Syntheses, structures and reactions of a series of β-diketiminatoyttrium compounds†

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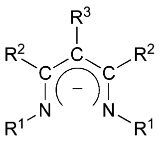
This paper describes the synthesis and selected reactions of a series of crystalline mono(β-diiminato)yttrium chlorides **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, **5c** and **9**. The X-ray structure of each has been determined, as well as of $[YCl(\mathbf{L}^4)_2]$ (**6**), $[Y(\mathbf{L}^1)_2OBu^t]$ (**7**) and $[Y\{CH(SiMe_3)_2\}(thf)(\mu\text{-}Cl)_2Li(OEt_2)_2(\mu\text{-}Cl)]_2$ (**8**). The *N*,*N*′-κ^2-β-diiminato ligands were $[\{N(R)C(Me)\}_2CH]^-$ [R = $C_6H_4Pr^i$-2 (**L**^{1}); R = $C_6H_4Bu^t$-2 (**L**^{2}); R = $C_6H_3Pr^i_2$-2,6 (**L**^{3})], $[\{N(SiMe_3)C(Ph)\}_2CH]^-$ (**L**^{4}) and $[\{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2CPh]^-$ (**L**^{5}). Equivalent portions of Li[**L**^{x}] and YCl_3 in Et_2O under mild conditions yielded $[Y(\mu\text{-}Cl)(\mathbf{L}^x)(\mu\text{-}Cl)_2Li(OEt_2)_2]_2$ [**L**^{x} = **L**^{1} (**3a**) or **L**^{2} (**3b**)] and $[Y(\mu\text{-}Cl)(\mathbf{L}^3)(\mu\text{-}Cl)Li(OEt_2)_2(\mu\text{-}Cl)]_2$ (**4a**) or its thf (instead of Et_2O) equivalent **4b**. Each of the $Li(OEt_2)_2Cl_2$ moieties is bonded in a terminal (**3**) or bridging (**4**) mode with respect to the two Y atoms; the difference is attributed to the greater steric demand of **L**^{3} than **L**^{1} or **L**^{2}. Under slightly more forcing conditions, YCl_3 and Li(**L**^{2}) (*via* **3b**) gave the lithium-free complex $[YCl_2(\mathbf{L}^2)(thf)_2]$ (**5b**). Two isoleptic compounds **5a** and **5c** (having in place of **L**^{2} in **5b**, **L**^{3} and **L**^{5}, respectively) were obtained from YCl_3 and an equivalent portion of K[**L**^{3}] and Na[**L**^{5}], respectively; under the same conditions using Na[**L**^{4}], the unexpected product was $[YCl(\mathbf{L}^4)_2]$ (**6**) (*i.e.* incorporating only one half of the YCl_3). A further unusual outcome was in the formation of **8** from **3a** and 2 $Li[CH(SiMe_3)_2]$. Compound $[Y(\mathbf{L}^5)\{N(H)\text{-}C_6H_3Pr^i_2\text{-}2,6\}(thf)(\mu_3\text{-}Cl)_2K]_2\cdot 4Et_2O$ (**9**), obtained from **5c** and $K[N(H)C_6H_3Pr^i_2\text{-}2,6]$, is noteworthy among group 3 or lanthanide metal (M) compounds for containing MClKCl (M = Y) moieties.

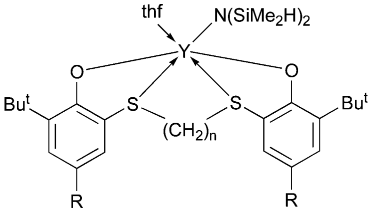
Introduction

β-Diiminates are important spectator ligands in coordination chemistry. Their use depends on their strong binding to metals, their widely tunable steric and electronic features by varying the substituents at the nitrogen and carbon atoms and the diversity of their bonding modes. In the present context, however, their general formula is limited to that shown in **L**^{1}–**L**^{5}, their binding to yttrium is invariably *N*,*N*′-chelating and their bonding mode is monoanionic and π-delocalised. Ligands **L**^{1}–**L**^{4} are β-diketiminates and **L**^{5} is a β-dialdiminate.



	R^1	R^2	R^3
L^1:	2-$Pr^iC_6H_4$	Me	H
L^2:	2-$Bu^tC_6H_4$	Me	H
L^3:	2,6-$Pr^i_2C_6H_3$	Me	H
L^4:	Me_3Si	Ph	H
L^5:	2,6-$Pr^i_2C_6H_3$	H	Ph

β-Diiminates of the majority of the natural elements have been described. In our 2002 review, however, such yttrium compounds were notable by their absence.[1] Subsequently, various **L**^{3} derivatives have been described: $[YI_2(\mathbf{L}^3)(thf)]$ (thf = tetrahydrofuran),[2] $[YI_2(\mathbf{L}^3)(dme)]$ (dme = 1,2-dimethoxyethane),[2] $[\{YI(\mathbf{L}^3)(\mu\text{-}OMe)\}_2]$,[2] $[YCl(\mathbf{L}^3)(\mu\text{-}Cl)_3Y(\mathbf{L}^3)(thf)]\cdot 2PhMe$,[3] and $[Y(\eta^3\text{-}C_3H_5)_2(\mathbf{L}^3)]$.[4] Furthermore, various yttrium compounds have featured as catalysts for ring-opening polymerisation of methyl methacrylate (MMA) or ε-caprolactone, or copolymerisation of carbon dioxide and an epoxide. Examples include $[Y(OOCR)_3]$ with $ZnEt_2$ and glycerol for CO_2/epoxide copolymerisation,[5a,b] $[Y\{(NPr^i)_2CN(SiMe_3)_2\}_2NPr^i_2]$[6] or $[Y\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiPh_2\}_2(\mu\text{-}K)(thf)_{0.5}(OEt_2)_{1.5}]_\infty$[7] for poly-MMA or poly-ε-caprolactone formation, and **I** (R = Me, *n* = 2; R = Bu^t, *n* = 3) for polylactide synthesis.[8] The complex $[Y(\eta^5\text{-}C_4PMe_2\text{-}3,4\text{-}Bu^t_2\text{-}2,5)(CH_2C_6H_4NMe_2\text{-}2)_2]$ with $[Ph_3C][B(C_6F_5)_4]$ was a catalyst for the syndiospecific polymerisation of styrene.[9] The above considerations have provided the stimulus for the present excursion into β-diiminatoyttrium chemistry.



I

Results and discussion

The β-diketimines $H[\{N(C_6H_4R\text{-}2)C(Me)\}_2CH]$ [R = Pr^i (**1a**) (≡ H**L**^{1});[10] R = Bu^t (**1b**) (≡ H**L**^{2})] were prepared from acetylacetone

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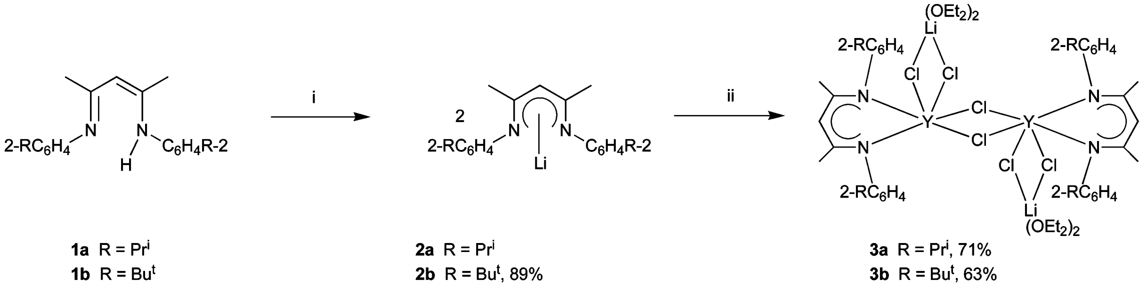
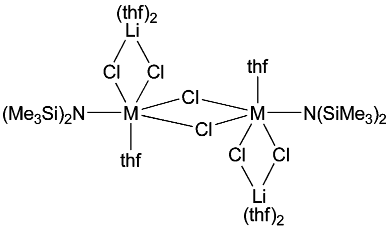


Scheme 1 *Reagents and conditions*: i, LiBu^n, C_6H_{14}; ii, YCl_3, Et_2O, −30 °C.

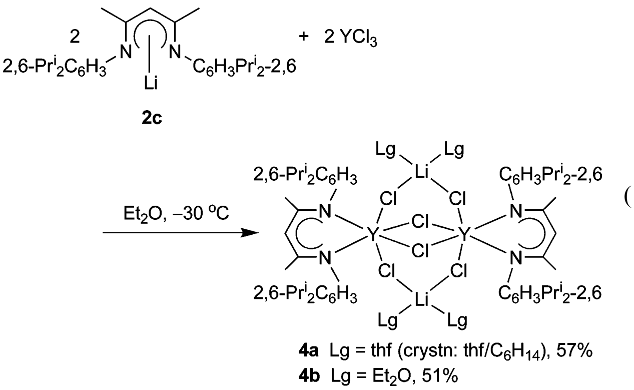
and the relevant amine 2-$RC_6H_4NH_2$, using the literature procedure outlined for $H[\{N(C_6H_3Pr^i_2\text{-}2,6)C(Me)\}_2CH]$ (≡ H$\mathbf{L}^3$).[11] The lithium salts Li[$\mathbf{L}^1$] (**2a**) (which had previously been prepared *in situ* as the first step *en route* to a zinc β-diketiminato derivative)[10] and Li[$\mathbf{L}^2$] were obtained from the appropriate β-diketimine and LiBu^n (i in Scheme 1); crystalline Li[$\mathbf{L}^3$] (**2c**) and its 1:1-diethyl ether or thf adducts had already been described.[12] The crystalline pentacyclic dimeric lithio(trichloro)(β-diketiminato)yttrium compounds **3a** or **3b** were synthesised (ii in Scheme 1) from equimolar portions of the respective compound **2a** or **2b** and yttrium(III) chloride.

The central $[(\mu\text{-Cl})M(\mu\text{-Cl})_2Li]_2$ motif of **3a** and **3b** (M = Y) resembles that found in the crystalline compounds **J** (M = Nd, Sm*, Eu*, Ho, Yb*; those marked with an asterisk were X-ray-characterised), obtained from $Li[N(SiMe_3)_2]$ and the corresponding compound MCl_3 in thf.[13]



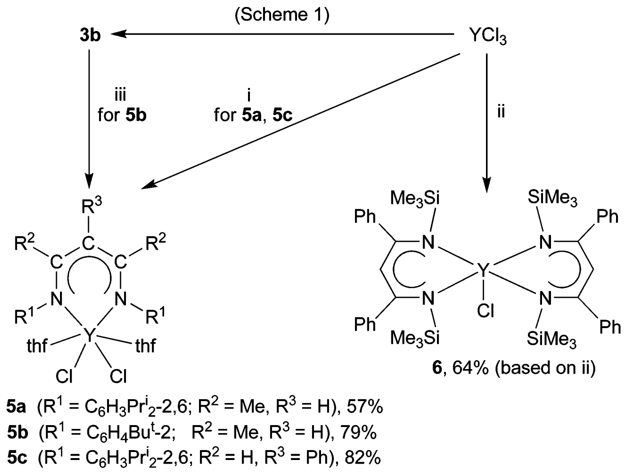
J

In contrast to step ii of Scheme 1, based on Li[$\mathbf{L}^1$] or Li[$\mathbf{L}^2$], treatment of YCl_3 with an equimolar portion of the more bulky lithium β-diketiminate **2c**[12] afforded [eqn (1)] the crystalline compounds **4a** or **4b**. Their central $[YCl_3Li]_2$ motif differs from that in **3a** or **3b**. Whereas in the latter each such moiety occupies a terminal site with respect to each yttrium atom, in **4a** and **4b** each functions as a bridge between its two yttrium atoms. Apart from the substituents on the nitrogen atoms, compounds **3** and **4** might be regarded as isomers.



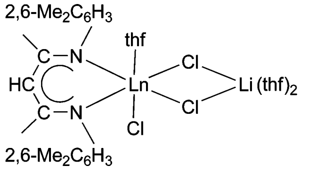
(1)

By using one of the heavier alkali metal salts, K[$\mathbf{L}^3$] or Na[$\mathbf{L}^5$] as a β-diiminato ligand-transfer reagent, a similar YCl_3/M[**L**] reaction in thf afforded (i in Scheme 2) the crystalline alkali metal-free, mononuclear dichloroyttrium β-diiminate **5a** or **5c**. A different outcome, again, resulted from treatment under mild conditions of equivalent portions of Na[$\mathbf{L}^4$] and YCl_3, which furnished (ii in Scheme 2) the crystalline chloroyttrium bis(β-diketiminate) [YCl($\mathbf{L}^4$)$_2$] (**6**). Related to **5a** and **5c**, the corresponding compound [YCl_2($\mathbf{L}^2$)(thf)$_2$] (**5b**) was obtained (iii in Scheme 2) by prolonged gentle heating of **3b**, with elimination of lithium chloride.



Scheme 2 *Reagents and conditions*: i, for **5a**: $K[\{N(C_6H_3Pr^i_2\text{-}2,6)C(Me)\}_2CH]$, Et_2O, −30 °C, crystd thf–Et_2O–C_6H_{14}; for **5b**: **3b**, 60 °C, 12 h, crystd thf–Et_2O; for **5c**: $Na[\{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2Ph]$, thf, 20 °C; ii, $Na[\{N(SiMe_3)C(Ph)\}_2CH$, thf, 20 °C, crystd thf–Et_2O; iii, C_6H_{14}, 60 °C, crystd C_6H_{14}–Et_2O–thf.

Regarding the binuclear β-diiminato-Y/Li chlorides **3a**, **3b**, **4a** and **4b**, there are some related 4f metal complexes in the recent literature. These include **K(a)**,[14] **K(b)**,[14] **K(c)**[15] and **K(d)**[14] obtained from Li[$\mathbf{L}^6$] and an equivalent portion of $LnCl_3$ in thf; treatment of **K(b)** with $H[\{N(C_6H_3Me_2\text{-}2,6)C(Me)\}_2CH]$ (≡ H$\mathbf{L}^6$) in toluene yielded [SmCl($\mathbf{L}^6$)(μ-Cl)$_3$Sm($\mathbf{L}^6$)(μ-Cl)Li($\mathbf{L}^6$)(thf)].[14] The compound [YCl($\mathbf{L}^3$)(μ-Cl)$_3$Y($\mathbf{L}^3$)(thf)]·2PhMe (mentioned in the Introduction) was prepared from equivalent portions of [YCl_3(thf)] and the lithium β-diketiminate in toluene at 90 °C.[3] Other tetrachlorobis(β-diketiminatolanthanide) complexes reported recently include [Ln($\mathbf{L}^6$)(thf)(μ-Cl)$_3$Ln(Cl)($\mathbf{L}^6$)] (Ln = Sm, Yb), obtained from the appropriate compound **K(b)** or **K(d)** in toluene.[14] The corresponding Sm_2–($\mathbf{L}^3$)$_2$ complex was prepared from $SmCl_3$ and K($\mathbf{L}^3$) in thf.[16] As for compounds **5a**, **5b** and **5c**, there are recent precedents for mononuclear β-diketiminatometal (M) dichlorides (M = Sc or Ln): [ScCl$_2$(**L**^{3})(thf)],[17] [Ln(**L**^{x})Cl$_2$(thf)$_2$] (Ln(**L**^{x}) = Yb(**L**^{3}),[18] Sm(**L**^{6}),[19a] Yb(**L**^{6}),[19a,b,c,d] and Ln[N(C$_6$H$_3$Pr$^i_2$-2,6)C(Me)C(H)C(Me)N(C$_6$H$_4$Cl-4)] (Ln = Sm, Yb)[19a,c]), and [YbCl$_2$(**L**^{3})(dme)].[20]



K(a) Ln = Nd
K(b) Ln = Sm
K(c) Ln = Tb
K(d) Ln = Yb

The formation of the five-coordinate bis(β-diketiminato)-yttrium chloride **6** from equivalent portions of YCl$_3$ and Na[**L**^{4}] (ii in Scheme 2) is surprising. It is attributed to disproportionation of the kinetically labile YCl$_2$(**L**^{4}) [eqn (2)]. An analogous situation involving an **L**^{4}-containing Ln compound was previously observed when the 1 : 1 reaction of [Ce(**L**^{4})$_2$Cl] with LiCH(SiMe$_3$)$_2$ gave a 1 : 2 product apparently *via* the ligand redistribution of the labile intermediate Ce(**L**^{4})Cl{CH(SiMe$_3$)$_2$} [eqn (3)]; it was suggested that [Ce(**L**^{4})$_2${CH(SiMe$_3$)$_2$}] was too sterically hindered to exist.[21]

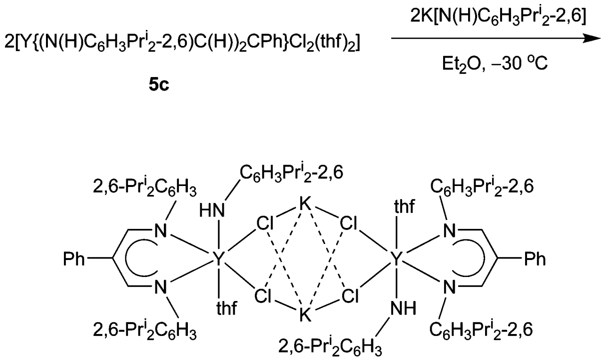
$$2\mathrm{YCL_2}(\mathbf{L}^4) \rightarrow [\mathrm{YCl}(\mathbf{L}^4)_2]\ (\mathbf{6}) + \mathrm{YCl_3} \qquad (2)$$

$$2[\mathrm{CeCl}(\mathbf{L}^4)_2] + 2\mathrm{LiCH(SiMe_3)_2} \rightarrow [\mathrm{Ce\{CH(SiMe_3)_2\}_2}(\mathbf{L}^4)] + [\mathrm{CeCl}(\mathbf{L}^4)_2] \qquad (3)$$

Treatment of the β-diketimine H[**L**^{1}] with K[N(SiMe$_3$)$_2$] yielded (ii in Scheme 3) K[**L**^{1}]. The latter with half an equivalent each of successively YCl$_3$ and K[OBu^t] furnished (iii in Scheme 3) in modest yield X-ray quality crystals of [Y(**L**^{1})$_2$OBu^t] (**7**). Several bis(β-diketiminato)lanthanide(III) compounds (but no alkoxides) have been reported, including [Ln(**L**^{4})$_2$Cl] (Ln = Ce,[21,22] Pr,[21] Nd,[21] Sm,[21] Yb[21]), [Ln(**L**^{7})$_2$Br] [**L**^{7} = {N(Pr)C(Ph)}$_2$CH; Ln = Sm, Gd],[23] and [Tm(**L**^{3})$_2$]X [X = BPh$_4$, B(C$_6$F$_5$)$_4$].[24]

X-Ray-quality crystals of **8** (i in Scheme 3) in moderate yield were obtained from [Y(μ-Cl)(**L**^{1})(μ-Cl)$_2$Li(OEt$_2$)$_2$]$_2$ (**3a**) and Li[CH(SiMe$_3$)$_2$]. It is interesting that, under the very mild reaction conditions used, the alkyl ligand displaced the β-diketiminate, especially as the alternative leaving groups (the bridging chlorides) were unaffected. This is a very rare occurrence. Another example is that shown in eqn (3), which, however, was attributed to the steric hindrance to the formation of [Ce{CH(SiMe$_3$)$_2$}(**L**^{4})$_2$];[21] and from [{Y(η^5-C$_5$H$_4$R)$_2$(μ-Cl)}$_2$] + 2LiMe in thf the only product isolated was Li[C$_5$H$_4$R] [R = (+)-neomenthyl].[25] Another possible route to **8** is that the first formed product from **3a** and the lithium alkyl was Y(**L**^{1})(μ-Cl)$_2$Li{CH(SiMe$_3$)$_2$} (suggested by a referee), which upon redistribution yields equivalent portions of **8** and Y(**L**^{1})Cl{CH(SiMe$_3$)$_2$} (which may have decomposed) and Li(**L**^{1}).

Addition of an equivalent portion of potassium 2,6-diisopropylanilide to [Y(**L**^{5})Cl$_2$(thf)$_2$] (**5c**) in diethyl ether at ambient temperature yielded [eqn (4)] the crystalline compound [Y(**L**^{5}){N(H)C$_6$H$_3$Pr$^i_2$-2,6}(thf)(μ$_3$-Cl)$_2$K]$_2$·4Et$_2$O (**9**). Heterobimetallic K–M [M = a group 3 or lanthanide(III) metal] complexes containing halide bridges between such two metals are exceedingly rare. Examples include the X-ray-characterised compounds [Dy(η^5-C$_5$H$_2$Bu$^t_3$-1,2,4)$_2$(μ-Cl)$_2$K(18-crown-6)],[26] [Ln(η^5-C$_5$Me$_5$)$_2$(μ-Cl)$_2$K(thf)]$_\infty$ (Ln = Ce,[27] Sm[28a,b]) and [Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(η^6-PhMe)$_2$].[29]

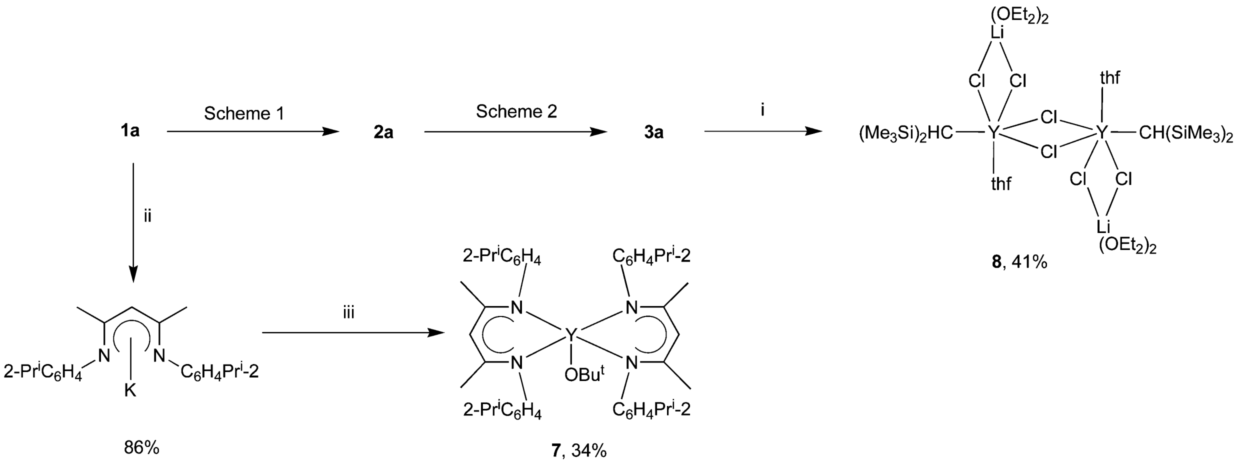


(4)

9, 67% (based on **5c**)

Molecular structures of the crystalline compounds 3a, 3b, 4a, 4b, 5a, 5b, 5c, 6, 7, 8 and 9

Each of the compounds, except **8**, is a mono- or bis- (**6**, **7**) di-iminatoyttrium complex, having the *N*,*N*′-centred ligand bonded to the metal in a terminal, chelating (κ^2) fashion. The endocyclic geometrical parameters of their six-membered $\overline{\mathrm{YNCCCN}}$ rings are shown in Table 1. The conformation of each such ring is that

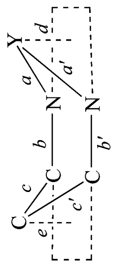


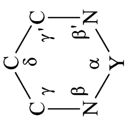
Scheme 3 *Reagents and conditions*: i, 2Li[CH(SiMe$_3$)$_2$], C$_6$H$_{14}$, 0 °C, crystd thf–Et$_2$O–C$_6$H$_{14}$; ii, K[N(SiMe$_3$)$_2$], PhMe; iii, YCl$_3$, Et$_2$O, −30 °C and KOBu^t, C$_6$H$_{14}$.

Table 1 Endocyclic bond distances *a*–*e* (Å) and angles α–δ (°) in the [Y{κ^2-(N(R^1)(R^2))$_2$CR^3}] moieties of **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, **5c**, **6**, **7** and **9**[a]

	3a	3b	4a	4b	5a	5b	5c	6	7	9
a	2.315(6), 2.300(7)	2.3427(19)	2.344(4), 2.361(4)	2.377(4)	2.380(3)	2.357(2)	2.3766(17)	2.3611(19), 2.3079(19)	2.395(8), 2.358(2)	2.400(2)
a'	2.317(6), 2.300(6)	2.3768(11)	2.356(4), 2.340(4)	2.367(4), 2.341(4)	2.360(3)	2.343(2)	2.3746(18)	2.3137(19), 2.3611(19)	2.347(2), 2.380(2)	2.473(2)
b	1.350(10), 1.332(10)	1.330(3)	1.336(6), 1.326(6)	1.337(7), 1.335(7)	1.334(5)	1.328(3)	1.324(3)	1.332(3), 1.338(3)	1.324(3), 1.335(3)	1.325(3)
b'	1.353(10), 1.342(10)	1.339(3)	1.330(6), 1.343(6)	1.337(7), 1.331(7)	1.330(5)	1.330(4)	1.320(3)	1.330(3), 1.329(3)	1.333(3), 1.327(3)	1.317(3)
c	1.414(11), 1.403(11)	1.410(3)	1.397(7), 1.406(7)	1.394(8), 1.402(8)	1.395(5)	1.407(4)	1.400(3)	1.422(3), 1.412(3)	1.407(3), 1.405(3)	1.401(4)
c'	1.388(12), 1.402(12)	1.399(3)	1.403(7), 1.396(7)	1.388(8), 1.385(8)	1.396(5)	1.398(4)	1.403(3)	1.415(3), 1.425(3)	1.405(3), 1.415(3)	1.408(4)
d	1.16, 1.17	0.91	0.84, 0.88	0.93, 0.80	0.59	0.77	0.11	1.67, 1.67	1.09, 1.27	0.68
e	0.12, 0.11	0.05	0.12, 0.14	0.12, 0.13	0.08	0.02	0.01	0.23, 0.23	0.13, 0.17	0.13
α	80.1(2), 78.5(2)	78.94(7)	81.58(14), 82.60(13)	82.45(15), 81.15(16)	79.94(10)	79.34(8)	80.52(6)	79.87(7), 80.31(7)	77.45(6), 77.91(16)	75.65(7)
β	117.7(5), 119.2(5)	124.39(16)	121.3(3), 123.3(3)	119.6(3), 122.7(4)	125.8(2)	125.70(18)	126.88(14)	97.55(14), 99.60(14)	120.95(14), 116.44(13)	128.53(18)
β'	117.6(6), 119.2(6)	122.17(15)	120.9(3), 119.2(3)	118.7(3), 122.6(4)	126.7(2)	125.50(18)	126.91(14)	100.93(14), 98.58(14)	122.32(13), 117.37(13)	127.02(17)
γ	123.5(8), 126.6(8)	123.6(2)	125.1(4), 124.7(4)	125.3(5), 124.7(5)	125.0(3)	124.0(3)	129.3(2)	124.2(2), 123.6(2)	124.1(2), 124.57(19)	129.5(2)
γ'	124.3(7), 123.9(7)	125.1(2)	125.2(5), 125.5(5)	125.1(5), 124.8(5)	124.5(3)	124.2(3)	129.3(2)	123.3(2), 123.8(2)	123.44(19), 123.1(2)	128.3(3)
δ	129.9(7), 129.8(7)	130.7(2)	131.4(5), 131.3(5)	132.1(5), 131.4(5)	131.5(4)	130.9(3)	126.5(2)	127.7(2), 128.0(2)	129.5(2), 129.1(2)	123.5(2)

[a] Parameters *a*–*e* and α–δ are defined as follows:





of a shallow boat; the central NCCN moiety is planar, with the Y and the apical carbon being out (Y > C) of that plane. The overall deviation from the plane is greatest for **YL^4** (**6**) and least for **YL^5** (**5c**, **9**); and for related compounds: **YL^1** (**3a**) > **YL^2** (**3b**) and **YL^2** (**5b**) > **YL^3** (**5a**). Each Y–N and Y–N′ bond length is closely similar for these compounds, the disparity being greatest for **YL^2** (**3b**) and **YL^5** (**9**). The average Y–N bond length in the **YL^5** dialdiminato complex **9** is by far the longest, unlike in the **YL^5** complex **5c**, and in both the C1–C2–C3 angle is the narrowest.

The structures of the isoleptic crystalline compounds [Y(μ-Cl)(L^x)(μ-Cl)$_2$Li(OEt$_2$)$_2$]$_2$ (**3a** (L^x = L^1; Fig. 1) and **3b** (L^x = L^2; Fig. 2) are similar, but there are significant differences as evident both from Table 1 (**L^1** *vs* **L^2**) and Table 2 [for endocyclic Y(**L^x**) data, see Table 1]. Each of **3a** and **3b** has a central YClY′Cl′ rhombus, but only **3b** is centrosymmetric. For both, the endocyclic angles are narrower at the Y atoms than at the Cl atoms. The four Y–Cl bond lengths in **3a** are closely similar, whereas the two in **3b** differ substantially; likewise the difference in the angles at Y/Y′ and Cl/Cl′ is greater in **3b** (*ca.* 11°) than **3a** (*ca.* 3°). The yttrium atoms are the spiro centres of YClY′Cl′ and YCl″LiCl‴ rings. Whereas

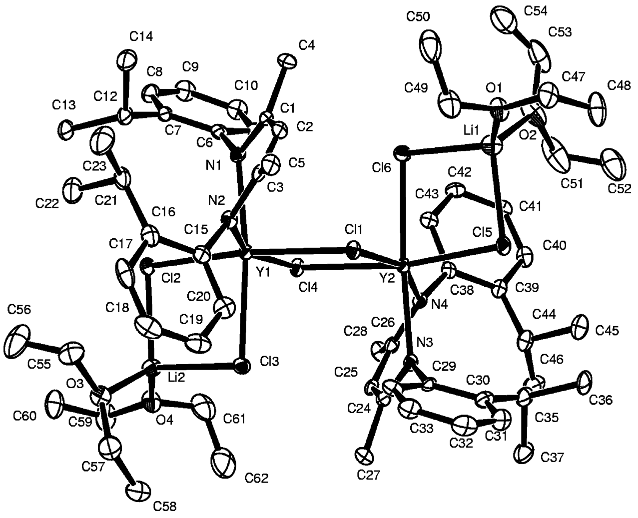


Fig. 1 Molecular structure of crystalline **3a** (20% thermal ellipsoids).

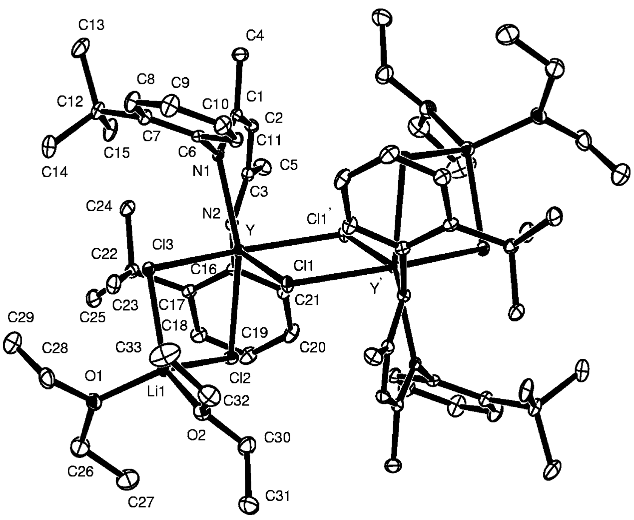


Fig. 2 Molecular structure of crystalline **3b** (20% thermal ellipsoids).

Table 2 Selected bond distances (Å) and angles (°) for the [Li(μ-Cl)$_2$Y(μ-Cl)]$_2$ moiety of **3a** and **3b**

3a				**3b**^{a}	
Y1–Cl1	2.705(2)	Y2–Cl1	2.684(2)	Y–Cl1′	2.6727(6)
Y1–Cl4	2.696(20	Y2–Cl4	2.707(2)	Y–Cl1	2.7462(6)
Y1–Cl2	2.611(2)	Y2–Cl5	2.616(2)	Y–Cl3	2.6169(6)
Y1–Cl3	2.660(2)	Y2–Cl6	2.660(2)	Y–Cl2	2.6294(6)
Li2–Cl2	2.391(15)	Li1–Cl5	2.391(17)	Li–Cl2	2.443(5)
Li2–Cl3	2.391(15)	Li1–Cl6	2.385(16)	Li–Cl3	2.384(4)
Y1–Cl1–Y2	101.55(6)	Y1–Cl4–Y2	101.17(6)	Y–Cl–Y′	104.48(2)
Cl1–Y1–Cl4	78.55(6)	Cl1–Y2–Cl4	78.73(6)	Cl1–Y–Cl1′	75.52(2)
Cl1–Y1–Cl2	171.26(7)	Cl4–Y2–Cl5	170.21(7)	Cl1′–Y–Cl3	158.09(2)
Cl1–Y1–Cl3	91.20(7)	Cl4–Y2–Cl6	88.60(7)	Cl1–Y–Cl3	83.341(19)
Cl2–Y1–Cl4	94.64(7)	Cl1–Y2–Cl5	96.30(7)	Cl1–Y–Cl2	87.37(2)
Cl3–Y1–Cl4	83.17(7)	Cl1–Y2–Cl6	89.10(7)	Cl1′–Y–Cl2	100.85(2)
Cl2–Y1–Cl3	83.17(7)	Cl5–Y2–Cl6	82.86(7)	Cl2–Y–Cl3	83.61(2)
Y1–Cl2–Li2	92.0(4)	Y2–Cl5–Li1	91.9(4)	Y–Cl2–Li	88.44(10)
Y1–Cl3–Li2	90.8(4)	Y2–Cl6–Li1	91.0(4)	Y–Cl3–Li	90.01(11)
Cl2–Li2–Cl3	94.1(5)	Cl5–Li1–Cl6	93.9(6)	Cl2–Li–Cl3	92.83(15)
N1–Y1–Cl1	96.22(16)	N3–Y2–Cl4	96.15(16)	N1–Y–Cl1	107.07(5)
N1–Y1–Cl4	91.30(17)	N3–Y2–Cl1	89.88(17)	N1–Y–Cl1′	94.75(5)
N1–Y1–Cl3	172.57(16)	N3–Y2–Cl6	174.83(16)	N1–Y–Cl2	161.05(5)
N1–Y1–Cl2	89.34(16)	N3–Y2–Cl5	92.23(16)	N1–Y–Cl3	85.92(5)
N2–Y1–Cl1	83.88(17)	N4–Y2–Cl4	85.61(16)	N2–Y–Cl1	158.67(5)
N2–Y1–Cl4	159.49(17)	N4–Y2–Cl1	159.90(17)	N2–Y–Cl1′	83.67(5)
N2–Y1–Cl3	101.77(19)	N4–Y2–Cl6	103.92(18)	N2–Y–Cl2	92.06(5)
N2–Y1–Cl2	103.77(17)	N4–Y2–Cl5	101.05(16)	N2–Y–Cl3	117.81(5)

[a] Symmetry transformations to generate equivalent atoms: ′ $-x + 1/2, -y + 3/2, -z$.

in **3a** the Y2Cl5Li1Cl6 ring is planar and the Y1Cl2Li2Cl3 ring is almost planar, in **3b** the YCl2LiCl3 ring is distinctly puckered, Cl3 being 0.72 Å out of the YCl2Li plane (*cf.*, for **3a**, Cl3 is 0.04 Å out of the Y1Cl2Li2 plane). Each of the yttrium atoms is at the centre of a distorted octahedron; the angle at the mutually transoid atoms for **3a** decrease in the sequence N1/Cl3 > Cl2/Cl1 ≫ N2/Cl4 for Y1 and N3/Cl6 > Cl4/Cl5 ≫ N4/Cl1 for Y2. In **3b** the mutually transoid pairs (N1/Cl2, N2/Cl1, Cl1′/Cl3) subtend at the yttrium atom more closely similar angles (*ca.* 159.5 ± 1.5°), whereas in **3a** they range from *ca.* 159.5 to *ca.* 172.5° for Y1 and *ca.* 159.5 to *ca.* 174.8° for Y2.

The structures of the isoleptic crystalline complexes [Y(μ-Cl)(**L**^{3}){(μ-Cl)Li(Lg)$_2$(μ-Cl)}]$_2$ [Lg = thf (**4a**), Fig. 3; OEt$_2$ (**4b**), Fig. 4a] are closely similar, as shown by the selected [excluding the Li(Lg)$_2$ fragments] geometrical parameters in Table 3; for endocyclic Y(**L**^{3}) data, see Table 1. As for **3a** and **3b**, the central core of **4a** and **4b** is a Y1Cl1Y2Cl2 rhombus; like for **3b**, the two Y–Cl bond lengths of **4a** and **4b** differ significantly (by *ca.* 0.07 Å). Essentially orthogonal to this plane is an eight-membered macrocycle, Li1Cl3Y1Cl4Li2Cl6Y2Cl5, shown for **4b** in Fig. 4b. As evident from the latter, this ring approximates to a boat with the atoms Li1 and Li2 out of the only slightly puckered Cl3Y1Cl4Cl6Y2Cl5 moiety (**4a**, the Cl1 and Cl2 are transposed relative to **4b**). Each of the Y1 and Y2 atoms is at the centre of a strongly distorted octahedron, with the atoms N1/Cl2, N2/Cl1 and Cl3/Cl4 being mutually transoid with respect to Y1 (at 166 ± 1.9°) and N3/Cl1, N4/Cl2 and Cl5/Cl6 with respect to Y2 (at 167 ± 2.5°) for **4a** (*cf.* 164 ± 1.5° for **4b**).

The structures of the isoleptic crystalline complexes [Y(**L**^{x})Cl$_2$(thf)$_2$] [**L**^{x} = **L**^{3} (**5a**), **L**^{2} (**5b**), **L**^{5} (**5c**)] are shown in Fig. 5, 6 and 7, respectively. Selected geometric parameters for the N1N2YCl1Cl2O1O2 fragments are shown in Table 4 [for endocyclic Y(**L**^{x}) data, see Table 1]. The pairs of Y–O and Y–Cl bonds are closely similar for **5b** and **5c**, but for **5a** the former are significantly longer and the latter shorter. The yttrium atom in each is at the centre of a severely distorted octahedron. The mutually transoid atoms are N1/O1, N2/O2 and Cl1/Cl2 for **5a** and **5b**, while for **5c** the O1 and O2 atoms are transposed; *trans* angles subtended at Y range from *ca.* 167 ± 8° (**5a**), 171 ± 2° (**5b**) and 170 ± 6° (**5c**). The geometric parameters of **5a** are similar to those for [Yb(**L**^{2})Cl$_2$(dme)].[20]

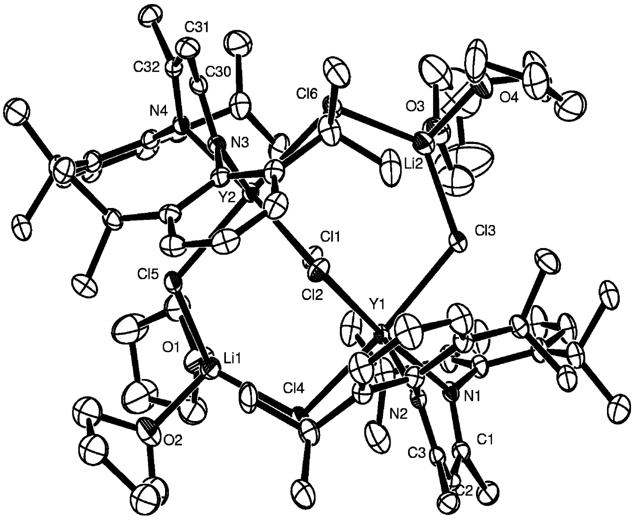


Fig. 3 Molecular structure of crystalline **4a** (20% thermal ellipsoids).

The structures of the crystalline five-coordinate bis(β-diketiminato)yttrium compounds [Y(**L**^{4})$_2$Cl] (**6**) and [Y(**L**^{1})$_2$(OBu^t)] (**7**) are illustrated in Fig. 8 and 9, respectively; selected exocyclic geometric parameters for the YXN1N2N3N4

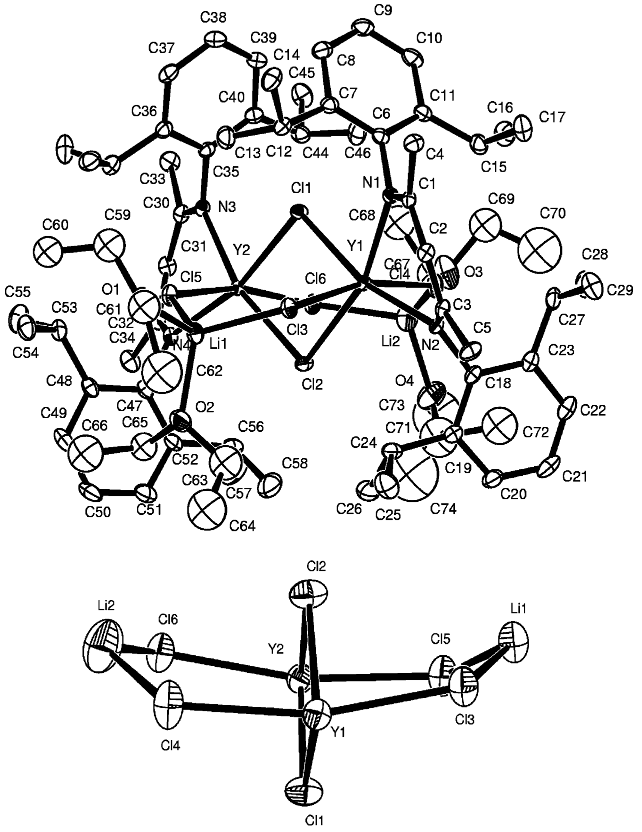


Fig. 4 (a) Molecular structure of crystalline **4b** (20% thermal ellipsoids) (top); (b) ORTEP representation of the Li1Cl3Y1Cl4Li2Cl6Y2Cl5 fragment of **4b** (bottom).

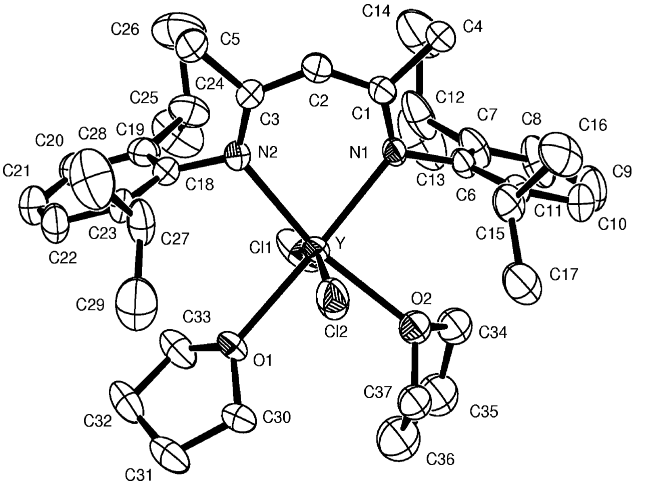


Fig. 5 Molecular structure of crystalline **5a** (20% thermal ellipsoids).

fragment of each are listed in Table 5 [for endocyclic $Y(\mathbf{L}^x)_2$ data, see Table 1]. The data for **6** are similar to those of $[Nd(\mathbf{L}^4)_2Cl]$,[21] allowing for the larger size of Nd^{3+} than Y^{3+}. The yttrium atom in both **6** and **7** is in a distorted trigonal bipyramid having N1 and N4 as the axial atoms.

The structure of the crystalline centrosymmetric complex $[Y(X)(\mu\text{-}Cl)(O)(\mu\text{-}Cl)_2Li]_2$ (**8**) is shown in Fig. 10. Selected geometric parameters for its core (X = C), together with its isoleptic analogue **J** (X = N) are listed in Table 6. The YCl2LiCl3 ring (as well as the YCl1Y′Cl1′ ring) is planar with the endocyclic angles centred at Y ≫ Cl2 > Cl3 > Li (ranging from *ca.* 84° at Y and *ca.* 94° at Li). Each yttrium atom is at the centre of a distorted octahedron, the *trans* angles being *ca.* 163.5 ± 4.5°; the angles at mutually transoid atoms decrease in the sequence C/Cl1′ > O1/Cl2 > Cl1/Cl3.

The structure of the crystalline centrosymmetric complex $[Y(\mathbf{L}^5)\{N(H)C_6H_3Pr^i{}_2\text{-}2,6\}(thf)(\mu_3\text{-}Cl)_2K]_2$ (**9**) is shown in

Table 3 Selected bond distances (Å) and angles (°) for the $[(N)(N)(\mu\text{-}Cl)Y(\mu\text{-}Cl)Li(\mu\text{-}Cl)]_2$ fragment of **4a** and **4b**

4a				**4b**			
Y1–Cl1	2.7543(13)	Y2–Cl1	2.7590(13)	Y1–Cl1	2.6793(14)	Y2–Cl1	2.6766(13)
Y1–Cl2	2.6740(13)	Y2–Cl2	2.6811(14)	Y1–Cl2	2.7397(14)	Y2–Cl2	2.7554(14)
Y1–Cl3	2.6189(15)	Y2–Cl6	2.6129(14)	Y1–Cl3	2.6326(15)	Y2–Cl5	2.6223(15)
Y1–Cl4	2.6180(14)	Y2–Cl5	2.6088(14)	Y1–Cl4	2.6286(15)	Y2–Cl6	2.6223(15)
Li2–Cl3	2.353(13)	Li1–Cl5	2.329(10)	Li1–Cl3	2.339(10)	Li2–Cl4	2.385(12)
Li1–Cl4	2.342(10)	Li2–Cl6	2.330(11)	Li1–Cl5	2.361(10)	Li2–Cl6	2.388(13)
Y1–Cl1–Y2	100.12(4)	Cl3–Li2–Cl6	118.9(5)	Y1–Cl1–Y2	102.66(4)	Cl3–Li1–Cl5	113.7(4)
Y1–Cl2–Y2	104.25(4)	Cl4–Li1–Cl5	122.6(4)	Y1–Cl2–Y2	99.10(4)	Cl4–Li2–Cl6	117.1(5)
Cl1–Y1–Cl2	77.91(4)	Cl1–Y2–Cl2	77.71(4)	Cl1–Y1–Cl2	79.20(4)	Cl1–Y2–Cl2	78.97(4)
Cl1–Y1–Cl3	83.50(5)	Cl1–Y2–Cl6	85.43(4)	Cl1–Y1–Cl3	99.21(5)	Cl2–Y2–Cl5	83.54(5)
Cl1–Y1–Cl4	84.44(4)	Cl1–Y2–Cl5	82.90(4)	Cl1–Y1–Cl4	87.41(5)	Cl2–Y2–Cl6	84.04(5)
Cl2–Y1–Cl3	89.09(5)	Cl2–Y2–Cl6	96.28(5)	Cl2–Y1–Cl3	84.59(5)	Cl1–Y2–Cl5	87.10(5)
Cl2–Y1–Cl4	97.11(4)	Cl2–Y2–Cl5	88.96(5)	Cl2–Y1–Cl4	84.62(5)	Cl1–Y2–Cl6	95.76(5)
Cl3–Y1–Cl4	164.98(5)	Cl5–Y2–Cl6	165.90(5)	Cl3–Y1–Cl4	166.06(5)	Cl5–Y2–Cl6	166.48(5)
Y1–Cl3–Li2	119.1(3)	Y2–Cl6–Li2	115.0(3)	Y1–Cl3–Li1	118.6(2)	Y2–Cl5–Li1	124.9(2)
Y1–Cl4–Li1	109.9(2)	Y2–Cl5–Li1	114.5(2)	Y1–Cl4–Li2	121.9(3)	Y2–Cl6–Li2	118.4(3)
N1–Y1–Cl1	113.45(11)	N3–Y2–Cl2	88.01(10)	N1–Y1–Cl1	84.26(11)	N3–Y2–Cl1	88.09(11)
N1–Y1–Cl2	167.47(10)	N3–Y2–Cl1	164.89(10)	N1–Y1–Cl2	163.05(11)	N3–Y2–Cl2	165.02(11)
N1–Y1–Cl3	87.12(10)	N3–Y2–Cl6	91.32(10)	N1–Y1–Cl3	89.23(11)	N3–Y2–Cl6	89.84(11)
N1–Y1–Cl4	89.49(10)	N3–Y2–Cl5	101.96(10)	N1–Y1–Cl4	103.51(11)	N3–Y2–Cl5	103.49(11)
N2–Y1–Cl1	163.72(9)	N4–Y2–Cl2	169.51(10)	N2–Y1–Cl1	165.84(11)	N4–Y2–Cl1	167.06(12)
N2–Y1–Cl2	87.82(10)	N4–Y2–Cl1	112.02(10)	N2–Y1–Cl2	113.16(11)	N4–Y2–Cl2	112.61(12)
N2–Y1–Cl3	104.28(10)	N4–Y2–Cl6	88.62(10)	N2–Y1–Cl3	89.18(11)	N4–Y2–Cl6	91.37(11)
N2–Y1–Cl4	89.66(10)	N4–Y2–Cl5	88.44(10)	N2–Y1–Cl4	86.96(11)	N4–Y2–Cl5	88.49(11)

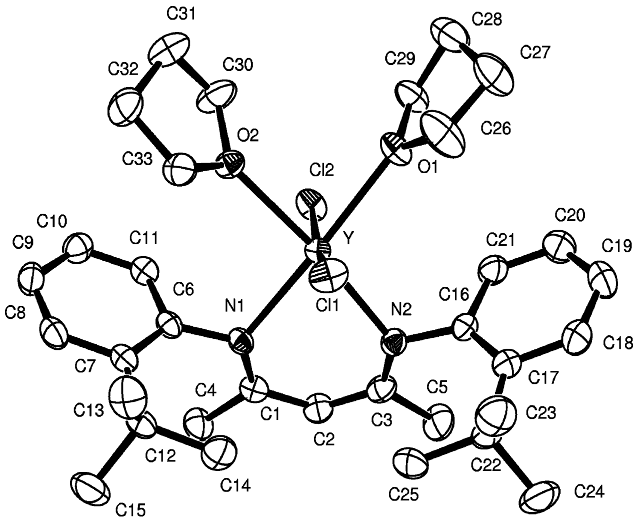


Fig. 6 Molecular structure of crystalline **5b** (50% thermal ellipsoids).

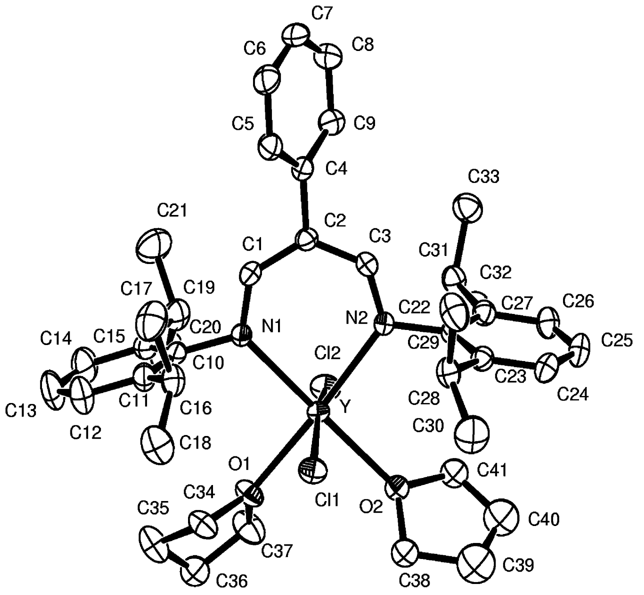


Fig. 7 Molecular structure of crystalline **5c** (50% thermal ellipsoids).

Fig. 11a. Selected geometric data are listed in Table 7 [for endocyclic **YL**^{5} data, see Table 1]. The eight atoms comprising the central core is shown in Fig. 11b, which contains two planar rings: the outer KYK′Y′ and the inner Cl2Cl1Cl2′Cl1′; each Cl atom bridges one Y and two K atoms. Each six-coordinate yttrium

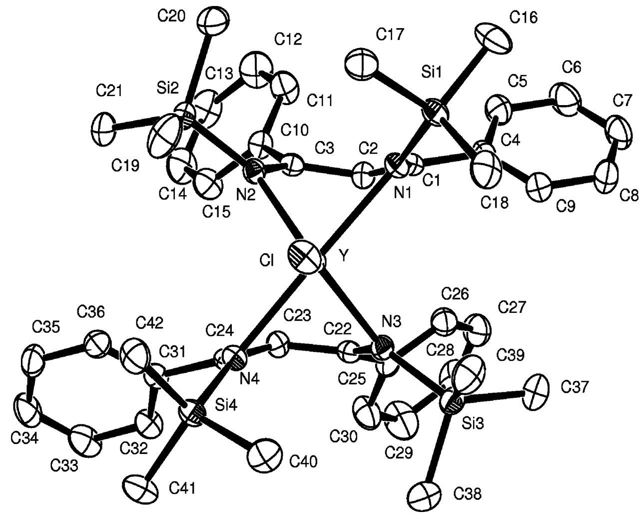


Fig. 8 Molecular structure of crystalline **6** (50% thermal ellipsoids).

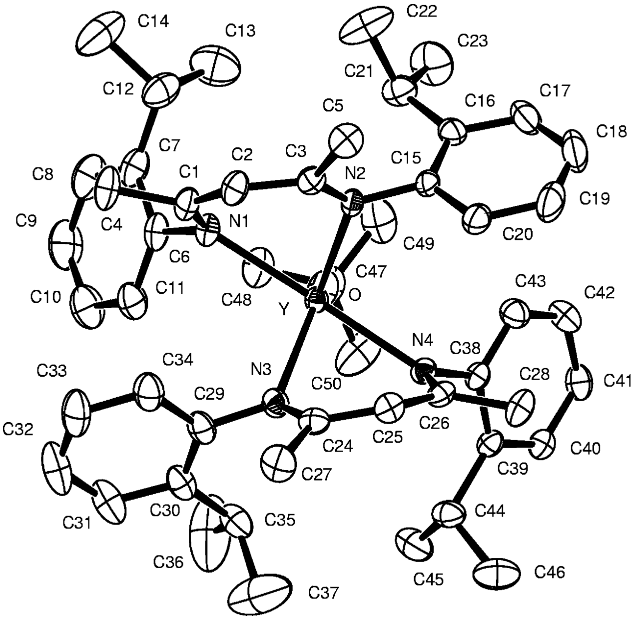


Fig. 9 Molecular structure of crystalline **7** (50% thermal ellipsoids).

Table 4 Selected bond distances (Å) and angles (°) for the N1N2YCl1Cl2O1O2 fragment of **5a**, **5b** and **5c**

	5a	**5b**	**5c**
Y–Cl1	2.5487(14)	2.5773(7)	2.5724(6)
Y–Cl2	2.5631(13)	2.5892(7)	2.5823(6)
Y–O1	2.426(3)	2.4015(18)	2.3586(16)
Y–O2	2.433(5)	2.3790(18)	2.381(4)
N2–Y–Cl1, N2–Y–Cl2	96.76(8), 98.76(8)	93.51(6), 93.42(6)	99.87(4), 92.75(4)
N1–Y–Cl1, N1–Y–Cl2	101.64(8), 94.75(7)	100.50(5), 88.36(5)	92.63(4), 99.69(5)
N1–Y–O1, N1–Y–O2	175.55(10), 88.33(13)	171.02(7), 95.68(7)	96.45(6), 176.80(13)
N2–Y–O1, N2–Y–O2	97.03(10), 168.15(15)	101.53(7), 173.78(7)	175.88(6), 97.70(13)
Cl1–Y–Cl2	159.14(5)	169.65(2)	163.63(2)
Cl1–Y–O1, Cl1–Y–O2	81.89(8), 87.21(14)	88.42(5), 83.99(5)	83.29(4), 84.83(10)
Cl2–Y–O1, Cl2–Y–O2	82.44(8), 80.39(13)	82.67(5), 89.85(5)	84.65(4), 83.18(10)

Table 5 The Y–X bond distances (Å) and angles (°) for the Y(X)N1N2N3N4 fragment of **6** (X = Cl) and **7** (X = O)

	6[a]	**7**[b]
Y–X	2.5566(6)	2.015(2)
N1–Y–N3	97.31(7)	93.96(7)
N1–Y–N4	178.48(7)	166.65(6)
N1–Y–X	89.11(5)	96.72(6)
N2–Y–X	114.29(5)	122.18(6)
N2–Y–N4	101.56(7)	95.03(6)
N2–Y–N3	125.66(7)	108.96(6)
N4–Y–X	89.81(5)	96.62(6)
N3–Y–X	120.04(5)	128.87(7)

[a] X = Cl. [b] X = O.

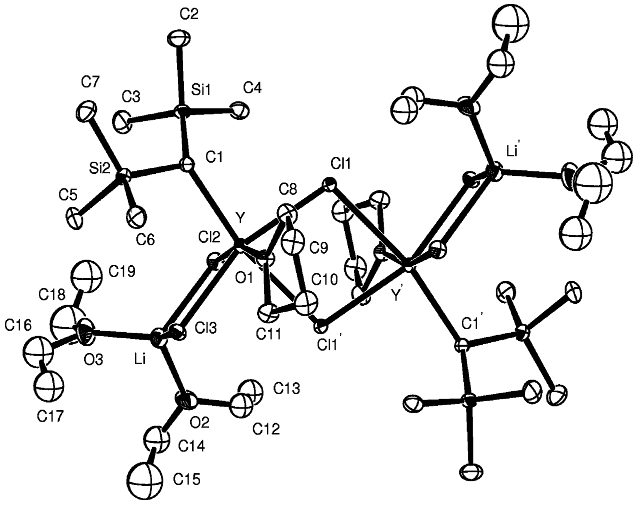


Fig. 10 Molecular structure of crystalline **8** (20% thermal ellipsoids).

atom is at the centre of a distorted octahedron; the *trans* angles range from *ca.* 162.5° (N2/N3) to *ca.* 170° (N1/Cl1), the third mutually *trans*-pair is O1/Cl2 (N1 and N2 belong to the $\mathbf{L}^5$ ligand).

In conclusion, the synthesis and characterisation of eleven new crystalline Y complexes (**3a**, **3b**, **4a**, **4b**, **5a**, **5b**, **5c**, **6**, **7**, **8**, **9**) is presented. Except for **8** and **9**, they are (κ^2-β-diiminato)yttrium chlorides, obtained from YCl_3 and an alkali metal β-diiminate M[$\mathbf{L}^x$], for which $\mathbf{L}^x$ = $\mathbf{L}^1$–$\mathbf{L}^5$: $[\{N(R)C(Me)\}_2CH]^-$ [R = $C_6H_4Pr^i$-2 ($\mathbf{L}^1$); R = $C_6H_4Bu^t$-2 ($\mathbf{L}^2$); R = $C_6H_3Pr^i_2$-2,6 ($\mathbf{L}^3$)], $[\{N(SiMe_3)C(Ph)\}_2CH)]^-$ ($\mathbf{L}^4$) and $[\{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2CPh]^-$ ($\mathbf{L}^5$). Several have unusual structures: $[Y(\mu\text{-}Cl)(\mathbf{L}^x)(\mu\text{-}Cl)_2Li(OEt_2)_2]_2$ [$\mathbf{L}^x$ = $\mathbf{L}^1$ (**3a**), $\mathbf{L}^2$ (**3b**)], $[Y(\mu\text{-}Cl)(\mathbf{L}^3)(\mu\text{-}Cl)Li(thf)_2(\mu\text{-}Cl)]_2$ (**4a**) or its (OEt_2) analogue (**4b**), $[Y\{(CH(SiMe_3)_2)(thf)(\mu\text{-}Cl)_2Li(OEt_2)_2\}_2(\mu\text{-}Cl)]_2$ (**8**) and $[Y(\mathbf{L}^5)\{N(H)C_6H_3Pr^i_2\text{-}2,6\}(\mu_3\text{-}Cl)_2K]_2\cdot 4Et_2O$ (**9**). Equivalent portions of YCl_3 and Na[$\mathbf{L}^x$] gave $[Y(\mathbf{L}^3)Cl_2(thf)_2]$ (**5a**) and $[Y(\mathbf{L}^5)Cl_2(thf)_2]$ (**5c**) but, unexpectedly, $[YCl(\mathbf{L}^4)_2]$ (**6**). The compound $[Y(\mathbf{L}^1)_2(OBu^t)]$ (**7**) is the first bis(β-diketiminato)metal (M) alkoxide (M = a group 3 or 4f metal). Formation of **8** *via* **3a** and $2Li[CH(SiMe_3)_2]$ is remarkable in that displacement by the carbanion of $\mathbf{L}^1$ rather than Cl^- was preferred.

Table 6 Selected bond distances (Å) and angles (°) for the $[M(X)(\mu\text{-}Cl)(O)(\mu\text{-}Cl)_2Li]_2$ fragment of **8** (X = C) and **J** (X = N)[13]

	8 (M = Y, X = C)	**J** (M = Sm, X = N)[13]
M–O1	2.340(3)	2.421(3)
M–X	2.412(5)	2.284(2)
M–Cl1, M–Cl1′	2.6665(13), 2.8107(12)	2.7276(7), 2.8937(7)
M–Cl2, M–Cl3	2.6169(12), 2.6272(13)	2.6928(8), 2.7276(7)
Li–Cl2, Li–Cl3	2.427(11), 2.368(10)	2.347(9), 2.359(7)
M–Cl1–M′	102.56(4)	102.92(2)
Cl1–M–Cl1′	77.44(4)	77.08(2)
X–M–O1	94.03(15)	93.22(10)
X–M–Cl1, X–M–Cl1′	91.34(12), 168.17(12)	97.12(6), 171.11(8)
X–M–Cl2, X–M–Cl3	99.17(12), 105.86(12)	102.33(6), 105.42(8)
O1–M–Cl1, O1–M–Cl1′	83.61(9), 81.13(9)	82.85(5), 79.48(5)
O1–M–Cl2, O1–M–Cl3	164.39(9), 84.63(9)	160.73(5), 88.35(5)
Cl1–M–Cl2, Cl1′–M–Cl2	104.27(4), 87.39(4)	99.21(3), 82.67(2)
Cl1–M–Cl3, Cl1′–M–Cl3	159.77(4), 84.53(4)	159.06(3), 82.35(3)
M–Cl2–Li, M–Cl3–Li	90.7(2), 91.7(3)	88.73(3), 89.21(3)
Cl2–Li–Cl3	93.8(3)	98.9(3)
Cl2–M–Cl3	83.77(4)	83.02(3)

Symmetry transformation to generate equivalent atoms for **8**: ′ $-x + 1, -y + 1, -z + 1$.

Experimental

General remarks

All manipulations were performed under argon using standard Schlenk techniques. Hexane and toluene were dried using sodium–potassium alloy. Diethyl ether and thf were dried and distilled from sodium–benzophenone and stored over a sodium mirror under argon. Deuterated solvents (C_6D_6, C_5D_5N and C_4D_8O) were freeze–thaw degassed and stored over dried 4 Å molecular sieves under an argon atmosphere. The compounds $Li[CH(SiMe_3)_2]$,[30] $H[\{N(C_6H_4R\text{-}2)C(Me)\}_2CH]$ [R = Pr^i (**1a**), Bu^t (**1b**)],[10] $Li[\{N(C_6H_3Pr^i_2\text{-}2,6)C(Me)\}_2CH]$ (**2c**),[12] Na[$\mathbf{L}^5$][31] and $K[N(H)C_6H_3Pr^i_2\text{-}2,6]$[32] were prepared as described in the literature

Table 7 Selected bond distances (Å) and angles (°) for the $[NNY\{N(H)C_6H_3Pr^i_2\text{-}2,6\}(thf)(\mu\text{-}Cl)_2K]_2$ fragment of **9**

Y–N3	2.259(2)	N3–Y–N1	91.81(8)	Cl1–Y–O1	82.99(5)	Cl1′–K–Cl2	68.83(2)
Y–Cl1	2.6134(7)	N3–Y–N2	162.65(8)	Cl2–Y–O1	165.17(5)	Cl1′–K–Cl2′	68.26(2)
Y–Cl2	2.6093(7)	N3–Y–Cl1	97.47(7)	Cl1–Y–Cl2	85.68(2)	Y–Cl1–K	82.67(2)
Y–O1	2.435(2)	N3–Y–Cl2	84.66(7)	N3–K–Cl1	69.29(5)	Y–Cl1–K′	98.80(3)
N3–C34	1.395(4)	N3–Y–O1	106.26(8)	N3–K–Cl2	61.76(5)	Y–Cl2–K	83.66(2)
K–Cl1	3.332(1)	N1–Y–O1	90.61(7)	N3–K–Cl1′	128.07(5)	Y–Cl2–K′	98.45(3)
K–Cl2	3.285(1)	N2–Y–O1	86.14(7)	N3–K–Cl2′	137.03(5)	K–Cl1–K′	76.21(2)
K–Cl1′	3.156(1)	N1–Y–Cl1	169.90(6)	Cl1–K–Cl2	64.92(2)	K–Cl2–K′	76.64(2)
K–Cl2′	3.173(1)	N2–Y–Cl1	96.05(5)	Cl1′–K–Cl2′	68.26(2)	Y–N3–C34	163.8(2)
		N1–Y–Cl2	99.21(6)	Cl1–K–Cl1′	103.79(2)		
		N2–Y–Cl2	85.57(5)	Cl1–K–Cl2′	68.04(2)		

Symmetry transformation used to generate equivalent atoms: ′ $-x + 1, -y + 1, -z$.

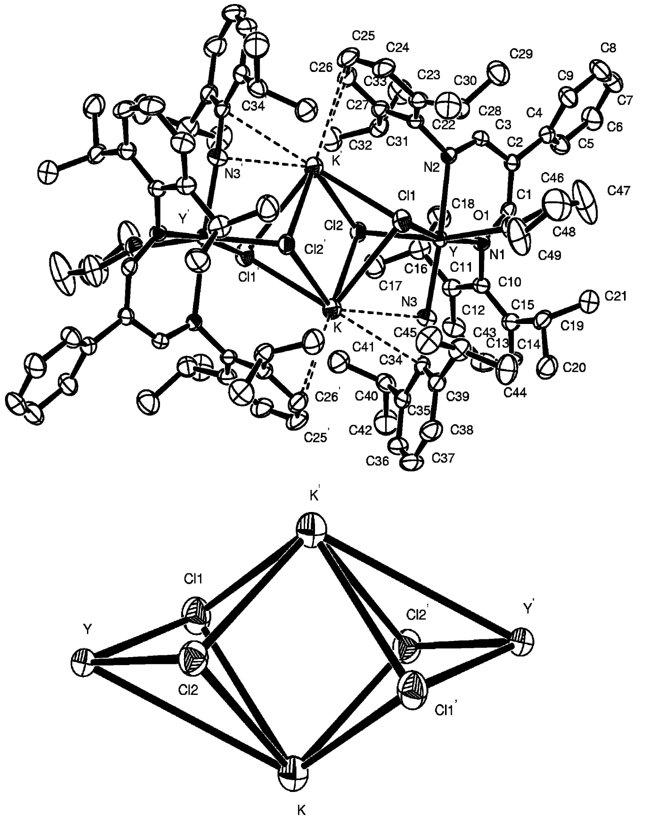


Fig. 11 (a) Molecular structure of crystalline **9** (50% thermal ellipsoids) (top); (b) ORTEP representation of the central KYK′Y′Cl1Cl1′Cl2Cl2′ core of **9** (bottom).

and LiBu, K[N(SiMe$_3$)$_2$], K[OBu^t] and YCl$_3$ were commercial samples (Aldrich). The NMR spectra were recorded on a Bruker DPX 300 (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C and 116.6 MHz for ^{7}Li) and referenced externally (^{7}Li, using LiCl) or internally to the residual solvent resonances. Unless otherwise stated, all NMR spectra were measured at 293 K in C$_6$D$_6$ and other than ^{1}H were proton-decoupled. Melting points were taken in sealed capillaries. Elemental analyses were determined by Medac Ltd., Brunel University.

Preparations

The lithium β-diketiminates Li[{N(C$_6$H$_4$R-2)C(Me)}$_2$CH] [R = Pr^i (2a), Bu^t (2b)]. The precursor β-diketimines **1a** (Found: C, 82.3; H, 9.01; N, 8.30%. $C_{23}H_{30}N_2$ requires: C, 82.6; H, 9.04; N, 8.37%) and **1b** (Found: C, 82.4; H, 9.26; N, 7.44%. $C_{25}H_{34}N_2$ requires: C, 82.9; H, 9.45; N, 7.73%) were prepared by literature procedures.[12] For **1a**: ^{1}H-NMR: δ 1.13 (d, 12 H, CH*Me*$_2$), 1.76 (s, 6 H, CCH$_3$), 3.35 (hept, 2 H, C*H*Me$_2$), 4.87 (s, 1 H, CH), 6.84 (m, 2 H, C$_6$H$_4$), 7.01 (m, 4 H, C$_6$H$_4$), 7.18 (m, 2 H, C$_6$H$_4$), 12.87 ppm (s, 1 H, NH); ^{13}C-NMR: δ 20.77 (CH$_3$), 23.34 (CH*Me*$_2$), 28.47 (*C*HMe$_2$), 97.19 (CH); 124.15, 124.69, 125.95, 126.23, 141.63, 143.81 (C$_6$H$_4$), 160.08 ppm (CN). For **1b**: ^{1}H-NMR: δ 1.37 (s, 18 H, CMe$_3$), 1.74 (s, 6 H, CH$_3$), 4.90 (s, 1 H, CH); 6.80 (d, 1 H), 6.82 (d, 1 H), 6.95 (d, $J = 1.46$ Hz, 1 H), 6.98 (d, 1 H), 7.02 (d, 1 H), 7.05 (d, 1 H), 7.29 (d, 1 H), 7.32 (d, 1 H) (C$_6$H$_4$), 12.88 ppm (s, 1 H, NH); ^{13}C-NMR: δ 21.14 (CH$_3$), 30.61 (C*Me*$_3$), 35.65 (*C*Me$_3$), 99.12 (CH); 124.12, 126.26, 128.33, 142.21, 144.22 (C$_6$H$_4$), 167.36 ppm (CN).

*Compound **2b**.* n-Butyllithium (8.6 cm^3 of a 1.6 mol dm^{-3} solution in C$_6$H$_{14}$) was added dropwise to a solution of **1b** (5.0 g, 13.81 mmol) in n-hexane (40 cm^3) at 0 °C. The mixture was stirred at 20 °C for 2 h, then cooled to 0 °C and filtered. The pale yellow **2b** (4.5 g, 89%) (Found: C, 81.1; H, 8.98; N, 7.24%. $C_{25}H_{33}LiN_2$ requires: C, 81.5; H, 9.03; N, 7.60%), mp 113–115 °C, was obtained from the precipitate after washing with cold hexane (3 × 10 cm^3) and drying *in vacuo*. ^{1}H-NMR: δ 1.32 (s, 18 H, CMe$_3$), 1.85 (s, 6 H, CH$_3$), 4.79 (s, 1 H, CH); 6.66 (d, 2 H), 7.03 (m, 2 H), 7.09 (d, 2 H), 7.40 ppm (d, 2 H, C$_6$H$_4$); ^{13}C-NMR: δ 21.13 (CH$_3$), 31.36 (C*Me*$_3$), 35.48 (*C*Me$_3$), 94.65 (CH); 122.51, 126.39, 126.92, 141.93, 153.57 (C$_6$H$_4$), 163.22 ppm (CN); ^{7}Li-NMR: δ −2.14 ppm.

*Compound **2a**.* Compound **2a** (86%) (Found: C, 80.6; H, 8.31; N, 8.02%. $C_{23}H_{29}LiN_2$ requires: C, 81.2; H, 8.59; N, 8.23%) was obtained from **1a** + LiBu^n in a similar fashion to **2b**. ^{1}H-NMR: δ 1.11 (d, 12 H, CH*Me*$_2$), 1.84 (s, 6 H CH$_3$), 3.32 (hept, 2 H, C*H*Me$_2$), 4.80 (s, 1 H, CH); 6.76 (m, 2 H), 7.04 (m, 4 H), 7.23 ppm (d, 2 H, C$_6$H$_4$); ^{13}C-NMR: δ 20.77 (CH$_3$), 23.38 (CH*Me*$_2$), 28.01 (*C*HMe$_2$), 93.96 (CH); 122.92, 124.81, 125.84, 126.06, 141.18, 152.13 (C$_6$H$_4$), 163.49 ppm (CN); ^{7}Li-NMR: δ −2.10 ppm.

The potassium β-diketiminate (K[L^1]). Potassium bis(trimethylsilyl)amide (1.60 g, 8.02 mmol) was added in small portions to a solution of the β-diketimine **1a** (2.68 g, 8.02 mmol) in toluene (35 cm^3) at 0 °C. The resulting mixture was stirred for 12 h at *ca.* 20 °C, then cooled to −25 °C and filtered. The precipitate was washed with hexane (3 × 15 cm^3) and dried *in vacuo* yielding the off-white powder (K[L^1]) (2.57 g, 86%) (Found: C, 74.4; H, 7.68; N, 7.36%. $C_{23}H_{29}KN_2$ requires: C, 74.1; H, 7.85; N, 7.52%). ^{1}H-NMR: δ 1.08 (d, 12 H, CH*Me*$_2$), 1.76 (s, 6 H, CH$_3$), 3.26 (hept, 2 H, C*H*Me$_2$), 4.68 (s, 1 H, CH); 6.72 (m, 2 H), 6.98 (m, 4 H), 7.08 ppm (d, 2 H, C$_6$H$_4$); ^{13}C-NMR: δ 20.07 (CH$_3$), 22.98 (CH*Me*$_2$), 28.00 (*C*HMe$_2$), 91.56 (CH); 122.63, 124.36, 125.57, 125.95, 141.02, 152.01 (C$_6$H$_4$), 161.38 ppm (CN).

The compounds [Y(μ-Cl){(N(C$_6$H$_4$R-2)C(Me))$_2$CH}(μ-Cl)$_2$Li(OEt$_2$)$_2$]$_2$ [R = Pr^i (3a), Bu^t (3b)]. Yttrium(III) chloride (0.88 g, 4.53 mmol) was added in small portions to a solution of **2a** (1.54 g, 4.53 mmol) in diethyl ether (30 cm^3) at −30 °C. The resulting mixture was warmed slowly to *ca.* 20 °C and stirred for 12 h. The volatiles were removed *in vacuo* and the residue was extracted into diethyl ether (40 cm^3). The filtered extract was concentrated *in vacuo* to *ca.* 15 cm^3 and stored at −25 °C to yield colourless crystals of **3a** (2.19 g, 71%) (Found: C, 54.0; H, 7.14; N, 4.08%. $C_{62}H_{98}Cl_6Li_2N_4O_4Y_2$ requires: C, 54.4; H, 7.22; N, 4.10%), mp 77 °C (decomp.). ^{1}H-NMR: δ 1.04 (t, 12 H, Et$_2$O), 1.14 (d, 12 H, CH*Me*$_2$), 1.68 (s, 6 H, CH$_3$), 3.23 (q, 8 H, Et$_2$O), 3.34 (hept, 2 H, C*H*Me$_2$), 5.09 (s, 1 H, CH), 6.66 (m, br, 4 H, C$_6$H$_4$), 7.24 ppm (br, 4 H, C$_6$H$_4$); ^{13}C-NMR: δ 15.29 (Et$_2$O), 20.73 (CH$_3$), 22.49 (CH*Me*$_2$), 29.32 (*C*HMe$_2$), 98.04 (CH); 124.12, 124.49, 125.95, 126.28, 140.63, 143.82 (C$_6$H$_4$), 164.26 ppm (CN); ^{7}Li-NMR: δ −2.35 ppm.

*Compound **3b**.* (3.05 g, 63%) (Found: C, 55.2; H, 7.42; N, 4.08%. $C_{66}H_{106}Cl_6Li_2N_4O_4Y_2$ requires: C, 55.7; H, 7.50; N, 3.93%), mp 71 °C (decomp.). ^{1}H-NMR: δ 1.07 (t, 12 H, Et$_2$O), 1.70 (s, 18 H, CMe$_3$), 1.75 (s, 6 H, CH$_3$), 3.23 (q, 8 H, Et$_2$O), 5.10 (s, 1 H, CH), 6.64 (m, br, 4 H, C$_6$H$_4$), 7.26 ppm (br, 4 H, C$_6$H$_4$); ^{13}C-NMR: δ 15.52 (Et$_2$O), 25.39 (CH$_3$), 31.66 (C*Me*$_3$), 33.65 (*C*Me$_3$), 65.82 (Et$_2$O), 98.35 (CH); 125.28, 125.58, 130.59, 130.93, 137.84, 140.56 (C$_6$H$_4$), 166.62 ppm (CN); ^{7}Li-NMR: δ 0.75 ppm.

The compounds [Y(μ-Cl){(N($C_6H_3Pr^i_2$-2,6)C(Me))$_2$CH}{(μ-Cl)Li(Lg)$_2$(μ-Cl)}]$_2$ [Lg = thf (4a), OEt_2 (4b)]. Yttrium(III) chloride (0.30 g, 1.55 mmol) was added in small portions to a solution of lithium β-diketiminate Li[**L**^{3}] (0.66 g, 1.55 mmol) in diethyl ether (20 cm^3) at −30 °C. The mixture was allowed to warm to *ca.* 20 °C and stirred for 18 h, whereafter the volatiles were removed *in vacuo*. The residue was extracted into hexane (40 cm^3)–thf (10 cm^3). The filtered extract was concentrated to *ca.* 15 cm^3 and stored at–25 °C, yielding colourless blocks of **4a** (0.61 g, 52%) (Found: C, 57.4; H, 7.06; N, 3.69%. $C_{74}H_{114}Cl_6Li_2N_4O_4Y_2$ requires: C, 58.2; H, 7.52; N, 3.67%), mp 126 °C (decomp.). ^{1}H-NMR: δ 0.87 (t, 8 H, thf), 1.16 (d, 12 H, J = 6.59, CH*Me*$_2$), 1.28 (d, 12 H, J = 6.59 Hz, CH*Me*$_2$), 1.90 (s, 6 H, CH_3), 2.67 (m, 8 H, thf), 3.41 (hept, 4 H, C*H*Me$_2$), 5.00 (s, 1 H, CH), 7.07 ppm (m, br, 6 H, C_6H_3); ^{13}C-NMR: δ 23.14 (CH_3), 23.46 (thf), 24.40 (CH*Me*$_2$), 24.70 (CH*Me*$_2$), 28.06 (*C*HMe$_2$), 67.86 (thf), 92.89 (CH); 122.99, 123.21, 140.81, 149.48 (C_6H_3), 163.48 ppm (CN); ^{7}Li-NMR: δ 0.58 ppm.

A solution of the lithium β-diketiminate **2c** (1.30 g, 3.06 mmol) in diethyl ether (20 cm^3) was added to a suspension of YCl_3 (0.62 g, 3.18 mmol) in Et_2O at *ca.* 20 °C. The mixture was stirred for 2 d, then filtered. The light brown filtrate was concentrated to *ca.* 10 cm^3 and stored at −27 °C, furnishing colourless crystals of **4b** (1.22 g, 51%) (Found: C, 57.9; H, 8.30; N, 3.64%. $C_{74}H_{122}Cl_6Li_2N_4O_4Y_2$ requires: C, 58.0; H, 8.41; N, 3.56%), mp 121–122 °C (decomp.). ^{1}H-NMR: δ 1.16 (d, 24 H, CH*Me*$_2$), 1.20 (d, 24 H, CH*Me*$_2$), 1.62 (s, 12 H, CH_3), 3.33 (m, 8 H, OEt_2), 5.07 (s, 2 H, CH), 7.11–7.24 ppm (m, 12 H, C_6H_3); ^{13}C-NMR: δ 15.0 (OEt_2), 23.46 (CH_3), 24.9 (CH*Me*$_2$), 25.3 (CH*Me*$_2$), 28.9 (*C*HMe$_2$), 65.8 (OEt_2), 99.1 (CH); 124.4, 126.4, 143.1, 143.9 (C_6H_3), 167.8 ppm (CN),^{7}Li-NMR: δ −2.34 ppm.

The dichloroyttrium β-diketiminates [YCl_2{(N(R^1)C(R^2))$_2$-CR^3}(thf)$_2$] [R^2 = Me, R^3 = H and R^1 = $C_6H_3Pr^i_2$-2,6 (5a) or $C_6H_4Bu^t$-2 (5b); R^1 = $C_6H_3Pr^i_2$-2,6, R^2 = H, R^3 = Ph (5c)]. Yttrium(III) chloride (0.38 g, 1.95 mmol) was added in small portions to a stirred suspension of the potassium β-diketiminate K[**L**^{3}] (0.88 g, 1.93 mmol) in diethyl ether (20 cm^3) at −78 °C. The mixture was set aside at *ca.* 20 °C for 18 h, then filtered. Removal of volatiles *in vacuo* from the filtrate yielded a yellow powder, which upon crystallisation from hexane (20 cm^3)–thf (5 cm^3) at −25 °C afforded colourless crystals of **5a** (0.79 g, 57%) (Found: C, 61.3; H, 8.02; N, 3.79%. $C_{37}H_{57}Cl_2N_2O_2Y$ requires: 61.6; H, 7.96; N, 3.88%), mp 143 °C (decomp.). ^{1}H-NMR: δ 1.16 (d, 12 H, J = 6.59 Hz, CH*Me*$_2$), 1.26 (d, 12 H, J = 6.59 Hz, CH*Me*$_2$), 1.38 (t, 8 H, thf), 1.71 (s, 6 H, CH_3), 3.62 (hept, 4 H, C*H*Me$_2$), 3.74 (q, 8 H, thf), 5.15 (s, 1 H, CH), 7.08 ppm (m, br, 6 H, C_6H_3); ^{13}C-NMR: δ 20.51 (CH_3), 23.14 (CH*Me*$_2$), 25.69 (thf), 28.45 (*C*HMe$_2$), 67.64 (thf), 94.00 (CH); 123.31, 123.42, 141.03, 148.61 (C_6H_3), 164.78 ppm (CN).

A suspension of **3b** (1.52 g, 1.07 mmol) in n-hexane (40 cm^3) was heated to 60 °C with stirring for 12 h. The hot mixture was filtered. Volatiles were removed from the filtrate *in vacuo* and the residue was extracted into hexane (30 cm^3)–diethyl ether (10 cm^3)–thf (5 cm^3). The extract was concentrated *in vacuo* to *ca.* 15 cm^3 and stored at −25 °C to afford colourless crystals of **5b** (1.12 g, 79%) (Found: C, 55.6; H, 7.26; N, 4.20%. $C_{33}H_{49}Cl_2N_2O_2Y$ requires: C, 59.55; H, 7.42; N, 4.21%), mp 158 °C (decomp.). ^{1}H-NMR: δ 1.18 (br, 8 H, thf), 1.65 (s, 18 H, CMe_3), 1.72 (s, 6 H, CH_3), 3.62 (br, 8 H, thf), 5.01 (s, 1 H, CH); 7.02 (br, 4 H), 7.42 (d, 2 H), 7.52 ppm (br, 2 H, C_6H_4); ^{13}C-NMR: δ 25.29 (CH_3), 25.54 (thf), 33.49 (C*Me*$_3$), 37.20 (*C*Me$_3$), 71.12 (thf), 98.19 (CH); 125.16, 128.32, 130.45, 144.41, 146.32 (C_6H_4), 166.84 ppm (CN).

A solution of the sodium β-diketiminate Na[**L**^{5}] (1.37 g, 2.80 mmol) in thf (20 cm^3) was added dropwise to a stirred suspension of YCl_3 (0.55 g, 2.81 mmol) in thf (10 cm^3) at *ca.* 20 °C. The mixture was set aside for 24 h, volatiles were removed *in vacuo* and the residue was extracted into diethyl ether. The extract was concentrated to *ca.* 10 cm^3 and maintained at −25 °C, yielding yellow crystals of **5c** (1.77 g, 82%) (Found: C, 62.1; H, 6.28; N, 3.59%. $C_{41}H_{57}Cl_2N_2O_2Y$ requires: C, 64.0; H, 7.46; N, 3.64%; $C_{37}H_{49}Cl_2N_2OY$ requires: C, 63.7; H, 7.08; N, 4.02% (*i.e.* **5c**–thf)); MS: m/z, 624 ([M − 2thf]$^+$, 100%), mp 141–148 °C (decomp.). ^{1}H-NMR: δ 1.15 (d, 12 H, J = 6.7, CH*Me*$_2$), 1.17 (s, 8 H, thf), 1.58 (d, 12 H, J = 6.7, CH*Me*$_2$), 3.59 (s, 8 H, thf), 4.23 (heptet, 4 H, J = 6.7, CH*Me*$_2$), 7.03 (t, 2 H, J = 7.4, *p*-H of C_6H_3), 7.05–7.23 (m, CH), 7.48 (d, 2 H, J = 7.8, *m*-H of C_6H_3), 7.97 ppm (d, 2 H, J = 2.0 Hz, *m*-H, of C_6H_3); ^{13}C-NMR: δ 23.2 (CH*Me*$_2$), 25.2 (CH*Me*$_2$), 26.3 (thf), 28.5 (*C*HMe$_2$), 71.2 (thf), 106.9 (*C*Ph); 124.1, 124.9, 143.0, 144.9, 147.9 (Ph and C_6H_3), 164.4 ppm (NCH).

The compound [YCl{(N(SiMe$_3$)C(Ph))$_2$CH}$_2$] (6). A solution of the sodium β-diketiminate Na[**L**^{4}] (3.13 g, 8.05 mmol) in thf (20 cm^3) was added to a stirred suspension of YCl_3 (1.68 g, 8.60 mmol) in thf (10 cm^3) at *ca.* 20 °C. The mixture was set aside for 48 h, volatiles were removed *in vacuo* and the residue was extracted into diethyl ether. The extract was concentrated to *ca.* 30 cm^3 and maintained at 25 °C, furnishing yellow crystals of **6** (2.17 g, 64% based on Na[**L**^{4}]). Recrystallisation from Et_2O provided X-ray quality crystals (Found: C, 59.2; H, 7.04; N, 6.50%. $C_{42}H_{58}ClN_4Si_4Y$ requires: C, 59.0; H, 6.83; N, 6.55%), mp 152–153 °C. ^{1}H-NMR (C_4D_8O): δ 0.05 [s, 36 H, Si(CH_3)$_3$], 5.35 (s, 2 H, CH), 7.14–7.56 ppm (m, 20 H, C_6H_5); ^{13}C-NMR (C_4D_8O): δ 1.4 [Si(CH_3)$_3$], 1.9 [Si(CH_3)$_3$], 3.0 [Si(CH_3)$_3$], 3.6 [Si(CH_3)$_3$], 97.6 (CH); 126.8, 127.8, 128.5,128.6, 128.9, 129.1, 129.4, 130.5, 130.6 ppm (C_6H_5, CN).

The compound [Y{(N($C_6H_4Pr^i$-2)C(Me))$_2$CH}$_2$OBu^t] (7). Yttrium(III) chloride (0.55 g, 2.81 mmol) was added in small portions to a solution of the potassium β-diketiminate K[**L**^{1}] (2.07 g, 5.56 mmol) in diethyl ether (50 cm^3) at −30 °C. The resulting mixture was stirred for 30 min at *ca.* 20 °C, whereafter KOBu^t (0.31 g, 2.77 mmol) was slowly added; stirring was continued for 24 h, followed by filtration. Volatiles were removed *in vacuo*; the residue was extracted into hexane. The extract was concentrated *in vacuo* to *ca.* 20 cm^3 and stored at 0 °C, yielding pale yellow crystals of **7** (0.78 g, 34%) (Found: C, 71.9; H, 8.03; N, 6.42%. $C_{50}H_{67}N_4OY$ requires: C, 72.4; H, 8.15; N, 6.76%), mp 171 °C (decomp.). ^{1}H-NMR: δ 0.46 (s, 9 H, $OCMe_3$), 1.14 (d, 12 H, CH*Me*$_2$), 1.39 (d, 12 H, CH*Me*$_2$), 1.72 (s, 12 H, CH_3), 3.34 (heptet, 4 H, C*H*Me$_2$), 4.90 (s, 2 H, CH); 6.13 (br, 4 H), 6.89 (t, 4 H), 6.93 (t, 4 H), 7.25 ppm (d, 4 H, C_6H_4); ^{13}C-NMR: δ 23.91 (CH_3), 24.33 (CH*Me*$_2$), 24.90 (CH*Me*$_2$), 27.75 (*C*HMe$_2$), 32.97 (OC*Me*$_3$), 71.90 (O*C*Me$_3$), 95.68 (CH); 125.04, 126.11, 126.19, 141.67, 148.61 (C_6H_4), 165.74 ppm (CN).

The compound [Y{CH(SiMe$_3$)$_2$}(thf){(μ-Cl)$_2$Li(OEt$_2$)$_2$}(μ-Cl)]$_2$ (8). Li[CH(SiMe$_3$)$_2$] (0.36 g, 2.17 mmol) was added in small portions to a solution of compound **3a** (1.48 g, 1.08 mmol) in hexane (50 cm^3) at 0 °C. The resulting mixture was stirred for 48 h at *ca.* 20 °C. Volatiles were removal *in vacuo.* The residue was extracted into hexane (40 cm^3)–diethyl ether (20 cm^3)–thf (10 cm^3). The extract was concentrated to *ca.* 15 cm^3 and stored at –25 °C. After 12 h, this yielded colourless crystals of **8** (0.51 g, 41%) (Found: C, 38.5; H, 7.98%; $C_{38}H_{94}Cl_6Li_2O_6Si_4Y_2$ requires: C, 3 9.2; H, 8.14%), mp 94 °C (decomp.). ^{1}H-NMR (C_6D_6–C_5D_5N): δ –0.40 (s, 1 H, CH), –0.09 [s, 18 H, Si(CH$_3$)$_3$], 1.06 (t, 12 H, OEt$_2$), 1.41 (t, 4 H, thf), 3.23 (q, 8 H, OEt$_2$), 3.54 ppm (t, 4 H, thf); ^{13}C-NMR (C_6D_6–C_5D_5N): δ –0.05 (CH), 1.36 [Si(CH$_3$)$_3$], 15.52 (OEt$_2$), 25.73 (thf), 65.82 (OEt$_2$), 67.77 ppm (thf); ^{7}Li-NMR (C_6D_6–C_5D_5N): δ –1.84 ppm.

The compound [Y{N(H)C$_6$H$_3$Pr$_2$^{i}-2,6}{(N(C$_6$H$_3$Pr$_2$^{i}-2,6)-C(H))$_2$CPh}(thf){μ-Cl}$_2$K}]$_2$·4Et$_2$O (9). The potassium amide K[N(H)C$_6$H$_3$Pr$_2$^{i}-2,6] (0.45 g, 2.09 mmol) was added in small portions to a solution of the dichloroyttrium β-diketiminate **5c** (1.51 g, 1.96 mmol) in diethyl ether (30 cm^3) at *ca.* 20 °C. The mixture was stirred for 24 h, then filtered. The filtrate, when concentrated and cooled at –27 °C, yielded the yellow crystalline **9** (1.20 g, 67%) (Found: C, 64.6; H, 7.55; N, 4.63%. $C_{98}H_{134}Cl_4K_2N_6O_2Y_2$ (ether-free) requires: C, 64.6; H, 7.41; N, 4.61%), mp 95–96 °C (decomp.). X-Ray quality crystals of **9** were obtained by crystallisation from Et$_2$O. ^{1}H-NMR (C_4D_8O): δ 0.85 (d, 24 H, J = 6.6, CH*Me*$_2$), 0.99 (d, 12 H, J = 6.6, CH*Me*$_2$), 1.04 [t, 24 H, O(CH$_2$C*H*$_3$)$_2$], 1.13 (d, 12 H, J = 6.6, CH*Me*$_2$), 1.25 (d, 24 H, J = 6.6, CH*Me*$_2$), 1.69 (t, 8 H, thf), 2.89 (m, 4 H, C*H*Me$_2$), 3.30 (q, 16 H, O(C*H*$_2$CH$_3$)$_2$), 3.54 (t, 8 H, thf), 3.63 (m, 8 H, C*H*Me$_2$), 3.94 (br, 2 H, NH), 6.13 (t, 2 H, J = 7.4, C$_6$H$_3$), 6.58 (d, 4 H, J = 7.4 Hz, C$_6$H$_3$), 6.80–7.18 (m, 22 H, C$_6$H$_5$), 7.56 ppm (s, 4 H, CH); ^{13}C-NMR (C_4D_8O): δ 14.9, 22.1, 22.6, 23.2, 23.6, 25.5, 26.3, 27.5, 28.4 [CHMe$_2$, O(CH$_2$*C*H$_3$)$_2$, thf], 65.5, 67.4 [O(*C*H$_2$CH$_3$)$_2$, thf], 105.2, 112.7 (CPh); 121.3, 122.2, 123.1, 123.6, 125.1, 125.2, 128.3, 135.0, 143.2, 144.2, 151.2 (C$_6$H$_3$, C$_6$H$_5$), 162.6 ppm (NCH).

Crystal data and refinement details for 3a, 3b, 4a, 4b, 5a, 5b, 5c, 6, 7, 8 and 9

Diffraction data were collected on a Nonius Kappa CCD diffractometer using monochromated Mo-Kα radiation, λ 0.71073 Å at 173(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas.

In **3a** diffraction was weak but with no apparent disorder in the structure. In **4a** all the thf ligands were included with 1,2 distance restraints and for the O2 thf disordered components were included with isotropic C atoms. In **4b** the Et$_2$O ligands were poorly defined and with disordered components for one thf. They were included with isotropic C atoms and 1,2 distance restraints and with an isotropic O atom for the disordered ligand. In **5a** and in **5c** the disordered components of the O2 thf ligand were included with isotropic displacement parameters and 1,2 distance restraints. In **8** the Et$_2$O ligands were poorly defined, discrete alternative positions defined only for C18; they were included with isotropic C atoms and 1,2 distance restraints. In all figures only the larger occupancy orientation is shown for disordered ligands. Absorption corrections using MULTISCAN were applied. Drawings are ORTEP-3 for Windows, with 20% ellipsoids for **3a**, **3b**, **4a**, **4b**, **5a**, and **8** and 50% ellipsoids for **5b**, **5c**, **6**, **7**, and **9**. The structures were refined on all F^2 atoms with H

Table 8 Crystal and structure refinement data for **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, **5c**, **6**, **7**, **8**, and **9**

Compound	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**	**5c**	**6**	**7**	**8**	**9**
Formula	$C_{62}H_{98}Cl_6Li_2N_4$-$O_4Y_2\cdot C_4H_{10}O$	$C_{66}H_{106}Cl_6Li_2N_4O_4Y_2\cdot C_4H_{10}O$	$C_{74}H_{114}Cl_6Li_2N_4O_4Y_2\cdot C_4H_{10}O$	$C_{74}H_{122}Cl_6Li_2N_4O_4Y_2\cdot 0.5C_4H_{10}O$	$C_{37}H_{57}Cl_2N_2O_2Y$	$C_{33}H_{49}Cl_2N_2O_2Y\cdot C_4H_{10}O$	$C_{41}H_{57}Cl_2N_2O_2Y$	$C_{42}H_{58}ClN_4Si_4Y$	$C_{50}H_{67}N_4OY$	$C_{38}H_{94}Cl_6Li_2N_2$-$O_6Si_4Y_2$	$C_{98}H_{134}Cl_4K_2N_6O_2Y_2\cdot 4C_4H_8O$
M	1441.96	1498.07	1602.21	1572.22	721.67	739.67	769.70	855.64	828.59	1163.89	2122.41
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (No. 14).	$C2/c$ (No. 15)	$P\bar{1}$ (No.2)	$P2_1/n$ (No. 14)	*Pbca* (No. 61)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14).	$P\bar{1}$ (No. 2)
a/Å	11.5518(3)	30.2936(30)	12.3174(20)	12.9001(20)	15.4162(1)	4.2932(2)	34.5375(4)	11.8676(2)	12.5959(1)	14.8150(3)	12.9490(1)
b/Å	26.9951(7)	13.7202(20)	15.3330(20)	26.5237(5)	24.0744(3)	13.5936(1)	11.3522(1)	12.4721(2)	17.9182(2)	20.0248(3)	14.4721(2)
c/Å	25.3522(7)	22.7889(2)	25.3952(50)	25.2112(4)	20.4590(2)	20.4397(3)	23.4944(3)	15.7658(3)	21.0703(2)	10.6476(2)	17.0897(2)
α/°			95.054(1)					84.567(10)			70.257(1)
β/°	95.090(1)	122.693(1)	99.880(1)	94.508(1)		94.757(1)	117.072(1)	86.136(1)	98.21(1)	99.532(1)	73.489(10)
γ/°			113.161(1)					89.915(1)			81.903(1)
U/Å^3	7873.5(4)	7971.26(16)	4279.75(12)	8599.5(3)	7593.07(13)	3957.67(9)	8202.3(2)	2317.77(7)	4706.78(8)	3115.18(10)	2886.47(6)
Z	4	4	2	4	8	4	8	2	4	2	1
Abs. coeff./mm^{-1}	1.71	1.70	1.58	1.58	1.71	1.64	1.59	1.45	1.28	2.22	1.22
Unique reflections, R_{int}	13 084, 0.082	6999, 0.047	14 282, 0.054	15 060, 0.065	6673, 0.080	9026, 0.066	9338, 0.059	8497, 0.045	10 732, 0.062	5466, 0.067	10 598, 0.050
Reflections with $I > 2\sigma(I)$	9362	6035	10 976	10 586	5210	6967	7598	7731	8417	4454	8871
Final R indices [$I > 2\sigma(I)$] R_1, wR_2	0.099, 0.192	0.034, 0.071	0.064, 0.142	0.066, 0.159	0.061, 0.104	0.047, 0.093	0.043, 0.089	0.035, 0.079	0.044, 0.081	0.055, 0.192	0.047, 0.095
R indices (all data) R_1, wR_2	0.139, 0.208	0.045, 0.075	0.090, 0.155	0.107, 0.181	0.084, 0.113	0.072, 0.102	0.060, 0.096	0.042, 0.081	0.067, 0.088	0.074, 0.139	0.062, 0.102

atoms in riding mode using SHELXL-97.[33] Further details are in Table 8.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b806451b

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