

Synthesis and structures of the ytterbium(II) β -diketiminates $[\text{Yb}\{\text{N}(\text{SiMe}_3)\text{C}(\text{R}^2)\text{C}(\text{H})\text{C}(\text{R}^4)\text{N}(\text{SiMe}_3)\}_2]$ ($\text{R}^2 = \text{R}^4 = \text{Ph}$, $\text{C}_6\text{H}_4\text{Me-4}$, or $\text{C}_6\text{H}_4\text{Ph-4}$; or $\text{R}^2 = \text{C}_6\text{H}_4\text{Me-4}$, $\text{R}^4 = 1\text{-adamantyl}$)

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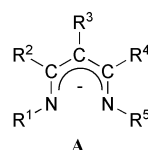
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Crystalline, homoleptic mononuclear ytterbium(II) β -diketiminates $[\text{Yb}\{\text{N}(\text{SiMe}_3)\text{C}(\text{R}^2)\text{C}(\text{H})\text{C}(\text{R}^4)\text{N}(\text{SiMe}_3)\}_2]$ ($\text{R}^2 = \text{R}^4 = \text{Ph}$ **1**, $\text{R}^2 = \text{R}^4 = \text{Tol}$ **2**, $\text{R}^2 = \text{R}^4 = \text{Dph}$ **3**, or $\text{R}^2 = \text{Tol}$ and $\text{R}^4 = \text{Ad}$ **4**) ($\text{Tol} = \text{C}_6\text{H}_4\text{Me-4}$, $\text{Dph} = \text{C}_6\text{H}_4\text{Ph-4}$, $\text{Ad} = 1\text{-adamantyl}$) have been prepared. They have a characteristic $^{171}\text{Yb}\{^1\text{H}\}$ chemical shift in the region $\delta 2650 \pm 200$ relative to $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{thf})]$, although for **2** and **3** this was only observed at low temperatures, indicative of a fast fluxional process at ambient temperature; data recorded earlier for **1** are shown to have been in error. The ^1H NMR spectra of **4** showed that two isomers were present in toluene solution, in a ratio of *ca.* 3 : 2, which interconverted on the spin saturation transfer scale of *ca.* 1 s^{-1} . NOE data are presented for each of **1–4**; these led to (i) assignments of the two types of SiMe_3 groups (adjacent to Tol or Ad) and (ii) the conclusion that the two isomers are conformers, one of which probably corresponds to that found in the crystal. The molecular structures of each of **1**, **3** and **4** have the ytterbium in a distorted tetrahedral environment, the two ligand planes (**1** and **3**) or boats (including the Yb atom, **4**) approximate to being either orthogonal (**1** and **3**) or parallel (**4**). The ligand-to-metal bonding is close to κ^2 (**1**, **3**) or η^5 (**4**) and the ligands are both π -delocalised (**1**, **3**) or only one of them in **4**.

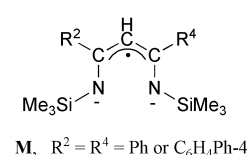
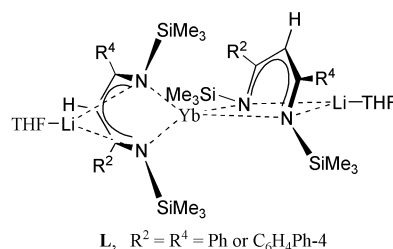
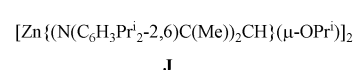
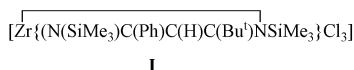
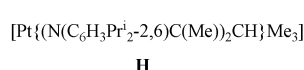
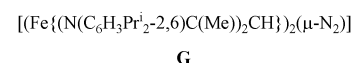
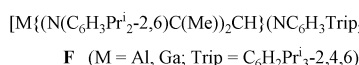
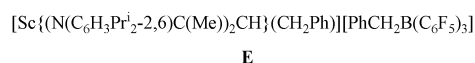
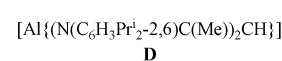
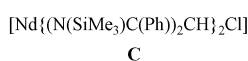
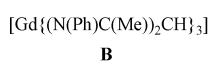
Introduction

The chemistry of metal β -diketiminates is of substantial current interest.¹ Up to the end of June 2002, there were about 180 publications, 38 of them in 2001 and 27 in the first half of 2002, dealing with compounds of 43 metals. The β -diketiminato ligand is shown as **A** in its delocalised general form.



Diketiminates are important spectator ligands by virtue of their strong binding to metals, their tuneable (*cf.* variations in $\text{R}^1\text{–R}^5$) and extensive steric demands and their diversity of bonding modes. The steric effects are well illustrated by the fact that (a) very few tris(diketiminato)metal complexes are known and

these have relatively small N,N' -substituents $\text{R}^1\text{–R}^5$, *e.g.*, **B**;² and (b) if $\text{R}^1 = \text{SiMe}_3 = \text{R}^5$, the 4f-metal complexes $[\text{Ln}(\text{A})_2\text{Cl}]$ are monomers, *e.g.*, **C**,³ whereas even the bulkiest lanthanocene chlorides, *e.g.*, $[\text{Pr}(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3})_2(\mu\text{-Cl})_2]$, are $(\mu\text{-Cl})_2$ -bridged dimers.⁴ The β -diketiminato ligands are thus not only able to stabilise compounds in an unusually low state of molecular aggregation, but also in a low oxidation state, as cations, and others containing multiply bonded coligands, as exemplified by **D**,⁵ **E**,⁶ and **F**,⁷ respectively. Many such complexes are coordinatively unsaturated, *e.g.*, **G**,⁸ and **H**,⁹ and this and other features are the key to their ability to function as catalysts (or procatalysts) for processes as varied as olefin oligo-, poly- and copoly-merisation, *e.g.*, **I** for polyethylene,¹⁰ **J** for ring-opening polymerisation of lactide,¹¹ and **K** for copolymerisation of cyclohexene oxide and carbon dioxide.¹² In each of **B–K**, the ligand **A** is bonded to the metal in a chelating terminal mode, approximating to κ^2 (**B**, **D**, **G**, **H**, **J**, **K**) or η^5 (**C**, **E**, **I**). In all these complexes, the ligands **A** have behaved in a monoanionic fashion,¹ but recently we have shown that the

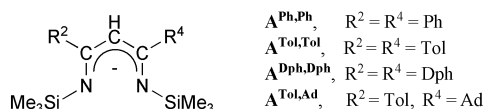


ytterbium(II) complexes **L** contain dianionic β -diketiminato ligands **M**.¹³

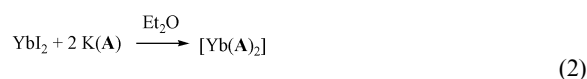
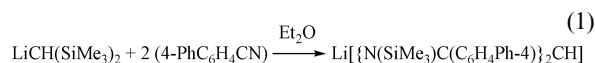
The synthesis and characterisation of several β -diketimino-lanthanoid(III) metal complexes have been reported, including crystallographic data not only for **B**² and **C**,³ but also for three further complexes of Ce,³ Sm^{14a} and Gd.^{14b} We now report data for the homoleptic Yb(II) β -diketimines **1–4**. The only previous record of Ln(II) β -diketimines (apart from the crystallographically characterised **L**¹³) is of [Ln{(N(SiMe₃)C(Ph))₂CH₂(thf)}₂] (Ln = Sm or Yb),³ [Yb{(N(SiMe₃)C(Ph))₂CH₂}₂] **1**^{3,15} and [Yb{N(SiMe₃)C(Ph)C(H)C(Bu^t)N(SiMe₃)}₂] **5**³ for which X-ray data were not available. A curious feature was that the ¹H, ¹³C{¹H}, ²⁹Si{¹H} and ¹⁷¹Yb{¹H} NMR spectra of **5** in C₆D₆/PhMe showed that at ambient temperature for each of these nuclei every signal was accompanied by one of closely similar chemical shift, the two coalescing upon heating.³ The ¹⁷¹Yb{¹H} chemical shifts for **5** at ambient temperature were at δ 2476 and 2513.5, whereas **1** showed a singlet at δ 870.4 {rel. to [Yb(η^5 -C₅Me₅)₂(thf)]¹⁶}.³ These observations were not convincingly rationalised,³ and hence the aim of the present investigation was to reinvestigate the NMR spectroscopic data in more detail and to gain access to crystallographic data for some homoleptic ytterbium(II) β -diketimines in which the ligand was either C₂- or C₁-symmetric, and examine further their solution behaviour.

Results and discussion

The homoleptic ytterbium(II) complexes described herein are derived from the bidentate β -diketiminato ligand **A** (R¹ = R⁵ = SiMe₃, R³ = H for all complexes): (a) **A**^{Ph,Ph},³ (b) **A**^{Tol,Tol} (Tol = C₆H₄Me-4), (c) **A**^{Dph,Dph} (Dph = C₆H₄Ph-4) and (d) **A**^{Tol,Ad} (Ad = 1-adamantyl). Thus, they have the molecular formulae [Yb(**A**^{Ph,Ph})₂] **1**, [Yb(**A**^{Tol,Tol})₂] **2**, [Yb(**A**^{Dph,Dph})₂] **3** and [Yb(**A**^{Tol,Ad})₂] **4**.



A precursor to complexes **1–4** was the corresponding potassium β -diketiminate. Of these, K(**A**^{Ph,Ph}), from $\frac{1}{2}$ [Li(**A**^{Ph,Ph})₂] + KOBu^t in Et₂O, has been described.¹⁷ The compounds K(**A**^{Tol,Tol}) and K(**A**^{Tol,Ad}) were made similarly from Li(**A**^{Tol,Tol})¹⁷ and the X-ray-characterised [Li(**A**^{Tol,Ad})],¹⁸ respectively. The lithium β -diketiminate Li(**A**^{Dph,Dph}) was prepared as shown in eqn. (1), by a general method established for [Li(**A**^{Ph,Ph})₂] and Li(**A**^{Tol,Tol}),¹⁷ and then converted with KOBu^t into K(**A**^{Dph,Dph}). Complexes **1–4** were prepared from ytterbium(II) iodide and the appropriate K(**A**) in diethyl ether, eqn. (2).



1 , 74%, green-brown	3 , 69%, green-brown
2 , 65%, green-brown	4 , 63%, brown

Each of the crystalline ytterbium(II) β -diketimines **1–4** gave satisfactory microanalyses, readily assignable (see Tables 2–5 and Experimental section) multinuclear NMR spectra and (not for **2**) single crystal X-ray diffraction data.

The molecular structure and atom numbering scheme, with selected geometrical parameters for each of **1**, **3** and **4** is shown in Figs. 1–3, respectively. Some comparative data for these and **L** (R² = R⁴ = Ph)¹³ are also listed in Table 1.

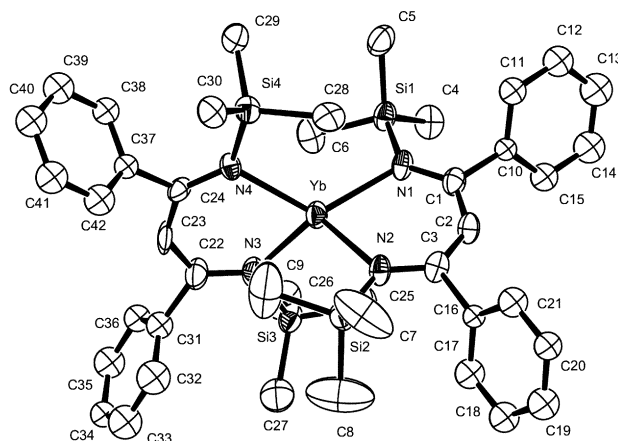


Fig. 1 The structure of **1** (20% ellipsoids). Selected bond lengths (Å) and angles (°): Yb–N1 2.423(9), Yb–N2 2.418(9), Yb–N3 2.396(10), Yb–N4 2.405(9), N1–C1 1.323(14), N2–C3 1.323(14), N3–C22 1.347(15), N4–C24 1.311(14), C1–C2 1.416(17), C2–C3 1.398(17), C22–C23 1.406(17), C23–C24 1.427(16); N1–Yb–N2 86.0(3), N3–Yb–N4 85.4(3).

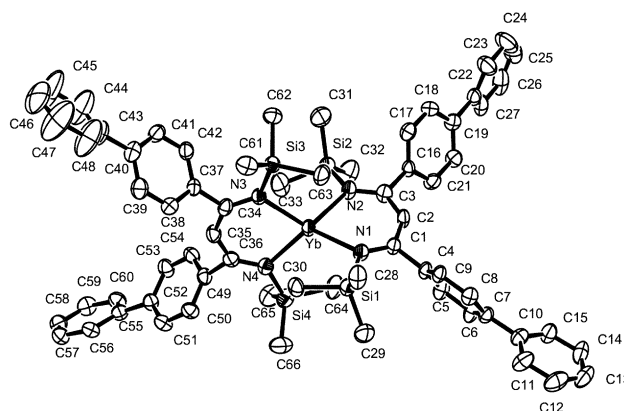


Fig. 2 The structure of **3** (20% ellipsoids). Selected bond lengths (Å) and angles (°): Yb–N1 2.396(4), Yb–N2 2.386(4), Yb–N3 2.393(4), Yb–N4 2.405(4), N1–C1 1.331(6), N2–C3 1.331(6), N3–C34 1.345(6), N4–C36 1.327(6), C1–C2 1.408(6), C2–C3 1.404(8), C34–C35 1.396(7), C35–C36 1.408(7); N1–Yb–N2 87.38(12), N3–Yb–N4 89.08(13).

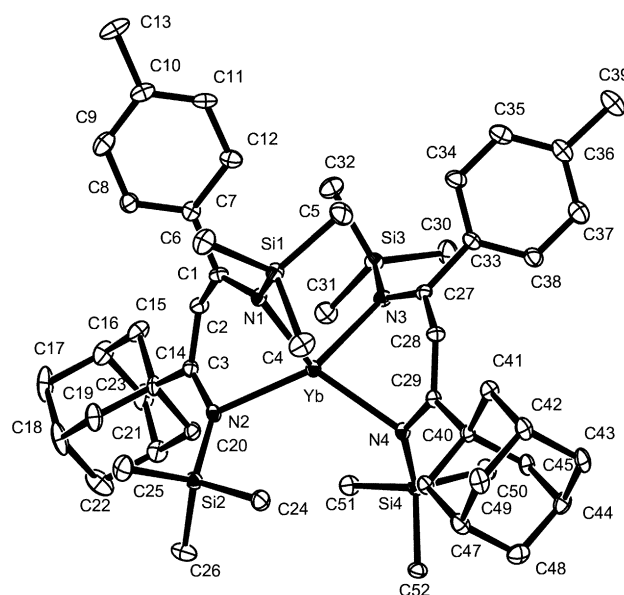


Fig. 3 The structure of **4** (20% ellipsoids). Selected bond lengths (Å) and angles (°): Yb–N1 2.371(7), Yb–N2 2.378(7), Yb–N3 2.412(7), Yb–N4 2.364(7), N1–C1 1.341(12), N2–C3 1.336(11), N3–C27 1.282(12), N4–C29 1.337(11), C1–C2 1.432(13), C2–C3 1.406(12), C27–C28 1.460(12), C28–C29 1.390(12); N1–Yb–N2 82.4(2), N3–Yb–N4 81.7(2).

Table 1 Selected average bond distances (Å) and an angle (°) for **1**, **3**, **4** and **L** ($R^2 = R^4 = \text{Ph}$)^{13a}

Compound	Yb–N	N–C	C–C	N–Yb–N
1	2.410 (–0.014)	1.326 (+0.021)	1.414 (–0.016)	85.7 (±0.3)
3	2.395 (+0.010)	1.334 (+0.012)	1.404 (–0.008)	88.2 (±0.9)
4	2.381 (+0.033)	1.324 (–0.042)	1.422 (+0.038)	82.0 (±0.4)
L ($R^2 = R^4 = \text{Ph}$) ¹³	2.326 (+0.015)	1.413 (+0.006)	1.427 (–0.002)	79.2 (±0.2)

^a In parentheses is shown the greatest deviation from the value of the mean bond length or angle.**Table 2** Selected NMR spectral chemical shifts (δ) at 298 K (unless otherwise indicated) for **1–5**

Compound	Si(C ¹ H ₃) ₃	Si(¹³ CH ₃) ₃ ^a	²⁹ Si(CH ₃) ₃ ^a	¹⁷¹ Yb ^a	Solvent
[Yb(A ^{Ph,Ph}) ₂] 1	0.19 (0.13) ³	2.99 (2.71) ³	–3.27 (–4.81) ³	2634 [950] ^c (840.4) ³	Toluene-d ₈ C ₆ D ₆ –PhMe
Yb(A ^{Tol,Tol}) ₂ 2	0.24	2.99	–5.18	2809 [2110] ^c	Toluene-d ₈ –thf
[Yb(A ^{Dph,Dph}) ₂] 3	0.37	3.26	–3.99	2529 [2120] ^c (at 273 K)	Toluene-d ₈ C ₆ D ₆ (¹ H, ¹³ C)
[Yb(A ^{Tol,Ad}) ₂] 4	0.57 ^b and 0.60 ^c 0.16 ^b and 0.21 ^c	4.51 ^b , 4.50 ^c 3.12 ^b , 3.17 ^c	–20.42 ^b , –20.16 ^c –4.32 ^b , –4.78 ^c	2588 [1960] ^c (at 203 K) 2641, 2629	Toluene-d ₈ –thf (²⁹ Si, ¹⁷¹ Yb) Toluene-d ₈ , C ₆ D ₆ (²⁹ Si)
[Yb(A ^{Tol,Bu}) ₂] 5 ³	0.39 ^d 0.03 ^d	4.05 ^d 3.03 ^d	–17.01, –17.51 –2.24, –2.91	[100, 150] ^c 2476, 2513 [220, 170] ^c	C ₆ D ₆ –PhMe

^a ¹³C, ²⁹Si and ¹⁷¹Yb: each ¹H-decoupled. ^b Major isomer. ^c Minor isomer. ^d Centre of two closely similar signals [for ¹H in ratio *ca.* 3 : 2 (low frequency)]; ^e Signal line width [*w*_{1/2}/Hz].**Table 3** Variable temperature NMR spectral chemical shifts (δ) for complex **2** in toluene-d₈–thf

<i>T</i> /K	¹³ C				
	¹⁷¹ Yb	²⁹ Si	NC(Tol)CH	CH(middle)	<i>ipso</i> -C of Tol
193	2388 [1050] ^a	–4.99	171.55	104.90	146.69
208	2350 [840] ^a	–5.01	171.75	104.95	146.67
223	2315 [420] ^a	–5.05	171.97	104.94	146.59
238	2324 [630] ^a	–5.09	172.17	104.85	146.45
253	2400 [1050] ^a	–5.15	172.29	104.68	146.21
268	2519 [1460] ^a	–5.23	172.29	104.52	145.99
283	2656 [1900] ^a	–5.33	172.24	104.42	145.84
298	2809 [2110] ^a	–5.49	172.20	104.32	145.71
318	3009 [2370] ^a	–5.59	172.17	104.25	145.63

^a Signal line width [*w*_{1/2}/Hz].**Table 4** Enhancement factors η (%) in ¹H NMR NOE spectral experiments on **1–3**

	Irradiation	
	SiMe ₃	CH
Complex 1		
SiMe ₃	n.a.	0
CH	2.0	n.a.
<i>m</i> -H and <i>p</i> -H of Ph	1.1	0
<i>o</i> -H of Ph	6.1	7.4
Complex 2		
SiMe ₃	n.a.	0.4
CH	2.4	n.a.
<i>m</i> -H of Tol	0.7	0
<i>o</i> -H of Tol	5.3	4.0
Complex 3		
SiMe ₃	n.a.	0
CH	1.4	n.a.
<i>p</i> '-H of Dph	0	0
<i>m</i> '-H of Dph	0	0
<i>m</i> - and <i>o</i> '-H of Dph	1.4	0
<i>o</i> -H of Dph	6.1	–1.1

In each of the crystalline compounds **1**, **3** and **4** the ytterbium atom is in a distorted tetrahedral environment, the angle between the N1–Yb–N2 and N3–Yb–N4 planes being 83° (**1**),

84° (**3**) and 58° (**4**). The ligands are disposed towards the metal in a κ^2 -mode for **1** and **3** but an approximately η^5 -fashion for **4**. Thus, the mean planes of the two ligands are almost orthogonal for **1** and **3**, the angle between them being 80° (**1**) or 84° (**3**), whereas in **4** it is 15°—the ligand planes (excluding the central C atom, *vide infra*) being almost parallel. The NCCCN atoms of the ligands are nearly coplanar in **1** and **3**, the rms deviations being 0.03 Å (**1**) and 0.01 Å (**3**). The N1–C1–C3–N2 atoms of one of the ligands of **4** and the N3–C27–C29–N4 atoms of the other are both almost coplanar with rms deviations of 0.07 Å, but the C2 and C28 atoms are out of their respective plane by 0.21 and 0.24 Å in the direction of the Yb atom. The endocyclic bond lengths show that the N1–C1–C2–C3–N2 ligand is essentially π -delocalised, whereas the other ligand approximates to the bonding illustrated in **N**. The molecule of **4** has approximate *C*₂ symmetry with the pseudo-principal axis along the bisector of the N2–Yb–N4 angle, and is the *rac*-diastereoisomer.

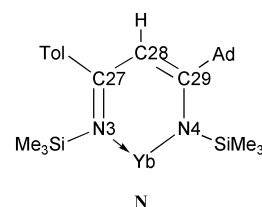


Table 5 Enhancement factors η (%) in ^1H NMR NOE spectral experiment on **4**

	Irradiation					
	$\text{SiMe}_3^{\text{Tol}}$ major	$\text{SiMe}_3^{\text{Tol}}$ minor	$\text{SiMe}_3^{\text{Ad}}$ major	$\text{SiMe}_3^{\text{Ad}}$ minor	CH major	CH minor
$\text{SiMe}_3^{\text{Tol}}$, major	n.a.	0	1.0	0	0	0
$\text{SiMe}_3^{\text{Tol}}$, minor	0	n.a.	0	1.5	0	0
$\text{SiMe}_3^{\text{Ad}}$, major	0	0	n.a.	0	0	0
$\text{SiMe}_3^{\text{Ad}}$, minor	0	0	0	n.a.	0	0
CH_2 of Ad	0	0	0	0	0	0
CH and CH_2 of Ad (+ CH_3 of Tol)	0	0	2.5	3.1	2.1	2.9
CH, minor	0	0.6	0	0	0	n.a.
CH, major	1.9	0	0	0	n.a.	0
<i>m</i> -H of Tol, minor	0	0.6	0	0	0	0
<i>m</i> -H of Tol, major	0.7	0	0	0	0	0
<i>o</i> -H of Tol, minor	0	4.7	0	0.6	0	3.1
<i>o</i> -H of Tol, major	4.5	0	0.8	0	2.7	0

The geometric parameters for the Yb β -diketimines **1** and **L** ($\text{R}^2 = \text{R}^4 = \text{Ph}$),¹³ both involving the same $[\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\}_2\text{CH}]^-$ ligand are now available for comparison, Table 1. The principal bond length differences are in the longer N–C and shorter Yb–N bond lengths in the latter. For Yb–N this is attributed to the fact that the ligand bridges Yb and Li atoms, but the longer N–C bond is consistent with the ligand in **L** being dianionic (*cf.* **M**), there being population of the $\pi^*(\text{CN})$ LUMO of the NCCCN array.¹³

To elucidate the solution structures of Yb(II) β -diketimines multinuclear NMR studies were performed on complexes **1–4**. Whereas the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral chemical shifts for **1** are in reasonable agreement with those previously recorded,³ this is not the case for the $^{29}\text{Si}\{^1\text{H}\}$ and $^{171}\text{Yb}\{^1\text{H}\}$ chemical shifts (Table 2). This table also summarises $^{171}\text{Yb}\{^1\text{H}\}$ and for the $\text{Si}(\text{CH}_3)_3$ groups ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ chemical shifts, as well as comparative data³ for **5**.

All five compounds showed $^{171}\text{Yb}\{^1\text{H}\}$ chemical shifts as broad signals (*cf.* $w_{1/2}$ in Table 2) in the range δ 2476–2809, although for **1**, **2** and **3** the signals became increasingly broad and weak when the temperature changed from 193 to 298 K. For **3** it was not found above 243 K and for **2** the observation of a $^{171}\text{Yb}\{^1\text{H}\}$ signal at room temperature was possible only with a more concentrated sample prepared using thf as a co-solvent. One possible explanation (suggested by a referee) of such a behaviour could be the presence in some NMR samples of a small amount of a paramagnetic Yb(III) impurity, which is in a dynamic equilibrium with diamagnetic Yb(II) complex at higher temperatures. To check this possibility the same NMR sample of **3** was mixed with the sample of **1** and $^{171}\text{Yb}\{^1\text{H}\}$ NMR spectra of the mixture were recorded in the 193–298 K temperature range. Only an $^{171}\text{Yb}\{^1\text{H}\}$ signal corresponding to complex **1** was observed in the entire temperature range while an ^1H NMR spectrum clearly showed the presence of both compounds in a 1.7 : 1 mixture of **1** : **3**. Thus, if a paramagnetic Yb(III) impurity in **3** was the reason of $^{171}\text{Yb}\{^1\text{H}\}$ signal broadening, it had no effect on the spectrum of complex **1**.

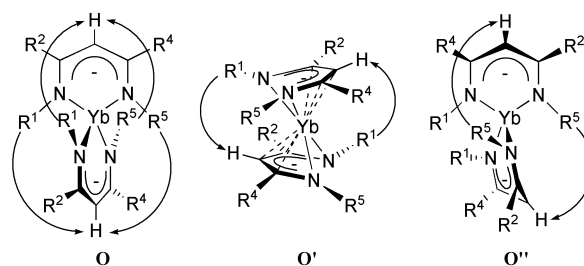
Variable temperature NMR spectra showed non-linear dependence of $^{171}\text{Yb}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ (ligand backbone carbon atoms) chemical shifts for **2** (Table 3) suggesting that some changes in the ligand coordination mode occurred at 220–260 K. At higher temperatures the ligands became labile, resulting in formation of a mixed-ligand complex when a mixture of **1** and **2** (or **1** and **3**) in C_6D_6 was heated at 363 K.

Having re-examined earlier such data for **1**, we now conclude that the ^{171}Yb chemical shift reported in 1997³ was in error and that the δ 2650 \pm 200 is characteristic for the homoleptic Yb(II) mononuclear β -diketimines $[\text{Yb}(\text{A}^{\text{R}^2, \text{R}^4})_2]$, even though these frequencies are much higher than any previously observed for Yb(II) complexes.

The solution NMR spectra of the C_2 -symmetric $[\text{Yb}(\text{A}^{\text{Tol, Ad}})_2]$

4 showed that, as for **5**, two isomers are present in the approximate ratio 3 : 2 (the former designated “major” in Table 2), which interconvert on the spin saturation transfer time scale of *ca.* 1 s^{−1}. Thus, spin saturation transfer experiments on the pair of CH protons (corresponding to δ 5.71 and 5.66 in toluene- d_8 at 298 K) displayed the following features: −20% at 303 K, −58% at 318 K and −89% at 333 K, thus showing an increasing rate at higher temperatures. However, the ratio of the two isomers did not change significantly in the studied temperature range showing that neither of them is thermodynamically preferred.

^1H NMR spectral NOE experiments were performed for each of the Yb(II) β -diketimines **1–3** (Table 4) and **4** (Table 5), in an attempt to establish their structures in toluene solution. The interligand contact observed was that between the protons of the SiMe_3 groups and the CH proton of the ligand **A**. As the distances between them are closely similar for both the coordination modes κ^2 (**O** and **O'**) and η^5 (**O''**) (Fig. 4, $\text{R}^1 = \text{SiMe}_3 = \text{R}^5$), these are not distinguishable by the NOE data. As reported above, crystalline **1** and **3** show κ^2 -bonding of ligands to metal, whereas **4** displays η^5 -bonding. The NOE experiments for **4** revealed that for both isomers there is a contact between the middle CH proton and SiMe_3 protons adjacent to the Tol, but not the Ad, substituent, therefore excluding the possible presence of the *meso*-isomer in solution. Only the *rac*-isomer with a similar substituent arrangement (SiMe_3 group adjacent to Tol substituent of one ligand is opposite to the middle CH of another ligand) is found in the crystal, suggesting that at least one of the isomers in solution has the same η^5 -coordination mode (**O'** in Fig. 4) as in the solid-state structure. Because the $^{171}\text{Yb}\{^1\text{H}\}$ chemical shifts for the two isomers of **4** are similar (Table 2), it is likely that they differ only in their conformation. We suggest that the second isomer adopts the κ^2 -mode, the Yb(NCCCN)-metallacycle being in the boat conformation (**O''** in Fig. 4). Each of the diketiminato ligands is bent towards the less crowded (*i.e.*, Tol-substituted) side of the other ligand with the middle CH proton of one ligand being close to the SiMe_3 group adjacent to the Tol substituent of the other (*cf.* **O'**, where the ligands are substituted symmetrically, $\text{R}^2 = \text{R}^4$).

**Fig. 4** Models demonstrating NOEs (shown as arrows) in κ^2 (**O** and **O'**) and η^5 (**O''**) bonded complexes.

Experimental

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled over sodium–potassium alloy (pentane, hexane) or sodium–benzophenone (Et_2O , THF) and stored over a K or Na mirror under argon. Microanalyses were carried out by Medac Ltd. (Brunel University). The NMR spectra were recorded using the DPX 300 and AMX 500 Bruker instruments and calibrated internally to residual solvent resonances for ^1H and ^{13}C ; external SiMe_4 and $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{thf})]$ were used for ^{29}Si and ^{171}Yb spectra, respectively. All NMR spectra other than ^1H were proton-decoupled and recorded at ambient temperature unless otherwise stated. Ytterbium(II) iodide, $^{19}\text{Li}(\text{A}^{\text{Ph,Ph}})$, 17 and $\text{Li}(\text{A}^{\text{Tol,Tol}})$ 17 were prepared by published procedures. The compound $[\text{Li}(\text{A}^{\text{Tol,Ad}})]$ was first made by Dr Bourget-Merle. 18

Preparations

$\text{Li}(\text{A}^{\text{Dph,Dph}})(\text{OEt}_2)$. 4-Phenylbenzonitrile (4.90 g, 27.4 mmol) was added to a cooled (0 °C) and stirred solution of $\text{LiCH}(\text{SiMe}_3)_2$ (2.12 g, 12.7 mmol) in diethyl ether (150 cm^3). The resulting solution was slowly warmed to ca. 25 °C and stirred for 2 h. Volatiles were removed *in vacuo* until onset of crystallisation, the mixture then set aside at –27 °C yielding yellow crystals of $\text{Li}(\text{A}^{\text{Dph,Dph}})(\text{OEt}_2)$ (6.41 g, 84%) (Found: C, 73.3; H, 7.92; N, 4.71. $\text{C}_{37}\text{H}_{47}\text{LiN}_2\text{OSi}_2$: requires C, 74.2; H, 7.91; N, 4.68%). ^1H NMR (δ , C_6D_6): 7.67 (d, $J = 8.78$ Hz, *o*-H of Dph, 4 H), 7.51 (m, *m*-H and *o'*-H of Dph, 8 H), 7.23 (m, *m'*-H and *o'*-H of Dph, 6 H), 5.69 (s, CH, 1 H), 3.37 (q, $J = 7.32$ Hz, OCH_2CH_2 , 4 H), 1.16 (t, $J = 7.32$ Hz, OCH_2CH_2 , 6 H), 0.21 (s, SiMe_3 , 18 H).

$\text{Li}(\text{A}^{\text{Tol,Ad}})$. 1-Adamantanecarbonitrile (1.64 g, 10.16 mmol) was added to a cooled (–20 °C) and stirred solution of $\text{LiCH}(\text{SiMe}_3)_2$ (1.69 g, 10.16 mmol) in diethyl ether (100 cm^3). The mixture was stirred at ca. 25 °C for 12 h, whereafter 4- $\text{MeC}_6\text{H}_4\text{CN}$ (1.19 cm^3 , 10.16 mmol) was slowly added. The resulting yellow solution was stirred for a further 12 h. Volatiles were removed at 50 °C/10 $^{-2}$ Torr. Crystallisation of the residue from *n*-hexane yielded yellow crystals of $\text{Li}(\text{A}^{\text{Tol,Ad}})$ (3.39 g, 75%) (Found: C, 69.9; H, 9.20; N, 6.26. $\text{C}_{26}\text{H}_{41}\text{LiN}_2\text{Si}_2$ requires C, 70.2; H, 9.29; N, 6.30%).

$\text{K}(\text{A}^{\text{Ph,Ph}})$. KOBu^t (0.70 g, 6.28 mmol) was added to a stirred solution of complex $\text{Li}(\text{A}^{\text{Ph,Ph}})$ (2.34 g, 6.28 mmol) in diethyl ether (100 cm^3). The orange solution was stirred for 2 h, then the solvent was pumped off and the residue was washed with hexane (2 \times 50 cm^3) and dried for 2 h at 50 °C/10 $^{-2}$ Torr giving $\text{K}(\text{A}^{\text{Ph,Ph}})$ (1.65 g, 65%) as a yellow powder (Found: C, 61.5; H, 7.20; N, 6.89. $\text{C}_{21}\text{H}_{29}\text{KN}_2\text{Si}_2$ requires C, 62.3; H, 7.22; N, 6.92%).

$\text{K}(\text{A}^{\text{Tol,Tol}})$. This was synthesised analogously (Found: C, 63.1; H, 7.61; N, 6.48. $\text{C}_{23}\text{H}_{33}\text{KN}_2\text{Si}_2$ requires C, 63.8; H, 7.69; N, 6.47%).

$\text{K}(\text{A}^{\text{Dph,Dph}})$. This was synthesised analogously (Found: C, 70.5; H, 6.72; N, 5.01. $\text{C}_{33}\text{H}_{37}\text{KN}_2\text{Si}_2$ requires C, 71.2; H, 6.70; N, 5.03%).

$\text{K}(\text{A}^{\text{Tol,Ad}})$. This was synthesised analogously (Found: C, 65.1; H, 8.59; N, 5.78. $\text{C}_{26}\text{H}_{41}\text{KN}_2\text{Si}_2$ requires C, 65.5; H, 8.67; N, 5.87%).

$[\text{Yb}(\text{A}^{\text{Ph,Ph}})_2]$ 1. YbI_2 (0.58 g, 1.36 mmol) was added to a stirred solution of $\text{K}(\text{A}^{\text{Ph,Ph}})$ (1.10 g, 2.72 mmol) in diethyl ether (100 cm^3). The dark brown suspension was stirred for 24 h and then filtered. The filtrate was concentrated to yield brown crystals of **1** (0.91 g, 74%) (Found: C, 55.3; H, 6.56; N, 6.31.

$\text{C}_{42}\text{H}_{58}\text{N}_4\text{Si}_4\text{Yb}$ requires C, 55.8; H, 6.46; N, 6.19%). ^1H NMR (δ , toluene- d_8): 7.49 (m, 8 H, *o*-H of Ph ring), 7.07 and 7.06 (two m, 12 H, *m*- and *p*-H of Ph ring), 5.52 (s, 2 H, CH), 0.19 (s, 36 H, $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (δ , toluene- d_8): 173.06 (s, NC-(Ph)CH), 148.40 (s, *ipso*-C of Ph ring), 128.30, 127.93, 127.83 (three s, C of Ph ring), 105.19 (s, CH), 2.99 (s, $\text{Si}(\text{CH}_3)_3$). ^{29}Si NMR (δ , toluene- d_8): –3.27. ^{171}Yb NMR (δ , toluene- d_8): 2634.

$[\text{Yb}(\text{A}^{\text{Tol,Tol}})_2]$ 2. A similar procedure, starting from YbI_2 (0.30 g, 0.69 mmol) and $\text{K}(\text{A}^{\text{Tol,Tol}})$ (0.65 g, 1.50 mmol), followed by crystallisation from hexane, yielded complex **2** (0.43 g, 65%) (Found: C, 57.2; H, 7.02; N, 5.70. $\text{C}_{46}\text{H}_{66}\text{N}_4\text{Si}_4\text{Yb}$ requires C, 57.5; H, 6.93; N, 5.83%). ^1H NMR (δ , toluene- d_8): 7.57 (d, $J = 7.32$ Hz, 8 H, *o*-H of Tol), 6.94 (d, $J = 7.32$ Hz, 8 H, *m*-H of Tol), 5.74 (s, 2 H, CH), 2.09 (s, 12 H, CH_3 of Tol), 0.24 (s, 36 H, $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (δ , toluene- d_8): 172.21 (s, NC(Tol)-CH), 145.80 (s, *ipso*-C of Tol), 138.09 (s, *p*-C of Tol), 128.58 and 128.12 (two s, *o*- and *m*-C of Tol), 104.51 (s, CH), 21.08 (s, CH_3 of Tol), 2.99 (s, $\text{Si}(\text{CH}_3)_3$). ^{29}Si NMR (δ , toluene- d_8): –5.18. ^{171}Yb NMR (δ , toluene- d_8 -thf) (273 K): 2529.

$[\text{Yb}(\text{A}^{\text{Dph,Dph}})_2]$ 3. A similar procedure, starting from YbI_2 (0.43 g, 1.02 mmol) and $\text{K}(\text{A}^{\text{Dph,Dph}})$ (1.17 g, 2.10 mmol), followed by crystallisation from hexane, yielded complex **3** (0.85 g, 69%) (Found: C, 65.2; H, 6.27; N, 4.80. $\text{C}_{66}\text{H}_{74}\text{N}_4\text{Si}_4\text{Yb}$ requires C, 65.6; H, 6.17; N, 4.63%). ^1H NMR (δ , C_6D_6): 7.67 (d, $J = 8.78$ Hz, 8 H, *o*-H of Dph), 7.43 (d, $J = 8.78$ Hz, 16 H, *m*-H and *o'*-H of Dph), 7.18 (t, $J = 7.32$ Hz, 8 H, *m'*-H of Dph), 7.14 (d, $J = 8.78$ Hz, 4 H, *o'*-H of Dph), 5.85 (s, 2 H, CH), 0.37 (s, 36 H, $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (δ , C_6D_6): 172.96 (s, NC(Dph)CH), 147.23 (s, *ipso*-C of Dph), 141.57 and 140.87 (two s, *p*-C and *ipso*-C of Dph), 129.03 and 128.54 (two s, *o*- and *m*-C of Dph), 127.61 (s, *p'*-C of Dph), 127.40 and 126.75 (two s, *o'*- and *m'*-C of Dph), 105.09 (s, CH), 3.26 (s, $\text{Si}(\text{CH}_3)_3$). ^{29}Si NMR (δ , C_6D_6): –3.99. ^{171}Yb NMR (δ , toluene- d_8 -thf) (203 K): 2588.

$[\text{Yb}(\text{A}^{\text{Tol,Ad}})_2]$ 4. A similar procedure, starting from YbI_2 (0.47 g, 1.10 mmol) and $\text{K}(\text{A}^{\text{Tol,Ad}})$ (1.10 g, 2.30 mmol), yielded complex **4** (0.72 g, 63%) (Found: C, 57.7; H, 7.80; N, 5.35. $\text{C}_{52}\text{H}_{82}\text{N}_4\text{Si}_4\text{Yb}$ requires C, 59.6; H, 7.88; N, 5.34%). ^1H NMR (δ , toluene- d_8): 7.54 (d, $J = 9.09$ Hz, 8 H, major *o*-H of Tol), 7.49 (d, $J = 8.86$ Hz, 8 H, minor *o*-H of Tol), 7.05 (d, $J = 5.81$ Hz, 8 H, major *m*-H of Tol), 6.98 (d, $J = 7.27$ Hz, 8 H, minor *m*-H of Tol), 5.71 (s, 2 H, major CH), 5.66 (s, 2 H, minor CH), 2.10 (m, 24 H, CH (6 H) of Ad + CH_2 (12 H) of Ad + CH_3 (6 H) of Tol), 1.79 (m, 12 H, CH_2 of Ad), 0.60 (s, 18 H, minor $\text{Si}(\text{CH}_3)_3$ connected to the Ad ligand side), 0.57 (s, 18 H, major $\text{Si}(\text{CH}_3)_3$ connected to the Ad ligand side), 0.21 (s, 18 H, minor $\text{Si}(\text{CH}_3)_3$ connected to the Tol ligand side), 0.16 (s, 18 H, major $\text{Si}(\text{CH}_3)_3$ connected to the Tol ligand side). ^{13}C NMR (δ , toluene- d_8): 176.20 (s, minor NC(Ad or Tol)CH), 175.27 (s, major NC(Ad or Tol)CH), 173.18 (s, major NC(Ad or Tol)CH), 172.81 (s, minor NC(Ad or Tol)CH), 145.49 (s, major *ipso*-C of Tol), 145.47 (s, minor *ipso*-C of Tol), 138.26 (s, major *p*-C of Tol), 138.23 (s, minor *p*-C of Tol), 128.58 (s, major *o*- or *m*-CH of Tol), 128.47 (s, minor *o*- or *m*-CH of Tol), 128.33 (s, minor *o*- or *m*-CH of Tol), 128.05 (s, major *o*- or *m*-CH of Tol), 99.07 (s, minor CH), 98.55 (s, major CH), 44.80 (s, major C_{quat} of Ad), 44.73 (s, minor C_{quat} of Ad), 41.39 (s, minor CH_2 of Ad), 41.36 (s, major CH_2 of Ad), 37.12 (s, major CH_2 of Ad), 37.08 (s, minor CH_2 of Ad), 29.43 (s, major CH of Ad), 29.38 (s, minor CH of Ad), 21.12 (s, major CH_3 of Tol), 21.06 (s, minor CH_3 of Tol), 4.51 (s, major $\text{Si}(\text{CH}_3)_3$ connected to the Ad ligand side), 4.50 (s, minor $\text{Si}(\text{CH}_3)_3$ connected to the Ad ligand side), 3.17 (s, minor $\text{Si}(\text{CH}_3)_3$ connected to the Tol ligand side), 3.12 (s, major $\text{Si}(\text{CH}_3)_3$ connected to the Tol ligand side). ^{29}Si NMR (toluene- d_8): –20.63 (s, major SiMe_3 connected to the Ad ligand side), –20.39 (s, minor SiMe_3 connected to the Ad ligand side), –4.92 (s, minor SiMe_3 connected

Table 6 Crystal data and structure refinement for **1**, **3** and **4**

Compound	1	3	4
Empirical formula	C ₄₂ H ₅₈ N ₄ Si ₄ Yb	C ₆₆ H ₇₄ N ₄ Si ₄ Yb	C ₅₂ H ₈₂ N ₄ Si ₄ Yb
Formula weight	904.32	1208.69	1048.62
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	<i>P</i> $\bar{1}$ (No.2)	<i>Pna</i> 2 ₁ (No.33)	<i>P</i> $\bar{1}$ (No.2)
<i>a</i> /Å	13.1217(14)	12.1373(3)	12.7363(5)
<i>b</i> /Å	13.6826(15)	22.1348(5)	13.1615(6)
<i>c</i> /Å	14.1141(16)	23.2872(3)	16.5277(11)
α /°	103.340(5)	90	85.738(3)
β /°	108.799(5)	90	82.722(4)
γ /°	100.987(6)	90	82.784(4)
<i>U</i> /Å ³	2235.5(4)	6256.3(2)	2721.6(2)
<i>Z</i>	2	4	2
<i>D_c</i> /Mg m ⁻³	1.34	1.28	1.28
μ (Mo-K α)/mm ⁻¹	2.23	1.61	1.84
Reflections collected	10932	38043	18527
Independent reflections	5369 [<i>R</i> (int) = 0.079]	13613 [<i>R</i> (int) = 0.057]	9531 [<i>R</i> (int) = 0.064]
Reflections with <i>I</i> > 2 σ (<i>I</i>)	4096	10281	7645
Data/restraints/parameters	5369/0/318	13613/1/676	9531/0/550
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.067, <i>wR</i> 2 = 0.152	<i>R</i> 1 = 0.041, <i>wR</i> 2 = 0.076	<i>R</i> 1 = 0.074, <i>wR</i> 2 = 0.185
<i>R</i> indices (all data)	<i>R</i> 1 = 0.094, <i>wR</i> 2 = 0.165	<i>R</i> 1 = 0.066, <i>wR</i> 2 = 0.085	<i>R</i> 1 = 0.094, <i>wR</i> 2 = 0.199

to the Tol ligand side), −4.44 (s, major SiMe₃ connected to the Tol ligand side). ¹⁷¹Yb NMR (δ , toluene-*d*₈): 2641, 2629.

¹H NMR NOE Spectroscopic experiments on complexes **1–4**

The results are summarised in Tables 4 and 5, showing the enhancement (η , %) of a designated ¹H signal upon irradiating the sample at the frequency of another, using C₆D₆ as solvent at ambient temperature.

Crystallography

Data for the crystal structure determination of each of **1**, **3** and **4** were collected on a Bruker AXS CCD area detector at 173(2) K with Mo-K α X-rays (λ = 0.71073 Å). Crystal data and refinement details are listed in Table 6. The structures were solved by direct methods and refined using SHELXL-97.²⁰ The phenyl groups of **1** were refined as rigid bodies with isotropic C atoms. For two of the rings (C16–C21) and (C31–C36) two alternative orientations were included. All other non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in riding mode.

CCDC reference numbers 191918, 192428 and 191917 for compounds **1**, **3** and **4**, respectively.

See <http://www.rsc.org/suppdata/dt/b3/b300204g/> for crystallographic data in CIF or other electronic format.

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