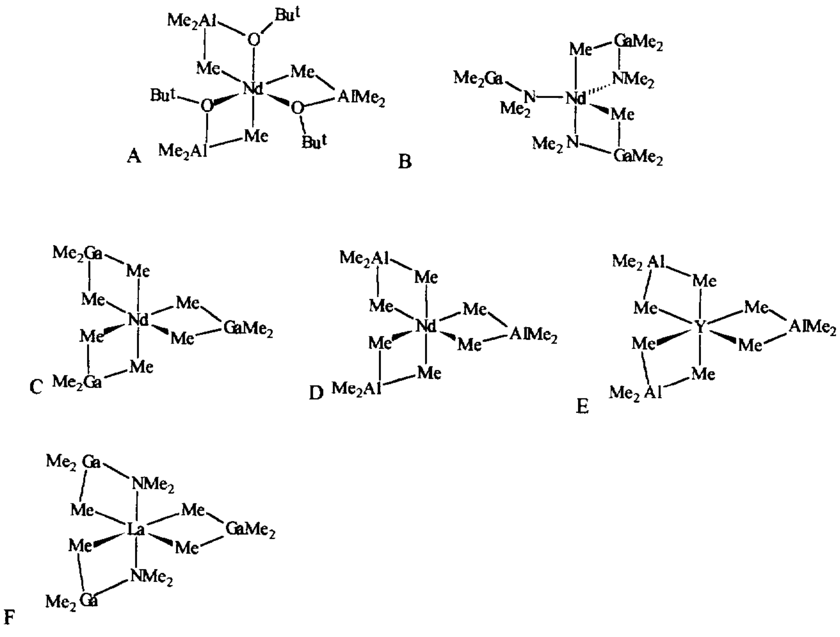


Fig. 9. The structure of alkyl-bridged lanthanide alkoxides and alkylamides.

Table 4
Bond lengths in bridged lanthanide methyls (Å)

Compound	Ln–C	Ln–C (av.) (homobridge)	Ln–C (av.) (hetero)
$[Nd\{(\mu\text{-}OBu^t)(\mu\text{-}Me)AlMe_2\}_3]$	2.784		2.784
$[Nd\{(\mu\text{-}Me)(\mu\text{-}NMe_2)GaMe_2\}_2\{(\mu\text{-}NMe_2)GaMe_2\}]$	2.749		2.749
$[Nd\{(\mu\text{-}Me)_2GaMe_2\}_3]$	2.581--2.619	2.599	
$[Nd\{(\mu\text{-}Me)_2AlMe_2\}_3$	2.563--2.609	2.589	
$[Y\{(\mu\text{-}Me)_2AlMe_2\}_3]$	2.505--2.510	2.508	
$[La\{(\mu\text{-}Me)(\mu\text{-}NMe_2)GaMe_2\}_2\ \{(\mu\text{-}Me)GaMe_2\}]$	2.746--2.992	2.76	2.941

2.2.3. *Other alkyls*

A red triphenylmethyl compound has been isolated as a cryptate [72]

$$Ph_3CLi + LaCl_3(B) \rightarrow Ph_3CLaCl_2(B) + LiCl$$

$$B = N\{(CH_2)_2O(CH_2)_2O(CH_2)_2\}_3N$$

Two groups have isolated anionic tetrabutyls, $[Li(THF)_n]^+$ $[LnBu^t_4]^-$ ($n=3$, Ln = Yb; $n=4$, Ln = Er, Lu) [73], $[Li(tmed)_2]^+$ $[LnBu^t_4]^-$ (Ln = Tb, Lu) and $[Li(Et_2O)_4]^+$ $[ErBu^t_4]^-$ [20,74]. These were prepared by two routes

$$LnCl_3 + 4Bu^tLi + n THF \rightarrow [Li(THF)_n][Ln(Bu^t)_4] + 3LiCl$$

$$Ln(OBu^t)_3 + 4Bu^tLi + 2tmed \rightarrow [Li(tmed)_2][Ln(Bu^t)_4]$$
$$+ 3Bu^tOH\ (Ln = Er, Yb)$$

$[Li(tmed)_2]^+$ $[LuBu^t_4]^-$ has tetrahedral coordination of lutetium with Lu–C = 2.32–2.43 Å (average 2.37(6) Å) [74], allowing for ionic radii differences, closely comparable with Y–C in the similarly tetrahedral $[Y(CH_2SiMe_3)_4]^-$ ion.

Simple benzyls are reportedly unstable with $[Nd(CH_2Ph)_3(Et_2O)_x]$ obtained in solution but not isolated [75]; further investigation in the area is merited, since under the conditions employed in some experiments, the workers did not isolate Me_3SiCH_2 derivatives of Y and Nd. Even with the possibility of some π-bonding between the lanthanide and the benzene ring, as is believed to be the case with $[(C_6H_5CH_2)_4Th]$ [76], it is likely that an anionic species of lutetium or scandium would offer the best chance of isolation. The high reactivity noted for benzyls may however militate against this [29].

A number of alkyls of scandium and lanthanide porphyrins have been made

$$[Sc(OEP)Cl] + MgR_2 \rightarrow [Sc(OEP)R] + MgRCl\ (R = Me, CH_2Me_3)$$

$$[Sc(OEP)Cl] + LiCH(SiMe_3)_2 \rightarrow [Sc(OEP)\{CH(SiMe_3)_2\}] + LiCl$$

$$OEP\ H_2 + [Ln\{CH(SiMe_3)_2\}_3] \rightarrow [Ln(OEP)\{CH(SiMe_3)_2\}] + 2CH_2(SiMe_3)_2$$
$$(Ln = Lu, Y)$$

Structures reported for three of these compounds show the expected 5-coordinate square pyramidal geometries. Bond lengths for [Sc(OEP){Me}] Sc–C = 2.246(3) Å (Sc–N = 2.151, 2.152, 2.157, 2.158 av. 2.1545 Å) and for [Sc(OEP){CH(SiMe$_3$)$_2$}] Sc–C 2.243(8) Å (Sc–N = 2.142, 2.151, 2.162, 2.196 av. 2.163 Å) show very similar Sc–C in an uncrowded environment [77]. Hence if significant differences between Ln–C distances for a methyl and a bis(trimethylsilyl)methyl are observed (presumably the same comment applies to to trimethylsilylmethyls), it may be taken as evidence of steric effects. In [Lu(OEP){CH(SiMe$_3$)$_2$}] [22] Lu–C 2.374 Å (Lu–N = 2.236, 2.256, 2.253, 2.296 av. 2.260 Å), M–C is increased by 0.131 Å compared with the scandium analogue; the ionic radius difference for the two metals is 0.116 Å.

An alkyl complex of the diazacrown macrocycle DAC (H$_2$DAC = 4,13-diaza-18-crown-6) has been made [78] by a proton transfer reaction of a homoleptic alkyl, as a suitable pure starting material such as [Y(DAC)Cl] was not available for metathesis

$$Y(CH_2SiMe_3)_3 \cdot 2THF + H_2DAC \rightarrow Y(DAC)CH_2SiMe_3 + 2SiMe_4 + 2THF$$

The crystal structure shows the presence of 7-coordinate yttrium (Fig. 10) with a Y–C distance of 2.468 Å, longer than might have been predicted by comparison with [Lu(OEP){CH(SiMe$_3$)$_2$}] and similar to that in [Cp$^*_2$Y{CH(SiMe$_3$)$_2$}], possibly indicative of steric congestion, though there was no evidence of agostic interaction. In the light of this, it is interesting that the compound reacts with phenylacetylene giving both the dimer [(DAC)Y(μ-C≡CPh)$_2$Y(DAC)] and the coupled species [(DAC)Y(μ-Ph–C=C=C=C–Ph)Y(DAC)] in an equilibrium mixture, coupling presumably induced by steric effects. The dimer is asymmetric, with the asymmetry less marked in the Y–C bond lengths than in the bond angles.

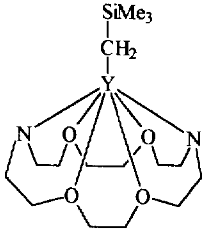


Fig. 10. The structure of [Ln(DAC)CH$_2$SiMe$_3$].

2.3. Alkynyls

Sc(C≡CPh)$_3$ was prepared by salt-elimination [49]

$$ScCl_3 + 3LiC{\equiv}CPh \rightarrow Sc(C{\equiv}CPh)_3 + 3LiCl$$

Other compounds of the lanthanides have been made by an exchange reaction starting with the bis(trimethylsilyl)amides [79].

$$[Ln(N(SiMe_3)_2)_3]+3HC\equiv CPh\rightarrow Ln(C\equiv CPh)_3+3HN(SiMe_3)_2$$

(Ln = Pr, Sm, Eu, Gd, Tb, Er, Yb)

Both neutral and anionic *t*-butylalkynyls have been made [38,73,80].

$$[Lu(o-C_6H_4CH_2NMe_2)_3]\xrightarrow{HC\equiv CCMe_3}[Lu(C\equiv CCMe_3)_3]$$

$$[Li(THF)_nLn(Bu^t)_4]+4HC\equiv CCMe_3\rightarrow[Li(THF)][LLn(C\equiv CCMe_3)_4]$$

$+4C_4H_{10}$ (Ln = Sm, Er, Lu, Y)

2.4. *Compounds involving chelating ligands*

These ligands have been used to attempt coordinative saturation and lessened lability of the resulting compounds. Scandium(III) chloride reacts with $LiCH_2C_6H_4NMe_2$ in THF [81] forming a pyrophoric compound assumed to have the structure shown in Fig. 11.

A similar approach has been used [82] to obtain 6-coordinate compounds [*mer*-$M(o\text{-}C_6H_4CH_2NMe_2)_3$] (M = Er, Yb, Lu) of the later lanthanides (Fig. 12) similar compounds could not be obtained for terbium or any lighter (and larger) lanthanides. The crystal structure of the lutetium compound confirmed the octahedral coordination with Lu–C = 2.425, 2.426 and 2.455 Å and Lu–N = 2.468, 2.478 and 2.588 Å.

Another approach utilized the deprotonation, using butyllithium, of lanthanide ylide complexes [83].

$$LnCl_3+3Me_3P{=}CH_2\rightarrow[Ln(CH_2{=}PMe_3)_3]Cl_3$$

$$[Ln(CH_2{=}PMe_3)_3]Cl_3+3BuLi\rightarrow[Ln\{(CH_2)_2PMe_2\}_3]+3C_4H_{10}+3LiCl$$

A di(*t*-butyl)phosphoniumbismethylide was made by salt elimination.

$$LuCl_3+3Li\{(CH_2)_2PBu^t_2\}\rightarrow[Ln\{(CH_2)_2PBu^t_2\}_3]+3LiCl$$

They are believed to have the structure shown in Fig. 13.

This approach has also sometimes been used in the presence of coligands like Cp.

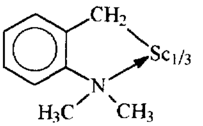


Fig. 11. The structure of $[Sc(CH_2C_6H_4NMe_2)_3]$.

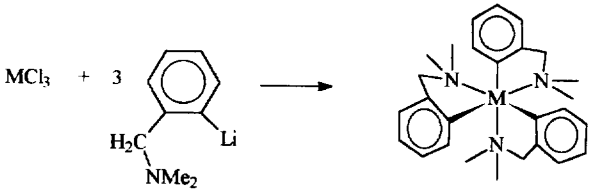


Fig. 12. The structure of $[M(o\text{-}C_6H_4CH_2NMe_2)_3$ (M = Er, Yb, Lu).

2.5. *The +2 oxidation state*

Reaction of alkyl and aryl iodides in THF solution with europium and ytterbium gives species analyzing as $RLn^{II}I$ (Ln = Eu, Yb; R, e.g., Me, Et, Ph) with Grignard-like properties [84]. No definite compounds could be isolated from the solutions. Some samarium compounds, though less well-defined, could be identified. These metals can react with C_6F_5Br, whilst if activated with methyl iodide, they also react with $C_8H_{17}X$ (X = Cl, Br, I) [85]. RYbI species react with stronger acids [86]

$$RYbI + R'H \rightarrow R'YbI + RH \ (R = Me, Ph; R' = PhC{\equiv}C, C_6F_5, \text{etc.})$$

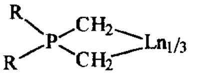
Europium and ytterbium react with mercury alkynyls [87] in THF to give $Ln^{II}(C{\equiv}CR)_2$ (R, e.g., Bu, Ph, C_6F_5) and other transmetallations are possible

$$Ln + Hg(C{\equiv}CR)_2 \rightarrow Ln(C{\equiv}CR)_2 + Hg$$

$$Ln + Hg(C_6F_5)_2 \rightarrow Ln(C_6F_5)_2 + Hg$$

The best known compound is $Yb(C_6F_5)_2$, whose stability may be increased by Yb–F interactions. Bis(pentafluorophenyl)ytterbium can be isolated [23,88] as a crystalline THF adduct $Yb(C_6F_5)_2 \cdot 4$. THF could structurally resemble the recently characterized $[Yb(QR_3)_2 \cdot (thf)_4]$ ($QR_3 = SnPh_3$, $Sn(SnMe_3)_3$) [89a] and $[Yb(PPh_2)_2(thf)_4]$ [89b], $[Sm(PPh_2)_2(N\text{-methylimidazole})_4]$ [89b] and $[Yb(P(mesityl)_2)_2(thf)_4]$ [89c], all having *trans*-octahedral structures.

Recently the first Ln^{II} alkyls to be isolated as solids have been reported [90]. Reaction of YbI_2 with $NaCH(SiMe_3)_2$ leads to a number of alkyls; those shown can be converted into alkylalkoxides and other species (Fig. 14(a)) $[NaYb\{CH(SiMe_3)_2\}_3]$ probably has a structure analogous to that of the alkylamides [91] $[NaLn\{N(SiMe_3)_2\}_3]$ (Ln = Eu, Yb), $[Na\{\mu\text{-}CH(SiMe_3)_2\}_2Yb\{CH(SiMe_3)_2\}]$. Similarly $[Yb\{CH(SiMe_3)_2\}_2(dmpe)]$ a monomeric struture like $[Yb\{N(SiMe_3)_2\}_2(dmpe)]$; these amides have short Yb···H and Yb···C contacts of the type familiar in alkyls.



R = Me, Bu^t

Fig. 13. The structure of $[Ln\{(CH_2)_2PR_2\}_3]$.

YbI_2 reacts with $KC(SiMe_3)_3$ in benzene forming orange crystals of $[Yb(C(SiMe_3)_3)_2]$ [14] (sublimeable at 95°/10^{-4} Torr). The crystal structure shows it to be a bent molecule (C–Yb–C 137°), with two coordinate ytterbium (Yb–C = 2.495(9) Å), but there are agostic Yb· · ·C interactions causing the bending; normally $M(CR_3)_2$ species are linear, but it is suggested that with the long Yb–C distance found here, repulsion between $SiMe_3$ groups that might enforce linearity is reduced [14].

On reaction with ether, dimeric $[(Et_2O)(R)Yb(\mu\text{-}OEt)_2Yb(R)(OEt_2)]$ forms $(R = (Me_3Si)_3C)$.

$$YbR_2 + 2Et_2O \rightarrow \tfrac{1}{2}[(Et_2O)(R)Yb(\mu - OEt)_2Yb(R)(OEt_2)] + RH + CH_2{=}CH_2$$

This has a Yb–C distance of 2.573(13) Å [90], rather long compared with the corresponding iodo-bridged species. Ytterbium undergoes a Grignard-like reaction [14] with $(Me_3Si)_3CI$ in ether forming $[(Et_2O)(R)Yb(\mu\text{-}I)_2Yb(R)(OEt_2)]$ with a Yb–C distance of 2.47(2) Å. These compounds are summarized in Fig. 14(b). Europium analogues to many of these should be possible.

Another type of alkyl has been obtained [92] starting with the poly(pyrazolyl)borate complex $[\{HB(bmpz)_3\}YbI(THF)]$ (bmpz = 3-*t*-butyl-5-methylpyrazolyl) which can be alkylated with KR $(R = Me_3SiCH_2, Me_3Si)_2CH)$ to form $[\{HB(bmpz)_3\}Yb(CH_2SiMe_3)(Et_2O)]$ and $[\{HB(bmpz)_3\}Yb(CH(SiMe_3)_2)]$. The Yb–C bond length in the latter is 2.55(6) Å.

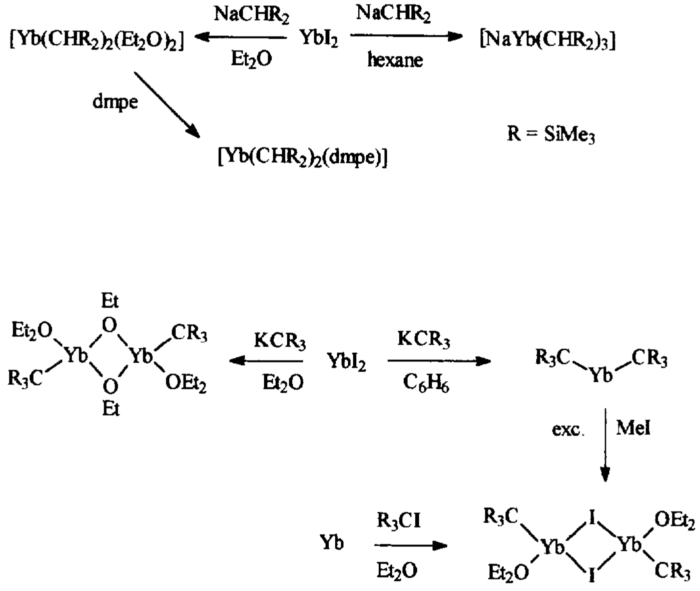


Fig. 14. Synthesis of ytterbium(II) alkyls.

3. Alkyls and aryls also containing π-bonding ligands

3.1. *Cyclopentadienyl alkyls, aryls and alkynyls*

3.1.1. *Syntheses*

Around the time of the synthesis [93] of UCp_3R from reactions of UCp_3Cl with LiR or RMgR (R = alkyl or aryl), analogous reactions with $LnCp_2Cl$ (which, strictly, should be written $[Cp_2Ln(\mu\text{-}Cl)_2LnCp_2]$) resulted in the synthesis of $LnCp_2R(THF)$ (R, e.g., Bu^n, Bu^t, CH_2SiMe_3, *p*-C_6H_4Me, CH_2Ph, etc.) for lutetium and certain of the later lanthanides [25,94]. Stable *tert*-butyls $LnCp_2Bu^t(THF)$ exist for Ln = Y, Er, Yb, Lu, and trimethylsilylmethyls $LnCp_2(CH_2SiMe_3)(THF)$ for Sm, Er, Yb, Lu; in addition there are some phenyls (Ln = Gd, Er, Yb).

$$[LnCp_2Cl]_2 + 2LiR \rightarrow 2LnCp_2R + 2LiCl$$

When this reaction is carried out in THF, the product is $LnCp_2R(THF)$ (Fig. 15). There is little evidence for monomers when no THF is present; $LnCp_2Me$ are dimers $[Cp_2Ln(\mu\text{-}Me)_2LnCp_2]$).

Few other simple alkyls have been isolated, possibly owing to β-elimination, though a few lutetium species have been characterized in solution, they tend to decompose at room temperature (R = Me, Et, Pr^i, Bu^n). The isolation and relative stability of $[LuCp_2Bu^t(THF)]$ may well be due to steric effects, a combination of the smallest lanthanide with a very bulky alkyl ligand. $[LuCp_2(CH_2)_3NMe_2]$ undoubtedly owes its stability [95] to chelation blocking a vacant site on the lutetium. (Fig. 16) The Lu–C distance of 2.22(1) Å is the shortest Lu–C σ-bond reported and must reflect an uncrowded environment around lutetium; the Lu–N distance of 2.37(1) Å is in line with those found in amides. Similar syntheses with Li(C≡CR) in THF afford dimers $[Cp_2Ln(\mu\text{-}C{\equiv}CR)_2LnCp_2]$ (Fig. 17) (R, e.g., Bu^n, Bu^t, Ph, Cy). The first structure of such an alkynyl to be reported was that of $[Cp_2Er(\mu\text{-}C{\equiv}CBu^t)_2ErCp_2]$ showing a slightly asymmetric bridge with Er–C = 2.42(2) and 2.47(2) Å [96], such asymmetry being typical of these systems, discussed in Section 3.1.2.3.

Reaction of $LnCp_2Cl$ with $LiAlMe_4$ gives a μ-dimethyl bridged species (Fig. 18) [97]. Similar, but less stable, ethyls can be made.

$$LnCp_2Cl + LiAlMe_4 \rightarrow LnCp_2(\mu - Me_2)AlMe_2 + LiCl$$

These heterometallic dimers undergo cleavage of the bridge with pyridine [30] to

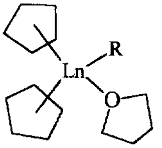


Fig. 15. The structure of $[LnCp_2R(THF)]$.

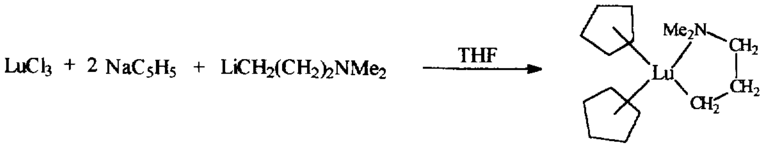


Fig. 16. The synthesis of [LuCp$_2$(CH$_2$)$_3$NMe$_2$].

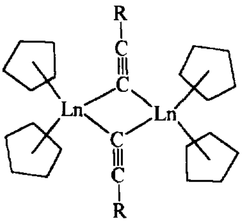


Fig. 17. The structure of [Cp$_2$Ln(μ-C≡CR)$_2$LnCp$_2$].

give [LnCp$_2$R]$_2$ (Fig. 19)

$$2\mathrm{LnCp_2(\mu-Me_2)AlMe_2} + 2\mathrm{py} \rightarrow \mathrm{Cp_2Ln(\mu-Me_2)LnCp_2} + 2\mathrm{AlMe_3 \cdot py}$$

3.1.2. Structural comments

3.1.2.1. LnCp$_2$R(THF) systems. The first structure to be reported was that of [LuCp$_2$Bu^t(THF)] [98]. Though few data were available for comparison and, moreover, the only Lu–C σ-bond length known was the "long" one in [Lu(2,6-dimethylphenyl)$_4$]$^-$, Evans et al. perceptively commented that both were longer than expected "perhaps due to steric crowding in both complexes". Data in Table 5 for Ln–C σ-bonds in related systems more recently determined show that the Lu–Bu^t σ-bond to be some 0.1 Å longer than predicted (indeed it is about the same length as the Lu–C bridge bonds in Cp$_2$Lu(μ-CH$_3$)$_2$Li(tmed) which are

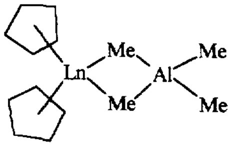


Fig. 18. The structure of [LnCp$_2$(μ-Me$_2$)AlMe$_2$].

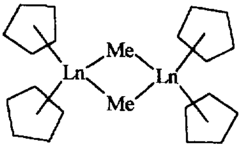


Fig. 19. The structure of [Cp$_2$Ln(μ-Me$_2$)LnCp$_2$].

Table 5
Bond lengths (Å) in lanthanide alkyls and related compounds, giving evidence for steric congestion

Compound	Ln–C (σ-)	Ln–O	Ref.
$LuCp_2(Bu^t)(THF)$	2.47 (2)	2.31 (2)	[98]
$LuCp_2(CH_2SiMe_3)(THF)$	2.376 (17)	2.288 (10)	[25]
$LuCp_2(p\text{-}MeC_6H_4)(THF)$	2.345(39)	2.265 (28)	[25]
$Cp_2Lu(\mu\text{-}Me_2)Li(tmed)$	2.461 (12)		[99]
$YCp_2(Me)(THF)$	2.362 (11)	2.31 (1)	[100]
$LuCp_2Cl(THF)$		2.27 (1)	[101]
$LuCp_3(THF)$		2.39 (2)	[102]
$YCp_2(CH_2SiMe_3)_2^-$	2.425 (23)		[103]

expected to be some 0.1–0.2 Å longer than terminal Lu–C (alkyl) bonds. Evans et al. estimated a Lu–O bond length by extrapolation from [$LnCp_3(THF)$] compounds; now that a considerable body of data is available, it is now known that the Ln–O distances in [$LnCp_3(THF)$] do tend to be unusually long, and it can now clearly be seen that the value for [$LuCp_2Bu^t(THF)$] is the longest known for a [$LuCp_2X(THF)$] molecule, again supporting the view of crowding.

3.1.2.2. Dialkyl bridges. In [$Cp_2Ln(\mu\text{-}Me)_2Li(tmed)$], the Ln–$CH_3$ distances at 2.46(2) Å (Ln = Er, Lu) are surprisingly short compared to those in the [MMe_6]$^{3-}$ ions although in both cases there are Ln–CH_3–Li bridges (see Fig. 20).

For the compounds [$LnCp_2(\mu\text{-}Me_2)AlMe_2$] and [$Cp_2Ln(\mu\text{-}Me_2)LnCp_2$], the lanthanide–carbon distances in the bridges are long compared to terminal Ln–C distances, as expected. The heterometallic bridges in the aluminium compounds look long in comparison (Table 6), and may reflect a polarization of the bond towards the more electropositive aluminium, though at a 3σ level of confidence such a conclusion is premature.

3.1.2.3. Dialkynyl bridges. Ln–C bridge distances for some bridged alkynyls are set out in Table 7. The bridges are significantly asymmetric; this is often more clearly reflected in the Ln–C≡C bond angles than the Ln–C distances. For most of these compounds, the Ln–C distances corrected for the different ionic radii of the lanthanides is roughly constant, though the Y–C distance for the DAC compound is surprisingly long and has been interpreted [78] in terms of steric congestion. Such

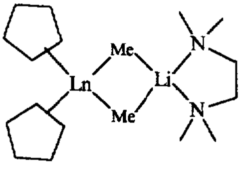


Fig. 20. The structure of [$Cp_2Ln(\mu\text{-}Me_2)Li(tmed)$].

Table 6
Lanthanide–carbon bridge bond lengths in bridged lanthanide alkyls (Å)

Compound	Ln–C	Ref.
$Cp_2Yb(\mu\text{-}Me)_2AlMe_2$	2.59(3)	[97]
$Cp_2Y(\mu\text{-}Me)_2YCp_2$	2.545(11)[a]	[30]
$Cp_2Yb(\mu\text{-}Me)_2YbCp_2$	2.511(35)[a]	[30]
$Cp_2Y(\mu\text{-}Me)_2AlMe_2$	2.58(3)	[104]
$Cp_2Er(\mu\text{-}C \equiv CBu^t)_2ErCp_2$	2.445(25)	[96]
$Cp_2Er(\mu\text{-}Me)_2Li(tmed)$	2.458(19)	[105]
$Cp_2Lu(\mu\text{-}Me)_2Li(tmed)$	2.461(12)	[99]

[a] Average.

steric congestion has been impliccated in alkynyl coupling reactions [41,109–111] such as

$$SmCp^*_2 + PhC \equiv CH \rightarrow [Cp^*_2Sm(\mu - \eta^2\text{:}PhC_4Ph)SmCp^*_2]$$

The short Y–C distance of 2.38 Å in the heterobridged compound $[Cp^*_2Y(C \equiv Bu^t)_2Li(THF)]$ (Fig. 21) has been attributed to the strong σ-donor properties of alkynyl ligands [108].

3.2. Pentamethylcyclopentadienyl alkyls and aryls

The C_5Me_5 ligand is sterically more demanding than C_5H_5; thus all $[LnCp_3]$ are known but, despite attempts, only $[SmCp^*_3]$ has been synthesized [112]. C_5Me_5 also is more electron-donating than C_5H_5; moreover, because it is more hydrocarbon-like, $C_5Me_5(Cp^*)$ complexes tend to be more hydrocarbon-soluble.

Table 7
Ln–C distances in bridged alkynyls

Compound	Ln–C (bridge) (Å)	Ref.
$[Cp_2Er(C \equiv CBu^t)]_2$	2.42(2) 2.47(2)	[96]
$[(MeCp)_2Sm(C \equiv CBu^t)]_2$	2.55(2)	[106]
$[(Bu^tCp)_2Sm(C \equiv CPh)]_2$	2.560(11) 2.617(13)	[42]
$[(Bu^tCp)_2Nd(C \equiv CPh)]_2$	2.602(4) 2.641(5)	[107]
$[(Bu^tCp)_2Gd(C \equiv CPh)]_2$	2.532(6) 2.601(7)	[107]
$[(DAC)_2Y(C \equiv CPh)]_2$	2.603(13) 2.627(12)	[78]
$[Cp^*_2Y(C \equiv Bu^t)_2Li(THF)]$	2.38(2)	[108]

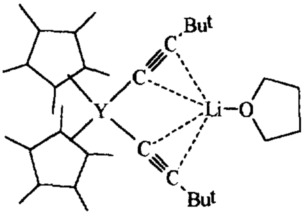


Fig. 21. The structure of [$Cp_2^*Y(\mu\text{-}C{\equiv}CBu^t)_2Li(THF)$].

3.2.1. *Bis(pentamethylcyclopentadienyl) systems*

3.2.1.1. Bis(trimethylsilyl)methyls. The extra bulk of the C_5Me_5 ligand increases the possibility of crowding in these compounds. $Cp_2^*LnR(THF)$ systems are less stable than the corresponding $Cp_2LnR(THF)$. [$Cp_2^*Ln\{CH(SiMe_3)_2\}$] are obtained THF-free, and even exhibit an agostic interaction between the lanthanide and one of the methyl carbons (Fig. 22). The agostic Ln· · ·C distance also decreases with increasing atomic number (decreasing size). The interaction is too weak to be seen on the NMR timescale [113–115] (see Table 8).

Obviously to confirm these trends, these is a need for a structure on [$Cp_2^*Lu\{CH(SiMe_3)_2\}$] [116] or [$Cp_2^*Sc\{CH(SiMe_3)_2\}$] [117]. Both [$Cp^*Ce\{CH(SiMe_3)_2\}_2$] and [$Cp_2^*Ce\{CH(SiMe_3)_2\}$] are isolable (also a THF complex of the former) suggesting that the steric requirements of the two ligands are similar [118]. (The La analogues [$Cp^*La\{CH(SiMe_3)_2\}_2$] (and its THF adduct) and [$Cp_2^*La\{CH(SiMe_3)_2\}$] can also be made [119].) However, it has not been possible to isolate [$Cp^*Lu\{CH(SiMe_3)_2\}_2$], though [$Cp^*Lu\{CH(SiMe_3)_2\}\{CH_2SiMe_3)(THF)$] has been isolated, as has [$Cp_2^*Lu\{CH(SiMe_3)_2\}$] [120]. This can scarcely be due to steric crowding since C_5Me_5 appears to take up more space than $CH(SiMe_3)_2$; thus [$Lu\{CH(SiMe_3)_2\}_3$] is readily isolable, but synthesis of $LnCp_3^*$

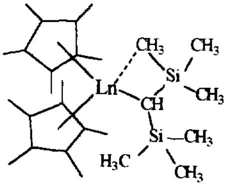


Fig. 22. The structure of [$Cp_2^*Ln\{CH(SiMe_3)_2\}$].

Table 8
Bond lengths in $Cp_2^*Ln[CH(SiMe_3)_2]$ (Å)

Lanthanide	Ln–C	(Ln–C)-radius Ln^{3+}	Ln· · ·C	Ln· · ·C-radius Ln^{3+}	Ref.
Ce	2.535(9)	1.525	2.917(5)	1.907	[113]
Nd	2.517(7)	1.534	2.895(7)	1.957	[114]
Y	2.468(7)	1.567	2.878(7)	1.979	[115]

has proved very difficult, only [SmCp$^*_3$] having been reported to date. If this is purely a steric phenomenom rather than a kinetic blockage in synthesis, the dividing line is fine since [Ln(η^5-C_5Me_4H)$_3$] (Ln = La, Nd, Sm, Tb) are all known [121].

Moreover, the Ce–C σ-bonds in [Cp*Ce{CH(SiMe$_3$)$_2$}$_2$] and [Cp$^*_2$Ce{CH(SiMe$_3$)$_2$}] (2.535(5), 2.532(av.) are slightly longer than La–C in La{CH(SiMe$_3$)$_2$}$_3$ (2.515(9)), suggesting crowding may be greater in these. The synthesis of the related [(C_5Me_4Et)$_2$Ln{CH(SiMe$_3$)$_2$}] (Ln = Y, Nd, Sm) have been reported, together with the structure of the samarium compound. Here Sm–C is 2.502 Å and the agostic Ln · · · C distance 2.953 Å; the former is in line with those in the pentamethylcyclopentadienyls [122].

3.2.1.2. Other bis(pentamethylcyclopentadienyl) alkyls. Structural data for a number of these are summarized below in Table 9.

The lengthening of the lanthanide–C(benzyl) bond relative to the other alkyls should be noted. A similar lengthening of U–benzyl distances compared to methyl is found in [U(CH_2Ph)$_3$Me(dmpe)], where U–CH_3 is 2.41(1) Å and U–CH_2Ph are 2.46(1), 2.51(1) and 2.54(1) Å [127], and has been attributed to resonance-stabilization of the benzylic carbon due to the electron-withdrawing effect of the phenyl group causing a lower electron density at this carbon and thus a weaker, longer, bond to the metal. The compound with the formula [LuCp$^*_2$Me] is in fact not [Cp$^*_2$Lu(μ-Me$_2$)LuCp$^*_2$] but is asymmetric [Cp$^*_2$Lu(μ-Me)LuCp$^*_2$Me] both in the solid state and solution (see Fig. 23); there is an equilibrium between dimer and monomer in solution. (A monomeric THF adduct can be made [128].)

The terminal Lu–C distance of 2.344(12) Å is significantly shorter than the Lu–C bridge distances, 2.440(9) and 2.756 (9) Å; it is in good agreement with the Lu–C distances found in [LuCp$_2$R(THF)] (R = CH_2SiMe_3, p-MeC_6H_4) systems, where the lutetium also has a formal coordination number of 8. The shorter of the two Lu–C bridge distances (2.440 Å) is very similar to that in the bridged compound [Cp$_2$Lu(μ-CH_3)$_2$Li(tmed)] (2.461 Å); a lengthening of some 0.12 Å compared with the terminal bond as expected [99]. The pronounced asymmetry in the methyl bridge almost suggests that the dimeric compound is made up of a loose association between two [LuCp$^*_2$Me] monomers. Coordinative unsaturation of the monomer in solution is doubtless [129] responsible for [LuCp$^*_2$Me] and [YCp$^*_2$Me] reacting with CH_4 considerably faster than does [ScCp$^*_2$Me].

Though resemblances between scandium and lutetium in their general chemistry

Table 9
Bond lengths (Å) in Cp$^*_2$LnR(THF)$_n$ systems

Compound	Ln–C (σ-)	(Ln–C)-radius Ln^{3+}	Ln–O	Ref.
Cp$^*_2$Ce(CH_2Ph)	2.596(5)	1.586	–	[123]
Cp$^*_2$Sm(CH_3)(THF)	2.464(14)	1.526	2.473(9)	[124]
Cp$^*_2$Sm(C_6H_5)(THF)	2.511(8)	1.553	2.511(4)	[34]
Cp$^*_2$Sm(CH_2Ph)(THF)	2.525(8)	1.567	2.498(5)	[125]
Cp$^*_2$Y(CH_3)(THF)	2.44(2)	1.44	2.379(8)	[126]

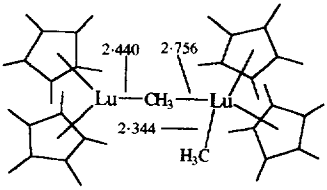


Fig. 23. The structure of [Cp$_2^*$Lu(μ-Me)LuCp$_2^*$(Me)].

are often marked [130], these two metals display a pronounced difference in their compounds with the formula [MCp$_2^*$Me] as [ScCp$_2^*$Me] is a monomer with Sc–C = 2.243(11) Å [129]; this is presumably due to crowding round the smaller scandium (though it does form a THF adduct that is stable enough to be isolated and the pyridinyl compound [ScCp$_2^*$(C,N-η^2-C_5H_4N) can be made). This illustrates nicely how small changes in atomic size can have profound repercussions on structure and reactivity. Compared with the Lu–C terminal distance in [Cp$_2^*$Lu(μ-Me)LuCp$_2^*$Me], the Sc–C distance is 0.10 Å less, in close agreement with what would be expected on ionic radii grounds.

Reaction of SmCp$_2^*$ with trialkyl aluminiums gives alkyl bridged species

$$3SmCp_2^* + 4AlEt_3 \rightarrow 3[SmCp_2^*(\mu-Et_2)AlEt_2] + Al$$

In the reation with trimethylaluminium, both [SmCp$_2^*$(μ-Me$_2$)AlMe$_2$] and a dimer can be obtained.

Analogues such as [LnCp$_2^*$(μ-Et$_2$)MMe$_2$] (Ln = Lu, Y; M = Al, Ga) have also been reported [131]. The bridged structure of [SmCp$_2^*$(μ-Et$_2$)AlEt$_2$] is similar to those of the cyclopentadienyls described in section with Sm–C(CH$_2$) distances averaging at 2.662 Å. A double AlMe$_3$ bridge is obtained in [Cp$_2^*$Sm{(μ-Me)AlMe$_2$(μ-Me)}$_2$SmCp$_2^*$] and the Y analogue (Fig. 24). Here the bridges are rather longer (Sm–C = 2.82–2.85 Å) and may reflect congestion [132].

3.3. *Ring-bridged alkyls*

A number of ring-bridged alkyls have been synthesised by conventional routes and the structures determined for four of these compounds [133–136].

$$[\{Me_2Si(C_5Me_4)_2\}LnCl_2Li(Et_2O)_2] + LiCH(SiMe_3)_2 \rightarrow [\{Me_2Si(C_5Me_4)_2\}$$
$$Ln(CH(SiMe_3)_2)] + 2LiCl + 2Et_2O \; (Ln = Sc, Nd, Sm, Lu, Y)$$

$$[\{Me_2Ge(C_5Me_4)_2\}LnCl_2Li(THF)_2] + LiCH(SiMe_3)_2 \rightarrow [\{Me_2Ge(C_5Me_4)_2\}$$
$$Ln(CH(SiMe_3)_2)] + 2LiCl + 2THF \; (Ln = Nd, Ho)$$

$$[\{R_2Si(C_5Me_4)(C_5H_4)\}LnCl_2Li(Et_2O)_2] + LiCH(SiMe_3)_2 \rightarrow$$
$$[\{R_2Si(C_5Me_4)(C_5H_4)\}Ln(CH(SiMe_3)_2)] + 2LiCl$$
$$+ 2Et_2O \; (R = Me, Ln = Lu; R = Et, Ln = Lu, Y)$$

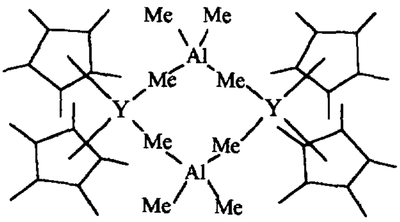


Fig. 24. The structure of [$Cp^*_2Y(\mu\text{-}Me_2AlMe_2)_2YCp^*_2$].

The compounds have structures (Fig. 25) of the same type as the alkyls with unbridged rings, even to the extent of featuring agostic Ln· · ·C interactions.

Examination of the structural data in Table 10 and comparison with bond lengths in the corresponding alkyls of unbridged cyclopentadienyls indicates the reduced steric demands of the cyclopentadienyl rings due to them being "tied back" allows the alkyls group to approach the lanthanide more closely [135]. The Lu–C distance in [{$Me_2Si(C_5Me_4)(C_5H_4)$}Lu(CH($SiMe_3)_2$)] in fact corresponds closely to those observed in unhindered alkyls. The closer approach of the alkyl group as the ionic radius of the metal decreases appears to be accompanied by a concomitant relative shortening of the Ln· · ·C agostic interaction where the methyl is bonded in a two-electron three-centred situation.

The crystal structure of the scandium analogue [{$Me_2Si(C_5Me_4)_2$}Sc-(CH($SiMe_3)_2$)] has no evidence for a Sc· · ·CH_3 bridge, probably due to steric congestion [137].

3.4. Mono Cp and Cp* alkyls

These are hard to make, as Schumann et al. [1] have pointed out, owing to a low degree of steric saturation with one unsubstituted cyclopentadienyl ligand. Apart from [Cp*Ln{CH($SiMe_3)_2$}$_2$] (Ln = La, Ce) discussed above, a number of such

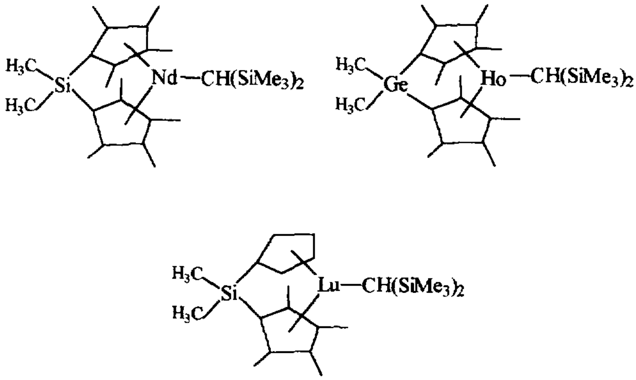


Fig. 25. The structure of ring bridged [{$Me_2Si(C_5Me_4)_2$}Nd(CH($SiMe_3)_2$)], [{$Me_2Ge(C_5Me_4)_2$}-Ho(CH($SiMe_3)_2$)] and [{$R_2Si(C_5Me_4)(C_5H_4)$}Lu(CH($SiMe_3)_2$)].

Table 10
Bond lengths (Å) in ring-bridged $Cp^*_2Ln(CH(SiMe_3)_2)$ systems

Compound	Ln–C	(Ln–C)-radius Ln^{3+}	Ln···C	Ln···C-radius Ln^{3+}	Ref.
$Me_2SiCp'_2NdR$	2.506(7)	1.523	2.862(8)	1.879	[133]
$Me_2GeCp'_2HoR$	2.418(7)	1.519	2.774(4)	1.873	[134]
$Me_2SiCpCp'LuR$	2.365(7)	1.504	2.820(8)	1.959	[135]
$Me_2SiCp'_2Y$	2.418(6)	1.519	2.816(7)	1.917	[133]

compounds have been isolated, of which some examples have been given here: $[(C_5H_5)Lu(CH_2SiMe_3)_2(THF)_3]$ is analogous in stoichiometry to the familiar compounds $[(C_5H_5)Lu(Cl)_2(THF)_3]$. It has been prepared thus:

$$(C_5H_5)Lu(OSO_2CF_3)_2(THF)_3 + 2LiCH_2SiMe_3 \rightarrow$$
$$(C_5H_5)Lu(CH_2SiMe_3)_2(THF)_3 + 2LiOSO_2CF_3$$

Though single crystals could not be obtained, the structure is firmly believed [138] to be as shown in Fig. 26.

Using a substituted cyclopentadienyl, the $[Cp^*LuMe_3]^-$ ion can be isolated [139]

$$LuCl_3 + NaCp^* + 2tmed + 3LiMe \rightarrow [Li(tmed)_2][Cp^*LuMe_3]^-$$
$$+ NaCl + 3LiCl$$

It has a piano-stool structure (Fig. 27) with some asymmetry in the reported Lu–C distances of 2.39(2), 2.56(2) and 2.59(2) Å; the average Lu–C distance of 2.51 Å is unexpectedly long compared with the terminal $Lu–CH_3$ distance in $[Cp^*_2Lu(\mu\text{-}Me)LuCp^*_2Me]$ [128].

A synthesis using a chelating ligand is [140]

$$LuCl_3 + NaCp + LiCH_2CH(Me)CH_2NMe_2 \rightarrow$$
$$[(C_5H_5)Lu(CH_2CH(Me)CH_2NMe_2)Cl(THF)_2] + NaCl + LiCl$$

The Lu–C distance of 2.411(7) and Lu–N distance of 2.637(8) Å are both substantially longer than the corresponding values of 2.22(1) and 2.37(1) Å. in $[LuCp_2(CH_2)_3NMe_2]$ but are not atypical (Fig. 28).

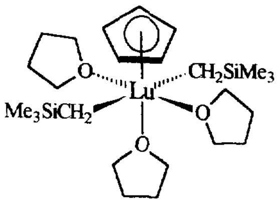


Fig. 26. The structure of $[(C_5H_5)Lu(CH_2SiMe_3)_2(THF)_3]$.

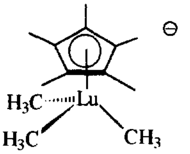


Fig. 27. The structure of the $[Cp^*LuMe_3]^-$ ion.

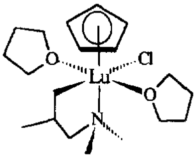


Fig. 28. The structure of $[(C_5H_5)Lu(CH_2CH(Me)CH_2NMe_2)Cl(THF)_2]$.

4. Carbene complexes

Carbene complexes are a recent development. A number of these have been made by direct reaction of the free carbene 1,3,4,5-tetramethyl-2-methyleneimidazoline with lanthanide compounds. Both mono- and bis-carbene derivatives of Cp^*_2Sm, which may be regarded (Fig. 29) as analogues of $Cp^*_2Sm(thf)_n$ ($n=1$, 2) have been reported as thermally stable solids; in $Cp^*_2Sm(carbene)_2$ Sm–C averages at 2.841(11) Å [141]. $Eu(tmhd)_3$ and $Y(tmhd)_3$ also form 1:1 adducts; in $[Eu(tmhd)_3(carbene)]$, Eu–C is 2.663(3) Å. Other structures have been reported for $[(C_5H_3(Bu^t)_2)_2Yb(carbene)]$ (Yb–C = 2.598(3) Å) [142], $[Ln(N(SiMe_3)_2)_3(carbene)]$ (Ln = La, Nd; Nd–C = 2.691(6) Å, Fig. 30) and $[(cot)Y(cp)(carbene)]$ (Y–C = 2.624(11) Å) [143].

There is no obvious pattern in the Ln–C (carbene) bond lengths when allowance is made for the ionic radius and oxidation state of the metal, as there is some variation in coordination number of the lanthanide.

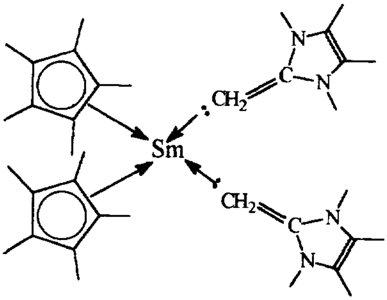


Fig. 29. The structure of the carbene complex $[Cp^*_2Sm\{1,3,4,5\text{-tetramethyl-2-methyleneimidazoline}\}]$.

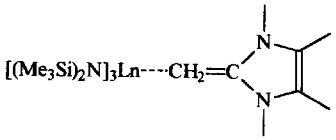


Fig. 30. The structure of the carbene complex [Ln(N(SiMe$_3$)$_2$)$_3$(1,3,4,5-tetramethyl-2-methyleneimidazoline)].

5. Future prospects

Even confined to simple homoleptic compounds, there are many avenues still unexplored. Can a simple neutral σ-aryl LnAr$_3$ be synthesised and characterised crystallographically? Can all the series [Ln{CH(SiMe$_3$)$_2$}$_3$] be made, and what are their properties? Do the bond lengths fit into the pattern that would be predicted following the "lanthanide contraction", observed for the analogous silylamides? What are the effects of using electron withdrawing substituents on bond length; can [Ln(C$_6$F$_5$)$_3$(THF)$_3$] be synthesised and compared to the analogous phenyls? Alternatively the synthesis and characterisation of porphyrin derivatives like [Sc(OEP)(CF$_3$)] would permit direct comparison. Can [LnCp$_2$(CF$_3$)] be made; if so are they dimeric or monomeric solvates? What are the decomposition pathways for simple alkyls? What is the relative importance of β-elimination and other routes?

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