

## Review

# BIS( $\eta$ -CYCLOPENTADIENYL) LANTHANOID(III) CHLORIDES \*

MICHAEL F. LAPPERT and ANIRUDH SINGH

*School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ  
(Great Britain)*

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## I. Introduction

The chemistry of bis( $\eta$ -cyclopentadienyl)lanthanoid(III) complexes has undergone substantial progress in recent years, as summarised in various reviews [1–8]. In this paper we shall restrict our scope to the bis(cyclopentadienyl)-lanthanoid(III) chlorides, otherwise named as lanthanocene(III) chlorides, which are key intermediates in these studies, and for which there have been particularly significant advances. Scandium and yttrium complexes will be included in this survey, because of their similarity to the related 4f derivatives, and “Ln” will be used as a generic symbol for any one of the Group IIIa metals. The name cyclopentadienyl will be taken to encompass not only  $\bar{C}_5H_5$  (abbreviated as  $\bar{Cp}$ ) but also substituted derivatives and the generic symbol we choose is  $\bar{Cp}^*$ .

## II. Bis( $\eta$ -cyclopentadienyl)lanthanoid(III) chlorides

These complexes fall broadly into two main classes: (i) homometallic complexes of formula [ {Ln( $\eta$ -Cp<sup>\*</sup>)<sub>2</sub>( $\mu$ -Cl)}<sub>2</sub> ] (Ln = a Group IIIa metal and  $\eta$ -Cp<sup>\*</sup>

\* Dedicated to Professor R.C. Mehrotra on the occasion of his sixtieth birthday (February 16th, 1982).

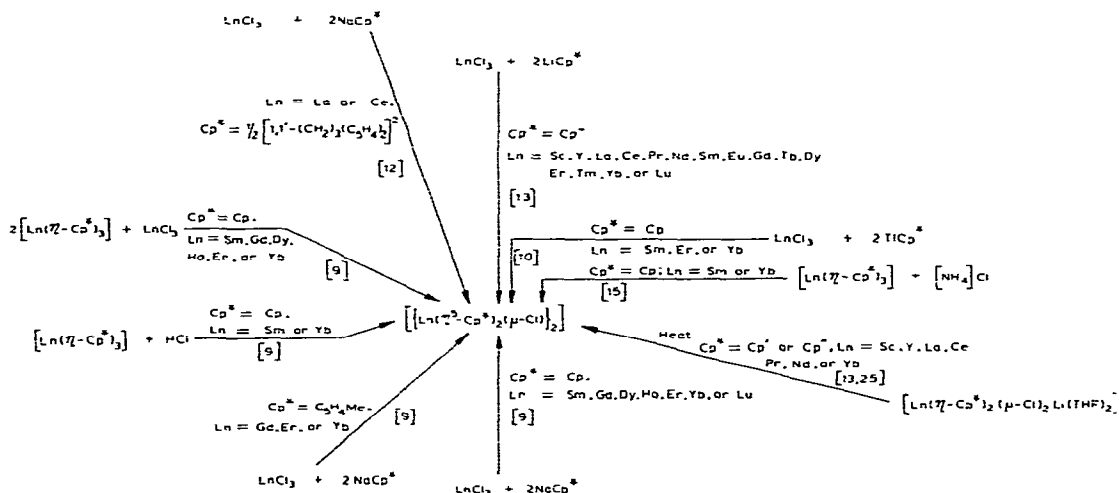
is a pentahapto cyclopentadienyl or substituted cyclopentadienyl ligand), and (ii) heterometallic complexes of formula  $[\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})_2\text{LiL}_2]$  [where L is a monodentate neutral ligand such as tetrahydrofuran (THF) or  $\text{L}_2$  is a bidentate neutral ligand such as tetramethylethylenediamine (TMEDA)], or a sodium analogue of the lithium compound, or  $[\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})_2\text{AlCl}_2]$ . Additionally there is a third class, the lanthanate(III) complex of formula  $[\text{Ln}(\eta\text{-Cp}^*)_2\text{Cl}_2]^-$ , first recognised for  $[\text{Y}(\eta\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_2]^-$  [25]. There is yet no crystal structural evidence for such complexes unless the chloride ligands are also bonding to lithium or aluminium, when we prefer to classify them in category (ii)\*.

### A. Homometallic complexes, $[\{\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})\}_2]$

#### 1. Preparation and properties

Most of the earlier preparations were directed at unsubstituted cyclopentadienyls, ( $\text{Cp} = \text{C}_5\text{H}_5$ ) [9,10], although in few instances simple derivatives such as  $\text{C}_5\text{H}_4\text{Me}$  analogues [9] were also sought. Currently, there is much interest in bulky or rigid cyclopentadienyl ligands [e.g.,  $\bar{\text{C}}_5\text{Me}_5$  (abbreviated as  $\bar{\text{Cp}}^{\text{Me}}$ ) [11],  $1,1'-(\text{CH}_2)_3(\text{C}_5\text{H}_4)_2^{2-}$  [12], or  $\bar{\text{C}}_5\text{H}_3(\text{SiMe}_3)_2$  (abbreviated as  $\bar{\text{Cp}}''$ ) [13] which may kinetically stabilise early ( $4f^0-4f^3$ ) lanthanocene(III) chlorides; the latter are inaccessible for  $\bar{\text{C}}_5\text{H}_5$  or simple derivatives. Various routes to these complexes are available, as illustrated in Scheme 1; they represent the following

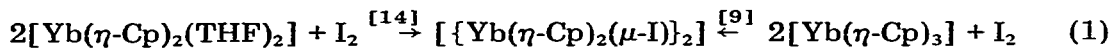
SCHEME 1



reaction types: (i) salt elimination (which may involve an intermediate heterometallic  $\text{Ln-Li}$  complex), (ii) ligand redistribution, or (iii)  $\text{Ln-Cp}^*$  cleavage using  $\text{HCl}$  or  $[\text{NH}_4]\text{Cl}$ . Additionally it is likely that two further types, (iv) and

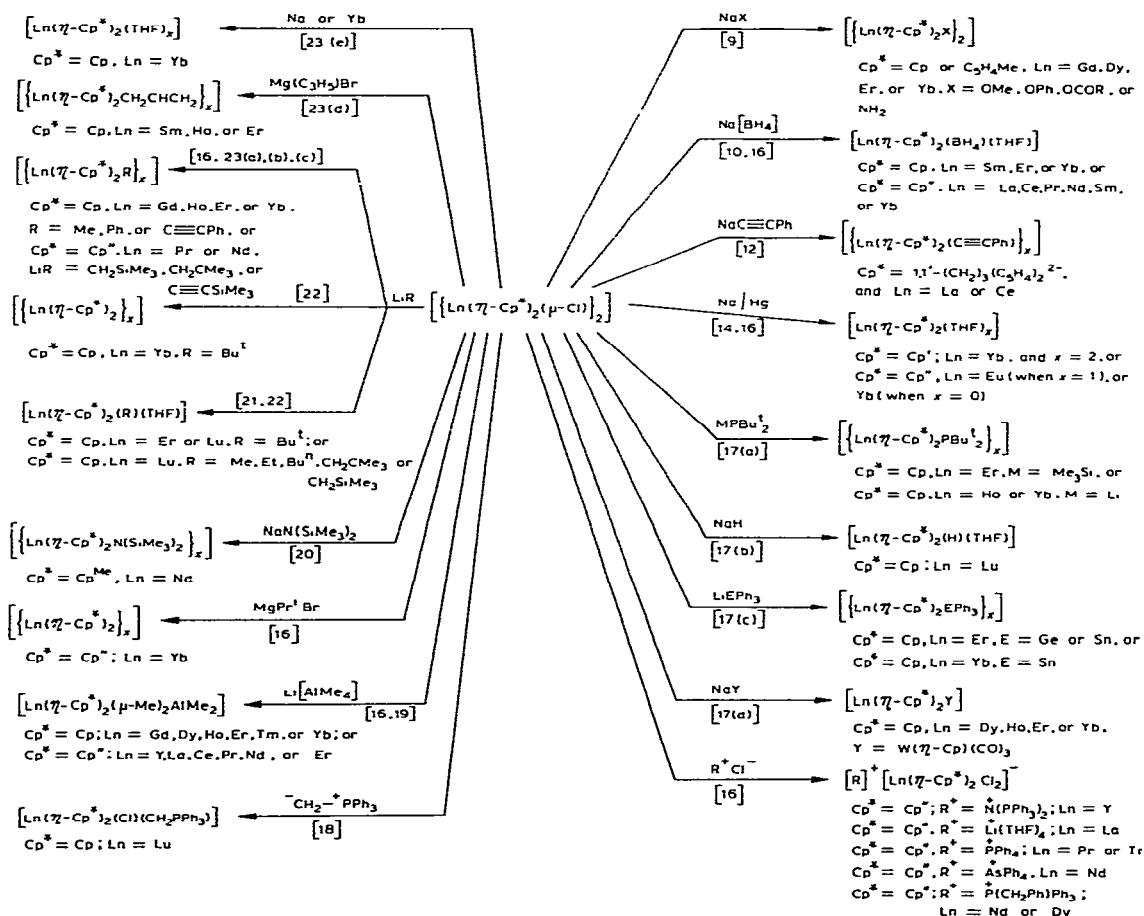
\* Note added in proof. Recently following seven complexes have been prepared and characterised [16]:  $[\text{N}(\text{PPh}_3)_2]^+[\text{YCp}_2^{\text{H}}\text{Cl}_2]^-$ ,  $[\text{Li}(\text{THF})_4]^+[\text{LaCp}_2^{\text{H}}\text{Cl}_2]^-$ ,  $[\text{PPh}_4]^+[\text{PrCp}_2^{\text{H}}\text{Cl}_2]^-$ ,  $[\text{AsPh}_4]^+[\text{NdCp}_2^{\text{H}}\text{Cl}_2]^-$ ,  $[\text{P}(\text{CH}_2\text{Ph})\text{Ph}_3]^+[\text{NdCp}_2^{\text{H}}\text{Cl}_2]^-$ ,  $[\text{P}(\text{CH}_2\text{Ph})\text{Ph}_3]^+[\text{DyCp}_2^{\text{H}}\text{Cl}_2]^-$ ,  $[\text{PPh}_4]^+[\text{TmCp}_2^{\text{H}}\text{Cl}_2]^-$ . The molecular structure of  $[\text{AsPh}_4]^+[\text{NdCp}_2^{\text{H}}\text{Cl}_2]^-$  has been confirmed by X-ray crystallography, in collaboration with Prof. J.L. Atwood.

(v), may become realised, as they already are available for ytterbocene(III) iodides (see eq. 1), namely (iv) Ln—Cp\* cleavage by Cl<sub>2</sub> and (v) Ln(Cp\*)<sub>2</sub> oxidative addition by Cl<sub>2</sub>.



The lanthanocene(III) chlorides (Table 1) are mostly coloured, volatile, air- and moisture-sensitive solids; three iodides, [ $\{\text{Yb}(\eta\text{-Cp}^*)_2\text{I}\}_2$ ] (Cp\* = Cp [9] or Cp' [14] and  $[\text{Yb}(\eta\text{-Cp}^{\text{Me}})_2(\mu\text{-I})_2\text{Li}(\text{OEt})_2]$  [27b] have also been made. The chlorides are monomeric in coordinating solvents (like THF), but dimeric in non-polar solvents (e.g., benzene) and in the solid state. The substituted derivatives (e.g., C<sub>5</sub>H<sub>4</sub>Me, Cp<sup>Me</sup>, 1,1'-(CH<sub>2</sub>)<sub>3</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>, or Cp'' complexes) are significantly more soluble in non-polar solvents than those of the Cp analogues, and the trimethylsilyl derivatives, Cp' and Cp'', offer particularly good hydrocarbon solubility. Magnetic moment data are in excellent agreement with the theoretical values for the corresponding Ln<sup>3+</sup> ions, and this has been offered as evidence for ionic metal—carbon bonding [7], although that view is clearly inconsistent both with the solubility data and also their volatility (the Cp' and Cp'' complexes are readily sublimable) [13]. It is widely held that ionic character increases with the magnitude of the metal radius. Thus the early (4f<sup>0</sup>—4f<sup>3</sup>) lanthanoid(III) complexes are probably the most ionic. It may well be that the

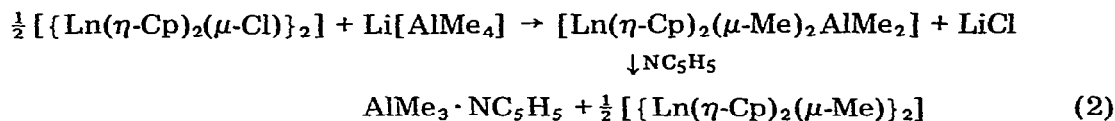
SCHEME 2



effect of trimethylsilyl substitution in the cyclopentadienyl ring is to increase covalent character relative to an unsubstituted derivative, especially for the ligand  $\overline{\text{C}}_5\text{H}_3(\text{SiMe}_3)_2$  (or  $\overline{\text{Cp}}''$ ). Indeed this proposition formed the strategic basis for the choice of the  $\overline{\text{Cp}}''$  ligand in order to synthesise the La, Ce, Pr, and Nd complexes [ $\{\text{Ln}(\overline{\text{Cp}}'')_2(\mu\text{-Cl})\}_2$ ] [13].

The chemistry of the lanthanocene(III) chlorides is predominantly associated with replacement of the chloride ligand. These are essentially nucleophilic displacements at the metal centre with  $\text{Cl}^-$  as the leaving group, and are illustrated in Scheme 2, which also features reductions (replacement of chlorine atoms). The latter are prominent for  $\text{Ln} = \text{Yb}, \text{Eu},$  or  $\text{Sm}$ ; this is probably due to their relatively stable electronic configurations,  $4f^{14}$ , (the most stable),  $4f^7$ , and  $4f^6$  (the most labile), respectively. The substitution reactions are noteworthy inter alia for providing routes to lanthanocene complexes having  $\text{Ln}-\text{C}$ ,  $\text{Ln}-\text{N}$ ,  $\text{Ln}-\text{P}$ ,  $\text{Ln}-\text{O}$ ,  $\text{Ln}-\text{H}$  (one example only,  $\text{Ln} = \text{Lu}$  and  $\text{Cp}^* = \text{Cp}$  [17b]; but data are incomplete and the  $\text{NaH}$  reaction is unlikely to prove a particularly useful method), or  $\text{Ln}-\text{M}$  [at present known [17d] only for  $\text{M} = \text{W}(\eta\text{-Cp})(\text{CO})_3$ ].

The "direct" alkylation and related  $\text{Ln}-\text{C}$ -forming reactions, using a Grignard or an organolithium reagent are complicated by the probable tendency of the main group metal to be bonded to the lanthanoid via two hydrocarbyl bridges. This is illustrated in eq. 2 for the well-characterised tetramethylaluminates [19]. Indeed the latter are useful intermediates in the planned synthesis of the lanthanocene methyls (eq. 2) ( $\text{Ln} = \text{Y}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm},$  or  $\text{Yb}$ ) [28]. The bridged dimethyls evidently represent a wider class of bridged binuclear complexes which are a feature of lanthanoid(III) chemistry [26], and of which the  $(\mu\text{-Cl})_2$ -complexes of Section B are a further manifestation.



## 2. X-Ray crystallographic data

Although a substantial number of lanthanocene chlorides is now available (Table 1), crystallographic data are sparse. To date, the structures of only four compounds [ $\{\text{Yb}(\eta\text{-C}_5\text{H}_4\text{Me})_2(\mu\text{-Cl})\}_2$ ] [24] and [ $\{\text{M}(\eta\text{-Cp}'')_2(\mu\text{-Cl})\}_2$ ] ( $\text{M} = \text{Sc}, \text{Yb}$  or  $\text{Pr}$ ) [13], have been published. The praseodymium complex is especially noteworthy because it provided structural verification for one of the first early lanthanocene(III) complexes [13]. The common structural pattern is that of a chloride-bridged dimer with centre of inversion symmetry, having non-parallel pentahapto-bonded cyclopentadienyl rings, and distorted tetrahedral geometry around each metal atom, Fig. 1.

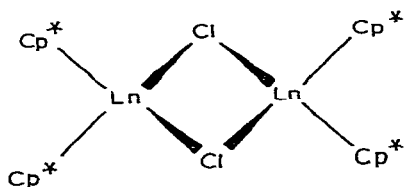


Fig. 1. Molecular structure of [ $\{\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})\}_2$ ] ( $\text{Ln} = \text{Sc}, \text{Pr}$  or  $\text{Yb}$ ,  $\text{Cp}^* = \text{Cp}''$ ; or  $\text{Ln} = \text{Yb}$ ,  $\text{Cp}^* = \text{C}_5\text{H}_4\text{Me}$ ).

TABLE 1

SOME BIS( $\eta$ -CYCLOPENTADIENYL)LANTHANOID(III) CHLORIDES<sup>a</sup>

Compound type	Specific examples	Ref.
1. [ $\{\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})\}_2$ ]	$\text{Cp}^* = \text{Cp}$ ; Ln = Sm, Gd, Dy, Ho, Er, Yb, or Lu	9
	$\text{Cp}^* = \text{C}_5\text{H}_4\text{Me}$ ; Ln = Gd, Er, or Yb	9
	$\text{Cp}_2^* = 1,1'-(\text{CH}_2)_3(\text{C}_5\text{H}_4)_2$ ; Ln = La or Ce	12a, b
	$\text{Cp}^* = \text{Cp}'$ ; Ln = Yb	14
	$\text{Cp}^* = \text{Cp}''$ ; Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb, or Lu	13
2. [ $\{\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})_2\text{ML}_2$ ]	$\text{Cp}^* = \text{Cp}''$ , M = Li; L = THF; Ln = Sc, Y, La, Ce, Pr, Nd, or Yb	26
	$\text{Cp}^* = \text{Cp}''$ , M = Li; L = TMEDA; Ln = Sc, Y, or La	26
	L <sub>2</sub> = DME (dimethoxyethane), and Ln = Sc, Y, or Nd	
	$\text{Cp}^* = \text{Cp}^{\text{Me}}$ , M = Li, Ln = Nd, L = THF	11
	$\text{Cp}^* = \text{Cp}^{\text{Me}}$ , M = Li, Ln = Yb, L = THF	27b
	$\text{Cp}^* = \text{Cp}^{\text{Me}}$ , M = Na, Ln = Yb, L = OEt <sub>2</sub>	20
	$\text{Cp}^* = \text{Cp}^{\text{Me}}$ , M = Li or Na; Ln = Sm or Yb; L <sub>2</sub> = TMEDA	20
	$\text{Cp}^* = \text{Cp}^{\text{Me}}$ , M = Li, Ln = Nd, L = TMEDA	20
	$\text{Cp}^* = \text{Cp}^{\text{Me}}$ , M = Na, Ln = Nd or Sm; L = OEt <sub>2</sub>	20
	$\text{Cp}^* = \text{Cp}^{\text{Me}}$ , M = Li, Ln = Nd or Yb; L = OEt <sub>2</sub>	20
	$\text{Cp}^* = \text{Cp}^{\text{Me}}$ , M = Li, Ln = Yb, L = OEt <sub>2</sub>	27b
	$\text{Cp}^* = \text{Cp}^{\text{Me}}$ , M = Li, Ln = Lu, L = OEt <sub>2</sub>	27b
	$\text{Cp}^* = \text{Cp}^{\text{Me}}$ , M = Li, Ln = Yb, L = absent	27b
	$\text{Cp}^* = \text{C}_5\text{H}_4\text{SiMePh}_2$ , M = Li, Ln = Yb	27b
	$\text{Cp}^* = \text{C}_5\text{H}_4\text{SiMePh}_2$ , M = Li, Ln = Lu, L is absent	27b
3. [ $\{\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})_2\text{AlCl}_2$ ]	Ln = Yb or Lu	27b

<sup>a</sup> For [ $\{\text{LnCp}_2^{\text{Me}}\text{Cl}_2\}^-$  (Ln = Y, La, Pr, Nd, Dy, or Tm)] see footnote in Section II, [16]. The following compounds have also been obtained [ $\{\text{Ln}(\eta\text{-C}_5\text{H}_3(\text{Bu}^t)\text{SiMe}_3)_2\text{Cl}\}_2$ ] (Ln = Sc, Y, Pr, or Nd) [16].

The bridging unit,  $\text{LnCl}_2\text{Ln}$ , is planar and approximately square. The angles between the centroids of the two cyclopentadienyl rings are significantly distorted (ca.  $130^\circ$ ) from an idealised tetrahedral geometry, due to the combined effect of the size of cyclopentadienyl rings and their occupation of more than one metal coordination site. The Cl—Ln—Cl angle is constrained to  $80 \pm 2^\circ$ , in part because of the  $\text{Ln}_2\text{Cl}_2$  ring. A comparison of some structural parameters for these complexes is described in Table 2.

TABLE 2

COMPARISON OF STRUCTURAL PARAMETERS FOR [ $\{\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})\}_2$ ]

Ln	Pr ( $\text{Cp}^* = \text{Cp}''$ )	Yb ( $\text{Cp}^* = \text{Cp}''$ or $\text{C}_5\text{H}_4\text{Me}^a$ )	Sc ( $\text{Cp}^* = \text{Cp}''$ )
$\text{Ln}^{3+}$ radius (Å)	1.14	0.98	0.68
Ln—Cl (Å)	2.81	2.65 (2.64)	2.58
Ln—C( $\eta$ -) (Å)	2.76	2.62 (2.58)	2.51
Cl—Ln—Cl (deg)	78	80 (82)	79
Ln—Cl—Ln (deg)	102	100 (98)	101
Cent—Ln—Cent (deg)	130	130 (127)	131

<sup>a</sup> Data for  $\text{Cp}^* = \text{C}_5\text{H}_4\text{Me}$  in parentheses.

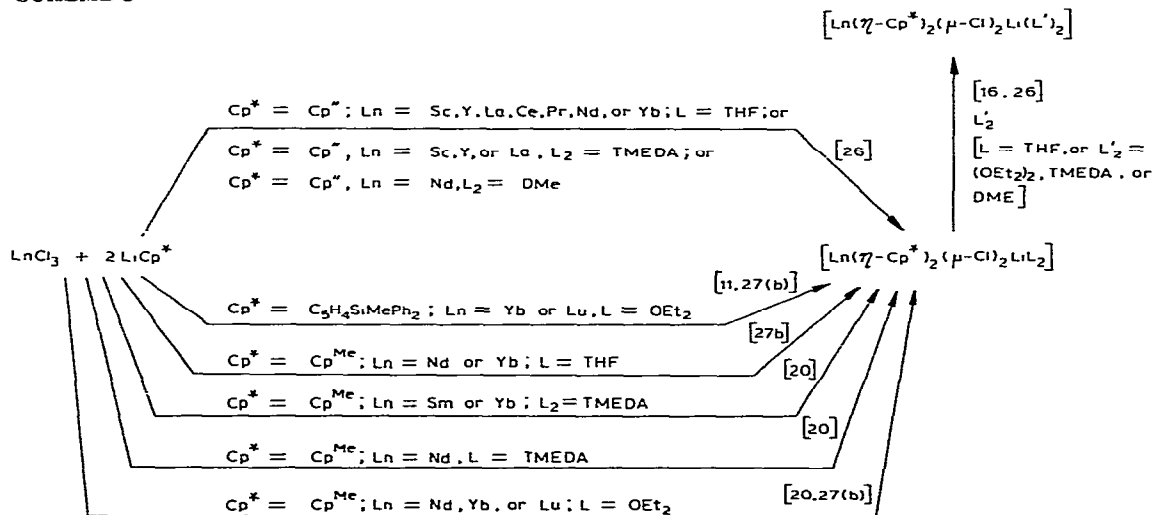
**B. Heterometallic complexes  $[Ln(\eta-Cp^*)_2(\mu-Cl)_2ML_2]$  ( $M = Li$  or  $Na$ ;  $L = a$  neutral monodentate ligand or  $L_2 = a$  neutral bidentate ligand) or  $[Ln(\eta-Cp^*)_2(\mu-Cl)_2AlCl_2]$**

**1. Preparation and properties**

The first complexes of this type were described in 1978 [25]. They had the composition  $Y(C_5H_4SiMe_3)_2Cl \cdot LiCl(L)_2$  (where  $L = THF$  or  $L_2 = TMEDA$ ) and the structure then proposed is illustrated in Fig. 2.

Preparative routes are summarised for the lithium complexes in Scheme 3

SCHEME 3



and generally depend on a metathetical  $Cl^-/\overline{Cp}^*$  exchange reaction using the lanthanoid(III) chloride and an appropriate lithium cyclopentadienide, and are salt eliminations; additionally, neutral ligand displacements are possible [26]. An alternative procedure for iodo-complexes has used the oxidative addition reaction of eq. 3 [27b], but these compounds are also accessible from  $LnI_3$  (with  $LiCp^{Me}$ , for  $Ln = Yb$ ) [27].

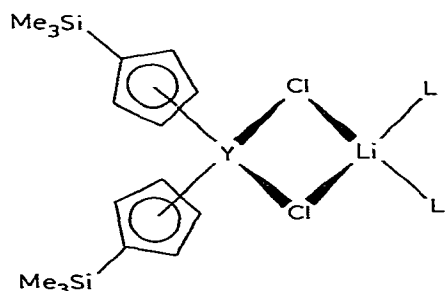
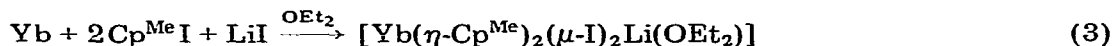
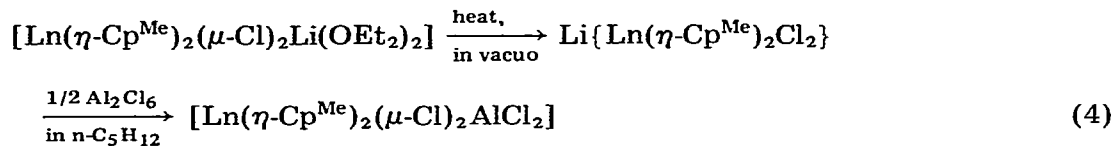


Fig. 2. Proposed [25] structure of  $[Y(\eta-C_5H_4SiMe_3)_2(\mu-Cl)_2LiL_2]$ .

The sodium analogues of the lithium complexes  $[\text{Ln}(\eta\text{-Cp}^{\text{Me}})_2(\mu\text{-Cl})_2\text{NaL}_2]$  have been obtained [for Ln = Nd, Sm, or Yb, and  $\text{L}_2 = \text{OEt}_2$  (not Yb) or TMEDA (not Nd), or Ln = Yb and  $\text{L} = \text{OEt}_2$ ] from  $\text{LnCl}_3$  and  $2\text{NaCp}^{\text{Me}}$  in presence of the ligand L [20]. The mixed lanthanoid-aluminium complexes have been prepared as shown in eq. 4 (Ln = Yb or Lu) [27(b)].



The heterometallic complexes (Table 1) are either colourless (La or Lu) or coloured crystalline solids, and in most cases melt with decomposition in the range 100–250°C. All are soluble in common organic solvents. The coordinated tetrahydrofuran molecules in  $[\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})_2\text{Li}(\text{THF})_2]$  can be displaced by  $\text{OEt}_2$  (excess) [16],  $\frac{1}{2}$  DME [26], or  $\frac{1}{2}$  TMEDA.

The effect of heat on the complexes  $[\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})_2\text{Li}(\text{THF})_2]$  is to drive off the tetrahydrofuran (e.g., see eq. 4) [16,27(b)]; the resulting solids have not been characterised in detail, but in some cases (see Scheme 1) crystallisation from a toluene extract [13], or sublimation [25], affords the homometallic complex  $[\{\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})_2\}]$  [16]. An alternative procedure for removing ligated THF or  $\text{OEt}_2$  is by prolonged vigorous stirring in *n*-hexane or toluene. Chemical properties are summarised in Scheme 4; additionally, we note that reactions of  $[\text{Yb}(\eta\text{-Cp}^{\text{Me}})_2(\mu\text{-I})_2\text{Li}(\text{OEt}_2)_2]$  with  $\text{LiMe}$  have been reported to yield  $[\text{Yb}(\eta\text{-Cp}^{\text{Me}})_2\text{X}]$  [where  $\text{X} = (\mu\text{-Me})_2\text{Li}(\text{OEt}_2)_2$ ,  $(\mu\text{-Me})(\mu\text{-I})\text{Li}(\text{OEt}_2)_2$ , or  $(\text{Me})(\text{THF})$ ] [27a].

SCHEME 4

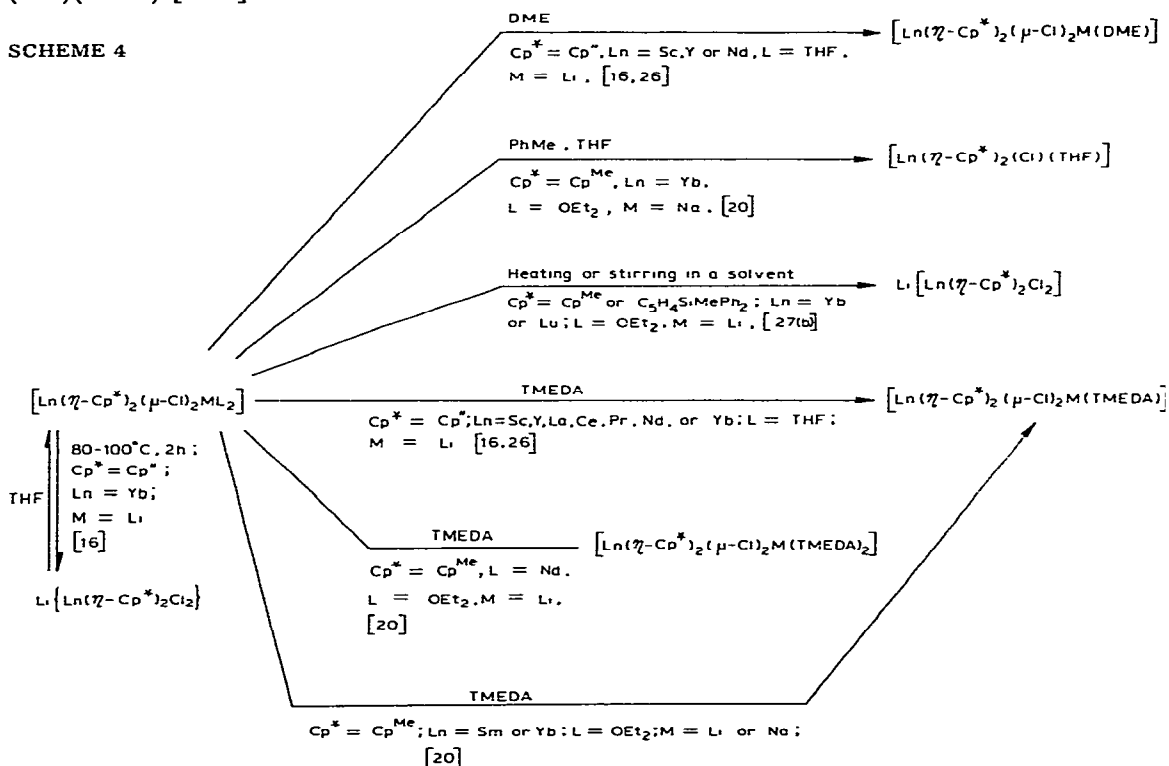


TABLE 3

COMPARISON OF STRUCTURAL PARAMETERS FOR A SERIES OF COMPLEXES OF FORMULA  $[\text{Ln}(\eta\text{-Cp}^*)_2(\mu\text{-X})_2\text{ML}_2]^{a,b}$ 

Compound	A	B	C	D	E
$\text{Ln}-\text{C}(\eta\text{-}) (\text{\AA})$	2.63	2.61(3)	2.63(2)	2.76(1)	2.58(3)
$\text{X}-\text{Ln}-\text{X}$ (deg)	86.1(2)	85.95(2)	87.14(3)	82.10(1)	73.6(3)
$\text{M}-\text{X}$ ( $\text{\AA}$ )	2.81(15)	2.40(6)	2.39(4)	2.41(3)	2.14
$\text{Ln}-\text{X}$ ( $\text{\AA}$ )	3.03(1)	2.59(1)	2.59(1)	2.74(3)	2.76(1)
$\text{M}-\text{O}$ ( $\text{\AA}$ )	1.90(15)	1.93(7)	1.96(4)	1.93(3)	—
$\text{X}-\text{M}-\text{X}$ (deg)	94.6(6)	95.4(2)	96.3(2)	97.2(9)	73.6(3)
$\text{Ln}-\text{M}$ ( $\text{\AA}$ )	4.12(12)	3.48(6)	3.51(6)	3.63(3)	3.65

<sup>a</sup> Complexes A–E and appropriate refs. in parentheses are: A, M = Yb, Cp\* = Cp<sup>Me</sup>, X = I, M = Li, L = OEt<sub>2</sub> [27(b)]; B, M = Yb, Cp\* = Cp<sup>Me</sup>, X = Cl, M = Li, L = OEt<sub>2</sub> [27(b)]; C, M = Yb, Cp\* = C<sub>5</sub>H<sub>4</sub>SiMePh<sub>2</sub>, X = Cl, M = Li, L = OEt<sub>2</sub> [27(b)]; D, M = Nd, Cp\* = Cp'', X = Cl, M = Li, L = THF [26]; E, M = Yb, Cp\* = Cp<sup>Me</sup>, X = Cl = L, M = Al [27(b)]. <sup>b</sup> Standard deviations in parentheses.

## 2. X-Ray crystallographic data

The X-ray structures of four heterometallic chloro-complexes have been elucidated:  $[\text{Nd}(\eta\text{-Cp}'')_2(\mu\text{-Cl})_2\text{Li}(\text{THF})_2]$  [26],  $[\text{Yb}(\eta\text{-Cp}^{\text{Me}})_2(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)_2]$  (also of the di-iodo-analogue) [27b],  $[\text{Yb}(\eta\text{-C}_5\text{H}_4\text{SiMePh}_2)_2(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)_2]$ , and  $[\text{Yb}(\eta\text{-Cp}^{\text{Me}})_2(\mu\text{-Cl})_2\text{AlCl}_2]$ . The molecular geometries of these complexes are all very similar and approximate to that shown for the Cp' complexes in Fig. 2. The common features are: (i) an approximate tetrahedral geometry about each lanthanoid, lithium, or aluminium atom, (ii) planarity of the bridging units LnCl<sub>2</sub>M, (iii) significant contraction in the Cl–Ln–Cl angles, (iv) comparable Li–O or Li–Cl bond distances, and (v) pentahapto bonding of the cyclopentadienyl rings. Further data are in Table 3.

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