DALTON

Synthesis, characterisation and alkylation reactions of lanthanide β-diketiminates; crystal structures of $[Nd(L–L)_2Cl]$ and $[Ce(L–L)(CHR_2)_2]$ [L–L = N(R)C(Ph)C(H)C(Ph)NR, R = $SiMe_3$]†

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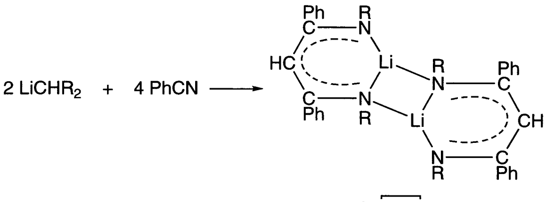
Treatment of two equivalents of the sodium β-diketiminate Na(L–L) **1** with a lanthanide metal(III) chloride, $LnCl_3$, yielded the mononuclear complex $[Ln(L–L)_2Cl]$ (Ln = Ce **3**, Pr, Nd **5**, Sm or Yb); similarly, two equivalents of **1** with TmI_3 gave $[Tm(L–L)_2I]$ [L–L = N(R)C(Ph)C(H)C(Ph)NR; R = $SiMe_3$]. When **3** was mixed with either one or two equivalents of $Li(CHR_2)$ in diethyl ether, the only new cerium-contaning product was $[Ce(L–L)(CHR_2)_2]$ **9**. Lanthanide metal(III) β-diketiminates $[Ln(L–L)_2(thf)_2]$ (Ln = Sm or Yb) or $[Yb(L–L)_2]$ and $[Yb(L–L')_2]$ **13** were obtained from $[LnI_2(thf)_2]$ (Ln = Sm or Yb) and K(L–L) in thf, or YbI_2 and K(L–L) or K(L–L′) in Et_2O [L–L′ = N(R)C(Ph)C(H)C(Bu^t)NR; thf = tetrahydrofuran]. The various lanthanide metal β-diketiminates were characterised by elemental analysis, mass spectrometry and multinuclear NMR spectra. The last of these indicated (by variable-temperature experiments) that for $[Yb(L–L')_2]$ **13** two isomers were present. X-Ray diffraction data for $[NdL–L)_2Cl]$ **5** and $[Ce(L–L)(CHR_2)_2]$ **9** revealed that for each of these crystalline mononuclear complexes the metal atom is well shielded, due to the extremely sterically demanding monoanionic $[L–L]^-$ ligand, which has some η^5 character in these molecules.

Monoanionic, tightly bound, bulky ligands L^- have an important role as 'spectator ligands', especially in early-transition and f-metal chemistry. A timely illustration relates to variously subsituted cyclopentadienyls in the context of their Group 4 metallocenes $[ML_2Cl_2]$ as catalysts or catalyst precursors for α-olefin polymerisation.[2] Other such spectator monoanionic ligands L^- or dianionic $[L'–L']^{2-}$ have come to the fore, including *ansa*-bis(cyclopentadienyls) (or analogues), diamides, benzamidinates, macrocyclic nitrogen-centred ligands (including Schiff bases, porphyrins or porphyrinogens), polypyrazolylborates and biphenoxy ligands;[3] these have rarely matched cyclopentadienyl-based metal complexes in their catalytic activity.

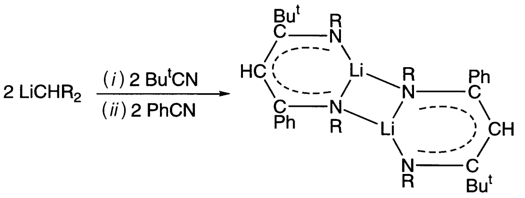
We have previously shown that *N*,*N*′-bis(trimethylsilyl)-β-diketiminato(trichloro)zirconium(IV) and related complexes (with methylaluminium oxide) are effective catalysts for α-olefin polymerisation.[4] The background to that work relates to the discovery that (*i*) bis(trimethyl)methylithium ($LiCHR_2$, R = $SiMe_3$) upon treatment with benzonitrile afforded the binculear lithium β-diketiminate $[Li\{N(R)C(Ph)C(H)C(Ph)NR\}]_2$ $\{[Li(L–L)]_2\}$, equation (1);[5] and (*ii*) $LiCHR_2$ with



(1)

$\{[Li(L–L)]_2\}$

successively Bu^tCN and PhCN gave an analogue $[Li\{N(R)C(Ph)C(H)C(Bu^t)NR\}]_2$ $\{[Li(L–L')]_2\}$, equation (2).[6] These lithium reagents were convenient ligand-transfer agents for β-diketiminates of K,[5] Sn^{II},[7] Sn^{IV},[5] Co^{II},[8] Ni^{II},[7] Cu^{II},[7] Zr^{IV},[4,6,8,9] U^{VI},[10] U^{III},[10] Th^{IV}[11] and Yb^{II},[12] including



(2)

$\{[Li(L–L')]_2\}$

$[Sn(L–L)Cl]$,[7] $[Sn(L–L)Br]$,[7] $[Sn(L–L)Me_2Cl]$,[5] $[M(L–L)_2]$ (M = Co, Ni or Cu),[7] $[Zr(L–L')Cl_3]$,[4,6,8,9] $[\{UCl(\mu\text{-}Cl)(L–L)(NR)\}_2][UCl_2(L–L)\{N(R)C(Ph)NC(Ph)CHR\}]$,[10] $[Th(L–L)_2Cl_2]$[11] and $[Yb(L–L)_2]$.[12]

Mononuclear lanthanide metal(III) complexes $[LnL_3]$, $[LnL_2X]$ or $[Ln(L)X_2]$ (L^- and X^- being monoanionic ligands) are rare,[13] because of the large Ln^{3+} radius. Examples of homoleptic complexes $[LnL_3]$ have L = $CH(SiMe_3)$, $N(SiMe_3)_2$, $OC_6H_2Bu^t_2$-2,6-Me-4, $SC_6H_2Bu^t_3$-2,4,6, η^5-$C_5H_3R'_2$-1,3 (R′ = $SiMe_3$ or Bu^t), $CH(PPh_2)_2$ or $OC(Bu^t)C(H)C(Bu^t)CO$;[13] the $[LnL_2X]$ type include $[Ln(\eta^5\text{-}C_5Me_5)_2(CHR_2)]$, $[Ln(\eta^5\text{-}C_5H_5)_2(acac)]$ (acac = acetylacetonate), $[Ln\{\eta^5\text{-}C_5H_4(CH_2)_3NMe_2\}_2Cl]$, $[Ln(\eta^5\text{-}C_5Me_5)_2(S_2CNMe_2)]$, $[Ln(oep)(CHR_2)]$ (H_2oep = octaethylporphyrin), $[Ln\{N(R)C(Ph)NR\}_2(CHR_2)]$[13] and $[Ln\{N(R)C(Bu^t)CHR\}_2I]$;[1] while $[Ln(L)X_2]$ complexes are represented for example by $[Ln(\eta^5\text{-}C_5Me_5)X_2]$ (X = CHR_2, NR_2 or $OC_2H_3Bu^t_2$-2,6);[13] and mononuclear $[LnL_2]$ complexes include $[Yb\{N(R)C(Bu^t)CHR\}_2]$[1] and $[Yb\{\eta^5\text{-}C_5H_4C(Me)_2CH_2C_5H_4N\text{-}2\}_2]$.[13] The bis(cyclopentadienyl)lanthanide(III) halides have to date invariably been binuclear $[\{LnCp^x_2(\mu\text{-}X)\}_2]$ (X = halide), even with bulky cyclopentadienyl ligands Cp^x such as C_5Me_5 or $C_5H_3R'_2$-1,3 (R′ = $SiMe_3$ or Bu^t).[13]

In preliminary publications we have described the synthesis of $[Nd(L–L)_2Cl]$[7] and $[Yb(L–L)_2]$[12] and the X-ray molecular structure of the former complex.[7] In this paper, we provide

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† Transformation of the bis(trimethylsilyl)methyl into the 1-aza-allyl and β-diketiminato ligands. Part 7.[1] No reprints available.

Table 1 Yields, colours and elemental analyses for complexes **3**–**9**, **12** and **13**

Compound*	Yield (%)	Colour	C (%) Found (Calc.)	H (%) Found (Calc.)	N (%) Found (Calc.)
[Ce(L–L)$_2$Cl] **3**	64	Pink	54.8 (55.6)	6.32 (6.45)	6.05 (6.2)
[Pr(L–L)$_2$Cl] **4**	58	Green yellow	54.7 (55.6)	6.25 (6.45)	5.59 (6.15)
[Nd(L–L)$_2$Cl] **5**	58	Yellow green	55.1 (55.4)	6.40 (6.4)	5.95 (6.15)
[Sm(L–L)$_2$Cl] **6**	54	Yellow	54.8 (55.0)	6.34 (6.35)	5.99 (6.1)
[Yb(L–L)$_2$Cl] **7**	57	Yellow	53.5 (53.7)	6.17 (6.2)	5.86 (5.95)
[Tm(L–L)$_2$I] **8**	61	Yellow	48.3 (49.1)	5.40 (5.7)	5.21 (5.45)
[Ce(L–L)(CHR$_2$)$_2$] **9**	30	Dark brown	49.8 (50.9)	7.96 (8.15)	3.23 (3.4)
[Yb(L–L)$_2$] **12**	85	Green	55.8 (55.8)	6.53 (6.45)	6.04 (6.2)
[Yb(L–L′)$_2$] **13**	67	Black green	52.0 (52.8)	7.70 (7.7)	6.26 (6.5)

* R = SiMe$_3$, L–L = N(R)C(Ph)C(H)C(Ph)NR, L–L′ = N(R)C(Ph)C(H)C(Bu^t)NR.

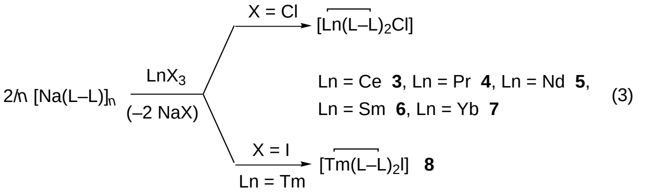
more detailed information on these compounds and substantial extensions to other aspects of bis(β-diketiminato)lanthanide-(II) or -(III) chemistry. Using related monoanionic ligands [L^1–L^1]$^-$, [L^2–L^2]$^-$ and [L^3–L^3]$^-$, the following complexes have been prepared and crystallographically characterised by Magull and co-workers: [Gd(L^1–L^1)Br$_2$(thf)$_2$],[14] [Ln(L^1–L^1)$_3$] (Ln = Sm or Gd), [Ln(L^2–L^2)$_2$Br] (Ln = Sm or Gd)[15] and [Gd(L^3–L^3)$_3$][16] [L^1–L^1 = N(Ph)C(Me)C(H)C(Me)NPh, L^2–L^2 = N(Pr^i)C(Me)C(H)C(H)C(Me)NPr^i, L^3–L^3 = (NC$_5$H$_4$-2)$_2$CH].

Results and Discussion

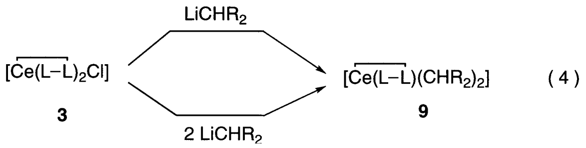
The β-diketiminatolanthanide metal-(II) or -(III) complexes reported below were prepared from the sodium or potassium β-diketiminates M(L–L) (M = Na **1** or K **2a**) or K(L–L′) **2b** [L–L = N(R)C(Ph)C(H)C(Ph)NR, L–L′ = N(R)C(Ph)C(H)C(Bu^t)NR, R = SiMe$_3$]. The corresponding lithium compounds have previously been obtained [equations (1)[5] and (2)[6]] and crystallographically characterised as binuclear compounds, while K(L–L) **2a** was prepared similarly from KCHR$_2$ and 2PhCN[5] or from [Li(L–L)]$_2$ + 2KOBu^t.[8] The Na(L–L) **1** and K(L–L′) **2b** used in the present study were made by similar techniques from (*i*) NaCHR$_2$[17] and 2PhCN and (*ii*) K{N(R)C(Bu^t)CHR}[6] and PhCN, respectively; details on these compounds and some of their neutral donor adducts will be presented in a future publication.

Synthesis and characterisation of the lanthanide β-diketiminates 3–13

Treatment of the appropriate lanthanide(III) chloride or iodide with two equivalents of the sodium β-diketiminate **1** in tetrahydrofuran (thf) afforded a coloured solution and a white precipitate of sodium halide. After filtration, removal of the solvents from the filtrate, extraction of the residue with diethyl ether and filtration, cooling of the filtrate gave in modest yield the microcrystalline coloured (Table 1) bis(β-diketiminato)lanthanide(III) chlorides or iodide **3**–**8**, equation (3), which were soluble in tetrahydrofuran, sparingly soluble in diethyl ether, but much less soluble in hydrocarbons.



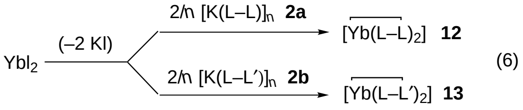
Attempts selectively to displace the chloride ligand from [Ce(L–L)$_2$Cl] **3** by $^-$CHR$_2$ failed, possibly because [Ce(L–L)$_2$(CHR$_2$)] would be too stericaly hindered; *cf.* the crystal structure of [Nd(L–L)$_2$Cl] **5**. The reaction of **3** with one equivalent of LiCHR$_2$ in Et$_2$O afforded the dark brown crystalline [Ce(L–L)(CHR$_2$)$_2$] **9** and unreacted **3**; the yield of **9** based on Ce was improved (Table 1) by using four equivalents of LiCHR$_2$, equation (4). Separation of **9** from **3** was facilitated by the greater hydrocarbon solubility of the former complex.



The green, microcrystalline (from toluene) bis(β-diketiminato)-samarium(II) **10** and -ytterbium(II) **11**–**13** complexes were obtained in good yield (Table 1) from two equivalents of K(L–L) **2a** or K(L–L′) **2b** and [LnI$_2$(thf)$_2$] (**2a** only) in thf [equation (5)] or YbI$_2$ in Et$_2$O, equation (6). Complexes

$$2/n\ [\text{K(L–L)}]_n \xrightarrow[(-2\ \text{KI})]{[\text{LnI}_2(\text{thf})_2],\ \text{thf}} [\text{Ln(L–L)}_2(\text{thf})_2] \qquad (5)$$

Ln = Sm **10**
Ln = Yb **11**



11–**13** were extremely soluble in pentane or toluene. Alternatively, [Yb(L–L)$_2$] **12** was accessible from [Yb(CHR$_2$)$_2$(OEt$_2$)$_2$] and four equivalents of PhCN, equation (7).

$$[\text{Yb(CHR}_2)_2(\text{OEt}_2)_2] + 4\ \text{PhCN} \longrightarrow \underset{\mathbf{12}}{[\text{Yb(L–L)}_2]} + 2\ \text{Et}_2\text{O} \qquad (7)$$

Complexes **3**–**13** were characterised by elemental analysis (Table 1; not **10** or **11**), ^{1}H NMR spectra (Table 2; not **8** or **9**), ^{13}C-{^{1}H} NMR (Table 3; not **4**, **7**, **8** or **9**) and mass spectra (Table 4; not **9** or **11**), which showed the molecular monomeric ion (M^+) as the highest *m*/*z* peak, except for **10**, that being $[M - \text{thf}]^+$.

Although each of the β-diketiminatolanthanide(III) complexes **3**–**9** and [Sm(L–L)$_2$(thf)$_2$] **10** was paramagnetic, clear (**3**–**5** showed significantly broad signals) ^{1}H and ^{13}C-{^{1}H NMR spectra were obtained (not for **8** or **9**) and are assigned where possible, Tables 2 and 3, respectively. The diamagnetic ytterbium(II) complexes **11**–**13** were further characterised by their ^{29}Si-{^{1}H} (likewise for the paramagnetic **4**–**6**) and ^{171}Yb-{^{1}H} (not **11**) NMR spectra, Table 5; the latter data are available for comparison with those on other Yb$^{\text{II}}$ complexes.[18]

It is noteworthy that the ^{1}H, ^{13}C-{^{1}H}, ^{29}Si-{^{1}H} and ^{171}Yb-

Table 2 ^{1}H NMR Spectral chemical shifts (δ) and assignments for complexes **3**–**7** and **10**–**13** (360 MHz, 293 K)

Compound	SiMe$_3$	CH	Phenyl ring	Others	Solvent
[Ce(L–L)$_2$Cl] **3**	1.72 (br)			4.88 (s), 3.88 (s), −1.30 (br), −1.43 (s), −8.70 (br)	$C_6D_5CD_3$
[Pr(L–L)$_2$Cl] **4**	3.35 (br)			4.41 (s), 3.98 (s), 1.54 (br)	$C_6D_5CD_3$
[Nd(L–L)$_2$Cl] **5**	2.36 (br)			5.18 (s), 4.13 (br), −27.0 (br)	$C_6D_5CD_3$
[Sm(L–L)$_2$Cl] **6**	0.52 (s, 18 H)	4.92 (s, 1 H)	5.95 (2 H), 6.40 (2 H), 6.62 (1 H)		$C_6D_5CD_3$
[Yb(L–L)$_2$Cl] **7**	−17.5 (s)			10.70 (s), 10.20 (s), 0.05 (s)	$C_6D_5CD_3$
[Sm(L–L)$_2$(thf)$_2$] **10**	−0.62 (18 H)	4.93 (1 H)	1.14 (4 H), 1.15 (4 H), −25.0 (2 H)	28.99 (4 H, thf), −7.40 (4 H, thf)	C_6D_6
[Yb(L–L)$_2$(thf)$_2$] **11**	−0.08 (18 H)	5.40 (1 H)	7.30 (4 H), 7.32 (4 H), 7.46 (2 H)	1.59 (4 H, thf), 3.36 (4 H, thf)	C_5D_5N
[Yb(L–L)$_2$] **12**	0.13 (18 H)	5.46 (1 H)	7.00 (4 H), 7.45 (4 H), 7.02 (2 H)		$C_6D_5CD_3$
[Yb(L–L′)$_2$] **13**	0.03 (d, 9 H), 1.20 (d, 9 H)	5.55 (d, 1 H)	7.43 (m, 2 H), 7.08 (m, 2 H), 7.06 (m, 1 H)	0.39 (d, 9 H, Bu^t)	$C_6D_5CD_3$

Table 3 ^{13}C-{^{1}H} NMR Spectral chemical shifts (δ) and assignments for complexes **3**, **5**, **6** and **10**–**13** (62.9 MHz, 293 K)*

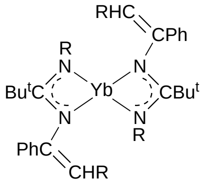
Compound	Si(CH$_3$)$_3$	Ph*C*N	CH	Phenyl ring	Others	Solvent
[Ce(L–L)$_2$Cl] **3**	5.24	155.0	15.00	124.49, 126.85, 127.32, 145.48		$C_6D_5CD_3$
[Nd(L–L)$_2$Cl] **5**	9.93	157.24	15.20	127.32, 128.06, 128.29, 143.67		$C_6D_5CD_3$
[Sm(L–L)$_2$Cl] **6**	3.58	191.42	48.0	85.61, 127.53, 128.71, 139.33		$C_6D_5CD_3$
[Yb(L–L)$_2$(thf)$_2$] **11**	3.20	174.01	104.93	127.43, 127.95, 128.50, 148.51	25.80 (thf) 67.83 (thf)	C_5D_5N
[Yb(L–L)$_2$] **12**	2.71	172.74	104.84	148.10, 128.05, 127.60, 127.14		$C_6D_5CD_3$
[Yb(L–L′)$_2$] **13**	3.03 (d) 4.05 (d)	173.0 (d) 176.5 (d)	98.95 (d)	147.97 (d), 127.90 (d), 128.00 (d) 128.45 (d)	30.13 (d, C*Me*$_3$) 42.78 (d, *C*Me$_3$)	$C_6D_5CD_3$

* [Sm(L–L)$_2$(thf)$_2$] **10** showed signals at 1.91, 14.31, 20.50, 22.99, 31.89, 94.50, 119.47, 121.29 and 130.13 which are not assigned; solvent C_6D_6.

Table 4 Mass spectral data (EI, 70 eV) for complexes **3**–**8**, **10**, **12** and **13** with assignments

Compound	Fragments and *m*/*z* (relative intensity, %)
[Ce(L–L)$_2$Cl] **3**	$[M]^+$, 904 (12); $[M - \mathrm{Cl}]^+$, 868 (6); $[M - (\mathrm{L–L})]^+$, 539 (40); $[(\mathrm{L–L})]^+$, 366 (100); $[\mathrm{SiMe_3}]^+$, 73 (60)
[Pr(L–L)$_2$Cl] **4**	$[M]^+$, 906 (10); $[M - \mathrm{Cl}]^+$, 871 (2); $[M - (\mathrm{L–L})]^+$, 541 (38); $[(\mathrm{L–L})]^+$, 365 (100); $[\mathrm{SiMe_3}]^+$, 73 (65)
[Nd(L–L)$_2$Cl] **5**	$[M]^+$, 910 (1); $[M - \mathrm{Cl} + 2]^+$, 876 (1.5); $[M - (\mathrm{L–L})]^+$, 545 (9); $[(\mathrm{L–L})]^+$, 365 (100); $[\mathrm{SiMe_3}]^+$, 73 (70)
[Sm(L–L)$_2$Cl] **6**	$[M]^+$, 918 (4); $[M - \mathrm{Cl}]^+$, 882 (5); $[M - (\mathrm{L–L})]^+$, 553 (35); $[(\mathrm{L–L})]^+$, 365 (100); $[\mathrm{SiMe_3}]^+$, 73 (65)
[Yb(L–L)$_2$Cl] **7**	$[M]^+$, 940 (9); $[M - \mathrm{Cl} + 2]^+$, 907 (9); $[M - (\mathrm{L–L})]^+$, 575 (23); $[(\mathrm{L–L})]^+$, 365 (100); $[\mathrm{SiMe_3}]^+$, 73 (61)
[Tm(L–L)$_2$I] **8**	$[M]^+$, 1026 (0.3); $[M - \mathrm{I}]^+$, 899 (87); $[M - (\mathrm{L–L})]^+$, 661 (31); $[(\mathrm{L–L})]^+$, 365 (56); $[\mathrm{SiMe_3}]^+$, 73 (100)
[Sm(L–L)$_2$(thf)$_2$] **10**	$[M - \mathrm{thf}]^+$, 954 (10); $[M - (\mathrm{thf})_2]^+$, 882 (14); $[\{\mathrm{Sm(L–L)_2}\} - \mathrm{SiMe_3}]^+$, 809 (8); $[(\mathrm{L–L}) - \mathrm{Me}]^+$, 350 (95); 130 (100); $[\mathrm{SiMe_3}]^+$, 73 (80)
[Yb(L–L)$_2$] **12**	$[M]^+$, 904 (13); $[M - \mathrm{SiMe_3}]^+$, 831 (0.4); $[M - (\mathrm{L–L})]^+$, 539 (3); $[(\mathrm{L–L})]^+$, 365 (90); $[\mathrm{SiMe_3}]^+$, 73 (100)
[Yb(L–L′)$_2$] **13**	$[M]^+$, 864 (12); $[(\mathrm{L–L'}) - \mathrm{Bu^t}]^+$, 289 (100); $[\mathrm{Bu^tSiMe_3}]^+$, 130 (26); $[\mathrm{SiMe_3}]^+$, 73 (80)

{^{1}H} NMR spectra of [Yb(L–L′)$_2$] **13** showed in each case that at ambient temperature every signal was accompanied by one of closely similar chemical shift, the two coalescing on heating. This is illustrated for the ^{1}H (298–343 K) and ^{29}Si-{^{1}H} (233–363 K) NMR spectra in Figs. 1 and 2, respectively. The observed values of the ^{171}Yb-{^{1}H} chemical shifts for **13** (δ 2475.8 and δ 2513.5) and [Yb(L–L)$_2$] **12** δ (870.4) were markedly different and those for **13** are well outside the 'normal' range (δ 0–1000) for Yb^{II} complexes; for **13**, this may have been due to a trace of Yb^{III} impurity. We note that (*i*) over the entire temperature range the two sets of SiMe$_3$ ^{1}H signals appeared to be in a 1 : 1 ratio, (*ii*) there was a substantial difference in δ(^{1}H) between the two sets, (*iii*) within each set, the two signals were of closely similar frequency and (*iv*) the two ^{171}Yb-{^{1}H} signals were of similar magnitude. We therefore conclude that at ambient temperature two isomes of **13** of closely similar structures were present which at higher temperatures were progressively converted into the thermodynamically preferred isomer. We suggest that the latter has the structure **13a**, the isomer **13b** having the exocyclic C(Ph)=CHR substituents in a closer proximity. From earlier studies,[8] it is known that the monoanionic [L–L′]$^-$ ligand is sterically more demanding than [L–L]$^-$ and furthermore that a β-diketaminato ligand can isomerise to a 1,3-diazaallyl ligand.[10] Attempts to obtain X-ray quality crystals of **13** have so far been unsuccessful.



13a

Table 5 ^{29}Si-{^{1}H} (49.7 MHz) and ^{171}Yb-{^{1}H} (87.5 MHz) NMR spectral chemical shifts (δ) for complexes **4–6** and **11–13**

Compound	^{29}Si-{^{1}H}	^{171}Yb-{^{1}H}	Solvent	Temperature/K
[Pr(L–L)$_2$Cl] **4**	0.49	—	$C_6D_5CD_3$	293
[Nd(L–L)$_2$Cl] **5**	−3.59	—	$C_6D_5CD_3$	293
[Sm(L–L)$_2$Cl] **6**	3.69	—	$C_6D_5CD_3$	293
[Yb(L–L)$_2$(thf)$_2$] **11**	−3.83		C_6D_6 + Et_2O	304
[Yb(L–L′)$_2$] **12**	−4.81	870.37	C_6D_6 + $C_6H_5CH_3$	293
[Yb(L–L′)$_2$] **13**	−2.24, 2.91 −17.01, −17.51	2475.75 2513.47	C_6D_6 + $C_6H_5CH_3$	298

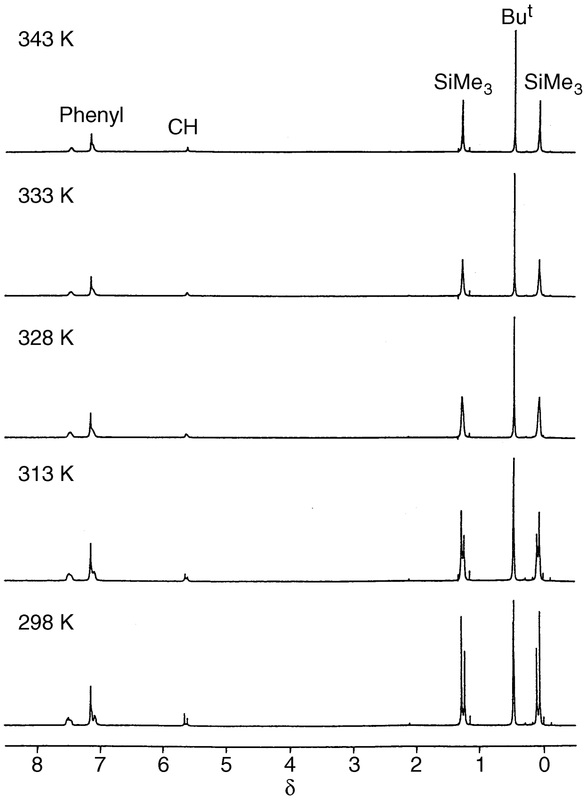


Fig. 1 Variable-temperature ^{1}H NMR spectra of [Yb(L–L′)$_2$] **13** (360 MHz, in $C_6D_5CD_3$)

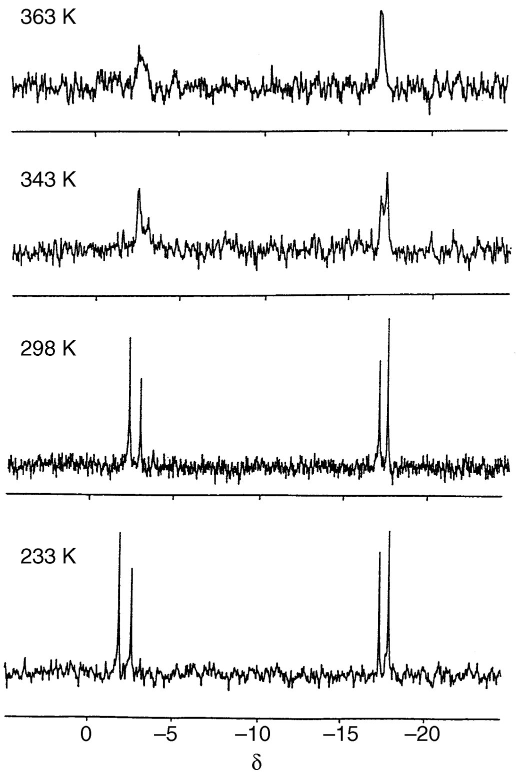


Fig. 2 Variable-temperature ^{29}Si-{^{1}H} NMR spectra of [Yb(L–L′)$_2$] **13** (49.7 MHz, in $C_6D_5CD_3$)

Crystal structures of [Nd(L–L)$_2$Cl] 5 and [Ce(L–L)(CHR$_2$)$_2$] 9

The molecular structure and atom numbering scheme for the crystalline complex **5** are shown in Fig. 3, and selected bond lengths and angles are listed in Table 6. The molecule is a monomer in the solid state. The geometry around the metal is trigonal bipyramidal: Nd–N(1) 2.447(6), Nd–N(2) 2.397(6), Nd–N(3) 2.464(6), Nd–N(4) 2.410(6) and Nd–Cl 2.665(2) Å. The Nd–N and Nd–Cl bond lengths may be compared with such data for the neodymium(III) complexes: [Nd{N(R)C(R′)NR}$_2$(μ-Cl)$_2$Li(thf)$_2$] [$R^1 = C_6H_2(CF_3)_3$-2,4,6], (Nd–N)$_{av}$ 2.53, Nd–Cl 2.710(2) Å; [Nd(η^5-$C_5H_4CH_2CH_2NMe_2$)$_2$Cl], Nd–N 2.804(2), 2.772(2), Nd–Cl 2.699(1) Å.[13] The three atoms Nd, N(1) and N(3) are almost linear, N(1)–Nd–N(3) 178.6(2)°. The angles N(1)–Nd–Cl and N(3)–Nd–Cl are both 90.4(1)°. The neodymium atom in **5** is above the planes of the two conjugated NCCCN fragments in such a way that to some degree it may be regarded as being η^5-bonded to Nd. The two N atoms and the adjacent C atoms in each NCCCN fragment are almost coplanar, but the central C atom of the ligand is situated slightly above the plane, with dihedral angles of 24.7 or 25.3°. A simplified η^5-bonding pattern for complex **5** is illustrated in Fig. 4.

The formation of a monomeric structure for **5** reveals that the *N,N′*-bis(trimethylsilyl)-β-diketiminato ligand [L–L]$^-$ is sterically more demanding than even the bulky substituted cyclopentadienyl ligands, such as $^-C_5Me_5$, $^-C_5H_3(SiMe_3)_2$-1,3 or $C_5H_3Bu^t_2$-1,3, as well as the *N,N′*-bis(trimethylsilyl)-benzamidinato ligand $Ph\bar{C}(NSiMe_3)_2$, since with these monoanionic ligands only chloride-bridged dimeric neodymocene(III) chloride or [bis(benzamidinato)]dichloroneodymate(III) complexes could be made;[13] no structural data on a monomeric, neutral, base-free neodymium(III) chloride have previously been reported, although the compounds [Ln(L^2–L^2)$_2$Br] [Ln = Sm or Gd, L^2–L^2 = N(Pr^i)C(Me)C(H)C(Me)NPr^i][15] are closely related.

The molecular structure and atom numbering scheme for the crystalline complex **9** is shown in Fig. 5, and selected bond lengths and angles are in Table 7. The molecule has a distorted tetrahedral geometry around the metal central with the bond distances Ce–N 2.442(6) and 2.421(7) Å and Ce–C 2.550(8) and 2.579(9) Å. The bonding pattern between the metal atom and the monoanionic [L–L]$^-$ ligand is similar to that found in **5**. The cerium atom is situated above the NCCCN fragment and the central C atom is above the plane with a dihedral angle of 24.2°. The C(sp^3)–Ce–C(sp^3) bond angle of 102.1(3)° is much smaller than the 132.3° in [Ce(η^5-C_5Me_5)(CHR$_2$)$_2$][19] indicating that the [L–L]$^-$ ligand is more bulky than $^-C_5Me_5$. A schematic

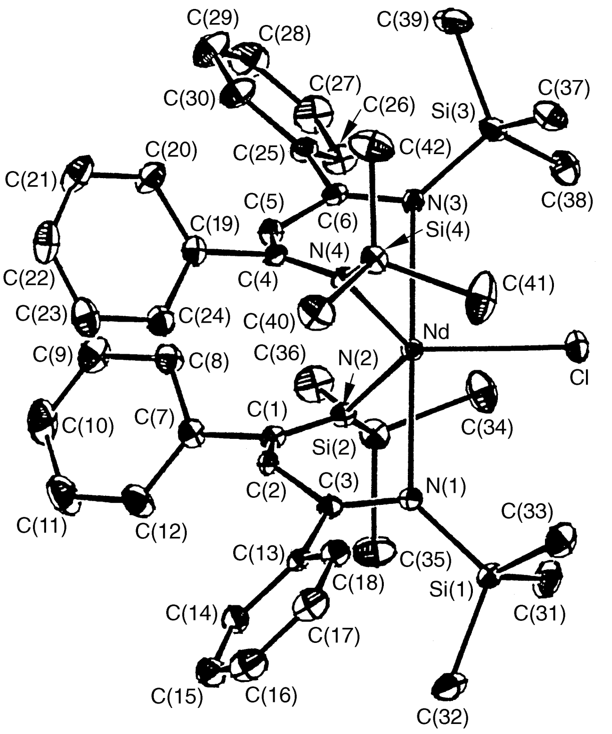


Fig. 3 Molecular structure and atom numbering scheme for [Nd(L–L)$_2$Cl] **5**

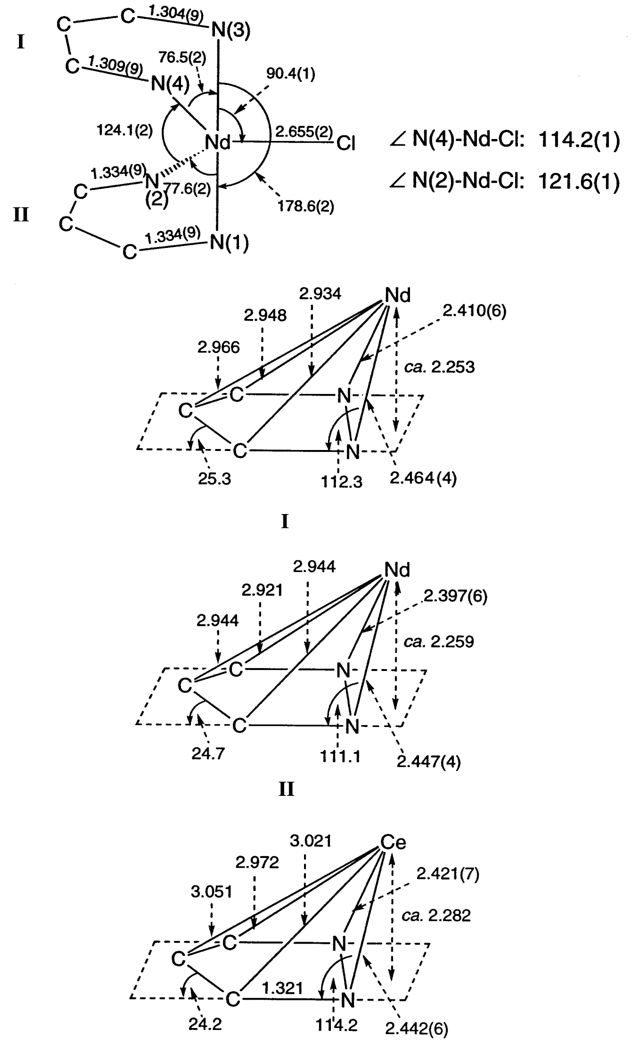


Fig. 4 Simplified η^5-bonding patterns of **5** and **9**, with selected bond distances (Å) and dihedral angles (°)

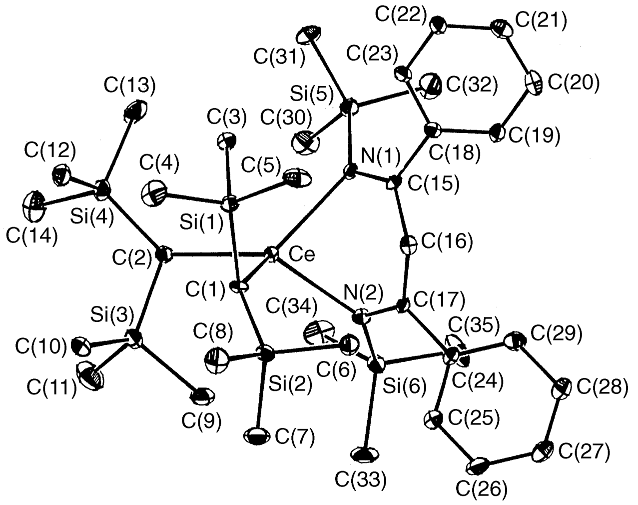


Fig. 5 Molecular structure and atom numbering scheme for [Ce(L–L)(CHR$_2$)$_2$] **9**

Table 6 Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for [Nd(L–L)$_2$Cl] **5**

Nd–Cl	2.655(2)	Nd–N(1)	2.447(6)
Nd–N(2)	2.397(6)	Nd–N(3)	2.464(6)
Nd–N(4)	2.410(6)	Si(1)–N(1)	1.770(6)
Si(2)–N(2)	1.755(6)	Si(3)–N(3)	1.751(6)
Si(4)–N(4)	1.762(6)	N(1)–C(3)	1.334(9)
C(2)–C(3)	1.455(10)	C(1)–C(2)	1.372(11)
N(2)–C(1)	1.334(9)	N(3)–C(6)	1.304(9)
C(5)–C(6)	1.431(10)	C(4)–C(5)	1.416(10)
N(4)–C(5)	1.309(9)		
Cl–Nd–N(1)	90.4(1)	Cl–Nd–N(2)	121.6(1)
Cl–Nd–N(3)	90.4(1)	Cl–Nd–N(4)	114.2(1)
N(1)–Nd–N(2)	77.6(2)	N(1)–Nd–N(3)	178.6(2)
N(1)–Nd–N(4)	104.3(2)	N(2)–Nd–N(3)	110.9(2)
N(2)–Nd–N(4)	124.1(2)	N(3)–Nd–N(4)	76.5(2)
N(3)–C(6)–C(5)	124.8(7)	C(4)–C(5)–C(6)	127.2(7)
N(4)–C(4)–C(5)	123.4(6)	N(1)–C(3)–C(2)	122.9(6)
C(1)–C(2)–C(3)	128.7(6)	N(2)–C(1)–C(2)	124.4(6)

Table 7 Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for [Ce(L–L){CH(SiMe$_3$)$_2$}$_2$] **9**

Ce–N(1)	2.442(6)	Ce–N(2)	2.421(7)
Ce–C(1)	2.550(8)	Ce–C(2)	2.579(9)
N(1)–C(15)	1.321(11)	N(2)–C(17)	1.323(12)
C(15)–C(16)	1.404(13)	C(15)–C(18)	1.493(13)
C(16)–C(17)	1.425(14)	C(17)–C(24)	1.502(13)
N(1)–Ce–N(2)	76.1(2)	N(1)–Ce–C(1)	123.0(3)
N(1)–Ce–C(2)	120.6(3)	N(2)–Ce–C(1)	112.6(3)
N(2)–Ce–C(2)	122.1(3)	C(1)–Ce–C(2)	102.1(3)
Ce–N(1)–C(15)	102.7(5)	Ce–N(2)–C(17)	101.0(6)
C(15)–C(16)–C(17)	126.5(9)		

η^5-bonding pattern between Nd or Ce and the $[\text{L–L}]^-$ ligand is presented in Fig. 4.

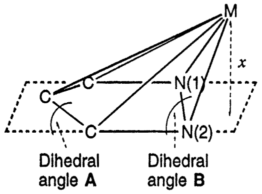
Some comparative data on various metal complexes containing the $[\text{L–L}]^-$ ligand are shown in Table 8.

Experimental

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$_2$ (M = Na or K),[17] K(L–L),[5] LnCl$_3$,[20] TmI$_3$,[21] YbI$_2$,[22] [SmI$_2$(thf)$_2$];[23] [the preparation and characterisation of Na(L–L)

Table 8 Selected bond distances (Å) and angles (°) for some *N*,*N*′-bis(trimethylsilyl)-β-diketiminatometal complexes

Compound[a]	M–N	M–C(Ph)[b]	M–C(H)[b]	N(1)–N(2)[b]	N–C(Ph)	*x* (M to N_2C_2 plane)[c]	N(1)–M–N(2)	Dihedral angle *A*[c,b]	Dihedral angle *B*[c,b]	Ref.
[Li(L–L)]$_2$	1.974(9) 1.956(9)	2.717 2.763	2.957	3.07	1.356(6) 1.315(6)	0.83	102.7(4)	12.6	145.2	5
[Sn(L–L)ClMe$_2$]	2.001(7) 2.311(8)	2.901 3.021	3.081	2.875	1.331(12) 1.357(12)	1.37	81.0(3)	13.5	125.3	5, 8
[Zr(L–L′)Cl$_3$]	2.138(5) 2.187(5)	2.602(7) 2.608(7)	2.535(7)		1.339(10) 1.331(9)	1.58	83.4(2)	27.8	101.658	8
[{UCl(μ-Cl)(L–L)(NR)}$_2$]$^{2+}$	2.35(2) 2.33(2)	2.882 2.842	2.862	2.932	1.32(3) 1.31(3)	1.75	77.4(7)	21.8	105.9	8, 10
[UCl$_2$(L–L)(L–L″)]$^-$	2.38(2) 2.36(2)	2.842 2.812	2.832	3.052	1.30(2) 1.30(3)	1.73	80.1(7)	23.7	109.0	8, 10
[Th(L–L)$_2$Cl$_2$]	2.472(4) 2.462(3)	2.959 2.997	2.956	2.959	1.318(5) 1.332(5)	1.872	73.7(1)	25.8	107.3	11
[Nd(L–L)$_2$Cl] **5**	2.447(6) 2.397(6)	2.934 2.948	2.966	3.011	1.334(9) 1.334(9)	2.253	77.6(2)	24.7	111.0	This work
	2.464(6) 2.410(6)	2.921 2.944	2.944	3.031	1.304(9) 1.309(9)	2.259	76.5(2)	25.3	112.3	
[Ce(L–L)(CHR$_2$)$_2$] **9**	2.442(6) 2.421(7)	3.021 2.972	3.051	2.997	1.321(11) 1.323(12)	2.828	76.1(2)	24.2	114.2	This work



[a] L–L = {N(R)C(Ph)}$_2$CH; L–L′ = N(R)C(Ph)CHC(Bu^t)NR; L–L″ = N(R)C(Ph)NC(Ph)CHR; R = SiMe$_3$. [b] Data without estimated standard deviations in parentheses were calculated from X-ray crystal data by Chem3D™. [c] Dihedral angles *A* and *B* and *x* (= M to N_2C_2 plane) are defined as shown above.

and K(L–L′) and other related alkali-metal β-diketiminates will be described in a future publication]. Others were purchased, and purified by standard procedures. Microanalyses were carried out by Medac Ltd (Brunel University). The NMR spectra were recorded on Bruker WM250, WM360 or WM500 instruments, mass spectra on a Fisons VG Autospec mass spectrometer operating in the electron impact (EI) model at 70 eV.

Preparations

[Ce(L–L)$_2$Cl] 3. A solution of Na(L–L) **1** (2.36 g, 6.08 mmol) in tetradydrofuran (20 cm^3) was added dropwise to a stirred suspension of CeCl$_3$ (0.78 g, 3.1 mmol) in tetrahydrofuran (100 cm^3) at room temperature. There was a change of colour from yellow to red. The mixture was stirred for 48 h, leaving a red-brown solution and a white precipitate, which was filtered off. The solvent was removed from the filtrate *in vacuo* and the residue was extracted with diethyl ether (2 × 50 cm^3) and filtered. The filtrate was concentrated to *ca.* 10 cm^3. Cooling to −30 °C afforded compound **3** (1.62 g, 64%) as pink microcrystals.

[Pr(L–L)$_2$Cl] 4. The reaction of Na(L–L) **1** (0.85 g, 2.2 mmol) with PrCl$_3$ (0.28 g, 1.13 mmol) in exactly the same way as that for **3** afforded **4** (0.58 g, 58%) as a green-yellow powder.

[Nd(L–L)$_2$Cl] 5. Similarly, **1** (2.36 g, 6.08 mmol) with NdCl$_3$ (0.78 g, 3.1 mmol) gave **5** (1.58 g, 58%) as yellow-green crystals.

[Sm(L–L)$_2$Cl] 6. Likewise, K(L–L) **1** (1.8 g, 4.64 mmol) with SmCl$_3$ (0.6 g, 2.33 mmol) afforded yellow crystals of **6** (1.15 g, 54%).

[Yb(L–L)$_2$Cl] 7. Similarly, **1** (0.97 g, 2.5 mmol) with YbCl$_3$ (0.36 g, 1.3 mmol) gave **7** (0.67 g, 57%) as a yellow powder.

[Tm(L–L)$_2$I] 8. Similarly from **1** (1.5 g, 3.86 mmol) and TmI$_3$ (1.4 g, 2.0 mmol), **8** (0.67 g, 61%) was obtained.

[Sm(L–L)$_2$(thf)$_2$] 10. A solution of K(L–L) **2a** (1.1 g, 2.72 mmol) in thf (20 cm^3) was added dropwise to a blue solution of [SmI$_2$(thf)$_2$] (0.75 g, 1.36 mmol) in thf (100 cm^3) at room temperature. There was a colour change from blue to green. The mixture was stirred for 24 h, leaving a deep green solution and a pale grey precipitate which was filtered off. The solvent was removed from the filtrate *in vacuo* and the green residue was extracted with toluene (30 cm^3) and filtered. Cooling the concentrated filtrate at −30 °C afforded green crystals of compound **10** (1.0 g, 73%).

[Yb(L–L)$_2$(thf)$_2$] 11. From **1** (1.0 g, 2.45 mmol) and YbI$_2$ (0.52 g, 1.23 mmol) using a procedure similar to that for **10**, yielded green crystals of **11** (1.0 g, 78%).

[Yb(L–L)$_2$] 12. Solid YbI$_2$ (1.3 g, 3.04 mmol) and K(L–L) **2a** (2.56 g, 6.3 mmol) were mixed together and diethyl ether (200 cm^3) was added. The suspension was stirred at room temperature for 2 d, leaving a green solution and a white precipitate which was filtered off. The solvent was removed from the filtrate *in vacuo* and the resultant green solid was extracted with toluene (50 cm^3) and filtered. The volume of the filtrate was reduced to *ca.* 10 cm^3. Cooling to −30 °C afforded dark green crystals of compound **12** (2.3 g, 85%).

Alternatively, **12** was obtained by the following procedure. A solution of [Yb(CHR$_2$)$_2$(OEt$_2$)$_2$] was prepared from Na(CHR$_2$) (1.04 g, 5.52 mmol) and YbI$_2$ (1.18 g, 2.67 mmol) in diethyl ether (150 cm^3), stiring at 25 °C for 2 d and filtering.[24] To this filtrate, benzonitrile (1.14 cm^3, 11 mmol) was added by syringe. There was an immediate colour change from red orange to green. The mixture was stirred for a further 16 h and filtered. Solvent was removed from the filtrate *in vacuo* to yield a green solid which was extracted into toluene (20 cm^3). The extract was filtered and the filtrate concentrated to *ca.* 5 cm^3. Cooling to −30 °C afforded green crystals of **12** (1.3 g, 52%).

[Yb(L–L′)$_2$] 13. A solution of K(L–L′) **2b** (0.85 g, 2.24 mmol) in diethyl ether (10 cm^3) was added to a suspension of YbI$_2$ (0.48 g, 1.12 mmol) in diethyl ether (100 cm^3) at room temperature. The colour gradually changed from yellow to intense green. The mixture was stirred for 20 h and a white precipitate was filtered off. Solvent was removed from the filtrate *in vacuo* and the green residue was extracted with hexane (50 cm^3) and filtered. The filtrate was concentrated and cooled to −30 °C to yield black-green crystals of compound **13** (0.65 g, 67%).

Reaction of [Ce(L–L)$_2$Cl] 3 with LiCHR$_2$ (R = SiMe$_3$). Solid LiCHR$_2$ (0.08 g, 0.48 mmol) was slowly added to a stirred suspension of **3** (0.43 g, 0.48 mmol) in diethyl ether (20 cm^3) at −78 °C. The mixture was allowed to warm to room temperature and was stirred for 4 h, the colour of the solution changing from red pink to brown. The reaction mixture was further stirred for 20 h, leaving a brown solution and a white precipitate. Some pink solid **3** remained unreacted which, together with the white precipitate, was filtered off. The volume of the filtrate was reduced under vacuum to *ca.* 5 cm^3. Cooling to −30 °C afforded dark brown crystals of [Ce(L–L)(CHR$_2$)$_2$] **9** (0.12 g, 30% based on **3**, or 61% based on LiCHR$_2$).

Table 9 Structure determination for complexes **5** and **9**

	[Nd(L–L)$_2$Cl] **5**	[Ce(L–L)(CHR$_2$)$_2$] **9**
Formula	$C_{42}H_{58}ClN_4NdSi_4$	$C_{35}H_{67}CeN_2Si_6$
M	910.99	824.6
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a,*b*,*c*/Å	11.986(4), 12.483(8), 16.006(10)	19.823(19), 12.283(7), 19.856(13)
α,β,γ/°	85.06(5), 86.16(3), 89.69(3)	90, 109.93(9), 90
U/Å^3, Z, D_c/g cm^{-3}	2380, 2, 1.26	4545.2, 4, 1.21
T/K	293	173
F(000)	942	1732
μ(Mo-Kα)/cm^{-1}	26.0	12.0
Crystal size/mm	0.3 × 0.3 × 0.15	0.3 × 0.2 × 0.2
Total unique reflections (2 < θ < 25°)	8363	8204
Significant reflections [$\|F^2\| > 2\sigma(F^2)$]	5613	4729
R, *R′* [a]	0.054, 0.060	0.065, 0.062

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

Similarly, from **3** (0.49 g, 0.54 mmol), $CeCl_3$ (0.13 g, 0.54 mmol) and $LiCHR_2$ (0.36 g, 2.16 mmol) in Et_2O (60 cm^3), there was obtained **9** (0.33 g, 74%).

Crystallography

In each case, unique data sets for compounds **5** and **9** were collected, for $2 < \theta < 25°$ from a crystal sealed in a Lindemann capillary under argon on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å). Two standard reflections monitored every hour showed no significant change. Data were corrected for Lorentz and polarisation effects (L_p) and also for absorption using DIFABS[25] after isotropic refinement. Reflections with $|F^2| > 2\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{\frac{1}{2}}/L_p$, were considered observed.

Each structure was solved using the heavy-atom routines of SHELXS-86.[26] Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares using programs from the Enraf-Nonius MOLEN package.[27] The hydrogen atoms were held fixed at calculated positions with $U_{iso} = 1.3U_{eq}$ for the parent atom. Further details are given in Table 9.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/480.

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