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The first examples of intermolecular weak (agostic) γ-methyl–metal interactions in organolanthanide complexes: the synthesis and X-ray structures of $[\{Yb(\eta\text{-}Cp'')_2\}_\infty]$ and $[\{Eu(\eta\text{-}Cp'')_2\}_\infty]$ $[Cp'' = C_5H_3(SiMe_3)_2\text{-}1,3]$ *

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Abstract

The lanthanocene(II) complexes $[\{Yb(\eta\text{-}Cp'')_2\}_\infty]$ (1) and $[\{Eu(\eta\text{-}Cp'')_2\}_\infty]$ (2) $[Cp'' = C_5H_3(SiMe_3)_2\text{-}1,3]$ were prepared by the desolvation via sublimation of $[Yb(\eta\text{-}Cp'')_2(OEt_2)]$ (3) and $[Eu(\eta\text{-}Cp'')_2(THF)]$ (4), respectively. The single crystal X-ray structures of 1 and 2 reveal that each complex has unique intermolecular agostic-like interactions. 1 adopts a bent metallocene conformation, Cent(Cp1)–Yb–Cent(Cp2) 138.0° and the mean Yb–C bond length 2.662 Å, and a close contact between the metal of one $YbCp''_2$ unit and a methyl group of a neighbouring such unit, Yb ··· C(9)″ 2.872(7) Å. For 2, the low temperature X-ray study shows a similar short intermolecular contact Eu(2′) ··· C(62) 3.091(6) Å [*cf.* the mean Eu(2)–C bond length of 2.804 Å], with the closest intermolecular metal-hydrogen distance Eu(2′) ··· H(62A) being 2.70 Å. Complex 2 also exhibits an unprecedented conformation with a cyclopentadienyl ring bridging η^5, η^3 between two non-equivalent europium atoms.

Introduction

The majority of first-row transition metals form homoleptic bis(cyclopentadienyl)metal-sandwich compounds [1]. It was a widely held view that for an f-element the appropriate ring size for a bis(carbocycle) sandwich complex should be eight-membered to fit the larger atomic radius of the metal, as in $[U(COT)_2]$ (COT = cyclooctatetraene) [2]. Consistent with this, the lanthanocene(II) complexes reported up to 1984 invariably had neutral adduct molecules occupying additional coordination sites at the metal [3–5]. The first X-ray characterised

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lanthanocene(II) derivatives were reported in 1980: $[Yb(\eta\text{-}C_5H_4SiMe_3)_2(THF)_2]$ [6], $[\{Yb(\eta\text{-}C_5H_4Me)_2(THF)\}_\infty]$ [7] and, $[Yb(\eta\text{-}C_5Me_5)_2(THF)]\cdot\frac{1}{2}PhMe$ [8] (THF = tetrahydrofuran).

The preparation of europocene(II) and ytterbocene(II) has been reported [9], but no structural details are yet known. Their insolubility, and the polymeric structure of crystalline $[\{Yb(\eta\text{-}C_5H_4Me)_2(THF)\}_\infty]$ [7] supports the notion that they are polymers with a high degree of ionic character [3–5]. (The attempted preparation of samarocene(II) failed [10]).

The base-free metallocene complexes $Yb(\eta\text{-}C_5H_4SiMe_3)_2$ [6], $Yb(\eta\text{-}C_5H_4CMe_3)_2$ [11] and $Sm(\eta\text{-}Cp'')_2$ [12] [$Cp'' = C_5H_3(SiMe_3)_2\text{-}1,3$], obtained by sublimation of the respective solvated lanthanocene(II) complex, have been reported, but their structures were not elucidated. Landmarks were reports of the synthesis and X-ray structures of the solvent-free crystalline decamethyllanthanocene(II) complexes $[Sm(\eta\text{-}C_5Me_5)_2]$ [13,14], $[Eu(\eta\text{-}C_5Me_{52}]$ [14], and $[Yb(\eta\text{-}C_5Me_5)_2]$ [15], having a bent monomeric conformation with some degree of close intermolecular contacts.

The use of lanthanide(II) complexes as one-electron reducing agents has been well documented [4,16]. A striking example is the conversion of $[Sm(\eta\text{-}Cp'')_2(THF)]$ or $[Yb(\eta\text{-}C_5H_4SiMe_3)_2(OEt_2)]$ into $[\{Sm(\eta\text{-}Cp'')_2(\mu\text{-}OH)\}_2]$ or $[\{Yb(\eta\text{-}C_5H_4SiMe_3)_2(\mu\text{-}OH)\}_2]$ [17]. In addition to acting as one-electron reductants, the chemistry of solvent-free lanthanocene(II) complexes is dominated by the coordinatively unsaturated nature of the metal. Their exceptional reactivity is demonstrated by $[Sm(\eta\text{-}C_5Me_5)_2]$ coordinating dinitrogen to give $[\{Sm(\eta\text{-}C_5Me_5)_2\}_2(\mu\text{-}\eta^2, \eta^2\text{-}N_2)]$ [18] and $[Yb(\eta\text{-}C_5Me_5)_2]$ reacting with C_6F_6 to give the Yb^{II}/Yb^{III} complex $[\{Yb(\eta\text{-}C_5Me_5)_2\}_2(\mu\text{-}F)]$ [19].

Experimental

Materials and procedures

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled over potassium-sodium alloy under argon prior to use. The following compounds were prepared by published procedures YbI_2 [20], $EuI_2(THF)_2$ [21], K(Cp″) [17] and (Cp″)H [22]. Microanalyses were carried out in the microanalytical department at the University of Sussex. NMR spectra were recorded using Bruker WM360 or WM500 spectrometers.

Preparation of $[\{Yb(\eta\text{-}Cp'')_2\}_\infty]$ (1)

The complex $[Yb(\eta\text{-}Cp'')_2(OEt_2)]$ (**3**) (1.05 g, 1.58 mmol) was placed in a horizontal sublimation apparatus, which in turn was inserted into a tubular oven. The temperature of the oven was slowly raised until the sublimation temperature of the compound (190°C/10^{-2} Torr) was reached. The compound was sublimed for 8 h at 10^{-2} Torr to yield purple X-ray quality single crystals of the title complex **1** (0.44 g, 47%). NMR spectroscopic data for **1**: ^1H (360 MHz) at 300 K in C_6D_6: δ 0.28 (s, 36H), 6.45 (t, 2H), 6.70 (d, 4H); ^{171}Yb [23] (63.01 MHz) at 297 K in $C_6D_5CD_3$: δ −15.67.

Preparation of $[\{Eu(\eta\text{-}Cp'')_2\}_\infty]$ (2)

By use of the procedure described for the preparation of **1**, $[Eu(\eta\text{-}Cp'')_2(THF)]$ (**4**) (0.72 g, 1.12 mmol) was sublimed for 6 h at 215°C/10^{-3} Torr, to yield red

X-ray quality crystals of the title complex **2** (0.33 g, 52%). Found: C, 46.6; H, 7.7. $C_{22}H_{42}EuSi_4$ calc.: C, 46.3; H, 7.4%. ^1H (360 MHz) NMR spectroscopic data for **2** at 300 K in $C_6D_5CD_3$: δ -0.12 (b, 36H), 6.35 (b, 2H), 6.64 (b, 4H).

Preparation of [Yb(η-Cp")$_2$(OEt$_2$)] (3)

Diethyl ether (ca. 200 cm^3) was added to a mixture of ytterbium(II) iodide (2.42 g, 5.67 mmol) and K(Cp") (2.65 g, 10.69 mmol). The mixture was stirred for *ca.* 20 h at *ca.* 20°C to give a dark green suspension, and was filtered. The solvent was removed from the filtrate *in vacuo* to give a green solid which was extracted into toluene (*ca.* 50 cm^3). Cooling to -30°C yielded dark green crystals of the title complex **3** (2.55 g, 72%). Found: C, 46.2; H, 7.0. $C_{26}H_{52}OSi_4Yb$ calc.: C, 46.9; H, 7.8%. NMR spectroscopic data for **3** in $C_6D_5CD_3$: ^1H (360 MHz) at 300 K: δ 0.23 (s, 36H), 0.91 (CH_3 t, 6H), 3.17 (CH_2 q, 8H), 6.39 (m, 2H), 6.58 (m, 4H); ^{171}Yb (87.51 MHz) at 297 K: δ -70.25.

Preparation of [Eu((η-Cp")$_2$(THF)] (4)

A solution of $EuI_2(THF)_2$ (3.25 g, 5.91 mmol) in THF (*ca.* 100 cm^3) was added to a stirred solution of Na(Cp") (**5**) (2.77 g, 11.94 mmol) in THF (*ca.* 100 cm^3); stirring was continued for *ca.* 20 h at *ca.* 20°C. The volatiles were removed *in vacuo* from this red solution to yield an orange solid which was extracted into toluene (*ca.* 100 cm^3). The extract was filtered and the filtrate concentrated to *ca.* 50 cm^3. Cooling to -30°C yielded brown crystals of the title complex **4** (3.11 g, 82%). Found: C, 49.4; H, 8.3. $C_{26}H_{50}EuOSi_4$ calc.: C, 48.6; H, 7.8%. ^1H (360 MHz) NMR spectroscopic data for **4** at 300 K in $C_6D_5CD_3$: δ -0.11 (b, 36H), 0.85 (b, 6H), 1.26 (b, 8H), 6.36 (b, 2H), 6.67 (b, 4H).

Preparation of Na(Cp") (5)

An excess of solid $NaNH_2$ (3.80 g, 97.44 mmol) was added to a stirred solution of 1,3-bis(trimethylsilyl)cyclopentadiene (12.24 g, 58.29 mmol) in THF (*ca.* 200 cm^3); stirring was continued for *ca.* 24 h at *ca.* 20°C. The mixture was filtered to remove unreacted $NaNH_2$. Tetrahydrofuran was removed *in vacuo* from the brown filtrate to yield a brown solid, which was washed with hexane (2 × 100 cm^3) and dried under vacuum to yield a free-flowing white powder of the title product **5** (7.01 g, 53%). NMR spectroscopic data for the pyridine adduct of **5** at 300 K in C_5D_5N: ^1H (360 MHz): δ 0.30 (s, 18H), 6.93 (d, 2H), 7.02 (t, 1H); ^{13}C (90.56 MHz): δ 2.02, 104.43, 107.53, 120.16: ^{29}Si (71.55 MHz): δ -14.10.

X-ray structure determination for [{Yb(η-Cp")$_2$}$_\infty$] (1) and [{Eu(η-Cp")$_2$}$_\infty$] (2)

Data were collected on a diffractometer at room temperature for **1** and low temperature for **2** using monochromated Mo-K_α X-radiation. Reflections were corrected for Lorentz and polarisation effects and also for absorption [24]. Structures were solved by heavy atom methods and refined with anisotropic thermal parameters for non-hydrogen atoms. For **1**, the hydrogen atoms were fixed at calculated positions with $U_{iso} = 1.3\ U_{eq}$ for the parent atom. For **2**, hydrogen atoms were defined as riding on their parent carbon atoms with fixed isotropic atomic displacement parameters. The hydrogen atoms of the methyl groups significant in inter-/intra-molecular interactions were tested using various models of fully independent isotropic refinement, but this stretched the data-to-parameter ratio with-

Table 1

Crystal and refinement parameters for **1** and **2**

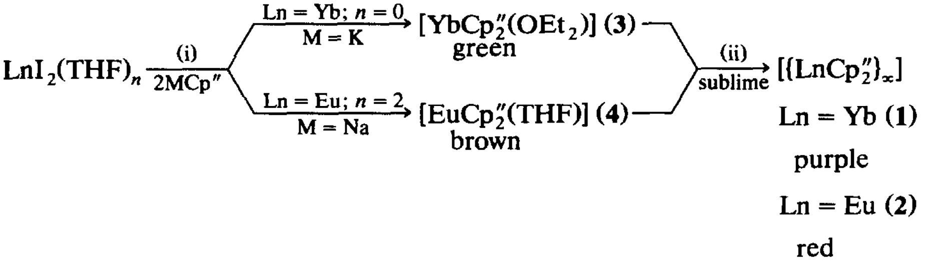
	1	**2**
Formula	$C_{22}H_{42}YbSi_4$	$C_{22}H_{42}EuSi_4$
MW	592.0	570.9
Crystal system and space group	monoclinic $P2_1/c$	orthorhombic $P2_12_12_1$
a/Å	11.038(2)	14.941(6)
b/Å	12.101(2)	17.422(7)
c/Å	22.421(9)	21.676(10) Å
β/°	102.06(2)	
U/Å^3	2929	5643(4)
Z	4	8
D_{calc}/g cm^{-3}	1.34	1.34
μ(Mo-K_α)/cm^{-1}	33.5	24.0
Diffractometer	Enraf-Nonius CAD4	Siemens R3m/v
θ_{max} for data/°	25	27.5
Unique reflections measured	5412	4083
Significance criterion	$I > 3\sigma(I)$	$I > 2\sigma(I)$
Significant reflections	3814	4037
R	0.031	0.024
R'	0.042	0.031
T/K	295	190

out meaningfully improving the model fit. Computer programs used were the Enraf–Nonius SDP package for **1** and the SHELXTL-PLUS package [25] for **2**. Tables of anisotropic thermal parameters, hydrogen atoms co-ordinates, and structure factors are available from the authors. Results for **2** correspond to the preferred absolute structure. Further details are included in Table 1.

Results and discussion

1. *Synthesis of* $[\{Yb(\eta\text{-}Cp'')_2\}_\infty]$ *(1) and* $[\{Eu(\eta\text{-}Cp'')_2\}_\infty]$ *(2)*

Desolvation of green $[Yb(\eta\text{-}Cp'')_2(OEt_2)]$ (**3**), and brown $[Eu(\eta\text{-}Cp'')_2(THF)]$ (**4**) (ii in Scheme 1), by a single sublimation afforded X-ray quality crystals of purple $[\{Yb(\eta\text{-}Cp'')_2\}_\infty]$ (**1**) or red $[\{Eu(\eta\text{-}Cp'')_2\}_\infty]$ (**2**). The reported desolvation of $[Yb(\eta\text{-}C_5Me_5)_2(OEt_2)]$ [15] occurred similarly. However, $[Eu(\eta\text{-}C_5Me_5)_2(THF)]$ [14] and $[Sm(\eta\text{-}Cp'')_2(THF)]$ [12] were only completely desolvated after repeated sublimations. This is consistent with steric effects being operative; thus, the Ln(II)



Scheme 1.

radii decrease in the sequence $Sm(4f^6) > Eu(4f^7) \gg Yb(4f^{14})$, and $^{-}Cp''$ is more bulky than $^{-}(\eta\text{-}C_5Me_5)$ [26], and Et_2O is sterically more demanding than THF.

2. *Synthesis of* $[Yb(\eta\text{-}Cp'')_2(OEt_2)]$ *(3) and* $[Eu(\eta\text{-}Cp'')_2(THF)]$ *(4)*

The solvated metallocenes **3** and **4** were prepared (i in Scheme 1), in a similar manner to that used previously for $[Yb(\eta\text{-}C_5H_4SiMe_3)_2(OEt_2)]$ and $[Sm(\eta\text{-}Cp'')_2(THF)]$, respectively [17]. Both reactions were between the appropriate lanthanide(II) iodide and an alkali metal cyclopentadienyl in an ethereal solution. Crystals of **3** and **4** were obtained by recrystallisation from toluene.

It is noteworthy that the reactions giving the products **3** and **4** were free from any bis-solvated complex $[Ln(\eta\text{-}Cp'')_2(L)_2]$. This is a contrast with observations concerning the preparation of $[Yb(\eta\text{-}C_5H_4SiMe_3)_2(OEt_2)]$ [17], $[Sm(\eta\text{-}Cp'')_2(THF)]$ [17], $[Yb(\eta\text{-}Cp'')_2(THF)$ [5], and $[Sm(\eta\text{-}C_5Me_5)_2(THF)]$ [27]; and confirms the significance of steric effects.

3. *Synthesis of* $Na(Cp'')$ *(5)*

Compound **5** was obtained by the reaction of excess $NaNH_2$ with bis(trimethylsilyl)cyclopentadiene in THF, using a procedure similar to that previously employed in the synthesis of $Na(C_5H_4SiMe_3)$ [17].

4. *X-ray structure of* $[\{Yb(\eta\text{-}Cp'')_2\}_\infty]$ *(1)*

The molecular structure and atom numbering scheme for $[\{Yb(\eta\text{-}Cp'')_2\}_\infty]$ (**1**) is shown in Fig. 1. Selected bond lengths and angles are shown in Table 2 and fractional atomic coordinates in Table 3.

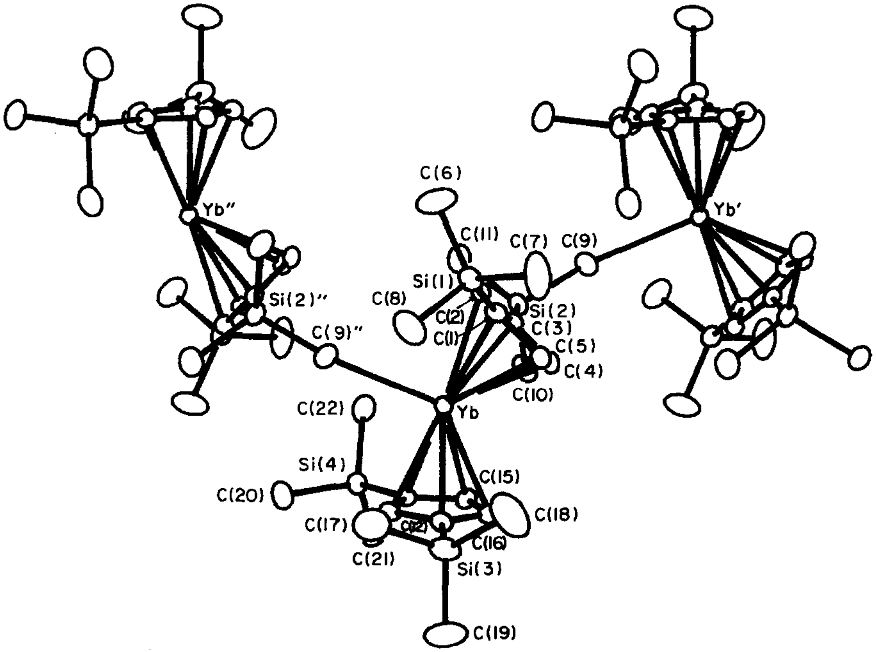


Fig. 1. X-Ray structure and atom labelling for $[\{Yb(\eta\text{-}Cp'')_2\}_\infty]$ (1).

Table 2

Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [{Yb(η-Cp″)$_2$}$_\infty$] (1) [a]

Bond lengths			
Yb–Cp1	2.382	Yb–Cp2	2.366
Yb–C(1)	2.684(6)	Yb–C(2)	2.674(5)
Yb–C(3)	2.678(5)	Yb–C(4)	2.654(5)
Yb–C(5)	2.657(6)	Yb–C(9)″	2.872(2)
Yb–C(12)	2.663(5)	Yb–C(13)	2.656(5)
Yb–C(14)	2.668(5)	Yb–C(15)	2.643(6)
Yb–C(16)	2.642(6)	Si(2)–C(3)	1.844(5)
Si(2)–C(9)	1.892(7)	Si(2)–C(10)	1.866(8)
Bond angles			
Cp1–Yb–Cp2	138.0	Cp1–Yb–C(9)″	111.9
Cp2–Yb–C(9)″	110.0	Yb′–C(9)–Si(2)	166.4(3)
C(9)–Si(2)–C(3)	106.8(3)	C(9)–Si(2)–C(10)	105.0(3)
C(9)–Si(2)–C(11)	109.3(3)	C(3)–Si(2)–C(10)	112.5(3)
C(3)–Si(2)–C(11)	110.7(3)	C(10)–Si(2)–C(11)	112.1(4)

[a] Cp1 is centroid of the ring C(1) to C(5), Cp2 is centroid of the ring C(10)–C(16); Symmetry element ′ is −x, 0.5+ y, 0.5−z; ″ is − x, 0.5+ y, 0.5− z.

Table 3

Atom coordinates (×10^4) for [{Yb(η-Cp″)$_2$}$_\infty$] (1)

	x	*y*	*z*
Yb	1769.1(2)	2213.5(2)	3451.3(1)
Si(1)	−1182.4(16)	2692.2(15)	4210.5(7)
Si(2)	90.8(15)	3680.7(13)	1872.1(7)
Si(3)	4161.0(20)	2252.3(20)	5038.8(8)
Si(4)	3895.7(15)	528.6(14)	2577.2(7)
C(1)	−301(5)	3190(5)	3642(2)
C(2)	−539(5)	2919(4)	3008(2)
C(3)	230(5)	3563(4)	2704(2)
C(4)	935(5)	4242(4)	3162(3)
C(5)	618(5)	4014(5)	3724(2)
C(6)	−2659(7)	2065(9)	3804(4)
C(7)	−1417(9)	3869(7)	4705(4)
C(8)	−342(8)	1612(8)	4732(3)
C(9)	−756(6)	5019(5)	1629(3)
C(10)	1624(6)	3835(6)	1655(3)
C(11)	−815(8)	2513(6)	1471(3)
C(12)	3988(5)	2192(5)	4198(3)
C(13)	3937(5)	1224(5)	3842(2)
C(14)	3913(5)	1499(5)	3223(2)
C(15)	3953(5)	2657(5)	3200(3)
C(16)	4000(5)	3084(5)	3798(3)
C(17)	3502(8)	945(9)	5317(4)
C(18)	3321(12)	3415(10)	5267(5)
C(19)	5800(9)	2278(11)	5430(4)
C(20)	4044(7)	−909(6)	2868(3)
C(21)	5208(7)	854(7)	2189(3)
C(22)	2430(8)	635(7)	2000(3)

Table 4

Selected structural data on solvated ytterbocene(II) complexes

Complex	Cent–Yb–Cent (°)	mean l(Yb–C) Å	Ref.
$[Yb(\eta\text{-}C_5H_5)_2(DME)]$	133.9	2.658	30
$[Yb(\eta\text{-}C_5H_5)_2(OPPh_3)_2]$	128.3(10)	2.76(2)	31
$[Yb(\eta\text{-}C_5Me_5)_2(THF)]\cdot\frac{1}{2}PhMe$	143.5(3)	2.663	8
$[Yb(\eta\text{-}C_5Me_5)_2(NC_5H_5)_2]$	136.3(3)	2.74(4)	32
$[Yb(\eta\text{-}C_5Me_5)_2(THF)(NH_3)]$	139.31	2.77	33
$[Yb(\eta\text{-}C_5H_4SiMe_3)_2(THF)_2]$	133	2.75	6
$[Yb(\eta\text{-}C_5H_4CMe_3)_2(THF)_2]$	134.0	2.723(15)	11

The structure of **1** exhibits the typical bent metallocene structure similar to that for $[Ln(\eta\text{-}C_5Me_5)_2]$ (Ln = Sm [13,14], Eu [14], or Yb [15]) and the alkaline earth metallocene complexes $[Ca(\eta\text{-}C_5Me_5)_2]$ [28] and $[Ba(\eta\text{-}C_5Me_5)_2]$ [28,29]. The Cent(Cp1)–Yb–Cent(Cp2) angle for **1** is 138.0°, and is available for comparison with (i) the corresponding angle for solvated ytterbocene(II) compounds, Table 4, and (ii) unsolvated lanthanocene(II), alkaline earth and Group XIV metallocene complexes, Table 5. Neither a variation in the bulk of the cyclopentadienyl ligand nor the presence of an added neutral donor seems to have a significant effect on this angle for a given metal.

The bent metallocene structure cannot be explained on steric or electrostatic grounds, as these would indicate that the most stable conformation for solvent-free lanthanocene(II) complexes should have, as in ferrocene, the two cyclopentadienyl rings parallel [14]. Neither is the bent structure due to crystal packing forces, as gaseous $[Yb(\eta\text{-}C_5Me_5)_2]$, like the alkaline earth metal analogues, retains the same conformation [38]. A polarisation argument is at present favoured to explain this aspect of the structure of lanthanocene(II) complexes [14,39], as for the similarly bent structures of the gaseous calcium halides [40].

Table 5

Selected structural data on lanthanide(II), alkaline earth and Group XIV metallocene complexes

Complex	Cent–M–Cent (°)	mean l(M–C) (Å)	closest intermolecular contact M···C (Å)	Ref.
$[Sm(\eta\text{-}C_5Me_5)_2]$	140.1	2.79(1)	3.22	13, 14
$[Eu(\eta\text{-}C_5Me_5)_2]$	140.3	2.79(1)	3.19	14
$[Yb(\eta\text{-}C_5Me_5)_2]$ [a]	145.7, 145.0	2.665(4)	2.98	15
$[Ca(\eta\text{-}C_5Me_5)_2]$ [a]	147.7, 146.3	2.64(2)	2.98	28
$[Ba(\eta\text{-}C_5Me_5)_2]$ [a]	131.0, 130.9	2.99(2)	3.35	28, 29
$[Sn(\eta\text{-}C_5H_5)_2]$ [a]	148.0, 143.7	2.68	4.02	34
$[Sn\{\eta\text{-}C_5H_2(SiMe_3)_3\}_2]$	162(2)	–	–	35
$[Sn(\eta\text{-}C_5Me_5)_2]$ [a]	143.6, 144.6	2.67	–	36
$[Ge\{\eta\text{-}C_5H_2(SiMe_3)_3\}_2]$ [a]	169.5, 171.8	2.56	–	37
$[\{Yb(\eta\text{-}Cp'')_2\}_\infty]$ (**1**)	138.0	2.662	2.872(7)	This work
$[\{Eu(\eta\text{-}Cp'')_2\}_\infty]$ (**2**) [a,b]	147, 122	2.828	3.091(6)	This work

[a] Two independent molecules exist in the unit cell. [b] Data given for η^5-Cp$''$ ligands.

The unsolvated crystalline decamethyllanthanocene(II) complexes showed some degree of close contact interaction between neighbouring monomeric units, Table 5. As the intermolecular Ln $\cdots$ C contacts were considerably greater than the l(Ln–C), these complexes were designated as monomers [13–15].

By contrast for **1** we now report that there is a close contact between a methyl group [Me(9)″] from one $YbCp''_2$ unit and a neighbouring Yb atom., the ytterbium-carbon distance l[Ln $\cdots$ C(9)″] = 2.872(7) Å, which is only 0.21 Å longer than the mean intramolecular l[Yb–C] of 2.662 Å and much shorter than the sum of the van der Waals radii (3.8 Å). The Si(2)″–C(9)″–Yb angle of 166.4(3)° shows a near linear arrangement and the Si(2)–C(9) bond [1.892(7) Å] is lengthened relative to the other Si–C (methyl) bonds. We interpret these findings as being indicative of the existence of γ-methyl–metal agostic-like intermolecular interactions. Such interactions are unprecedented in organolanthanide chemistry, and only two organometallic complexes showing similar features have been reported, $[\{Mg(CH(SiMe_3)_2)_2\}_\infty]$ [41] and $[\{Li[C(SiMe_3)_2PMe_2]\}_2]$ [42].

The overall geometric effect of these intermolecular interactions is to provide a "herring bone weave" pattern for the polymer. This packing arrangement was first noted in $Sm(\eta\text{-}C_5Me_5)_2$ [13,14] and $Ba(\eta\text{-}C_5Me_5)_2$ [28,29].

The difference between **1** and $[Ln(\eta\text{-}C_5Me_5)_2]$ may be due to the absence of γ-methyl groups in the latter, the β-effects being less significant.

5. *The low temperature X-ray structure of* $[\{Eu(\eta\text{-}Cp'')_2\}_\infty]$ *(2)*

The ambient temperature X-ray study of **2** suggested a polymeric array with an unprecedented intermolecular interaction between the europium atom and the γ-methyl group of a neighbouring $Eu(Cp'')_2$ unit. Subsequently low temperature X-ray data were collected and these show that the metallocene **2** possesses a unique structure, encompassing *intra*molecular and *inter*molecular agostic-like interactions with an η^5, η^3-bridging cyclopentadienyl ligand.

The molecular structure and atom numbering scheme for $[\{Eu(\eta\text{-}Cp'')_2\}_\infty]$ (**2**) is shown in Figs. 2 and 3. Selected bond lengths and angles are given in Table 6 and fractional coordinates in Table 7.

There are two crystallographically independent europium atoms in the unit cell with a unique and different environment around each one.

Eu(2) is η^5-bonded to two $^-$Cp″ ligands in a bent metallocene arrangement, the Cent(Cp3)–Eu(2)–Cent(Cp4) angle is 147.0° and the two metal–centroid separations are 2.504 Å (Cp4) and 2.558 Å (Cp3). The longer separation is observed for the $^-$Cp″ ligand, Cp3, which bridges the two independent europium atoms.

Eu(1), by contrast as seen clearly in Fig. 2, is joined to *three* Cp″ units at distances of 2.576 (Cp1), 2.610 (Cp2), and 2.897 Å (Cp3). The longest separation was again observed for Eu $\cdots$ the bridging Cp″ (Cp3). The angles [(Cpn) $\cdots$ Eu(1) $\cdots$ (Cpm)] for the 3 $^-$Cp″ ligands around Eu(1) are 122, 113, and 122°; the smallest lies between Cp3 and Cp2. The bridging $^-$Cp″, Cp3, is not symmetrically situated between the two europium atoms, being η^5-linked to Eu(2) and only η^3-linked to Eu(1). The two remaining carbon atoms, C(11) and C(12) of Cp3, lie further away from Eu(1) at 3.315 and 3.328 Å, respectively. In the bridging $^-$Cp″ ligand (Cp3), the Eu(2) $\cdots$ C(Cp3) distances range from 2.772–2.903 Å compared with those in the 'terminally' bound Cp4, namely Eu(2) $\cdots$ C(Cp4) of 2.724–2.828(6) Å. The shortest connections for Cp3 to Eu(2) are seen for C(11), and

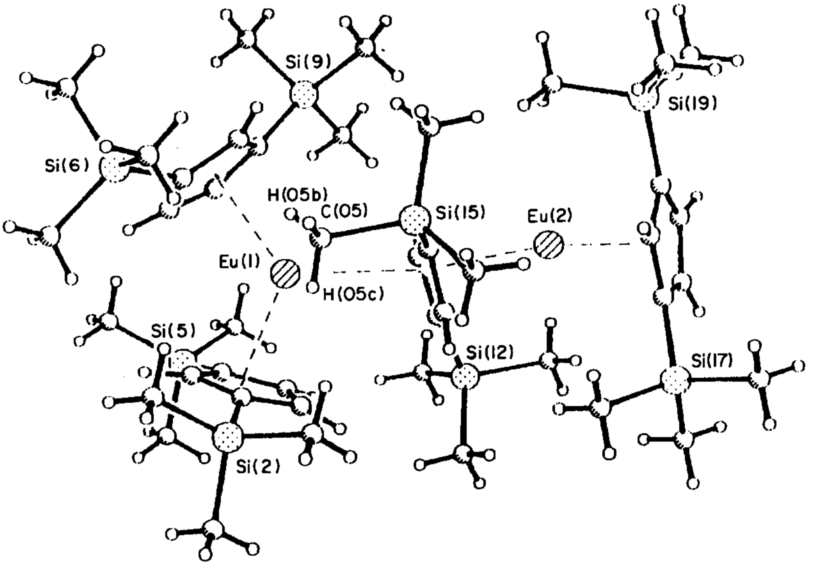


Fig. 2. X-Ray structure and atom labelling for [{Eu(η-Cp$''$)$_2$}$_\infty$] (2).

C(12), *i.e.* the "non-bonded" atoms with respect to Eu(1). These Eu(2) · · · C(Cp) values can be compared with the range 2.776–2.956 Å observed for the ten [Eu(1) · · · C(Cp1,2)] separations.

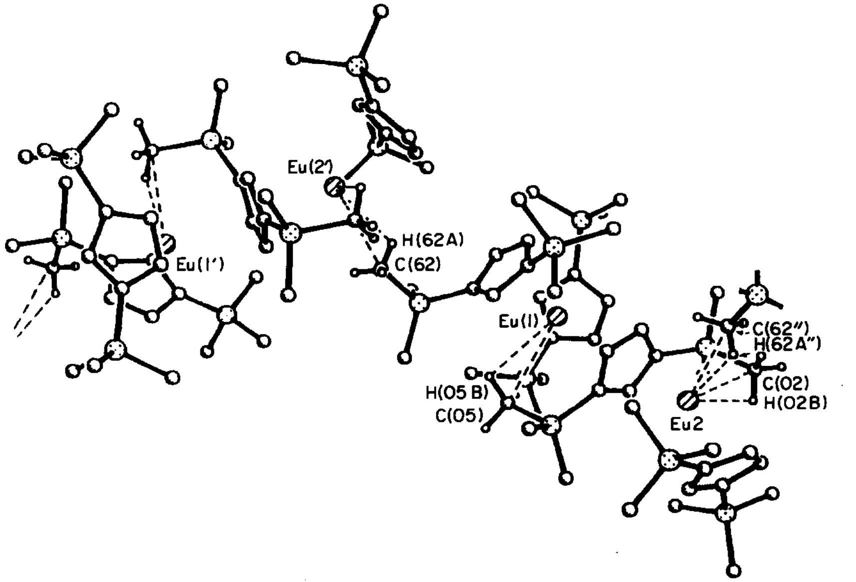


Fig. 3. X-Ray structure of [{Eu(η-Cp$''$)$_2$}$_\infty$] (2) showing intra- and intermolecular agostic-like interactions. Relevant bond distances: Eu(1) · · · H(05B) 3.137, Eu(1) · · · H(05C) 2.932, Eu(1) · · · C(05) 3.297, Eu(2) · · · H(02A) 2.849, Eu(2) · · · H(02B) 2.854, Eu(2) · · · C(02) 3.160, Eu(2′) · · · H(62A) 2.70, Eu(2′) · · · H(62B) 3.07, Eu(2′) · · · H(62C) 3.02; Eu(2′) · · · C(62) 3.091 Å. [Eu(2′) generated by ($\frac{1}{2} - x$, $- y$, $\frac{1}{2} + z$).]

Table 6

Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[\{Eu(\eta\text{-}Cp'')_2\}_\infty]$ (2) [a]

Bond lengths			
Eu(1)–Cp1	2.576	Eu(1)–Cp2	2.610
Eu(1)–Cp3	2.897	Eu(2)–Cp3	2.558
Eu(2)–Cp4	2.504	Eu(1)–C(1)	2.795(6)
Eu(1)–C(2)	2.803(6)	Eu(1)–C(3)	2.850(6)
Eu(1)–C(4)	2.870(6)	Eu(1)–C(5)	2.854(5)
Eu(1)–C(6)	2.886(5)	Eu(1)–C(7)	2.776(6)
Eu(1)–C(8)	2.795(5)	Eu(1)–C(9)	2.941(6)
Eu(1)–C(10)	2.956(6)	Eu(1)–C(13)	3.042(6)
Eu(1)–C(14)	2.897(6)	Eu(1)–C(15)	3.076(5)
Eu(2)–C(11)	2.802(5)	Eu(2)–C(12)	2.772(6)
Eu(2)–C(13)	2.814(6)	Eu(2)–C(14)	2.870(6)
Eu(2)–C(15)	2.903(5)	Eu(2)–C(16)	2.816(6)
Eu(2)–C(17)	2.828(6)	Eu(2)–C(18)	2.766(6)
Eu(2)–C(19)	2.724(6)	Eu(2)–C(20)	2.749(6)
Eu(2)–C(02)	3.161(6)	Eu(2′)–C(62)	3.091(6)
Si(2)–C(3)	1.857(6)	Si(6)–C(6)	1.849(6)
Si(6)–C(61)	1.859(7)	Si(6)–C(62)	1.896(6)
Si(6)–C(63)	1.864(7)	Si(12)–C(12)	1.869(6)
Si(12)–C(01)	1.863(6)	Si(12)–C(02)	1.889(6)
Si(12)–C(03)	1.849(6)	Si(15)–C(15)	1.864(6)
Si(15)–C(04)	1.845(10)	Si(15)–C(05)	1.852(7)
Si(15)–C(06)	1.853(8)	C(11)–C(12)	1.411(8)
C(11)–C(15)	1.409(8)	C(12)–C(13)	1.429(8)
C(13)–C(14)	1.429(8)	C(14)–C(15)	1.432(8)
Bond angles			
Cp1–Eu(1)–Cp2	122	Cp1–Eu(1)–Cp3	113
Cp2–Eu(1)–Cp3	122	Cp3–Eu(2)–Cp4	147
C(6)–Si(6)–C(61)	115.3(3)	C(6)–Si(6)–C(62)	104.4(3)
C(61)–Si(6)–C(62)	108.4(3)	C(6)–Si(6)–C(63)	111.6(3)
C(61)–Si(6)–C(63)	109.4(3)	C(62)–Si(6)–C(63)	107.3(3)
C(12)–Si(12)–C(01)	110.7(3)	C(12)–Si(12)–C(02)	107.9(3)
C(01)–Si(12)–C(02)	107.8(3)	C(12)–Si(12)–C(03)	111.0(3)
C(01)–Si(12)–C(03)	113.8(3)	C(02)–Si(12)–C(03)	105.4(3)
C(15)–Si(15)–C(04)	112.4(3)	C(15)–Si(15)–C(05)	106.9(3)
C(04)–Si(15)–C(05)	107.5(3)	C(15)–Si(15)–C(06)	110.0(3)
C(04)–Si(15)–C(06)	111.0(4)	C(05)–Si(15)–C(06)	108.8(3)

[a] Cp1 is the centroid of ring C(1) to C(5); Cp2 is the centroid of ring C(6) to C(10); Cp3 is the centroid of ring C(11) to C(15); Cp4 is the centroid of ring C(16) to C(20). Eu(2′) is generated by ($\frac{1}{2} - x$, $-y$, $\frac{1}{2} + z$).

In addition to these obvious links from the europium atoms to the $^{-}$Cp″ ligands, for which M ··· C(Cp) < 3.1 Å, the low temperature X-ray study revealed weaker, secondary, agostic-like interactions between the unsaturated europium atoms and certain hydrogen atoms of the $(SiMe_3)$ methyl groups; Fig. 3 shows how these inter- and intra-molecular interactions arise. The Eu ··· H distances range from 2.70–3.14 Å, while the Eu ··· parent C atom values vary from 3.09–3.29 Å; the individual data are given in the Fig. 3 caption. The C–H separations involved in the *intra*molecular interactions are slightly elongated from the normally accepted value (0.96 Å), although within the limitations of X-ray data the variation

Table 7

Atom coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for [{Eu(η-Cp″)$_2$}$_x$] (2)

	x	y	z	U_{eq} [a]
Eu(1)	6409(1)	6512(1)	1668(1)	22(1)
Eu(2)	8361(1)	6607(1)	3782(1)	25(1)
Si(2)	6008(1)	8769(1)	920(1)	40(1)
Si(5)	3591(1)	6314(1)	1644(1)	32(1)
Si(6)	7005(1)	5923(1)	−246(1)	29(1)
Si(9)	7140(1)	4077(1)	1942(1)	28(1)
Si(12)	6067(1)	7326(1)	3758(1)	26(1)
Si(15)	8897(1)	7146(1)	1886(1)	35(1)
Si(17)	9158(1)	8862(1)	4297(1)	33(1)
Si(19)	10712(1)	5823(1)	3846(1)	33(1)
C(1)	4948(4)	7300(3)	2165(3)	31(2)
C(2)	5542(4)	7881(3)	1993(3)	29(2)
C(3)	5569(4)	7922(3)	1337(3)	27(2)
C(4)	4958(4)	7347(3)	1118(3)	27(2)
C(5)	4576(3)	6969(3)	1624(3)	23(2)
C(6)	6739(4)	5646(3)	557(2)	27(2)
C(7)	5847(4)	5496(3)	761(3)	27(2)
C(8)	5880(4)	5048(3)	1288(3)	26(2)
C(9)	6795(4)	4882(3)	1439(3)	28(2)
C(10)	7301(4)	5262(3)	981(3)	25(2)
C(11)	7494(3)	7367(3)	2812(2)	24(2)
C(12)	6818(4)	6966(3)	3133(2)	23(2)
C(13)	6953(4)	6173(3)	2993(3)	24(2)
C(14)	7718(4)	6110(3)	2600(2)	25(2)
C(15)	8051(4)	6866(3)	2476(2)	24(2)
C(16)	9138(4)	7313(3)	4821(3)	28(2)
C(17)	9372(4)	7810(3)	4313(3)	32(2)
C(18)	9961(4)	7381(3)	3938(3)	28(2)
C(19)	10083(4)	6634(3)	4194(3)	29(2)
C(20)	9563(4)	6611(4)	4742(3)	32(2)
C(01)	5810(5)	8363(3)	3644(3)	42(2)
C(02)	6682(4)	7227(4)	4515(3)	37(2)
C(03)	5063(4)	6713(3)	3834(3)	34(2)
C(04)	9760(6)	6401(6)	1772(4)	78(4)
C(05)	8290(5)	7259(4)	1146(3)	46(2)
C(06)	9412(6)	8077(5)	2096(3)	64(3)
C(07)	10231(4)	9361(4)	4499(3)	44(2)
C(08)	8801(6)	9225(4)	3526(3)	61(3)
C(09)	8268(4)	9107(4)	4856(3)	45(2)
C(010)	11716(5)	6181(4)	3425(4)	52(2)
C(011)	10998(5)	5129(4)	4459(3)	49(2)
C(012)	9957(5)	5322(4)	3292(3)	53(2)
C(21)	5189(6)	9571(4)	981(4)	54(3)
C(22)	7037(6)	9143(5)	1315(6)	88(4)
C(23)	6245(9)	8541(4)	107(4)	101(5)
C(51)	2560(4)	6904(4)	1768(3)	48(2)
C(52)	3679(5)	5630(4)	2298(3)	49(2)
C(53)	3447(5)	5773(4)	915(3)	53(2)
C(61)	8056(5)	6480(4)	−346(3)	46(2)
C(62)	7129(5)	4976(3)	−668(3)	39(2)
C(63)	6060(5)	6451(40	−613(3)	45(2)
C(91)	6911(5)	3173(3)	1500(3)	48(2)
C(92)	6495(5)	4054(3)	2673(3)	45(2)
C(93)	8364(4)	4080(4)	2128(3)	49(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

cannot be claimed to be highly significant (1.00–1.20 Å). Similarly, the Si–C–H angles while showing deviations from tetrahedral are not all bent towards the metal atoms. Nonetheless, this form of intramolecular agostic interaction has been reported previously to exist in the homoleptic lanthanide(III) alkyls [LnR_3] [L = La or Sm; R = $CH(SiMe_3)_2$] [31].

Interestingly, but again not significantly, the *inter*molecular link through C(62)–H(62A) to an adjacent Eu(2), shows the shortest Eu ··· H and Eu ··· C separations of 2.70 and 3.09 Å, respectively, and the shortest C–H, 0.87 Å, but the longest C(methyl)–Si, 1.896(6) Å [*cf.* Si(12)–C(02), 1.889(6) Å and Si(15)–C(05), 1.852(7) Å]. The intermolecular angle, [Eu(2′) ··· C(62)–Si(6)] is clearly non-linear at 159.9°. As reported for the Mg complex [41], the intermolecularly associated C atom appears to approximate to a trigonal bipyramidal 5-coordinate arrangement.

The polymeric character conferred on the solid state structure, derives from these novel inter- and intra-molecular agostic-like interactions, in addition to the unusual bridging η^5,η^3-$(Cp'')^-$ ligands.

The intermolecular agostic-like interactions in both **1** and **2** may involve two-electron three-centre bonds between Ln ··· C ··· H but alternatively Ln ··· C ··· Si; the latter possibility would be consistent with a trigonal bipyramidal geometry at the central carbon atom.

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