

Synthesis, characterisation and reactions of 1,3-bis(trimethylsilyl)-1-aza-allyl-lanthanide complexes; X-ray structures of $[\text{Sm}(\text{LL}')_2\text{I}(\text{thf})]$, $[\text{Yb}(\text{LL}')_2]$ and $[\text{RN}=\text{C}(\text{Bu}^t)\text{CH}(\text{R})_2]$ (thf = tetrahydrofuran, $\text{LL}' = \eta^3\text{-N}(\text{R})\text{C}(\text{Bu}^t)\text{CHR}$, $\text{R} = \text{SiMe}_3$)¹

Peter B. Hitchcock, Michael F. Lappert^{*}, Shun Tian

The Chemistry Laboratory, University of Sussex, Brighton BN1 9QJ, UK

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Abstract

Several lanthanide(II) and lanthanide(III) complexes of formula $[\text{Ln}(\text{LL}')_2\text{X}(\text{thf})_n]$ ($\text{LL}' = \eta^3\text{-N}(\text{R})\text{C}(\text{Bu}^t)\text{CHR}$, $\text{R} = \text{SiMe}_3$; $\text{X} = \text{Cl}$, $n = 1$ and $\text{Ln} = \text{Ce}$ **1** or Nd **2**; or $\text{X} = \text{I}$, $n = 1$ and $\text{Ln} = \text{Sm}$ **3**; or $\text{X} = \text{I}$, $n = 0$ and $\text{Ln} = \text{Yb}$ **4**), $[\text{Sm}(\text{LL}')_2(\text{thf})]$ **5** and $[\text{Yb}(\text{LL}')_2]$ **6** have been synthesised by the reaction of the appropriate lanthanide(II) or lanthanide(III) halide with two equivalents of 1,3-bis(trimethylsilyl)-1-aza-allyl-potassium $[\text{K}(\text{LL}')]$. Oxidation of **6** with $\text{Ag}(\text{OTf})$ afforded $[\text{Yb}(\text{LL}')_2(\text{OTf})]$ **7** ($\text{Tf} = \text{SO}_2\text{CF}_3$). The reaction of **6** with half an equivalent of I_2 yielded as the main oxidative product **4** but also led to ligand coupling, forming $[\text{RN}=\text{C}(\text{Bu}^t)\text{CH}(\text{R})_2]$ **8**, which was also prepared by the reaction of $[\text{K}(\text{LL}')]$ with I_2 . Treatment of **6** with two equivalents of PhCN yielded the previously known β -diketiminato $[\text{Yb}(\text{L}'\text{L}'')_2]$ [$\text{L}'\text{L}'' = \text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Bu}^t)\text{NR}$]. Complexes **1–8** were identified by C, H and N elemental analysis, multinuclear (^1H , ^{13}C , ^{29}Si (^1H), ^{17}Yb or ^{19}F) NMR and mass spectra, of which **3**, **6** and **8** were additionally characterised by single crystal X-ray diffraction. © 1997 Elsevier Science S.A.

Keywords: Lanthanides; 1,3-Bis(trimethylsilyl)-1-aza-allyls; Crystal structure

1. Introduction

The ubiquitous η^3 -allyl ligand has been shown to play an important role in many transition metal-mediated reactions [1,2]. In recent years, the chemistry of heteroallylmetal complexes has attracted great interest; in these complexes the metal tends to bond asymmetrically to the ligand because of the differing electronic nature of the heteroatom. Among the latter are oxygen, phosphorus or nitrogen. Several η^3 -1-oxa-allyl- and η^3 -1-phospha-allyltransition metal complexes have been reported [3–8]. Heteroallyl species containing two terminal nitrogens (i.e. η^3 -1,3-diaza-allyls) or one centrally located nitrogen (i.e. η^3 -2-aza-allyls) have also been prepared [9–11]. The former include the well-

known N,N' -bis(trimethylsilyl)benzamidinato ligands $[4\text{-R}'\text{C}_6\text{H}_4\text{C}(\text{NR})_2]^-$ ($\text{R} = \text{SiMe}_3$ and $\text{R}' = \text{H}$, Me , OMe , CF_3 or Ph), from which inter alia a series of f-element complexes has been made [12–18]. Numerous η^3 -1-aza-allylmetal complexes of alkali metals [19–24] and transition metals [25–27] have been synthesised and structurally characterised.

We have recently reported that the reaction of MCHR_2 ($\text{M} = \text{Li}$ or K , $\text{R} = \text{SiMe}_3$) with Bu^tCN afforded the appropriate metal complex containing the 1,3-bis(trimethylsilyl)-1-aza-allyl ligand $[\eta^3\text{-N}(\text{R})\text{C}(\text{Bu}^t)\text{CR}]^- (= [\text{LL}']^-)$ [28,29], and we have synthesised and structurally characterised the corresponding lithium, zirconium and thorium complexes, $[\text{Li}(\text{LL}')_2]$ [28], $\text{rac-}[\text{Zr}(\text{LL}')_2\text{Cl}_2]$ [28,30], $[\text{Zr}(\text{LL}')\text{Cl}_2(\mu\text{-Cl})_2]$ [30] and $\text{rac-}[\text{Th}(\text{LL}')_2\text{Cl}_2]$ [31]. Some of these papers are Parts 2 [30], 3 [29] and 5 [31] of this series; Part 1 [32] dealt with a uranium β -diketiminato and 1,3-diaza-allyls of potassium and uranium, while Part 4 [33] dealt with β -diketiminates but also 1-aza-allyls of tin(II), lead(II), iron(II), cobalt(II) and copper(I).

^{*} Corresponding author.

¹ Transformation of the bis(trimethylsilyl)methyl into the 1-aza-allyl and β -diketiminato ligands. Part 6. For Part 5, see Ref. [31]. No reprint available.

The work described in this paper is concerned with the use of the 1-aza-allyl ligand in lanthanide chemistry. We have previously briefly communicated the preparation and X-ray structure of $[\text{Yb}(\text{LL}')_2] \mathbf{6}$ [34]; we report here details, including new data on $\mathbf{6}$ and the synthesis and characterisation of other lanthanide(III) and samarium(II) bis(trimethylsilyl)-1-aza-allyl complexes.

2. Experimental details

2.1. 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 known procedures: MCHR_2 ($\text{M} = \text{Na}$ or K) [35], $[\text{K}(\text{LL}')_n]$ [28], CeCl_3 [36], NdCl_3 [36], $\text{TmI}_3(\text{thf})_2$ [37], YbI_3 [37], YbI_2 [38] and $\text{SmI}_2(\text{thf})_2$ [39]. Others were purchased, and purified by standard procedures. Microanalyses were carried out by Medac Ltd. (Brunel University). NMR spectra were recorded with Bruker WM250, WM360 or WM500 instruments. Mass spectra were recorded on a Fisons VG Autospec mass spectrometer operating in the EI mode at 70 eV.

2.2. Synthesis of $[\text{Ce}(\text{LL}')_2\text{Cl}(\text{thf})] \mathbf{(1)}$

A colourless solution of $[\text{K}(\text{LL}')_n]$ (1.7 g, 6.1 mmol) in tetrahydrofuran (50 ml) was added to a stirred suspension of CeCl_3 (0.75 g, 3.04 mmol) in tetrahydrofuran (100 ml). The mixture was stirred at room temperature for 12 h and refluxed for another 12 h, leaving a yellow solution and a white precipitate which was filtered off. Solvent was removed from the filtrate in vacuo and the yellow residue was extracted with hexane (50 ml) and filtered. The volume of the filtrate was reduced under vacuum to ca. 10 ml. Cooling to -30°C afforded the title compound $\mathbf{1}$ (1.4 g, 63%) as a yellow powder. Anal. Found: C, 46.4; H, 8.84; N, 3.87. $\text{C}_{28}\text{H}_{64}\text{ClN}_2\text{OSi}_4\text{Sm}$ Calc.: C, 46.9; H, 9.00; N, 3.91%. MS: m/e 660 (1.5%, $[\text{M} - \text{thf}]^+$); 587 (18%, $[\text{M} - \text{SiMe}_3]^+$); 603 (12%, $[\text{M} - \text{Bu}]^+$); 228 (22%, $[(\text{LL}') - \text{Me}]^+$); 186 (100%, $[(\text{LL}') - \text{Bu}]^+$); 73 (96%, $[\text{SiMe}_3]^+$).

2.3. Synthesis of $[\text{Nd}(\text{LL}')_2\text{Cl}(\text{thf})] \mathbf{(2)}$

A colourless solution of $[\text{K}(\text{LL}')_n]$ (0.5 g, 1.77 mmol) in tetrahydrofuran (50 ml) was added to a stirred suspension of NdCl_3 (0.22 g, 0.88 mmol) in tetrahydrofuran (100 ml). The mixture was stirred at room temperature for 12 h and refluxed for another 8 h, leaving a blue-green solution and a white precipitate which was filtered off. Solvent was removed from the filtrate in

vacuo and the yellow residue was extracted with hexane (50 ml) and filtered. The volume of the filtrate was reduced under vacuum to ca. 10 ml. Cooling to -30°C afforded the title compound $\mathbf{2}$ (0.5 g, 77.8%) as a blue powder. Anal. Found: C, 46.0; H, 8.66; N, 3.65. $\text{C}_{28}\text{H}_{64}\text{ClN}_2\text{NdOSi}_4$ Calc.: C, 46.6; H, 8.94; N, 3.89%. MS: m/e 664 (0.05%, $[\text{M} - \text{thf}]^+$); 591 (2%, $[\text{M} - \text{SiMe}_3]^+$); 607 (10%, $[\text{M} - \text{Bu}]^+$); 228 (15%, $[(\text{LL}') - \text{Me}]^+$); 186 (85%, $[(\text{LL}') - \text{Bu}]^+$); 73 (100%, $[\text{SiMe}_3]^+$).

2.4. Synthesis of $[\text{Sm}(\text{LL}')_2\text{I}(\text{thf})] \mathbf{(3)}$

A colourless solution of $[\text{K}(\text{LL}')_n]$ (1.2 g, 4.27 mmol) in diethyl ether (50 ml) was added to a stirred suspension of $\text{SmI}_2(\text{thf})_2$ (1.43 g, 2.1 mmol) in diethyl ether (100 ml). The mixture was stirred at room temperature for 36 h, leaving a yellow solution and a white precipitate which was filtered off. Solvent was removed from the filtrate in vacuo and the yellow solid residue was extracted with pentane (75 ml) and filtered. The filtrate was concentrated to ca. 10 ml. Cooling to -30°C afforded the title compound $\mathbf{3}$ (1.0 g, 57%) as orange crystals. Anal. Found: C, 38.1; H, 7.37; N, 3.54. $\text{C}_{28}\text{H}_{64}\text{IN}_2\text{OS}_4\text{Sm}$ Calc.: C, 40.3; H, 7.73; N, 3.36%. MS: m/e 764 (1.5%, $[\text{M} - \text{thf}]^+$); 638 (2%, $[\text{Sm}(\text{LL}')_2]^+$); 521 (36%, $[\text{Sm}(\text{LL}')\text{I}]^+$); 394 (13%, $[\text{Sm}(\text{LL}')]^+$); 228 (22%, $[(\text{LL}') - \text{Me}]^+$); 186 (92%, $[(\text{LL}') - \text{Bu}]^+$); 73 (100%, $[\text{SiMe}_3]^+$).

2.5. Synthesis of $[\text{Yb}(\text{LL}')_2\text{I}] \mathbf{(4)}$

The reaction of $[\text{K}(\text{LL}')_n]$ (0.7 g, 2.4 mmol) with YbI_3 (0.62 g, 1.12 mmol) using the procedure described for $\mathbf{3}$ afforded the title compound $\mathbf{4}$ (0.6 g, 58.2 mmol) as dark red crystals. Anal. Found: C, 36.2; H, 7.17; N, 3.48. $\text{C}_{24}\text{H}_{56}\text{IN}_2\text{Si}_4\text{Yb}$ Calc.: C, 36.7; H, 7.19; N, 3.57%. MS: m/e 786 (8%, $[\text{M}]^+$); 658 (28%, $[\text{M} - \text{I} - \text{I}]^+$); 543 (15%, $[\text{M} - (\text{LL}')^+]^+$); 486 (13%, $[\text{Yb}(\text{LL}')\text{I} - \text{Bu}]^+$); 416 (32%, $[\text{Yb}(\text{LL}')^+]^+$); 243 (32%, $[(\text{LL}')^+]^+$); 228 (70%, $[(\text{LL}') - \text{Me}]^+$); 186 (94%, $[(\text{LL}') - \text{Bu}]^+$); 73 (100%, $[\text{SiMe}_3]^+$).

2.6. Synthesis of $[\text{Sm}(\text{LL}')_2(\text{thf})] \mathbf{(5)}$

A colourless solution of $[\text{K}(\text{LL}')_n]$ (0.92 g, 3.26 mmol) in tetrahydrofuran (50 ml) was added to a stirred green-blue solution of $\text{SmI}_2(\text{thf})_2$ (0.9 g, 1.65 mmol) in tetrahydrofuran (150 ml). The mixture was stirred at room temperature for 18 h; the colour of the solution became red-brown. After filtration, solvent was removed from the filtrate in vacuo to yield a green solid which was extracted with pentane and filtered. The filtrate was concentrated to ca. 5 ml. Cooling to -30°C afforded the dark green crystalline $\mathbf{5}$ (1.0 g, 83.2%). Anal. Found: C, 47.1; H, 8.86; N, 3.80.

$C_{28}H_{64}N_2OSi_4Sm$ Calc.: C, 47.5; H, 9.12; N, 3.98%. NMR: 1H (C_6D_6 , $25^\circ C$): δ -2.95 (s, 9H, $SiMe_3$), -2.21 (s, 9H, $SiMe_3$), 9.28 (s, 9H, Bu^1), 39.47 (s, 1H, CH), 3.85 (s, 2H, thf), -3.40 (s, 2H, thf). ^{13}C (1H) (C_6D_6 , $25^\circ C$): δ -39.15 and -38.26 ($SiMe_3$), 56.41 (d, CMe_3), 22.06 (d, CMe_3), 52.21 (CH), 303.65 (Bu^1CN), 16.16 and -32.00 (thf). ^{29}Si (1H) (C_6D_6 15% + $C_6H_5CH_3$ 85%, $25^\circ C$): δ 83.74 and 79.4. MS: m/e 636 (7.5%, $[M - thf]^+$); 579 (0.2%, $[Sm(LL')_2 - Bu^1]^+$); 394 (5%, $[Sm(LL')^+]$); 228 (23%, $[(LL') - Me]^+$); 186 (100%, $[(LL') - Bu^1]^+$); 73 (98%, $[SiMe_3]^+$).

2.7. Synthesis of $[Yb(LL')_2]$ (6)

2.7.1. From the reaction of YbI_2 and $[K(LL')]_n$

A solution of $[K(LL')]_n$ (1.95 g, 6.8 mmol) in diethyl ether (50 ml) was added to a stirred suspension of YbI_2 (1.44 g, 3.37 mmol) in diethyl ether (150 ml). The mixture was stirred at room temperature for 24 h, leaving a red solution and a white precipitate which was filtered off. Solvent was removed from the filtrate in vacuo and the residue was extracted with pentane (30 ml) and filtered. The volume of the filtrate was reduced to ca. 5 ml and cooled to $-30^\circ C$ to yield the title compound **6** (2.1 g, 95%) as dark red crystals. Anal. Found: C, 42.7; H, 8.54; N, 4.20. $C_{24}H_{56}N_2Si_4Yb$ Calc.: C, 43.8; H, 8.58; N, 4.26%. NMR: 1H (C_6D_6 , $25^\circ C$): δ 0.26 (d, 9H, $SiMe_3$), 0.33 (d, 9H, $SiMe_3$), 1.21 (d, 9H, Bu^1), 3.84 (d, 1H, CH). ^{13}C (1H) (C_6D_6 , $25^\circ C$): δ 1.09 (d, $SiMe_3$), 4.60 (d, $SiMe_3$), 30.49 (d, CMe_3), 41.22 (d, CMe_3), 77.9 and 80.00 (CH, $^1J_{C-Yb} = 17.0$ Hz), 192.50 (Bu^1CN). ^{29}Si (1H) (C_6D_6 15% + $C_6H_5CH_3$ 85%, $25^\circ C$): δ -14.3, -14.5, -20.0 and -21.1. ^{171}Yb (C_6D_6 15% + $C_6H_5CH_3$ 85%, $25^\circ C$): δ 829.57 ($w_{1/2} = 42$ Hz), 820.04 ($w_{1/2} = 54$ Hz). MS: m/e 658 (22%, $[M]^+$); 416 (45%, $[Yb(LL')^+]$); 186 (78%, $[(LL') - Bu^1]^+$); 73 (100%, $[SiMe_3]^+$).

2.7.2. From the reaction of $[Yb(CHR_2)_2(OEt_2)_2]$ and Bu^1CN

A solution of $NaCHR_2$ (0.81 g, 4.3 mmol) in diethyl ether (50 ml) was added to a suspension of YbI_2 (0.92 g, 2.15 mmol) in diethyl ether (50 ml). The mixture was stirred at ca. $25^\circ C$ for 2 days and the resulting white precipitate was filtered off. To the filtrate was added Bu^1CN (0.48 ml, 4.3 mmol) by syringe. The mixture was stirred for 20 h, and the colour of the solution gradually changed to dark red. Solvent was removed from the solution in vacuo and the resultant red residue was extracted with hexane (20 ml) and filtered. The filtrate was concentrated to ca. 5 ml. Cooling to $-30^\circ C$ afforded red crystalline **6** (0.6 g, 42%).

2.8. Reaction of $[Yb(LL')_2]$ (6) with $Ag(OTf)$

Solid $Ag(OTf)$ ($Tf = SO_2CF_3$) (0.37 g, 1.52 mmol) was added to a stirred solution of **6** (1.0 g, 1.52 mmol)

in toluene (75 ml). The mixture was stirred at room temperature for 12 h and a silver mirror was formed on the walls of the Schlenk flask. The colour of the solution changed from dark red to light pink. After filtration, the filtrate was concentrated to ca. 5 ml. Cooling to $-30^\circ C$ afforded $[Yb(LL')_2(OTf)]$ **7** (0.6 g, 49%) as a pink powder. Anal. Found: C, 36.5; H, 8.54; N, 3.31. $C_{25}H_{56}F_3N_2O_3SSi_4$ Calc.: C, 37.2; H, 6.99; N, 3.47%. MS: m/e 808 (30%, $[M]^+$); 659 (57%, $[M - (OTf)]^+$); 565 (100%, $[M - (LL')^+]$); 508 (77%, $[Yb(LL')(OTf) - Bu^1]^+$); 416 (42%, $[Yb(LL')^+]$); 228 (50%, $[(LL') - Me]^+$); 186 (95%, $[(LL') - Bu^1]^+$); 73 (90%, $[SiMe_3]^+$).

2.9. Reaction of $[Yb(LL')_2]$ (6) with I_2

A brown solution of I_2 in diethyl ether (10.0 ml of a 0.03 mol dm^{-3} solution in Et_2O , 0.3 mmol) was added to a stirred red solution of **6** (0.4 g, 0.6 mmol) in diethyl ether (50 ml). The mixture was stirred at room temperature for 12 h, leaving a pink solution. Solvent was removed in vacuo from the solution and the red solid residue was extracted with pentane (30 ml) and filtered. The volume of the filtrate was reduced under vacuum to ca. 5 ml. Cooling to $-30^\circ C$ afforded pink needles identified as **4** (0.3 g, 63.3%). From the mother liquor, a mixture of pink needles **4**, red cubic crystals (trace amount) and white crystals identified as $[RN=C(Bu^1)CH(R)]_2$ ($R = SiMe_3$) (**9**) (a trace amount) were further isolated.

2.10. Reaction of $[Yb(LL')_2]$ (6) with $PhCN$

$PhCN$ (0.13 ml, 1.25 mmol) was added by a syringe to a red solution of **6** (0.4 g, 0.61 mmol) in diethyl ether (50 ml) at room temperature. There was an immediate colour change from red to blue, then to green. The mixture was stirred at room temperature for 12 h. Solvent was removed in vacuo and the resultant green residue was dissolved in hexane (5 ml). The solution was reduced under vacuum to ca. 3 ml and cooled to $-30^\circ C$, yielding dark green crystals which were identified by 1H , ^{13}C and ^{171}Yb NMR spectra as $[Yb(LL')_2][L'L' = N(R)C(Ph)C(H)C(Bu^1)NR, R = SiMe_3]$ (0.33 g, 63%).

2.11. Synthesis of $[RN=C(Bu^1)CH(R)]_2$ (8) from $[K(LL')]_n$ and I_2

A solution of I_2 in diethyl ether (62 ml of a 0.03 mol dm^{-3} solution in Et_2O , 1.86 mmol) was added to a stirred solution of $[K(LL')]_n$ (1.05 g, 3.73 mmol) in diethyl ether (100 ml). The red-brown colour was immediately discharged; the mixture was stirred for 8 h, leaving a cloudy milky suspension. After filtration, the filtrate was concentrated to ca. 10 ml. Cooling to $-30^\circ C$

Table 1
X-ray crystal structure details

	[Sm(LL') ₂](thf) (3)	[Yb(LL') ₂] (6)	[RN=C(Bu')CH(R)] ₂ (8)
Formula	C ₂₈ H ₆₄ IN ₂ OSi ₄ Sm	C ₂₄ H ₅₆ N ₂ Si ₄ Yb	C ₂₄ H ₅₆ N ₂ Si ₄
<i>M</i>	834.4	658.1	824.6
Crystal system, space group	triclinic, <i>P</i> $\bar{1}$ (No. 2)	monoclinic <i>P</i> 2 ₁ / <i>c</i> (No. 14)	triclinic <i>P</i> $\bar{1}$ (No. 2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.163(6), 12.300(1), 17.030(2)	19.890(6), 16.259(4), 23.095(5)	9.054(2), 9.794(8), 10.252(3)
α , β , γ (°)	75.83(1), 88.32(3), 63.24(3)	90, 114.90(2), 90	93.90(4), 101.76(2), 114.57(5)
<i>U</i> (Å ³), <i>Z</i> , <i>D</i> _c (g cm ⁻³)	2015, 2, 1.38	6774.2, 8, 1.29	797.4, 1, 1.01
<i>T</i> (K)	293	173	293
<i>F</i> (000)	850	2720	270
X-radiation	Mo K α	Mo K α	Cu K α
μ (cm ⁻¹)	23.6	29.0	18.3
Crystal size (mm ³)	0.4 × 0.15 × 0.2	0.3 × 0.3 × 0.3 cut from needle	0.2 × 0.2 × 0.2
$\theta_{\max}$ (°)	25	22	75
Total unique reflections	7085	8629	3711
Significant reflections [<i>F</i> ²] > 2 σ (<i>F</i> ²)	6172	4612	2559
<i>R</i> , <i>R</i> ' ^a	0.030, 0.039	0.066, 0.067	0.050, 0.060

$$^a R = \sum(|F_o| - |F_c|)/\sum(|F_o|); R' = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}.$$

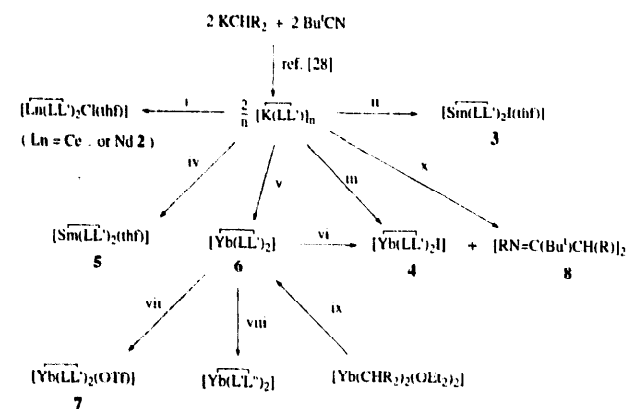
afforded the white microcrystalline **8** (0.6 g, 66%). Anal. Found: C, 58.8; H, 11.6; N, 5.62. C₂₄H₅₆N₂Si₄ Calc.: C, 59.4; H, 11.4; N, 5.78%. NMR: ¹H (C₆D₆, 25 °C): δ 0.16 (s, 18H, SiMe₃), 0.37 (s, 18H, SiMe₃), 1.16 (s, 18H, Bu'), 3.50 (s, 2H, CH), ¹³C{¹H} (C₆D₆, 25 °C): δ 2.01 (SiMe₃), 2.79 (SiMe₃), 29.86 (CMe₃), 43.66 (CMe₃), 42.66 (CH), 186.46 (Bu'C=N), ²⁹Si{¹H} (C₆D₆, 15% + C₆H₅CH₃, 85%, 25 °C): δ 4.7, -16.1.

2.12. X-ray structure determination for [Sm(LL')₂](thf) (3), [Yb(LL')₂] (6) and [RN=C(Bu')CH(R)]₂ (8)

In each case, unique data sets were collected from a crystal sealed in a capillary under argon on an Enraf–Nonius CAD4 diffractometer in the θ – 2θ mode with monochromated radiation; Mo K α for **3** and **6** and Cu K α for **8**. Two standard reflections monitored every

hour showed no significant change. Data were corrected for Lorentz and polarisation effects (Lp), and also for absorption for **3** and **6** based on psi-scan measurements [40]. Reflections with $|F^2| > 2\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$, were considered observed.

Each structure was solved using the heavy atom routines (**3** and **6**) or direct methods (**8**) of SHELXS-86 [41]. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares using programs from the Enraf–Nonius MOLEN package. For **6**, only Yb and Si atoms were anisotropic. For **3** and **6**,



Scheme 1. Reagents and conditions: i, LnCl₃ (Ln = Ce or Nd), thf, reflux, 12h; ii, Sml₃(thf)₂, Et₂O, 36h, 298 K; iii, YbI₃, Et₂O, 36h, 298 K; iv, Sml₃(thf)₂, thf, 18h, 298 K; v, YbI₃, Et₂O, 24h, 298 K; vi, 1/2 I₂, Et₂O, 12h, 298 K; vii, Ag(OTf), toluene, 12h, 298 K; viii, 2 PhCN, Et₂O, 12h, 298 K; ix, 2 Bu'C/N, Et₂O, 12h, 298 K; x, I₂, Et₂O, 8h, 298 K.

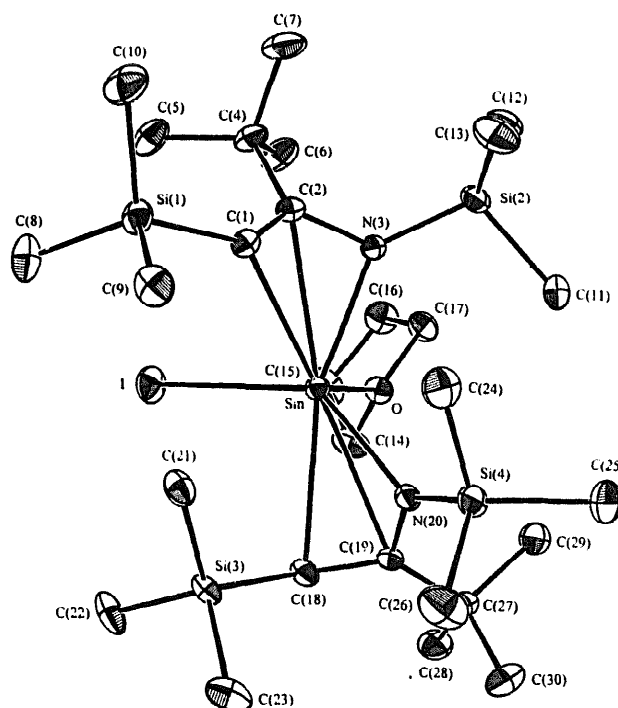


Fig. 1. X-ray structure and atom labelling scheme for [Sm(LL')₂](thf) (**3**) (LL' = η^1 -N(R)C(Bu')CHR, R = SiMe₃).

Table 2

Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for [Sm(LL')₂I(thf)] (3)

Bonds			
Sm–I	3.092(1)	Sm–O	3.452(3)
Sm–C(1)	2.876(4)	Sm–C(2)	2.772(3)
Sm–N(3)	2.311(3)	Sm–C(18)	2.814(3)
Sm–C(19)	2.791(4)	Sm–N(20)	2.348(3)
C(1)–C(2)	1.372(5)	C(2)–N(3)	1.403(6)
C(18)–C(19)	1.370(7)	C(19)–N(20)	1.380(5)
Angles			
I–Sm–O	82.76(8)	C(1)–Sm–C(2)	28.0(1)
C(1)–Sm–N(3)	53.2(1)	C(2)–Sm–N(3)	30.3(1)
N(3)–Sm–N(20)	112.1(1)	C(18)–Sm–C(19)	28.3(1)
C(18)–Sm–N(20)	53.1(1)	C(19)–Sm–N(20)	29.6(1)
C(1)–C(2)–N(3)	56.4(2)	Sm–N(3)–C(2)	93.3(2)
Sm–C(1)–C(2)	118.0(3)	C(18)–C(19)–N(20)	117.1(4)
Sm–N(20)–C(19)	93.3(2)	Sm–C(18)–C(19)	74.9(2)

the hydrogen atoms were held fixed at calculated positions with $U_{\text{iso}} = 1.3 U_{\text{eq}}$ for the parent atom, except for H1 and H18 in **3** which were fixed at positions from a difference map. For **8**, H atoms were freely refined isotropic.

Further details are given in Table 1.

3. Results and discussion

The synthesis and some reactions of the 1,3-bis(trimethylsilyl)- η^3 -1-aza-allyllanthanide complexes are illustrated in Scheme 1 [LL' = N(R)C(Bu')CHR, L'L'' = N(R)C(Ph)C(H)C(Bu')NR, R = SiMe₃].

Table 3

Fractional atomic coordinates and equivalent isotropic thermal parameters for [Sn(LL')₂I(thf)] (3)

Atom	x	y	z	U_{eq}
Sm	–0.24980(2)	–0.02359(2)	–0.21722(1)	0.031(1)
I	–0.42827(3)	–0.15378(3)	–0.15571(2)	0.066(1)
Si(1)	–0.19219(12)	–0.23643(10)	–0.40355(7)	0.050(1)
Si(2)	0.12827(11)	–0.17854(11)	–0.19614(8)	0.047(1)
Si(3)	–0.57321(10)	0.20025(11)	–0.31110(7)	0.043(1)
Si(4)	–0.20669(11)	0.24390(10)	–0.35200(8)	0.049(1)
O	–0.2119(3)	–0.0458(2)	–0.0718(2)	0.044(2)
C(1)	–0.1330(4)	–0.1917(3)	–0.3203(2)	0.038(3)
C(2)	–0.0589(4)	–0.2475(3)	–0.2459(2)	0.038(3)
N(3)	–0.0273(3)	–0.1726(2)	–0.2087(2)	0.036(2)
C(4)	–0.0152(5)	–0.3867(3)	–0.1982(3)	0.051(3)
C(5)	–0.1109(6)	–0.4356(4)	–0.2202(3)	0.070(4)
C(6)	–0.0129(6)	–0.4009(4)	–0.1071(3)	0.066(4)
C(7)	0.1254(6)	–0.4666(4)	–0.2200(4)	0.077(5)
C(8)	–0.3441(5)	–0.2613(4)	–0.3872(3)	0.077(4)
C(9)	–0.2351(5)	–0.0997(5)	–0.4942(3)	0.063(4)
C(10)	–0.0550(6)	–0.3720(5)	–0.4341(3)	0.076(5)
C(11)	0.0949(4)	–0.0266(4)	–0.1757(3)	0.063(4)
C(12)	0.2490(5)	–0.3018(5)	–0.1088(4)	0.072(5)
C(13)	0.2175(5)	–0.1974(6)	–0.2894(4)	0.082(5)
C(14)	–0.3206(5)	–0.0121(5)	–0.0181(3)	0.063(4)
C(15)	–0.2836(5)	–0.1325(5)	0.0470(3)	0.075(5)
C(16)	–0.1287(5)	–0.1992(4)	0.0557(3)	0.065(4)
C(17)	–0.0888(4)	–0.1275(4)	–0.0175(3)	0.052(4)
C(18)	–0.4831(4)	0.2031(3)	–0.2222(2)	0.041(3)
C(19)	–0.3789(4)	0.2336(3)	–0.2256(2)	0.037(3)
N(20)	–0.2792(3)	0.1820(3)	–0.2745(2)	0.037(2)
C(21)	–0.4639(4)	0.0844(4)	–0.3681(3)	0.054(4)
C(22)	–0.7158(4)	0.1675(5)	–0.2782(3)	0.070(4)
C(23)	–0.6466(5)	0.3596(5)	–0.3830(3)	0.073(5)
C(24)	–0.1064(5)	0.1164(4)	–0.4009(3)	0.069(4)
C(25)	–0.0905(5)	0.3044(5)	–0.3262(4)	0.083(5)
C(26)	–0.3329(6)	0.3733(5)	–0.4322(4)	0.092(6)
C(27)	–0.3698(4)	0.3174(3)	–0.1734(3)	0.051(3)
C(28)	–0.4677(5)	0.3393(4)	–0.1089(3)	0.069(4)
C(29)	–0.2273(5)	0.2610(4)	–0.1323(3)	0.065(4)
C(30)	–0.4070(6)	0.4480(4)	–0.2315(4)	0.080(5)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

3.1. Synthesis and characterisation of $[\text{Ce}(\text{LL}')_2\text{Cl}(\text{thf})]$ (1), $[\text{Nd}(\text{LL}')_2\text{Cl}(\text{thf})]$ (2), $[\text{Sm}(\text{LL}')_2\text{I}(\text{thf})]$ (3) and $[\text{Yb}(\text{LL}')_2\text{I}(\text{thf})]$ (4)

Reaction of CeCl_3 or NdCl_3 with two equivalents of 1,3-bis(trimethylsilyl)- η^3 -1-aza-allyl-potassium, $[\text{K}(\text{LL}')_n]$, in tetrahydrofuran under reflux yielded yellow $[\text{Ce}(\text{LL}')_2\text{Cl}(\text{thf})]$ 1 or blue $[\text{Nd}(\text{LL}')_2\text{Cl}(\text{thf})]$ 2. Each was isolated from hexane as a microcrystalline solid. Both were very soluble in ether and hydrocarbon solvents, and were extremely air- and moisture-sensitive. The reactions were fairly slow and refluxing was required.

Using the lanthanide(III) iodide as starting material, two bis[1,3-bis(trimethylsilyl)- η^3 -1-aza-allyl]lanthanide(III) iodide complexes, $[\text{Sm}(\text{LL}')_2\text{I}(\text{thf})]$ 3 and $[\text{Yb}(\text{LL}')_2\text{I}(\text{thf})]$ 4 were prepared. The reactions proceeded readily without refluxing, and the resultant products had better crystallinity; both 3 and 4 afforded X-ray quality crystals. Since compounds 1–4 are paramagnetic, their ^1H NMR spectral signals were very broad and are difficult to assign. Compound $[\text{Sm}(\text{LL}')_2\text{I}(\text{thf})]$ 3 was authenticated by single crystal X-ray diffraction.

3.2. The single crystal X-ray structure of $[\text{Sm}(\text{LL}')_2\text{I}(\text{thf})]$ (3)

The molecular structure of 3 and the atom numbering scheme are shown in Fig. 1. Selected bond distances and angles and atomic coordinates are presented in Tables 2 and 3 respectively.

The molecular structure, taking each $[\text{LL}']^-$ ligand as occupying either a single or a C,N-chelating site, shows a distorted tetrahedral or octahedral geometry respectively around the samarium atom; however, the attachment of the Sm to the $\text{C}_1 \cdots \text{C}_2 \cdots \text{N}$ moiety can

perhaps best be described as involving η^3 -bonding. The bond distances between samarium and the two carbons (terminal C_1 and central C_2) are similar. $\text{Sm}-\text{C}_1$ 2.876(4) [2.814(3)] and $\text{Sm}-\text{C}_2$ 2.772(3) [2.791(4)] Å; it is noteworthy that the latter is slightly the shorter, as is the case for classical η^3 -allyls, e.g. of Pd(II) [42].

3.3. Synthesis and spectroscopic characterisation of $[\text{Sm}(\text{LL}')_2(\text{thf})]$ (5) and $[\text{Yb}(\text{LL}')_2]$ (6)

Reaction of $\text{SmI}_2(\text{thf})_2$ or YbI_2 with two equivalents of $[\text{K}(\text{LL}')_n]$ in diethyl ether yielded (iv or v in Scheme 1) the bis(η^3 -1-aza-allyl)lanthanide(II) complexes $[\text{Sm}(\text{LL}')_2(\text{thf})]$ (5) and $[\text{Yb}(\text{LL}')_2]$ (6). Complex 6 had previously been prepared (ix in Scheme 1) by the reaction of $[\text{Yb}(\text{CHR})_2(\text{OEt})_2]$ ($\text{R} = \text{SiMe}_3$) [34] with two equivalents of Bu^tCN in diethyl ether.

Complexes 5 and 6 were extremely soluble in ether or hydrocarbon solvents. Complex 5 was red-brown in thf, green in diethyl ether or a hydrocarbon and was isolated as green microcrystals from pentane. Complex 6 readily crystallised from pentane as red crystals.

Each of the complexes 5 and 6 was characterised by C, H and N elemental analysis and ^1H , ^{13}C , $^{29}\text{Si}\{^1\text{H}\}$ and ^{171}Yb (for 6) NMR spectroscopy and mass spectrometry. Complex 6 was also authenticated by single crystal X-ray diffraction. Unlike the Sm(III) analogue 3, complex 5 showed very sharp ^1H NMR spectral signals, although the chemical shifts appeared over a wide range (–5 to 40 ppm). The integration of the ^1H NMR spectral peaks confirmed 5 to be a mono-thf adduct.

The diamagnetic complex 6 showed unexceptional ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$ and $^{171}\text{Yb}\{^1\text{H}\}$ NMR spectra in C_6D_6 , but each group gave rise to two signals, which is attributed to the asymmetry of the $[\text{LL}']^-$ ligand (C-3 of the 1-aza-allyl ligand is a chiral centre, causing the

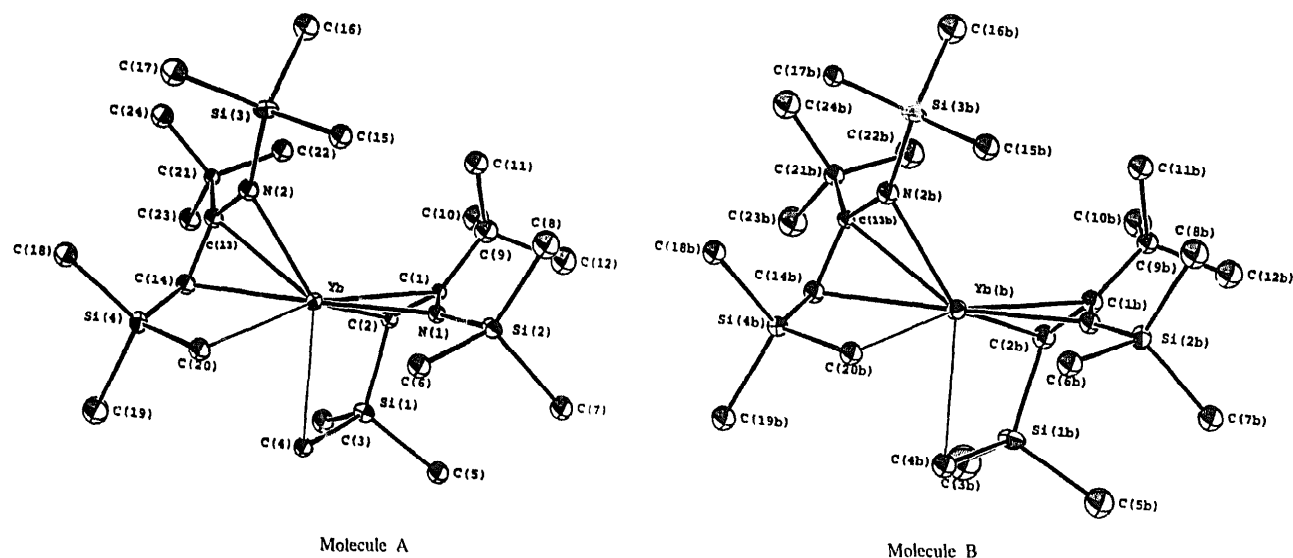


Fig. 2. X-ray structure and atom labelling scheme for $[\text{Yb}(\text{LL}')_2]$ (6) (Molecule A and Molecule B) $[\text{LL}' = \eta^3\text{-N(R)C}(\text{Bu}^t)\text{CHR}]$, $\text{R} = \text{SiMe}_3$].

Table 4

Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for [Yb(LL')₂] (**6**)

Bonds			
Molecule A			
Yb–N(1)	2.326(14)	Yb–N(2)	2.344(12)
Yb–C(1)	2.78(2)	Yb–C(2)	2.68(2)
Yb–C(4)	2.84(2)	Yb–C(13)	2.66(2)
Yb–C(14)	2.63(2)	Yb–C(20)	2.90(2)
Si(1)–C(2)	1.86(2)	Si(2)–N(1)	1.69(2)
Si(3)–N(2)	1.729(15)	Si(4)–C(14)	1.87(2)
C(13)–C(21)	1.57(3)	C(1)–C(9)	1.53(3)
C(13)–C(14)	1.36(3)	N(2)–C(13)	1.35(3)
C(1)–C(2)	1.38(3)	N(1)–C(1)	1.36(2)
Molecule B			
Yb(b)–N(1b)	2.35(2)	Yb(b)–N(2b)	2.350(13)
Yb(b)–C(1b)	2.73(2)	Yb(b)–C(2b)	2.70(2)
Yb(b)–C(4b)	2.81(2)	Yb(b)–C(13b)	2.68(2)
Yb(b)–C(14b)	2.67(2)	Yb(b)–C(20b)	2.92(2)
Si(1b)–C(2b)	1.87(2)	Si(2b)–N(1b)	1.68(2)
Si(3b)–N(2b)	1.72(2)	Si(4b)–C(14b)	1.85(2)
C(13b)–C(21b)	1.52(3)	C(1b)–C(9b)	1.50(3)
C(13b)–C(14b)	1.41(3)	N(2b)–C(13b)	1.31(3)
C(1b)–C(2b)	1.35(3)	N(1b)–C(1b)	1.36(2)
Angles			
Molecule A			
N(1)–Yb–N(2)	125.6(5)	N(1)–C(1)–C(2)	116(2)
N(1)–Yb–C(1)	29.2(5)	N(1)–Yb–C(2)	54.7(5)
N(1)–Yb–C(4)	90.0(5)	N(1)–Yb–C(14)	158.4(5)
N(2)–Yb–C(13)	30.4(5)	N(2)–Yb–C(14)	55.3(5)
N(2)–Yb–C(20)	83.5(5)	C(4)–Yb–C(20)	84.7(5)
C(1)–Yb–C(2)	29.2(6)	C(1)–Yb–C(4)	89.0(5)
C(13)–Yb–C(14)	29.7(6)	C(13)–Yb–C(20)	86.2(5)
C(14)–Yb–C(20)	69.0(6)	N(2)–C(13)–C(14)	119(2)
Molecule B			
N(1b)–Yb(b)–N(2b)	125.9(6)	N(1b)–C(1b)–C(2b)	118(2)
N(1b)–Yb(b)–C(1b)	29.9(6)	N(1b)–Yb(b)–C(2b)	54.3(6)
N(1b)–Yb–C(4)	90.0(5)	N(1b)–Yb(b)–C(4b)	89.2(5)
N(2b)–Yb(b)–C(13b)	29.2(5)	N(2b)–Yb(b)–C(14b)	54.6(6)
N(2b)–Yb(b)–C(20b)	83.7(5)	C(4b)–Yb(b)–C(20b)	84.8(5)
C(1b)–Yb(b)–C(2b)	28.6(6)	C(1b)–Yb(b)–C(4b)	88.9(6)
C(13b)–Yb(b)–C(14b)	30.6(6)	C(13b)–Yb(b)–C(20b)	86.7(5)
C(14b)–Yb(b)–C(20b)	68.4(6)	N(2b)–C(13b)–C(14b)	117(2)

complex to be a mixture of *meso*- and *rac*-diastereoisomers). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, $^1J(^{13}\text{C}-^{171}\text{Yb}) = 17\text{ Hz}$ and $^1J(^{13}\text{C}-^{29}\text{Si}) = 64.6\text{ Hz}$ coupling was observed, involving the CH moiety. There was no obvious $^{171}\text{Yb}-^1\text{H}$ coupling. However, the proton-decoupled $^{171}\text{Yb}\{^1\text{H}\}$ NMR signal was sharper than the ^1H coupled analogue. The ^{171}Yb NMR chemical shifts were temperature-dependent.

3.4. The single crystal X-ray structure of [Yb(LL')₂] (**6**)

Large crystals of **6**, obtained from a hexane solution of **6** at -30°C , were cut into smaller single crystals suitable for X-ray studies. A specimen of the latter was coated with Nujol and placed on the diffractometer under a cooled (173 K) nitrogen stream. The molecular

structure and atom numbering scheme for compound **6** are shown in Fig. 2. Selected bond distances and angles and atomic coordinates are given in Tables 4 and 5 respectively.

The structure shows that **6** is a monomer in the solid state. There are two independent molecules (A and B) in the unit cell, with essentially the same geometry. The η^3 -bonding between Yb and the $[\text{LL}']^-$ ligand is similar to that in compound **3**, except that the Yb distance to the central carbon is slightly longer than to the terminal carbon. The Yb–C bond distances for the central and terminal carbons in molecule A are 2.78(2) [2.66(2)] and 2.68(2) [2.63(2)] Å respectively. There is 'agostic' intramolecular interaction between the ytterbium atom and two of the methyls in the trimethylsilyl groups bonded to the terminal carbons of the $[\text{LL}']^-$ ligand.

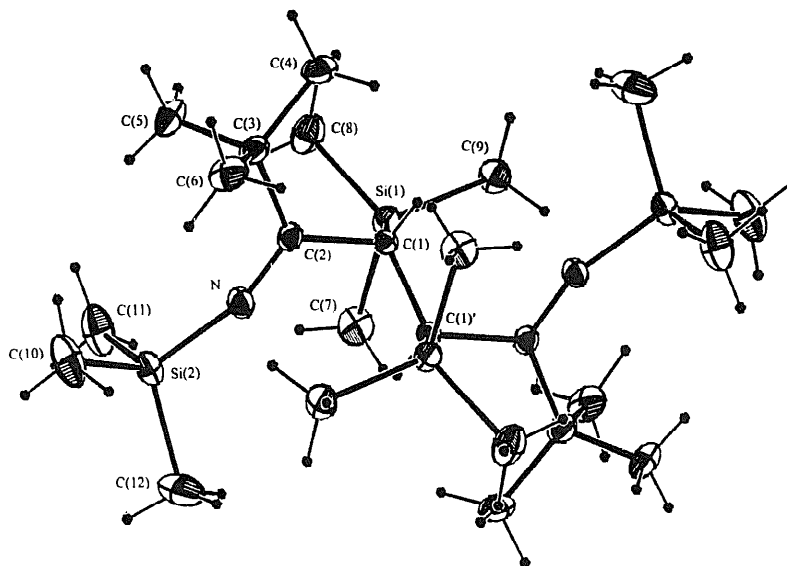
Table 5
Fractional atomic coordinates and equivalent isotropic thermal parameters for [Yb(LL')₂] (6)

Atom	x	y	z	U _{iso}
Molecule A				
Yb	0.11209(4)	0.13317(6)	0.20533(3)	0.024(1) ^a
Si(1)	−0.0502(3)	0.1972(3)	0.1061(3)	0.031(3) ^a
Si(2)	0.1401(3)	0.0842(3)	0.0688(2)	0.029(2) ^a
Si(3)	0.2990(3)	0.1765(3)	0.3225(3)	0.030(2) ^a
Si(4)	0.1043(3)	0.0509(3)	0.3309(2)	0.026(2) ^a
N(1)	0.1076(6)	0.1554(8)	0.1043(6)	0.023(4)
N(2)	0.2048(7)	0.1811(9)	0.3015(6)	0.029(4)
C(1)	0.0895(8)	0.2363(10)	0.1028(7)	0.018(4)
C(2)	0.0374(9)	0.2549(11)	0.1257(8)	0.026(5)
C(3)	−0.1123(10)	0.2635(13)	0.1283(9)	0.045(6)
C(4)	−0.0418(9)	0.0967(12)	0.1496(8)	0.028(5)
C(5)	−0.0965(10)	0.1727(12)	0.0194(9)	0.038(6)
C(6)	0.1442(10)	−0.0137(12)	0.1160(9)	0.035(5)
C(7)	0.0725(9)	0.0679(12)	−0.0156(9)	0.037(6)
C(8)	0.2331(10)	0.0948(14)	0.0694(9)	0.050(6)
C(9)	0.1337(10)	0.3044(13)	0.0890(9)	0.045(6)
C(10)	0.1047(11)	0.3908(14)	0.0923(10)	0.057(7)
C(11)	0.2145(10)	0.2988(13)	0.1311(9)	0.042(6)
C(12)	0.1191(11)	0.2900(14)	0.0170(10)	0.056(7)
C(13)	0.1507(9)	0.2121(11)	0.3156(8)	0.027(5)
C(14)	0.0932(9)	0.1627(11)	0.3096(8)	0.030(5)
C(15)	0.3102(9)	0.1115(12)	0.2588(9)	0.038(6)
C(16)	0.3520(10)	0.2725(14)	0.3251(10)	0.049(6)
C(17)	0.3469(10)	0.1278(14)	0.4032(9)	0.048(6)
C(18)	0.1784(10)	0.0331(13)	0.4120(9)	0.039(6)
C(19)	0.0152(11)	0.0146(14)	0.3274(10)	0.051(7)
C(20)	0.1259(9)	−0.0166(12)	0.2778(8)	0.030(5)
C(21)	0.1525(8)	0.3054(10)	0.3339(7)	0.020(5)
C(22)	0.1713(9)	0.3583(14)	0.2882(8)	0.039(5)
C(23)	0.0807(10)	0.3356(12)	0.3328(9)	0.042(6)
C(24)	0.02147(10)	0.3122(13)	0.4006(9)	0.041(6)
Molecule B				
Yb(b)	0.65393(4)	0.14024(6)	0.21094(4)	0.029(1)
Si(1b)	0.8193(3)	0.1807(4)	0.3170(3)	0.040(3)
Si(2b)	0.6318(3)	0.0494(4)	0.3425(2)	0.033(3)
Si(3b)	0.4675(3)	0.2011(4)	0.1087(3)	0.033(3)
Si(4b)	0.6486(3)	0.0897(3)	0.0707(2)	0.00
N(1b)	0.6606(7)	0.1316(10)	0.3148(6)	0.031(4)
N(2b)	0.5596(7)	0.2051(10)	0.1235(7)	0.034(4)
C(1b)	0.6812(9)	0.2121(12)	0.3257(8)	0.033(5)
C(2b)	0.7352(9)	0.2391(12)	0.3099(8)	0.035(5)
C(3b)	0.8842(13)	0.2508(18)	0.3061(12)	0.088(9)
C(4b)	0.8642(10)	0.0964(13)	0.2593(9)	0.042(6)
C(5b)	0.8643(11)	0.1343(16)	0.3993(10)	0.062(7)
C(6b)	0.6185(11)	−0.0317(13)	0.2816(9)	0.045(6)
C(7b)	0.7006(10)	0.0127(13)	0.4214(9)	0.044(6)
C(8b)	0.5410(11)	0.0550(14)	0.3487(10)	0.055(7)
C(9b)	0.6457(9)	0.2697(12)	0.3552(8)	0.031(5)
C(10b)	0.6711(10)	0.3571(15)	0.3585(9)	0.052(6)
C(11b)	0.5625(10)	0.2718(13)	0.3183(9)	0.043(6)
C(12b)	0.6641(11)	0.2418(14)	0.4236(10)	0.052(7)
C(13b)	0.6100(8)	0.2429(11)	0.1107(7)	0.020(5)
C(14b)	0.6663(9)	0.1932(12)	0.1066(8)	0.031(5)
C(15b)	0.4596(10)	0.1187(13)	0.1601(9)	0.047(6)
C(16b)	0.4213(11)	0.2928(15)	0.1214(10)	0.059(7)
C(17b)	0.4097(9)	0.1696(11)	0.0241(8)	0.029(5)
C(18b)	0.5668(9)	0.0887(12)	−0.0089(9)	0.038(5)
C(19b)	0.7347(10)	0.0570(12)	0.0617(9)	0.040(6)
C(20b)	0.6322(10)	0.0074(12)	0.1198(9)	0.037(6)

Table 5 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
Molecule B				
C(21b)	0.6110(9)	0.3358(11)	0.1027(8)	0.030(5)
C(22b)	0.6066(11)	0.3750(15)	0.1602(10)	0.061(7)
C(23b)	0.6816(11)	0.3673(16)	0.0980(10)	0.060(7)
C(24b)	0.5436(10)	0.3579(15)	0.0410(9)	0.053(6)

^a *U*_{eq} is defined as one third of the trace of the orthogonalised *U*_{*ij*} tensor.

Fig. 3. X-ray structure and atom labelling scheme for [RN = C(Buⁱ)CH(R)]₂ (**8**) (R = SiMe₃).

Yb–C(20) 2.90(2) and Yb–C(4) 2.84(2) Å. The Yb–N bond lengths of 2.326(14) and 2.344(12) Å in molecule **A** are shorter than those of 2.468(2) and 2.478(2) Å in the benzamidinate [Yb{(NR)₂CPh}₂(thf)₂] (R = SiMe₃), which is not unexpected since the latter is a thf-solvate [16].

Table 6

Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for [RN = C(Buⁱ)CH(R)]₂ (**8**)

Bonds			
Si(1)–C(1)	1.933(2)	Si(1)–C(7)	1.863(4)
Si(1)–C(8)	1.869(3)	Si(1)–C(9)	1.866(3)
Si(2)–N	1.686(2)	Si(2)–C(10)	1.872(5)
Si(2)–C(11)	1.848(5)	Si(2)–C(12)	1.851(5)
N–C(2)	1.256(3)	C(1)–C(1')	1.562(4)
C(1)–C(2)	1.528(3)	C(2)–C(3)	1.565(3)
C(3)–C(4)	1.524(4)	C(3)–C(5)	1.535(4)
C(3)–C(6)	1.527(4)	C(1)–H1	0.85(2)
Angles			
Si(2)–N–C(2)	161.0(2)	Si(1)–C(1)–C(1')	112.7(2)
Si(1)–C(1)–C(2)	104.6(1)	C(1)'–C(1)–C(2)	113.2(2)
N–C(2)–C(1)	118.1(2)	N–C(2)–C(3)	122.0(2)
C(1)–C(2)–C(3)	119.9(2)	Si(1)–C(1)–H1	109(1)
C(1)'–C(1)–H1	104(1)	C(2)–C(1)–H1	114(1)

Symmetry element *i* = *x*, – *y*, – *z*.

3.5. Reactions of [Yb(LL')₂] (**6**) with Ag(OTf), I₂ and PhCN

Oxidation of [Yb(LL')₂] (**6**) with Ag(OTf) (Tf = SO₂CF₃) in toluene afforded (vii in Scheme 1) the pink powder of [Yb(LL')₂(OTf)] (**7**) and a silver mirror.

Table 7

Fractional atomic coordinates and equivalent isotropic thermal parameters for [RN = C(Buⁱ)CH(R)]₂ (**8**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Si(1)	0.24638(7)	0.13909(7)	–0.06644(6)	0.045(1)
Si(2)	0.16124(9)	0.37460(8)	0.29276(7)	0.059(1)
N	0.1430(2)	0.2134(2)	0.2061(2)	0.047(1)
C(1)	0.0924(2)	0.0137(2)	0.0302(2)	0.036(1)
C(2)	0.1643(2)	0.0974(2)	0.1765(2)	0.039(1)
C(3)	0.2636(3)	0.0393(3)	0.2838(2)	0.051(1)
C(4)	0.3010(3)	–0.0864(3)	0.2248(3)	0.066(1)
C(5)	0.4308(3)	0.1725(3)	0.3619(3)	0.076(1)
C(6)	0.1601(3)	–0.0208(3)	0.3853(3)	0.074(1)
C(7)	0.2018(3)	0.3035(3)	–0.1043(3)	0.068(1)
C(8)	0.4712(3)	0.2242(3)	0.0321(3)	0.070(1)
C(9)	0.2406(3)	0.0256(3)	–0.2228(3)	0.064(1)
C(10)	0.1550(5)	0.3678(4)	0.4737(3)	0.105(2)
C(11)	0.3632(5)	0.5296(4)	0.2853(4)	0.096(2)
C(12)	–0.0142(4)	0.4160(4)	0.2113(5)	0.123(2)

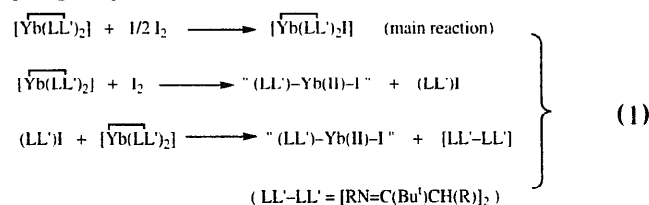
*U*_{eq} is defined as one third of the trace of the orthogonalised *U*_{*ij*} tensor.

Table 8
Selected bond lengths and angles for some η^3 -1-aza-allylmetal complexes

Compounds (R = SiMe ₃)	M–C _{term} (Å)	M–C _{cent} (Å)	M–N (Å)	C _{term} –M–N (°)	C _{term} –C _{cent} –N	Ref.
[Sn(N(R)C(Bu')CHR) ₂]	2.295(2)	2.730(2)	2.510(2)	57.99(6)	115.5(2)	[44]
[Th(N(R)C(Bu')CHR) ₂ (μ ₃ -Cl)(μ-Cl) ₂ K(OTf) ₂]	2.99(2)	2.89(2)	2.25(2)	48(1)	103(2)	[31]
	2.91(2)	2.87(2)	2.16(2)	44(1)	106(2)	
[Zr(N(R)C(Bu')CHR) ₂ Cl ₂]	2.379(13)	2.554(14)	2.225(12)	59.2(5)	115(1)	[30]
	2.381(14)	2.563(14)	2.265(12)	60.5(5)	117(1)	
[[Zr(N(R)C(Bu')CHR)Cl ₂ (μ-Cl)] ₂]	2.525(4)	2.387(5)	2.115(4)	61.2(2)	113.2(4)	[30]
	2.598(3)	2.494(3)	2.048(3)	59.7(1)	117.0(3)	
[[Zr(N(R)C(Bu')CHPh)Cl ₃]	2.621(3)	2.449(3)	2.050(3)	59.3(1)	117.6(3)	[45]
	2.470(3)	2.561(4)	2.175(3)	59.2(1)	114.4(3)	
[Zr(N(R)C(Bu')CH)(C ₆ H ₄ -2)Cl ₂]	2.509(3)	2.560(3)	2.167(3)	58.7(1)	114.6(3)	This work
	2.876(4)	2.772(3)	2.311(3)	53.2(1)	118.0(3)	
[Sm(N(R)C(Bu')CHR) ₂ I(thf)] (3)	2.814(3)	2.791(4)	2.348(3)	53.1(1)	117.1(4)	
[Yb(N(R)C(Bu')CHR) ₂] (6) Molecule A	2.63(2)	2.66(2)	2.326(14)	55.3(5)	116(2)	This work
	2.68(2)	2.78(2)	2.344(12)	54.7(5)	119(2)	
Molecule B	2.67(2)	2.68(2)	2.35(2)	54.6(6)	117(2)	This work
	2.70(2)	2.73(2)	2.350(13)	54.3(6)	118(2)	

Compound **7** was characterised by C, H and N elemental analysis, mass spectrum and ^{19}F NMR spectrum. Since Yb(III) is paramagnetic, the ^{19}F NMR signal of **7** was very broad.

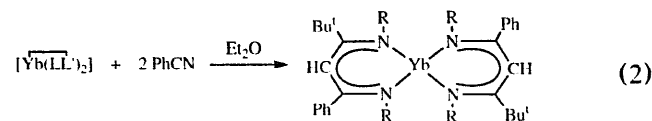
The reaction of **7** with half an equivalent of I_2 was complicated, leading not only to its oxidation but also to ligand coupling. The main product isolated from a hexane solution was **4**, as pink needles, as determined by elemental analysis and mass spectrometry. From the mother liquor, small amounts of red cubic crystals and white crystals were also isolated. Single crystal X-ray analysis showed the white crystals to be the ligand-coupled product, $[\text{RN}=\text{C}(\text{Bu}^t)\text{CH}(\text{R})]_2$ ($\text{R} = \text{SiMe}_3$) (**8**), which was probably formed by a ligand radical coupling, Eq. (1).



The red crystals might have been an $(\text{LL}')\text{-Yb(II)-I}$ complex, but due to the small amount of sample its full characterisation was not achieved.

In order to throw light on the coupling reaction, $[\text{K}(\text{LL}')_n]$ was treated with half an equivalent of I_2 in diethyl ether solution. The violet colour of I_2 was immediately discharged and a white crystalline solid was obtained, which was identified as **8** by C, H and N elemental analysis, ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR and mass spectra.

Treatment of **6** with two equivalents of PhCN in Et_2O yielded (viii in Scheme 1) the green solid $[\text{Yb}(\text{L}'\text{L}'')_2]$, which we had independently (Part 7) synthesised by reaction of YbI_2 with two equivalents of $[\text{K}(\text{L}'\text{L}'')_n]$ [$\text{L}'\text{L}'' = \text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Bu}^t)\text{NR}$, $\text{R} = \text{SiMe}_3$] [43], Eq. (2). The ^1H , ^{13}C and ^{171}Yb NMR and MS spectra of both products were identical.



3.6. The single crystal X-ray structure of $[\text{RN}=\text{C}(\text{Bu}^t)\text{CH}(\text{R})]_2$ ($\text{R} = \text{SiMe}_3$) (**8**)

The molecular structure of **8** and the atom numbering scheme are shown in Fig. 3. Selected bond distances and angles and atomic coordinates are presented in Tables 6 and 7 respectively.

The molecule **8** lies on a crystallographic inversion centre.

3.7. Some comparative structural data for 1-aza-allylmethylmetal complexes

Available $\text{M}-\text{C}_{\text{terminal}}$, $\text{M}-\text{C}_{\text{central}}$ and $\text{M}-\text{N}$ bond lengths with $\text{C}_{\text{term}}-\text{M}-\text{N}$ and $\text{C}_{\text{term}}-\text{C}_{\text{central}}-\text{N}$ bond angles for 1-aza-allylmethylmetal complexes, including data for **3** and **6** are listed in Table 8.

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References

- [1] J.P. Collman, L.S. Hegehus, J.R. Norton and R.G. Finke, *Principles and Application of Organotransition Metal Chemistry*, University Science Books, Mill Valley, 2nd edn., 1987.
- [2] S.L. Blystone, *Chem. Rev.*, **89** (1989) 1663.
- [3] J.J. Doney, R.G. Bergman and C.H. Heathcock, *J. Am. Chem. Soc.*, **107** (1985) 3724.
- [4] E.R. Burkhardt, J.J. Doney, R.G. Bergman and C.H. Heathcock, *J. Am. Chem. Soc.*, **109** (1987) 2022.
- [5] F. Mercier, J. Fischer and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, **25** (1986) 357.
- [6] F. Mercier, C. Hugel-Le Goff and F. Mathey, *Organometallics*, **7** (1988) 955.
- [7] C. Hugel-Le Goff, F. Mercier, L. Ricard and F. Mathey, *J. Organomet. Chem.*, **363** (1989) 325.
- [8] F. Mercier and F. Mathey, *Organometallics*, **9** (1990) 863.
- [9] H.R. Keable and M. Kilner, *J. Chem. Soc., Dalton Trans.*, (1972) 153.
- [10] T. Inglis, M. Kilner, T. Reynoldson and E.E. Robertson, *J. Chem. Soc., Dalton Trans.*, (1975) 924.
- [11] T. Inglis and M. Kilner, *J. Chem. Soc., Dalton Trans.*, (1975) 930.
- [12] M. Wedler, H.W. Roesky and F.T. Edelmann, *J. Organomet. Chem.*, **345** (1988) C1.
- [13] M. Wedler, M. Noltemeyer, U. Pieper, H.-G. Schmidt, D. Stalke and F.T. Edelmann, *Angew. Chem., Int. Ed. Engl.*, **29** (1990) 894.
- [14] M. Wedler, F. Knösel, M. Noltemeyer, F.T. Edelmann and U. Behrens, *J. Organomet. Chem.*, **388** (1990) 21.
- [15] M. Wedler, A. Recknagel, J.W. Gilje, M. Noltemeyer and F.T. Edelmann, *J. Organomet. Chem.*, **426** (1992) 295.
- [16] A. Recknagel, F. Knösel, H. Gornitzka, M. Noltemeyer, F.T. Edelmann and U. Behrens, *J. Organomet. Chem.*, **417** (1991) 363.
- [17] M. Wedler, F. Knösel, U. Pieper, D. Stalke, F.T. Edelmann and H.-D. Amberger, *Chem. Ber.*, **125** (1992) 2171.
- [18] R.T. Boeré, R.T. Oakley and R.W. Reed, *J. Organomet. Chem.*, **331** (1987) 161.
- [19] K.N. Houk, R.W. Strozier, N.G. Rondan, R.R. Fraser and N. Chuaqui-Offermanns, *J. Am. Chem. Soc.*, **102** (1980) 1426.
- [20] R.R. Fraser, M. Bresse, N. Chuaqui-Offermanns, K.N. Houk and N.G. Rondan, *Can. J. Chem.*, **61** (1983) 2729.
- [21] R.R. Fraser, in I. Bunell and T. Durst (eds.), *Comprehensive Carbanion Chemistry, Part B*, Elsevier, Amsterdam, 1984, Chap. 2.

- [22] R.I. Papasergio, C.L. Raston and A.H. White, *J. Chem. Soc., Chem. Commun.*, (1983) 1419.
- [23] D. Colgan, R.I. Papasergio, C.L. Raston and A.H. White, *J. Chem. Soc., Chem. Commun.*, (1984) 1708.
- [24] P.C. Andrews, D.R. Armstrong, M. MacGregor, R.E. Mulvey and D. Reed, *J. Chem. Soc., Chem Commun.*, (1989) 1341.
- [25] M. Green, R.J. Mercer, C.E. Morton and A.G. Orpen, *Angew. Chem., Int. Ed. Engl.*, 24 (1985) 422.
- [26] G.-M. Yang, G.-H. Lee, S.-M. Peng and R.-S. Liu, *Organometallics*, 10 (1991) 1305.
- [27] A.C. Filippou, W. Grünleitner and P. Kiprof, *J. Organomet. Chem.*, 410 (1991) 175.
- [28] P.B. Hitchcock, M.F. Lappert and D.-S. Liu, *J. Chem. Soc., Chem. Commun.*, (1994) 2637.
- [29] M.F. Lappert and D.-S. Liu, *J. Organomet. Chem.*, 500 (1995) 203.
- [30] P.B. Hitchcock, M.F. Lappert, D.-S. Liu and E.J. Ryan, *Polyhedron*, 14 (1995) 2745.
- [31] P.B. Hitchcock, M.F. Lappert, J. Hu and S. Tian, *J. Organomet. Chem.*, in press.
- [32] P.B. Hitchcock, M.F. Lappert and D.-S. Liu, *J. Organomet. Chem.*, 488 (1995) 241.
- [33] P.B. Hitchcock, J. Hu, M. Layh, M.F. Lappert, D.-S. Liu, J. Severn and S. Tian, *Anal. Quim., Int. Ed. Engl.*, 92 (1996) 186.
- [34] P.B. Hitchcock, S.A. Holmes, M.F. Lappert and S. Tian, *J. Chem. Soc., Chem. Commun.*, (1994) 2691.
- [35] P.B. Hitchcock, M.F. Lappert, W.-P. Leung, D.-S. Liu and S. Tian, *J. Chem. Soc., Chem. Commun.*, (1993) 1386.
- [36] M.D. Taylor and C.P. Carter, *J. Inorg. Nucl. Chem.*, 24 (1962) 387.
- [37] N. Haeberle, *Tech.-Wiss. Abh. Osram-Ges.*, 11 (1973) 285; *Chem. Abstr.*, 81 (1974) 71961x.
- [38] T.D. Tilley, J.M. Boncella, D.J. Berg, C.J. Burns and R.A. Andersen, *Inorg. Synth.*, 27 (1990) 146.
- [39] P.L. Watson, T.H. Tulip and I. Williams, *Organometallics*, 9 (1990) 1999.
- [40] N. Walker and D. Stuart, *Acta Crystallogr.*, A39 (1983) 158.
- [41] G.M. Sheldrick, in G.M. Sheldrick, C. Krüger and R. Goddard (eds.), *Crystallographic Computing 3*, Oxford University Press, 1985, pp. 175–189.
- [42] P.M. Maitlis and M.J.H. Russell, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Pergamon, Oxford, 1982, Chap. 38.7, p. 406.
- [43] P.B. Hitchcock, J. Hu, M.F. Lappert and S. Tian, *J. Chem. Soc., Dalton Trans.*, in press.
- [44] P.B. Hitchcock, J. Hu and M.F. Lappert, unpublished results, 1996.
- [45] M.F. Lappert and D.-S. Liu, *Neth. Pat. Appl.*, 9500085 (1995).
- [46] M.F. Lappert and D.-S. Liu, *Neth. Pat. Appl.*, 9400919 (1994).