Crystalline di- or trianionic metal (Al, Sm) β-diketiminates†‡

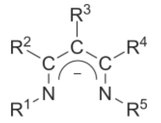
Martyn P. Coles, Peter B. Hitchcock, Alexei V. Khvostov, Michael F. Lappert* and Andrey V. Protchenko

Received 4th March 2010, Accepted 25th May 2010
First published as an Advance Article on the web 21st June 2010
DOI: 10.1039/c0dt00071j

The new [Al($\mathbf{L}^{\mathrm{Tol}}$)Br$_2$] (**1**) and the known [Al($\mathbf{L}^{\mathrm{Ph}}$)Me$_2$] (**2**) were prepared as potential precursors to more novel aluminium compounds. In the event, only the latter was effective. Thus **2** and two equivalents of potassium was the source of [{Al($\mathbf{L}^{\mathrm{Ph}}$)Me$_2$K$_2$(OEt$_2$)}$_2$] (**3**). The complexes [{KSm($\mathbf{L}^{\mathrm{Ph}}$)$_2$}$_2$] (**4**), [Sm$_2$($\mathbf{L}^{\mathrm{Dph}}$)$_3$] (**5**) and [Sm($\mathbf{L}^{\mathrm{Tol,Ad}}$)($\mathbf{L}^{\mathrm{Tol,Ad}}$–H)] (**6**) were obtained from SmI$_2$ and two equivalents of the appropriate potassium β-diketiminate [$\mathbf{L}^{\mathrm{Ph}}$ or $\mathbf{L}^{\mathrm{Tol}}$ or $\mathbf{L}^{\mathrm{Dph}}$ = {N(SiMe$_3$)C(Ar)}$_2$CH, Ar = Ph or C$_6$H$_4$Me-4 or C$_6$H$_4$Ph-4; $\mathbf{L}^{\mathrm{Tol,Ad}}$ = N(SiMe$_3$)C(C$_6$H$_4$Me-4)C(H)C(Ad)NSiMe$_3$, $\mathbf{L}^{\mathrm{Tol,Ad}}$–H = N(SiMe$_3$)C(C$_6H_4$Me-4)C(H)C(Ad)NSiMe$_2CH_2$, Ad = 1-adamantyl]. Crystalline complexes **3–6** were isolated in very low (**4**, **5**) or satisfactory (**3**, **6**) yield and characterised by X-ray diffraction. From comparisons of the M–N, N–C, C–C and C–C$_{\mathrm{Ar}}$ bond lengths with suitable standards, complexes **3–5** are assigned as containing Al^{3+}/($\mathbf{L}^{\mathrm{Ph}}$)$^{3-}$ for **3**, Sm^{3+}/($\mathbf{L}^{\mathrm{Ph}}$)$^{-}$/($\mathbf{L}^{\mathrm{Ph}}$)$^{3-}$ for **4**, and {Sm^{3+}}$_2$/($\mathbf{L}^{\mathrm{Dph}}$)$^{-}$/($\mathbf{L}^{\mathrm{Dph}}$)$^{2-}$/($\mathbf{L}^{\mathrm{Dph}}$)$^{3-}$ for **5**. Complex **6** is best formulated as a Sm^{3+} compound with one “normal” ($\mathbf{L}^{\mathrm{Tol,Ad}}$)$^{-}$ and one deprotonated ($\mathbf{L}^{\mathrm{Tol,Ad}}$–H)$^{2-}$ ligand.

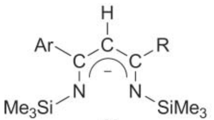
Introduction

β-Diketiminates, shown in their most generalised monoanionic π-delocalised form in **A**, are important spectator ligands. They bind strongly to a metal or bridge two metals and usually are *N*,*N*′, but rarely also *N*,*C*-centred. Their steric and electronic demands can be varied widely, particularly by choice of the substituents R^1 and R^5. Their substantial steric effects are well illustrated by noting that very few tris(β-diketiminato)metal complexes are known. Many such species are coordinatively unsaturated, which is crucial to their frequent use as catalysts or pro-catalysts for systems ranging from numerous olefinic transformations to ring-opening polymerisation of lactide. In a 2002 review we noted that *ca.* 180 publications, including 65 post-2000, dealt with complexes of 43 metals.[1] The significance of β-diketiminato ligands continues apace.



A

The four ligands, which feature as samarium and aluminium complexes in the present study, are a sub-class **A’** of **A** (R^1 = SiMe$_3$ = R^5):



A'

L^{Ph}: Ar = Ph = R
$\mathrm{L}^{\mathrm{Tol}}$: Ar = C$_6H_4$Me-4 = R
$\mathrm{L}^{\mathrm{Tol,Ad}}$: Ar = C$_6H_4$Me-4, R = Ad
$\mathrm{L}^{\mathrm{Dph}}$: Ar = C$_6H_4$Ph-4 = R

The first β-diketiminatosamarium complexes to be described were [Sm({N(Pr^i)C(Me)}$_2$CH)$_2$Br],[2] [Sm({N(Ph)C(Me)}$_2$CH)$_3$] (obtained from SmI$_2$ and the appropriate Li β-diketiminate),[3] [Sm($\mathbf{L}^{\mathrm{Ph}}$)$_2$Cl][4] and [Sm($\mathbf{L}^{\mathrm{Ph}}$)$_2$(thf)$_2$].[4] More recent examples were [Sm({N(C$_6$H$_2$Me$_3$-2,4,6)C(Me)}$_2$CH)Cl(thf)(μ-Cl)$_2$Li(thf)$_2$] and three derivatives,[5] and [Sm($\mathbf{L}^{\mathrm{NDipp}}$)Cl(μ-Cl)$_3$Sm($\mathbf{L}^{\mathrm{NDipp}}$)(thf)] and nine products [$\mathbf{L}^{\mathrm{NDipp}}$ = {N(C$_6$H$_3$Pr$^i_2$-2,6)C(Me)}$_2$CH].[6] The heteroleptic compound [SmCp’($\mathbf{L}^{\mathrm{NTol}}$)(BH$_4$)] [Cp′ = C$_5Me_4$Pr^n, $\mathbf{L}^{\mathrm{NTol}}$ = {N(C$_6$H$_4$Me-4)C(Me)}$_2$CH] was studied as a stereospecific isoprene polymerisation catalyst,[7] while [Sm($\mathbf{L}^{\mathrm{NDipp}}$)(η^3-C$_3H_5$)$_2$][8] and [Sm($\mathbf{L}^{\mathrm{NClPh}}$)$_3$][9] [$\mathbf{L}^{\mathrm{NClPh}}$ = {N(C$_6$H$_4$Cl-4)C(Me)}$_2$CH] were effective initiators for the ring-opening polymerisation of ε-caprolactone and *rac*-lactide. The Sm(III) derivative [Sm($\mathbf{L}^{\mathrm{NPend}}$)Br$_2$] [$\mathbf{L}^{\mathrm{NPend}}$ = {N(CH$_2$CH$_2$NMe$_2$)C(Me)}$_2$CH] of a ligand possessing two pendant arms has been described.[10] About sixty β-diketiminatoaluminium(III) complexes were cited in the 2002 review,[1] as well as the first aluminium(I) β-diketiminate [Al($\mathbf{L}^{\mathrm{NDipp}}$)];[11] some of its oxidative adducts were later disclosed.[12] The dicationic Al(III) salt [Al({N(C$_6$F$_5$)C(Me)}$_2$CH)(tren)][OTf]$_2$ is of interest.[13]

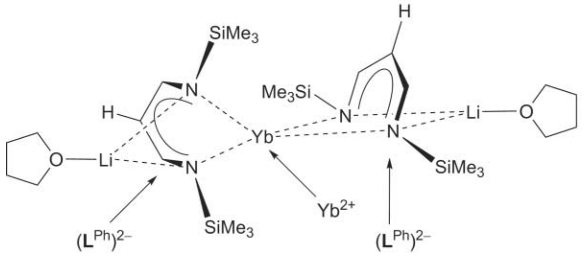
More than 500 β-diketiminatometal complexes have been reported. Apart from three lithium and five ytterbium *N*,*N*′bis(trimethylsilyl) compounds, all have been monoanionic. The Li compounds have been the dianionic [Li(tmeda)(μ-$\mathbf{L}^{\mathrm{Ph}}$)Li(OEt$_2$)] and the [$\mathbf{L}^{\mathrm{Ph,t\text{-}Bu}}$]$^{2-}$ analogue [$\mathbf{L}^{\mathrm{Ph,t\text{-}Bu}}$ = N(SiMe$_3$)C(Ph)C(H)C(Bu^t)NSiMe$_3$] and the trianionic [{Li$_3$({N(SiMe$_3$)C(C$_6$H$_4$Bu^t-4)}$_2$CH)(tmeda)}$_2$];[14] the precursors in each case included the appropriate Li β-diketiminate and one or two equivalents of the metal. The ytterbium complexes were [Yb{(μ-$\mathbf{L}^{\mathrm{Ph}}$)Li(thf)}$_2$] (**B**) and the $\mathbf{L}^{\mathrm{Dph}}$ analogue,[14,15] [Yb$_3$($\mathbf{L}^{\mathrm{Ph}}$)$_3$(thf)] (**C**)[14,16] and [Yb$_3$($\mathbf{L}^{\mathrm{Ph}}$)$_2$(dme)$_2$];[14] compounds **B** and **C** were prepared from [Yb($\mathbf{L}^{\mathrm{Ph}}$)$_2$Cl] + 3Li and [Yb(C$_{10}$H$_8$)(thf)$_3$] + [Yb($\mathbf{L}^{\mathrm{Ph}}$)$_2$], respectively. A final Yb compound [Yb$_5$($\mathbf{L}^{\mathrm{Ph}}$)(L^1)(L^2)(L^3)(thf)$_4$], isolated in very low yield from 2Yb + [Yb($\mathbf{L}^{\mathrm{Ph}}$)$_2$], contained ($\mathbf{L}^{\mathrm{Ph}}$)$^{3-}$ and three, L^1 to L^3, polyanionic $\mathbf{L}^{\mathrm{Ph}}$ fragments: [$\mathbf{L}^{\mathrm{Ph}}$ minus H$^+$]$^{4-}$, [NC(Ph)CHC(Ph)H]$^{3-}$ and [N(SiMe$_2$CH$_2$)]$^{3-}$, respectively.[14] Cyclic

---

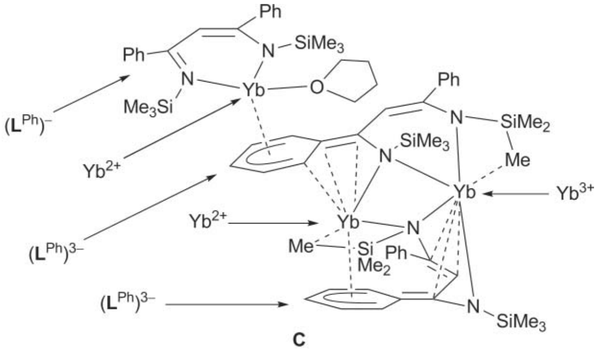
Department of Chemistry and Biochemistry, University of Sussex, Brighton, UK BN1 9QJ. E-mail: m.f.lappert@sussex.ac.uk; Fax: +44 1273 876687; Tel: +44 1273 678316

† Dedicated to Professor David W. H. Rankin on the occasion of his retirement.

‡ CCDC reference number 768769–768772. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00071j



B



C

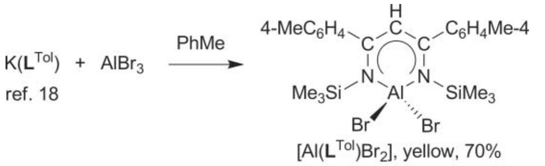
voltammetry showed that the primary reduction potential in thf containing [NBu$_4$][PF$_6$] decreased in the sequence (i) Li($\mathbf{L}^{\mathrm{Ph}}$) > Li($\mathbf{L}^{\mathrm{Ph,t\text{-}Bu}}$) ≫ Li($\mathbf{L}^{\mathrm{Dipp}}$) and (ii) [Yb($\mathbf{L}^{\mathrm{Ph}}$)$_2$] ≫ [Yb($\mathbf{L}^{\mathrm{Dipp}}$)$_2$], consistent with the notion that two ($\mathbf{L}^{\mathrm{Ph}}$) or one ($\mathbf{L}^{\mathrm{Ph,t\text{-}Bu}}$) *C*-phenyl substituents are available for π-electron delocalisation of the reduced species, whereas the bulky *N*-aryl groups are sterically unable to participate in such conjugation.[17]

Results and discussion

The paper deals with the synthesis, structure and bonding of selected aluminium and samarium β-diketiminates and their one- or two-electron reduction products. These elements have two stable oxidation states in some of their β-diketiminates, Al(I)/Al(III) and Sm(II)/Sm(III), while certain *C*-aryl or *C*,*C′*diaryl β-diketiminates such as $\mathbf{L}^{\mathrm{Ph}}$ are readily reduced. Hence the nature of the bonding in some of their reduced β-diketiminates was the major objective of the present study.

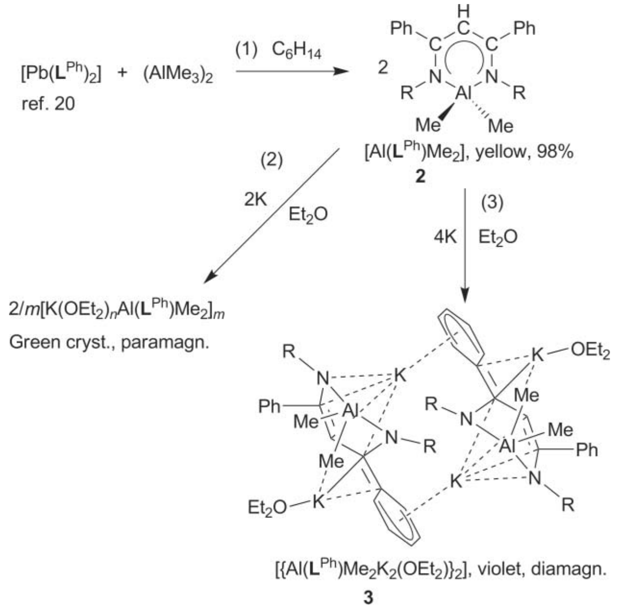
Experiments in aluminium chemistry

The β-diketiminatoaluminium(III) complex, originally chosen as a prospective precursor to a reduced species, was the new, yellow β-diketiminatoaluminium(III) dibromide **1**, prepared as shown in eqn. (1). Attempts to obtain characterisable products from **1** and metallic potassium were unsuccessful. Thus from **1** and an equivalent portion of K, as a mirror in C$_6$D$_6$ or PhMe, there was a rapid colour change from yellow to green and then to brown; the green intermediate was too unstable to be characterised while only non-crystalline material was isolated from the brown solution.



1

We next turned to the known[19] yellow complex [Al($\mathbf{L}^{\mathrm{Ph}}$)Me$_2$] (**2**); it was prepared by a new method (step 1 of Scheme 1) using [Pb($\mathbf{L}^{\mathrm{Ph}}$)$_2$][20] as the source of the $\mathbf{L}^{\mathrm{Ph}}$ ligand. Treatment of **2** with an equivalent portion of potassium in diethyl ether resulted in dissolution of potassium and formation of a green solution; cooling at −27 °C afforded dark green paramagnetic (^{1}H NMR) crystals (not of X-ray quality) believed to be of a 1 : 1-complex (step 2 of Scheme 1). Finally, the stoichiometry was altered so that (step 3 of Scheme 1) an Et$_2$O solution of **2** was added to a K mirror prepared from slightly more than two equivalents of potassium; lustrous violet crystals of [{Al($\mathbf{L}^{\mathrm{Ph}}$)Me$_2$K$_2$(OEt$_2$)}$_2$] (**3**) precipitated at room temperature. The low solubility of **3** in Et$_2$O or hydrocarbons and its extremely high sensitivity to moisture and air prevented preparation of an analytically pure sample. The ^{1}H NMR spectrum of **3** in thf-d$_8$ showed low frequency shifted signals for *ortho*- and *para*- protons of the Ph substituents, consistent with the β-diketiminato ligand being doubly reduced.[14]



Scheme 1 Synthesis of [Al($\mathbf{L}^{\mathrm{Ph}}$)Me$_2$] (**2**) and its reduction to [{Al($\mathbf{L}^{\mathrm{Ph}}$)Me$_2$K$_2$(OEt$_2$)}$_2$] (**3**) (R = SiMe$_3$)

The molecular structure of the crystalline centrosymmetric dimeric compound **3** is shown as an ORTEP representation in Fig. 1. Selected bond lengths and angles are listed in Table 1. The two monomeric units are joined by short K···η^6-C$_6$H$_5$ contacts (K1···M1′ and M1···K1′ of 2.901(3) Å; M1 and M1′ are the centroids of the transoid C$_6$H$_5$ groups of units containing K1 and K1′, respectively); thus, K1 is sandwiched between the NCCCN backbone of an $\mathbf{L}^{\mathrm{Ph}}$ ligand of one unit and a C$_6$H$_5$ group of the second. The second potassium atom K2 is in a five-coordinate environment, having short contacts to the oxygen atom of an Et$_2$O ligand, the β-carbon atom (C3) of the $\mathbf{L}^{\mathrm{Ph}}$ ligand, the adjacent *ipso*-carbon atom (C10) of the C$_6$H$_5$ group, and the AlMe$_2$ methyl carbon atoms C22 of the same and C23′ of the neighbouring molecule. The relative magnitude of the two C$_{ipso}$–C($\mathbf{L}^{\mathrm{Ph}}$) bond

Table 1 Selected bond distances (Å) and angles (°) for $[\{Al(\mathbf{L}^{Ph})Me_2K_2(OEt_2)\}_2]$ (**3**)

Al–N1	1.888(2)	K1–M1′	2.901(3)
Al–N2	1.902(2)	K1–N1	2.934(2)
Al–C22	1.990(3)	K1–N2	3.033(2)
Al–C23	1.992(3)	K1–C1	3.054(2)
N1–C1	1.430(3)	K1–C2	2.973(3)
N2–C3	1.459(3)	K1–C3	2.959(3)
C1–C2	1.376(4)	K2–O	2.644(3)
C2–C3	1.438(3)	K2–C10	2.839(2)
C1–C4	1.480(3)	K2–C3	2.968(3)
C3–C10	1.425(4)	K2–C22	3.021(4)
N1–Si1	1.718(2)	K2–C23″	3.061(3)
N2–Si2	1.720(2)		
N1–Al–N2	99.75(10)	N1–C1–C4	119.6(2)
C22–Al–C23	104.03(17)	N2–C3–C10	122.4(2)
Al–N1–C1	105.28(16)	C2–C3–C10	117.6(2)
Al–N2–C3	110.95(15)	C2–C1–C4	117.7(2)
N1–C1–C2	121.5(2)	N1–K1–M1′	157.62(5)
N2–C3–C2	117.8(2)	O–K2–C10	112.93(9)
C1–C2–C3	132.7(2)	O–K2–C3	121.72(8)

M1′ is centroid of the C10′ to C15′ ring. Symmetry transformations used to generate equivalent atoms: ′ −x, −y, −z; ″ $-x - \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$

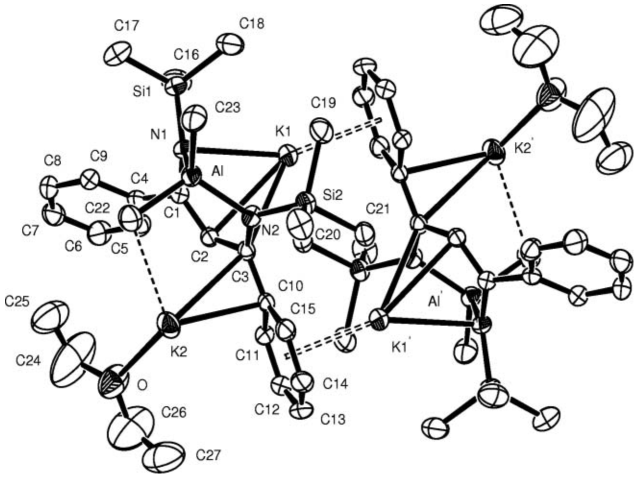


Fig. 1 Molecular structure of crystalline **3** (50% ellipsoids).

lengths indicates that C3–C10, unlike C1–C4, is a double bond (the formal single/double bond distribution is shown in Scheme 1). The C–C distances in the backbone of the $\mathbf{L}^{Ph}$ ligand are unequal, with C2–C3 > C1–C2, consistent with the notion that the latter is a double bond; the N–C bonds are significantly longer than those in **2** (av. 1.334 Å).[19] The $\mathbf{L}^{Ph}$: Al : K 1 : 1 : 2 stoichiometry would be appropriate either for an $(\mathbf{L}^{Ph})^{3-}/Al^{3+}$ or $(\mathbf{L}^{Ph})^{-}/Al^{+}$ assignment; the former is preferred not only on the basis of the above discussion, but also because the Al–N distances in **3** are significantly shorter than the 1.921(4) Å in **2**,[19] and the Al–CH_3 length (av. 1.991 Å) is longer than in **2** (apparently due to the presence of additional K···CH_3 interactions in **3**).

Synthesis and structures of three crystalline β-diketiminatosamarium compounds 4, 5 and 6

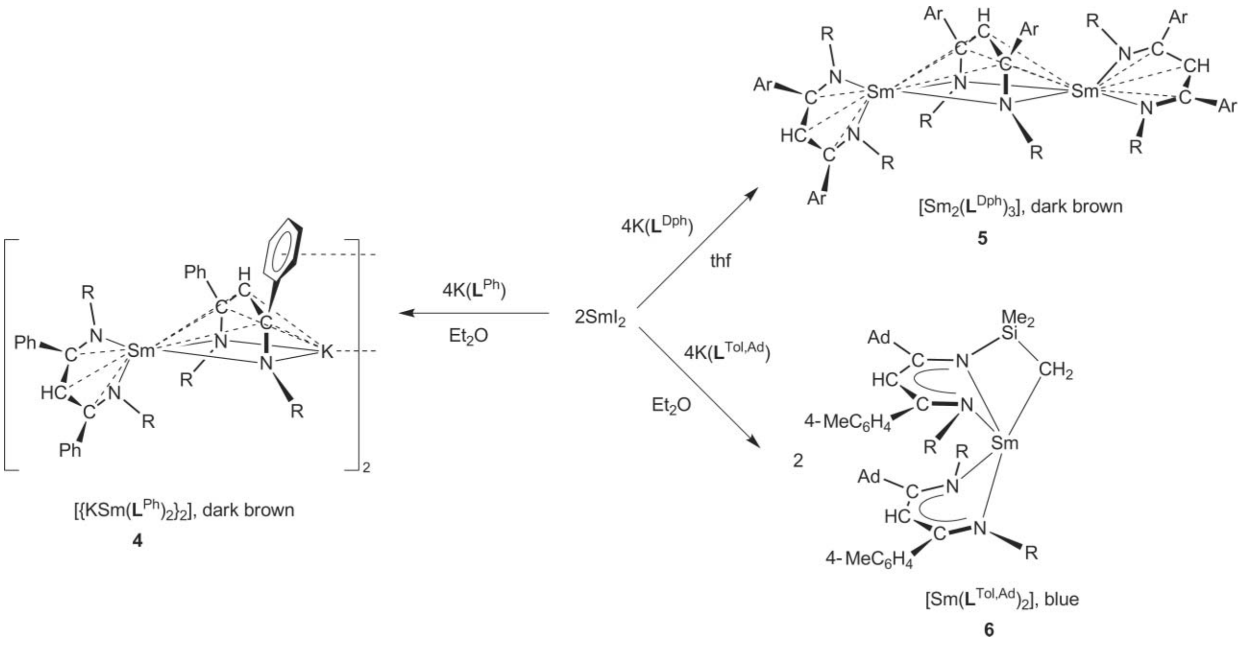
Table 2 Selected bond distances (Å) and angles (°) for $[\{KSm(\mathbf{L}^{Ph})_2\}_2]$ (**4**)

Sm–N1	2.412(3)	Sm–N3	2.309(3)
Sm–N2	2.391(3)	Sm–N4	2.308(3)
Sm···C1	2.919(4)	Sm···C22	2.562(4)
Sm···C2	2.940(4)	Sm···C23	2.611(4)
Sm···C3	2.905(4)	Sm···C24	2.601(4)
N1–C1	1.335(5)	N3–C22	1.422(5)
N2–C3	1.324(5)	N4–C24	1.428(5)
C1–C2	1.423(6)	C22–C23	1.418(6)
C2–C3	1.422(6)	C23–C24	1.448(6)
C1–C4	1.501(6)	C22–C25	1.484(6)
C3–C10	1.489(6)	C24–C31	1.463(6)
N1–Si1	1.740(4)	N3–Si3	1.703(3)
N2–Si2	1.741(4)	N4–Si4	1.688(4)
K···C22	2.940(4)	K–N3	2.812(3)
K···C23	2.923(4)	K–N4	2.873(3)
K···C24	2.987(4)	K···M′	2.928(5)
N1–Sm–N2	78.08(12)	N3–Sm–N4	83.07(11)
Sm–N1–C1	98.2(2)	Sm–N3–C22	83.1(2)
Sm–N2–C3	98.8(2)	Sm–N4–C24	84.8(2)
N1–C1–C2	123.9(4)	N3–C22–C23	122.2(4)
N2–C3–C2	123.3(4)	N4–C24–C23	120.0(3)
C1–C2–C3	128.7(4)	C22–C23–C24	134.6(4)
C2–C3–C10	115.3(4)	C23–C22–C25	116.4(4)
C2–C1–C4	115.7(4)	C23–C24–C31	117.6(4)
M′–K–N3	150.97(12)	M′–K–N4	140.79(12)

M′ is centroid of the C31′ to C36′ ring. Symmetry transformations used to generate equivalent atoms: ′ −x,−y,−z

Treatment of a suspension of SmI_2 in diethyl ether (**4**, **6**) or tetrahydrofuran (**5**) with two equivalents of the appropriate potassium β-diketiminate and successive filtration, concentration of the green (**4**, **5**) or blue (**6**) filtrate, addition of pentane (**4**, **6**) or hexane (**5**), and cooling at −10 °C afforded (Scheme 2), in low (**4**, **5**) or significant (60% for **6**) yield, X-ray quality crystals of the dark brown (**4**, **5**) or blue (**6**) samarium complexes $[\{KSm(\mathbf{L}^{Ph})_2\}_2]$ (**4**), $[Sm_2(\mathbf{L}^{Dph})_3]$ (**5**) and $[Sm(\mathbf{L}^{Tol,Ad})(\mathbf{L}^{Tol,Ad}{-}H)]$ (**6**). The ^{1}H NMR spectra of each of the compounds **4** and **5** showed one set of paramagnetically shifted (sharp and having the appropriate multiplicity) signals characteristic for the appropriate ligand ($\mathbf{L}^{Ph}$ and $\mathbf{L}^{Dph}$) and another set of broad signals which could not be integrated separately due to increased line-width. This fact is indicative of the presence of two types (terminal and bridging) of ligands in compounds **4** and **5**. The ^{1}H NMR spectrum of complex **6** was unassignable.

The molecular structure of the crystalline centro-symmetric dimeric compound **4** is shown in an ORTEP representation in Fig. 2a and for a monomer fragment in greater detail in Fig. 2b; selected bond lengths and angles are listed in Table 2. The two monomeric units are joined by the close K···η^6-C_6H_5 contacts (K···C31′ to 36′ at 3.24 ± 0.10 Å). The potassium atom also has short contacts to the five backbone atoms of the bridging $\mathbf{L}^{Ph}$ ligand N3C22C23C24N4 of 2.84 ± 0.03 Å (N3/N4) and 2.87 ± 0.06 Å (C22/C23/C24); the K–N distances may be compared to those in $[K(\mu\text{-}\mathbf{L}^{Ph})(thf)_2]_\infty$ (2.827(3) and 2.833(3) Å).[21] This virtually planar ligand is bound in an η^5-fashion to the Sm atom *via* very short Sm–N and Sm–C interactions. Thus, the Sm–N3 and Sm–N4 distances are shorter than similar distances in the Sm(III) β-diketiminates $[Sm(\mathbf{L}^{NDipp})Cl(NR_2)]$ and $[Sm(\mathbf{L}^{NDipp})(NR_2)_2]$ (2.344 ± 0.010 and 2.465 ± 0.038 Å, respectively),[6] but very close to the Sm(III)-N_{amide} distances in the above-mentioned compounds [2.276(3) and 2.311 ± 0.013 Å, respectively],[6] and in the bulky triamides $[Sm(NCy_2)_3(thf)]$ (2.27 ± 0.01 Å)[22] and $[Sm(NR_2)_3]$ (2.284(3) Å)[23] (R = $SiMe_3$). The Sm–C distances (C22/C23/C24, 2.59 ± 0.03 Å)



Scheme 2 Synthesis of samarium complexes **4**, **5** and **6** (R = $SiMe_3$, Ar = C_6H_4Ph-4)

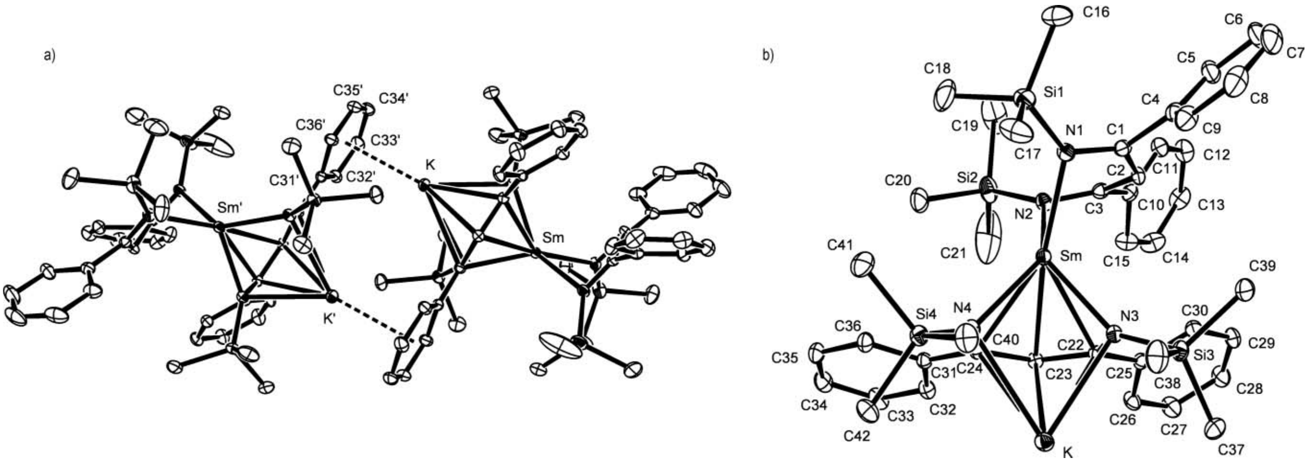


Fig. 2 Molecular structure of crystalline **4** (20% ellipsoids): (a) dimeric molecule (left); (b) monomeric unit (right).

are much shorter than the Sm–C(Cp*) distances in the bulky Sm(III) compounds [Sm($\mathbf{L}^{NDipp}$)(CH_2R)(Cp*)] [2.746(5) Å][6] or [Sm$(Cp^*)_2$Me(thf)] [2.711(6) Å][24] (Cp* = C_5Me_5), and similar to the shortest Sm–C(allyl) distances in [Sm($\mathbf{L}^{NDipp}$)(η^3-C_3H_5)$_2$] (2.606(4) and 2.612(4) Å).[8] The second, terminal, $\mathbf{L}^{Ph}$ ligand is attached to the Sm atom in an η^5-fashion with the Sm–N distances being *ca.* 0.1 Å longer and the Sm···C contacts *ca.* 0.3 Å longer than those for the bridging $\mathbf{L}^{Ph}$ ligand. The Sm–($\mathbf{L}^{Ph}$)$_{terminal}$ bonding situation is very similar to that in [Nd($\mathbf{L}^{Ph}$)$_2$Cl],[4] where the appropriate Nd–N and Nd···C distances are *ca.* 0.03 Å longer, consistent with the difference in the Sm^{+3} and Nd^{+3} ionic radii.[25] The backbone N–C and (to a lesser extent) C–C bond lengths are longer in the bridging ligand, consistent with its being reduced; the slightly shorter backbone-to-phenyl C–C bonds in this ligand suggest some delocalisation of the negative charge to the Ph rings, especially to the potassium-bound ring, which is nearly coplanar with the ligand backbone. The $\mathbf{L}^{Ph}$: Sm : K 2 : 1 : 1 stoichiometry would be appropriate either for an Sm^{2+}/($\mathbf{L}^{Ph}$)$^-$/($\mathbf{L}^{Ph}$)$^{2-}$ or Sm^{3+}/($\mathbf{L}^{Ph}$)$^-$/($\mathbf{L}^{Ph}$)$^{3-}$ assignment (as the terminal ligand is certainly monoanionic); to assign the Sm atom oxidation state the Sm–N bond lengths are compared with those in Sm formamidinate complexes (in the absence of a well-characterised Sm(II) β-diketiminate in the literature) for which both Sm(II) and Sm(III) complexes have been prepared.[26] Thus, the Sm–N bonds in [Sm(Form)$_2$(thf)$_2$] (2.58 ± 0.05 Å) are significantly longer than those in [SmF(Form)$_2$(thf)] (2.449 ± 0.005 Å) or in [Sm(Form)$_3$] (2.46 ± 0.01 Å) [Form = {N($C_6H_3Pr^i_2$-2,6)}$_2$CH], which is in good agreement with the difference in Sm^{2+} and Sm^{3+} ionic radii.[25] It is noteworthy that [Sm(Form)$_3$] was obtained from [Sm(Form)$_2$(thf)$_2$], [SmI_2(thf)$_2$] and NaI with no oxidant added (formally [SmI_2(thf)$_2$] (a well-known reducing agent) was regarded as the oxidant yielding a Sm^0 co-product) as in the case of the reactions of Scheme 2. None of the Sm complexes **4**, **5** or **6** have Sm–N bond lengths approaching the values found in the Sm(II)

Table 3 Selected bond distances (Å) and angles (°) for $[Sm_2(\mathbf{L}^{Dph})_3]$ (**5**)

Sm1–N1	2.411(7)	Sm2–N5	2.320(7)	Sm1–N3	2.317(7)
Sm1–N2	2.380(8)	Sm2–N6	2.303(7)	Sm1–N4	2.464(7)
Sm1 ··· C1	2.803(10)	Sm2 ··· C67	2.694(9)	Sm2–N3	2.488(7)
Sm1 ··· C2	2.772(10)	Sm2 ··· C68	2.742(9)	Sm2–N4	2.407(7)
Sm1 ··· C3	2.784(9)	Sm2 ··· C69	2.763(9)	Sm1 ··· C34	2.623(9)
N1–C1	1.328(12)	N5–C67	1.420(9)	Sm1 ··· C35	2.644(9)
N2–C3	1.353(12)	N6–C69	1.390(9)	Sm1 ··· C36	2.590(9)
C1–C2	1.430(13)	C67–C68	1.408(12)	Sm2 ··· C34	2.697(9)
C2–C3	1.424(13)	C68–C69	1.431(12)	Sm2 ··· C35	2.726(9)
C1–C10	1.521(14)	C67–C76	1.450(13)	Sm2 ··· C36	2.730(8)
C3–C22	1.508(13)	C69–C88	1.484(13)	N3–C34	1.447(9)
N1–Si1	1.758(8)	N5–Si5	1.732(8)	N4–C36	1.417(9)
N2–Si2	1.759(8)	N6–Si6	1.720(8)	C34–C35	1.427(12)
N3–Si3	1.728(7)			C35–C36	1.421(12)
N4–Si4	1.738(7)			C34–C43	1.484(12)
				C36–C55	1.497(13)
N1–Sm1–N2	79.1(3)	N5–Sm2–N6	85.3(3)	N3–Sm1–N4	75.1(2)
Sm1–N1–C1	92.5(6)	Sm2–N5–C67	88.8(4)	Sm1–N3–C34	85.0(3)
Sm1–N2–C3	92.3(6)	Sm2–N6–C69	93.5(4)	Sm1–N4–C36	78.7(4)
N1–C1–C2	124.2(9)	N5–C67–C68	121.6(8)	N3–C34–C35	118.8(7)
N2–C3–C2	124.6(9)	N6–C69–C68	122.6(7)	N4–C36–C35	121.2(7)
C1–C2–C3	127.7(9)	C67–C68–C69	135.3(9)	C34–C35–C36	132.1(8)
C2–C3–C22	115.6(8)	C68–C67–C76	118.3(8)	C35–C34–C43	119.4(8)
C2–C1–C10	113.6(9)	C68–C69–C88	115.6(8)	C35–C36–C55	117.1(8)
N1–Sm1–N3	116.6(2)	Sm2–N3–C34	81.9(4)	N4–Sm2–N5	121.4(3)
N1–Sm1–N4	133.8(2)	Sm2–N4–C36	87.1(3)	N4–Sm2–N6	124.7(3)
N2–Sm1–N3	121.4(3)	N3–Sm2–N5	128.2(2)		
N2–Sm1–N4	135.7(3)	N3–Sm2–N6	129.9(2)		

formamidinate $[Sm(Form)_2(thf)_2]$[26] or guanidinate $[Sm(Giso)_2]$ [Giso = $\{N(C_6H_3Pr^i{}_2\text{-}2,6)\}_2CN(C_6H_{11})_2$; Sm–N 2.55 ± 0.02 Å].[27] Hence, complex **4** is best formulated as $Sm^{3+}/(\mathbf{L}^{Ph})^-/(\mathbf{L}^{Ph})^{3-}$.

An ORTEP representation of the structure of the crystalline dinuclear complex **5** is presented in Fig. 3 and selected geometrical parameters are shown in Table 3. Each samarium atom has a terminal β-diketiminato ligand $\mathbf{L}^{Dph}$, and the two Sm atoms are each attached to the N3, C34, C35, C36 and N4 atoms of a bridging $\mathbf{L}^{Dph}$. The two terminal ligands differ significantly, most notably by the magnitude of the N–C bond lengths of *ca.* 1.34 ± 0.013 Å for N1–C1/N2–C3 and 1.405 ± 0.015 Å for N5–C67/N6–C69 and their distances to the η^5-coordinated Sm atoms of *ca.* 2.396 ± 0.016 Å for Sm1–N1/N2 and 2.78 ± 0.02 Å for Sm1–C1/C2/C3 and 2.312 ± 0.009 Å for Sm2–N5/N6 and 2.73 ± 0.04 Å for Sm2–C67/C68/C69. The η^5:η^5-bridging $\mathbf{L}^{Dph}$ ligand has very short Sm–C34/C35/C36 contacts to the Sm1 atom of *ca.* 2.62 ± 0.03 Å and slightly longer from C34, C35, C36 to the Sm2 of 2.72 ± 0.02 Å, the former being similar to those in **4**. The Sm–N(bridging) bond lengths vary widely from *ca.* 2.32 to 2.49 Å increasing in the sequence Sm1–N3 < Sm2–N4 < Sm1–N4 < Sm2–N3. Within the three $\mathbf{L}^{Dph}$ ligands the N–C bond lengths decrease in the sequence N3–C4 > N5–C67 ≈ N4–C36 > N6–C69 ≫ N2–C3 > N1–C1, while each of the six C–C distances fall in a narrow range centred on 1.420 ± 0.012 Å. The variation of the backbone-to-aryl C–C bond lengths (C1–C10 > C3–C22 > C36–C55 > C34–C43 ≈ C69–C88 ≫ C67–C76) is somewhat greater and is centred on 1.485 ± 0.035 Å.

Based on the comparison of Sm–N bond lengths (as in the case of complex **4**) and the notion that all three ligands in complex **5** are different, the formal charge distribution for **5** is formulated as $\{Sm^{3+}\}_2/(\mathbf{L}^{Dph})^-/(\mathbf{L}^{Dph})^{2-}/(\mathbf{L}^{Dph})^{3-}$.

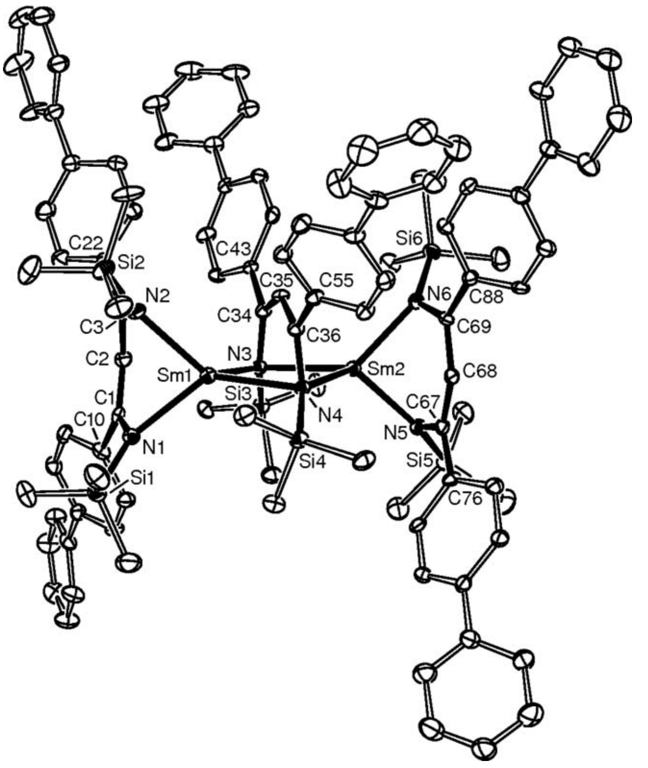


Fig. 3 Molecular structure of crystalline **5** (20% ellipsoids).

For the complex **6**, the first structure refinement was made assuming that it was a Sm(II) compound with two monoanionic $\mathbf{L}^{Tol,Ad}$ ligands, as its preparation was similar to that of the known ytterbium(II) compound $[\mathrm{Yb}(\mathbf{L}^{\mathrm{Tol,Ad}})_2]$.[18] However, this model had inexplicably short contacts Sm···C(Me) of 2.643(6) Å and Sm···H of 1.81 Å, which were considerably shorter than expected for an agostic interaction. Thus, the structure was re-refined as $[\mathrm{Sm}(\mathbf{L}^{\mathrm{Tol,Ad}})(\mathbf{L}^{\mathrm{Tol,Ad}}\text{–H})]$ considering one ligand being deprotonated and the Sm atom having a Sm–C σ-bond (although the difference map showed three peaks near the C52 atom, one was of a lower intensity and deviated from the expected tetrahedral geometry).

The molecular structure of the crystalline samarium β-diketiminate **6** is illustrated in an ORTEP representation in Fig. 4, and selected geometrical parameters are listed in Table 4 together with those of the ytterbium compound $[\mathrm{Yb}(\mathbf{L}^{\mathrm{Tol,Ad}})_2]$.[18] The Sm–N bond lengths in **6** are very similar to the Yb–N bond lengths in the Yb(II) complex having a similar coordination environment. However, due to the *ca.* 0.13 Å difference in the Sm^{+3} and Yb^{+2} ionic radii,[25] the Sm–N bonds are expected to be considerably longer, as was found in $[\mathrm{Sm}(\{\mathrm{N}(\mathrm{C_6H_3Pr^i{}_2}\text{-}2,6)\}_2\mathrm{CH})_2(\mathrm{thf})_2]$ with Sm–$\mathrm{N_{av.}}$ of 2.58 ± 0.05 Å,[26] or the Sm(II) bis-guanidinate $[\mathrm{Sm(Giso)_2}]$ [Giso = $\{\mathrm{N}(\mathrm{C_6H_3Pr^i{}_2}\text{-}2,6)\}_2\mathrm{CN}(\mathrm{C_6H_{11}})_2$] with Sm–$\mathrm{N_{av.}}$ of 2.55 ± 0.02 Å.[27] On the other hand these distances are very close to the Sm–N distances in most of the known Sm(III) β-diketiminates or the Sm(III) formamidinate $[\mathrm{Sm}(\{\mathrm{N(Ar)}\}_2\mathrm{CH})_3]$ (Ar = $\mathrm{C_6H_3Pr^i{}_2}$-2,6,[26] $\mathrm{C_6H_3Me_2}$-2,6,[28] $\mathrm{C_6H_3Et_2}$-2,6,[28] $\mathrm{C_6H_4Ph}$-2[28]). The N–C and C–C bond lengths of the ligand backbone are similar to those in $[\mathrm{Yb}(\mathbf{L}^{\mathrm{Tol,Ad}})_2]$[18] and for the terminal ligand in **4**, indicating that the ligands in **6** are not reduced. The Sm–C52 distance is slightly longer than such distances in Sm(III) alkyl complexes but is similar to the Sm–C bond lengths in the allyl complex $[\mathrm{Sm}(\mathbf{L}^{\mathrm{NDipp}})(\eta^3\text{-}\mathrm{C_3H_5})_2]$ (2.606(4) and 2.612(4) Å).[8] Involvement of the C52 atom in bonding with the Sm atom has caused a significant change in the geometry of the adjacent Si4 atom with the N4–Si4–C52 angle being considerably reduced compared to the N4–Si4–C50 and N4–Si4–C50 angles.

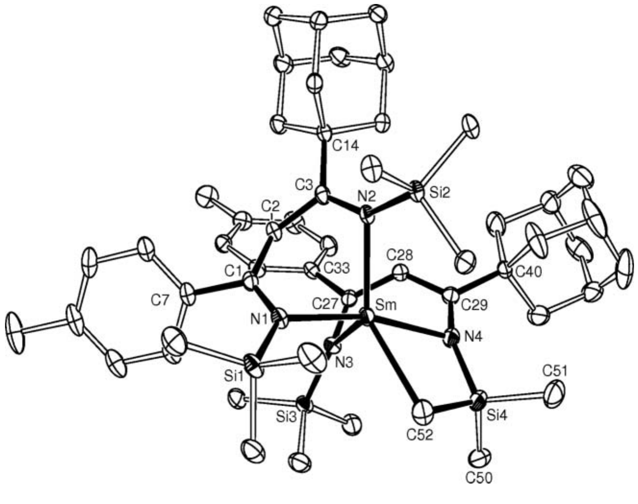


Fig. 4 Molecular structure of crystalline **6** (20% ellipsoids).

Table 4 Selected bond distances (Å) and angles (°) for $[\mathrm{Sm}(\mathbf{L}^{\mathrm{Tol,Ad}})(\mathbf{L}^{\mathrm{Tol,Ad}}\text{–H})]$ (**6**) and the Yb complex $[\mathrm{Yb}(\mathbf{L}^{\mathrm{Tol,Ad}})_2]$.[18]

	6 (M = Sm)	$[\mathrm{Yb}(\mathbf{L}^{\mathrm{Tol,Ad}})_2]$ (M = Yb)
M–N1	2.420(4)	2.412(7) (Yb–N3)
M–N2	2.417(4)	2.364(7) (Yb–N4)
M–N3	2.350(4)	2.378(7) (Yb–N2)
M–N4	2.363(4)	2.371(7) (Yb–N1)
N1–C1	1.322(6)	1.282(12) (N3–C27)
N2–C3	1.330(6)	1.337(11) (N4–C29)
N3–C27	1.355(6)	1.336(11) (N2–C3)
N4–C29	1.313(6)	1.341(12) (N1–C1)
C1–C2	1.424(6)	1.460(12) (C27–C28)
C2–C3	1.418(6)	1.390(12) (C28–C29)
C27–C28	1.411(6)	1.406(12) (C2–C3)
C28–C29	1.438(6)	1.432(13) (C1–C2)
Sm–C52	2.627(6)	
N1–M–N2	77.67(12)	81.7(2) (N3–Yb–N4)
N3–M–N4	78.96(13)	82.4(2) (N1–Yb–N2)
N1–C1–C2	125.9(4)	127.0(8) (N3–C27–C28)
N3–C27–C28	123.8(4)	125.6(8) (N1–C1–C2)
M–N1–C1	94.4(3)	99.8(5) (Yb–N3–C27)
M–N3–C27	95.6(3)	96.3(5) (Yb–N2–C3)
N4–Si4–C50	106.4(3)	
N4–Si4–C51	115.7(3)	
N4–Si4–C52	100.4(2)	

Angle between N1–M–N2 and N3–M–N4 planes: 58° (M = Sm), 58° (M = Yb). Angle between N1C1C3N2 and N3C27C29N4 planes: 10° (M = Sm), 15° (M = Yb). C2 out of N1C1C3N2 plane: 0.22 Å (M = Sm), 0.21 Å (M = Yb). C28 out of N1C27C29N2 plane: 0.21 Å (M = Sm), 0.24 Å (M = Yb).

Conclusions

The unusual X-ray-characterised crystalline metal complexes $[\{\mathrm{Al}(\mathbf{L}^{\mathrm{Ph}})\mathrm{Me_2K_2(OEt_2)}\}_2]$ (**3**), $[\{\mathrm{KSm}(\mathbf{L}^{\mathrm{Ph}})_2\}_2]$ (**4**), $[\mathrm{Sm_2}(\mathbf{L}^{\mathrm{Dph}})_3]$ (**5**) and $[\mathrm{Sm}(\mathbf{L}^{\mathrm{Tol,Ad}})(\mathbf{L}^{\mathrm{Tol,Ad}}\text{–H})]$ (**6**) have been prepared *via* potassium reduction (**3**) or a salt metathesis/disproportionation (**4**, **5**, **6**) route. Their novelty arises because a β-diketiminato ligand in each is other than monoanionic, a situation without precedent except in lithium and ytterbium chemistry. Noteworthy is the formation of Sm(III) products from a Sm(II) precursor. The assignment of charges $[\mathrm{Al}^{3+}/(\mathbf{L}^{\mathrm{Ph}})^{3-}$ for **3**, $\mathrm{Sm}^{3+}/(\mathbf{L}^{\mathrm{Ph}})^{-}/(\mathbf{L}^{\mathrm{Ph}})^{3-}$ for **4**, and $\{\mathrm{Sm}^{3+}\}_2/(\mathbf{L}^{\mathrm{Dph}})^{-}/(\mathbf{L}^{\mathrm{Dph}})^{2-}/(\mathbf{L}^{\mathrm{Dph}})^{3-}$ for **5**] is based on analysis of selected bond lengths and comparisons with those in known Al/N compounds for **3** and Sm/N compounds for **4**, **5** and **6**.

Experimental

General methods

The preparations of $[\mathrm{Al}(\mathbf{L}^{\mathrm{Tol}})\mathrm{Br_2}]$ (**1**), $[\mathrm{Al}(\mathbf{L}^{\mathrm{Ph}})\mathrm{Me_2}]$ (**2**), $[\{\mathrm{Al}(\mathbf{L}^{\mathrm{Ph}})\mathrm{Me_2K_2(OEt_2)}\}_2]$ (**3**), $[\{\mathrm{KSm}(\mathbf{L}^{\mathrm{Ph}})_2\}_2]$ (**4**), $[\mathrm{Sm_2}(\mathbf{L}^{\mathrm{Dph}})_3]$ (**5**) and $[\mathrm{Sm}(\mathbf{L}^{\mathrm{Tol,Ad}})(\mathbf{L}^{\mathrm{Tol,Ad}}\text{–H})]$ (**6**) were carried out under an atmosphere of argon or in a vacuum, using Schlenk apparatus and vacuum line techniques. The compounds $\mathrm{K}(\mathbf{L}^{\mathrm{Ph}})$,[14] $\mathrm{K}(\mathbf{L}^{\mathrm{Tol}})$,[14] $\mathrm{K}(\mathbf{L}^{\mathrm{Dph}})$,[14] $\mathrm{K}(\mathbf{L}^{\mathrm{Tol,Ad}})$,[14] and $[\mathrm{Pb}(\mathbf{L}^{\mathrm{Ph}})_2]$[16] were prepared by published procedures; $\mathrm{AlBr_3}$, $\mathrm{AlMe_3}$ in PhMe, K and $\mathrm{SmI_2}$ were commercial samples (Aldrich). The solvents employed were dried and distilled over sodium-potassium alloy (pentane, hexane) or sodium-benzophenone ($\mathrm{Et_2O}$, thf) and stored over a sodium mirror under argon. The NMR spectra were recorded using the DPX 300 and AMX 500 Bruker instruments and calibrated internally to residual solvent resonances for ^{1}H and ^{13}C{^{1}H}.

Synthesis of $[\mathrm{Al}(\mathbf{L}^{\mathrm{Tol}})\mathrm{Br_2}]$ (1)

Potassium β-diketiminate, $\mathrm{K}(\mathbf{L}^{\mathrm{Tol}})$, (0.455 g, 1.05 mmol) was added to a stirred suspension of $\mathrm{AlBr_3}$ (0.305 g, 1.14 mmol) in toluene

Table 5 Crystal data and structure refinement for **3**, **4**, **5** and **6**

Compound	**3**	**4**	**5**·C_6H_{14}	**6**
Empirical formula	$C_{27}H_{45}AlK_2N_2OSi_2$	$C_{84}H_{116}K_2N_8Si_8Sm_2$	$C_{105}H_{125}N_6Si_6Sm_2$	$C_{52}H_{81}N_4Si_4Sm$
Formula weight	575.01	1841.47	1940.35	1024.92
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$(No. 2)	$P2_1/c$ (No. 14)
a/Å	13.8525(7)	13.0232(5)	14.3495(6)	16.0256(6)
b/Å	14.1721(8)	20.0158(5)	16.7924(9)	18.5440(9)
c/Å	16.9078(7)	17.9052(7)	24.5587(14)	20.9627(7)
α (°)	90	90	97.177(3)	90
β (°)	101.807(3)	94.925(2)	95.469(3)	104.300(2)
γ (°)	90	90	111.259(3)	90
U/Å^3	3249.1(3)	4650.1(3)	5408.2(5)	6036.6(4)
Z	4	2	2	4
D_c/Mg m^{-3}	1.18	1.32	1.19	1.13
μ/mm^{-1}	0.41	1.49	1.19	1.09
Independent reflections	6334 [R(int) = 0.049]	8199 [R(int) = 0.063]	12909 [R(int) = 0.074]	8331 [R(int) = 0.058]
Reflections with $I > 2\sigma(I)$	4600	6183	9200	6791
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.051$, w$R_2 = 0.100$	$R_1 = 0.039$, w$R_2 = 0.080$	$R_1 = 0.059$, w$R_2 = 0.141$	$R_1 = 0.041$, w$R_2 = 0.091$
R indices (all data)	$R_1 = 0.081$, w$R_2 = 0.112$	$R_1 = 0.064$, w$R_2 = 0.089$	$R_1 = 0.094$, w$R_2 = 0.158$	$R_1 = 0.057$, w$R_2 = 0.101$

(20 mL) at −30 °C. The mixture was slowly warmed up to ambient temperature and stirred overnight. A white precipitate was filtered off; the solvent was removed *in vacuo* from the filtrate and the residue was washed with cold pentane (2 × 10 mL). The resulting yellow solid was dried *in vacuo*, yielding pure (by NMR) [Al(**L**^{Tol})Br$_2$] (**1**) (0.425 g, 0.73 mmol, 70%). ^{1}H-NMR (C_6D_6): δ 7.03 (d, 4H, *m*-H of tolyl), 6.72 (d, 4H, *o*-H of tolyl), 5.51 (s, 1H, middle CH), 1.96 (s, 6H, CH$_3$ of tolyl), 0.29 ppm (s, 18H, SiMe$_3$). ^{13}C-NMR (C_6D_6): δ 179.10 (s, N*C*(Tol)CH), 140.62 and 139.71 (two s, *ipso*-C and *p*-C of tolyl), 129.00 and 127.56 (two s, *m*- and *o*-CH of tolyl), 110.79 (s, middle CH), 21.09 (s, CH$_3$ of tolyl), 4.07 ppm (s, SiMe$_3$).

Synthesis of [Al(L^{Ph})Me$_2$] (2)

Excess AlMe$_3$ (1 mL of a 2 *M* solution in toluene, 2.0 mmol) was added to a stirred solution of the lead β-diketiminate [Pb(**L**^{Ph})$_2$] (0.618 g, 0.66 mmol) in toluene (10 mL) at ambient temperature. The mixture was stirred for 1 h (a black powder started to precipitate after 10 min) and then filtered. The volatiles were removed from the filtrate *in vacuo* and the resulting yellow crystalline solid was dried *in vacuo* at 60 °C, yielding pure (by NMR) [Al(**L**^{Ph})Me$_2$] (**2**) (0.550 g, 1.30 mmol, 98% based on **L**^{Ph}). ^{1}H-NMR (C_6D_6): δ 7.16–7.21 (m, 4H, Ph), 6.91–6.98 (m, 6H, Ph), 5.39 (s, 1H, middle CH), 0.09 (s, 18H, SiMe$_3$), −0.02 ppm (s, 6H, AlCH$_3$). ^{13}C-NMR (C_6D_6): δ 177.93 (s, N*C*(Ph)CH), 144.75 (s, *ipso*-C of Ph), 129.08 (s, *p*-CH of Ph), 128.20 and 127.76 (two s, *m*- and *o*-CH of Ph), 109.53 (s, middle CH), 3.29 (s, SiMe$_3$), −4.86 ppm (s, AlCH$_3$).

Reduction of 2

(i) A solution of [Al(**L**^{Ph})Me$_2$] (**2**) (0.195 g, 0.46 mmol) in diethyl ether (10 mL) was added to a potassium mirror (0.019 g, 0.49 mmol) at ambient temperature. The solution immediately turned green; after stirring for 2 h, the potassium had disappeared. Upon storing the concentrated (to *ca.* 3 mL) mixture at −27 °C overnight, dark green crystals (tentatively assigned as [K(OEt$_2$)$_x$Al(**L**^{Ph})Me$_2$]) precipitated. The quality of these crystals was insufficient for an X-ray diffraction study; the crystals decomposed quickly after being removed from the mother solution.

(ii) A solution of [Al(**L**^{Ph})Me$_2$] (**2**) (0.173 g, 0.41 mmol) in diethyl ether (10 mL) was added to a potassium mirror (0.040 g, 1.02 mmol) at ambient temperature. The solution first turned green and then blue-violet with the formation of extremely air-sensitive, dark violet with a bronze lustre, crystals of [Al(**L**^{Ph})Me$_2$K$_2$(OEt$_2$)] (**3**) on the surface of the K metal (0.165 g, 70%). X-ray quality crystals were obtained by storing the decanted solution at −10 °C overnight. ^{1}H-NMR (thf-d$_8$): δ 6.58 (d, $^3J_{H-H} = 7.5$, 4H, *o*-CH of Ph), 6.48 (t, $^3J_{H-H} = 7.0$, 4H, *m*-CH of Ph), 5.79 (s, 1H, middle CH), 5.65 (t, $^3J_{H-H} = 6.3$ Hz, 2H, *p*-CH of Ph), 3.39 (q, 4H, OC*H*$_2$CH$_3$), 1.12 (t, 6H, OCH$_2$C*H*$_3$), 0.01 (s, 18H, SiMe$_3$), −1.07 ppm (s, 6H, AlCH$_3$).

Synthesis of [{KSm(L^{Ph})$_2$}$_2$] (4)

Potassium β-diketiminate K(**L**^{Ph}) (0.83 g, 2.05 mmol) was added to a stirred suspension of SmI$_2$ (0.41 g, 1.01 mmol) in Et$_2$O (80 mL) at ambient temperature; stirring was continued overnight. A white precipitate was filtered off; *ca.* three quarters of the solvent was removed *in vacuo* from the green filtrate, which was layered with pentane and stored at −10 °C resulting in the formation of dark brown crystals of [{KSm(**L**^{Ph})$_2$}$_2$] (**4**) (0.092 g, 10%), which gave a purple solution in deuterated benzene. ^{1}H-NMR (C_6D_6): δ (i) sharp signals: 23.13 (s, 1H, middle CH), 5.96 (t, $^3J_{H-H} = 7.3$, 2H, *p*-CH of Ph), 4.92 (t, $^3J_{H-H} = 7.6$, 4H, *m*-CH of Ph), 2.33 (d, $^3J_{H-H} = 7.3$ Hz, 4H, *o*-CH of Ph), −7.47 ppm (s, 18H, SiMe$_3$); (ii) broad signals: 29.3, 7.1, 1.14, −0.7 ppm.

Synthesis of [Sm$_2$(L^{Dph})$_3$] (5)

Potassium β-diketiminate K(**L**^{Dph}) (1.52 g, 2.73 mmol) was added to a stirred solution of SmI$_2$ (0.55 g, 1.36 mmol) in thf (80 mL) at ambient temperature and stirred overnight. A white precipitate was filtered off; the solvent was removed *in vacuo* from the dark green filtrate; the residue was dissolved in hexane and stored at −10 °C resulting in the formation of dark brown crystals of [Sm$_2$(**L**^{Dph})$_3$] (**5**) (0.264 g, 20%). ^{1}H-NMR (C_6D_6): δ (i) sharp signals: 26.64 (s, 1H, middle CH), 6.67 (t, $^3J_{H-H} = 7.3$, 2H, *p*-CH of Ph), 6.57 (t, $^3J_{H-H} = 7.3$, 4H, *m*-CH of Ph), 6.36 (d, $^3J_{H-H} = 7.3$, 4H, *o*-CH of Ph), 5.28 and 2.61 (two d, $^3J_{H-H} = 8.8$ Hz, 4H + 4H, *o*- and *m*-CH of C_6H_4), −7.29 ppm (s, 18H, $SiMe_3$); (ii) broad signals: 33.2, 27.5, 11.1, 1.33 (~36H, $SiMe_3$), −0.8, −4.5 ppm.

Synthesis of [Sm($\mathbf{L}^{\mathrm{Tol,Ad}}$)($\mathbf{L}^{\mathrm{Tol,Ad}}$–H)] (6)

Potassium β-diketiminate K($\mathbf{L}^{\mathrm{Tol,Ad}}$) (0.30 g, 0.63 mmol) was added to a stirred suspension of SmI_2 (0.13 g, 0.32 mmol) in Et_2O (50 mL) at ambient temperature and stirred overnight. A white precipitate was filtered off; the dark blue filtrate was evaporated *in vacuo*; pentane was added to the oily residue, which only partially dissolved. Storing the mixture at −10 °C resulted in the formation of blue crystals of [Sm($\mathbf{L}^{\mathrm{Tol,Ad}}$)($\mathbf{L}^{\mathrm{Tol,Ad}}$–H)] (**6**) (0.197 g, 60%).

X-ray crystallographic studies for 3, 4, 5 and 6

Diffraction data were collected on a Nonius Kappa CCD diffractometer using monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å at 173(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. The structures were refined by a full-matrix least-squares procedure based on F^2, using SHELXL-97;[29] absorption corrections were applied using MULTISCAN. For **3** there are K···Me contacts to C22 and C23 and for both groups hydrogen atoms were refined; all other H atoms were in riding mode. For **4** distance (SADI) and DELU constraints were applied to the $Si2Me_3$ group. In **5** the hexane solvate molecule was poorly defined and only five carbon atoms were included with isotropic displacement parameters. In **6** for C52 a difference map showed three regions of density, initially suggesting a methyl group. However, a free refinement of these three H atoms was unsuccessful and including them with idealised geometry but with the torsion angle refined led to an inexplicably short Sm···H bond (1.81 Å). The group was therefore modelled as a methylene carbon with the two hydrogen atoms in idealised positions. There are two regions of poorly defined residual density, presumably due to uncharacterised solvate molecules; this was modelled by including seven isotropic carbon atoms in the refinement. Further details on the four structures are in Table 5.

Acknowledgements

We are grateful for the support of EPSRC and the Leverhulme Trust with fellowships for A.V.K. and A.V.P.

Notes and references

1 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031.
2 D. Drees and J. Magull, *Z. Anorg. Allg. Chem.*, 1995, **621**, 948.
3 D. Drees and J. Magull, *Z. Anorg. Allg. Chem.*, 1994, **620**, 814.
4 P. B. Hitchcock, M. F. Lappert and S. Tian, *J. Chem. Soc., Dalton Trans.*, 1997, 1945.
5 Z.-Q. Zhang, Y.-M. Yao, Y. Zhang, Q. Shen and W.-T. Wong, *Inorg. Chim. Acta*, 2004, **357**, 3173.
6 C. Cui, A. Shafir, J. A. R. Schmidt, A. G. Oliver and J. Arnold, *Dalton Trans.*, 2005, 1387.
7 F. Bonnet, M. Visseaux, D. Barbier-Baudry, E. Vigier and M. M. Kubicki, *Chem.–Eur. J.*, 2004, **10**, 2428.
8 L. F. Sánchez-Barba, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Organometallics*, 2005, **24**, 3792.
9 M. Xue, R. Jiao, Y. Zhang, Y. Yao and Q. Shen, *Eur. J. Inorg. Chem.*, 2009, 4110.
10 A. M. Neculai, D. Neculai, H. W. Roesky and J. Magull, *Polyhedron*, 2004, **23**, 183.
11 C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao and F. Cimpoesu, *Angew. Chem. Int. Ed.*, 2000, **39**, 4274.
12 S. Nagendran and H. W. Roesky, *Organometallics*, 2008, **27**, 457.
13 D. Vidovic, M. Findlater, G. Reeske and A. H. Cowley, *J. Organomet. Chem.*, 2007, **692**, 5683.
14 A. G. Avent, P. B. Hitchcock, A. V. Khvostov, M. F. Lappert and A. V. Protchenko, *Dalton Trans.*, 2004, 2272.
15 A. G. Avent, A. V. Khvostov, P. B. Hitchcock and M. F. Lappert, *Chem. Commun.*, 2002, 1410.
16 O. Eisenstein, P. B. Hitchcock, A. V. Khvostov, M. F. Lappert, L. Maron, L. Perrin and A. V. Protchenko, *J. Am. Chem. Soc.*, 2003, **125**, 10790.
17 S. K. Ibrahim, A. V. Khvostov, M. F. Lappert, L. Maron, L. Perrin, C. J. Pickett and A. V. Protchenko, *Dalton Trans.*, 2006, 2591.
18 A. G. Avent, P. B. Hitchcock, A. V. Khvostov, M. F. Lappert and A. V. Protchenko, *Dalton Trans.*, 2003, 1070.
19 F. Coslédan, P. B. Hitchcock and M. F. Lappert, *Chem. Commun.*, 1999, 705.
20 P. B. Hitchcock, M. F. Lappert and A. V. Protchenko, *Chem. Commun.*, 2005, 951.
21 P. B. Hitchcock, M. F. Lappert, D.-S. Liu and R. Sablong, *Chem. Commun.*, 2002, 1920.
22 R. K. Minhas, Y. Ma, J.-I. Song and S. Gambarotta, *Inorg. Chem.*, 1996, **35**, 1866.
23 E. D. Brady, D. L. Clark, J. C. Gordon, P. J. Hay, D. W. Keogh, R. Poli, B. L. Scott and J. G. Watkin, *Inorg. Chem.*, 2003, **42**, 6682.
24 W. J. Evans, L.R. Chamberlain, T. A. Ulibarry and J. W. Ziller, *J. Am. Chem. Soc.*, 1988, **110**, 6423.
25 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1976, **32**, 751.
26 M. L. Cole and P. C. Junk, *Chem. Commun.*, 2005, 2695.
27 D. Heitmann, C. Jones, P. C. Junk, K.-A. Lippert and A. Stasch, *Dalton Trans.*, 2007, 187.
28 M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, K. Konstas and J. Wang, *Chem.–Eur. J.*, 2007, **13**, 8092.
29 G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany.