

Synthesis and characterization of mono β -diketiminatosamarium amides and hydrocarbyls[†]

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Reaction of SmCl₃ with 1 eq of KL (L = [DippNC(Me)CHC(Me)NDipp]; Dipp = 2,6-*i*-Pr₂C₆H₃) in THF afforded the dimeric samarium dichloride LSmCl₂(THF)Cl₂SmL (**1**) in high yield. Reactions of **1** with NaN(SiMe₃)₂, KNHAr (Ar = 2,4,6-*t*-Bu₃C₆H₂), KBHET₃, and KCp* (Cp* = C₅Me₅) yielded various new complexes: LSmCIN(SiMe₃)₂ (**2**), LSm[N(SiMe₃)₂]₂ (**3**), LSmNHAr(HBEt₃) (**4**), LSm(NHAr)₂ (**5**), and LSmCp*Cl (**6**). Reaction of **1** with one eq of NaN(SiMe₃)₂ followed by treatment with excess AlMe₃ afforded a unique bimetallic samarium tetramer Cl₃L₂Sm₂(AlMe₃)₂Sm₂L₂Cl₃ (**7**). Reaction of **6** with LiMe or LiCH₂SiMe₃ afforded LSmCp*Me (**8**) and LSmCp*CH₂SiMe₃ (**9**) in excellent yield. Methyl abstraction from **8** with B(C₆F₅)₃ in toluene yielded the cationic borate species (LSmCp*)[MeB(C₆F₅)₃] (**10**). Molecular structures of **1–7** and **9** were determined by X-ray single crystal analysis.

Introduction

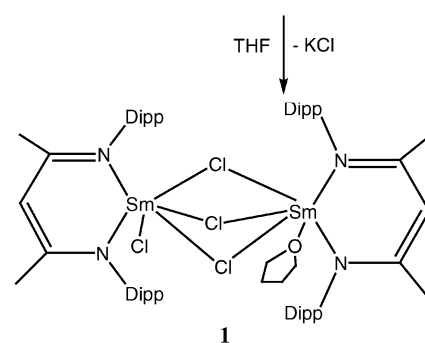
Recent efforts in the design and synthesis of new ligand systems for lanthanide chemistry have been aimed to a large degree at extending organolanthanide chemistry beyond the realm of lanthanocene species. A major impetus for such studies can be traced to the well known applications of lanthanide complexes in homogeneous catalysis.^{1,2} Our recent efforts in this area have been to apply bulky, kinetically-stabilizing monoanionic ligand systems to the lanthanide metals^{3,4} in the hope that they will allow the isolation of low-coordinate metal complexes showing unique bonding or patterns of reactivity.

In this paper we are concerned with the chemistry of samarium compounds containing the monoanionic β -diketiminato (or nacnac) ligand L {L = [DippNC(Me)CHC(Me)NDipp], Dipp = 2,6-*i*-Pr₂C₆H₃}.⁵ This general class of ligands has been the subject of intense interest in recent years,⁶ especially the more bulky variants which seem unique in stabilizing some unusual complexes of main group^{7–9} and transition metals.^{10–13} Piers and co-workers^{14–16} have extensively investigated the scandium chemistry with such bulky ligands, and recent reports continue to extend the less-developed chemistry of other lanthanide metals.^{17–26} Herein, we describe some new chemistry of samarium with β -diketiminato ligands^{6,17,25–27} including amide and alkyl complexes, several X-ray structures and some reaction chemistry.²⁸

Results and discussion

The potassium salt of the ligand L {L = [DippNC(Me)CHC(Me)NDipp] (Dipp = 2,6-*i*-Pr₂C₆H₃) employed in this study was obtained by reaction of the free ligand LH⁵ with KN(SiMe₃)₂. Reaction of KL with SmCl₃ in THF was conducted at room temperature (Scheme 1) to yield the dimeric samarium species LSmCl₂(THF)Cl₂SmL (**1**) in high yield.

Crystals of **1** were obtained from toluene at –40 °C. The crystallographic model features two molecules of **1**, as well as 4.5 eq of incorporated toluene solvent. The structure of



Scheme 1

one of the two dimeric molecules of **1** is shown in Fig. 1. The compound adopts a dimeric structure with three chlorine atoms bridging the two samarium centers while one chlorine atom resides in a terminal position on one samarium atom; the coordination sphere of the other samarium atom is completed by a coordinated THF molecule. Each diketiminato ligand binds to a samarium atom in the typical chelating fashion, with acute

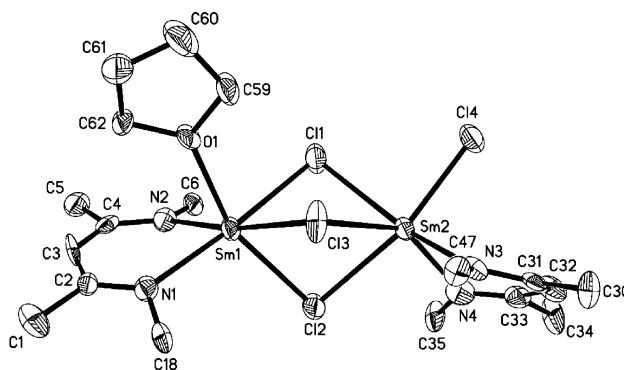


Fig. 1 Ortep drawing of complex **1** (50% probability). Hydrogen atoms and the two Dipp groups on the nitrogen atoms have been omitted for clarity.

[†] Dedicated to the memory of Professor Ian Rothwell.

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N–Sm–N angles (N101–Sm11–N102 = 75.9(2)° and N103–Sm12–N104 = 77.9(3)°). The chloride ligands bridge asymmetrically across the two Sm atoms, such that the bonds to the Sm ligated by THF are *ca.* 0.05 Å shorter than those to the Sm with the terminal chloride. As expected, the Sm–Cl (terminal) distance (2.605(3) Å) is quite short compared to the Sm–Cl (bridging) (2.72–2.83 Å).

Compound **1** serves as a good starting synthon for LSm derivatives *via* simple metathesis chemistry. For example, **1** reacted with the sodium amide NaN(SiMe₃)₂ in 1 : 2 and 1 : 4 ratios at room temperature to afford LSmN(SiMe₃)₂(Cl) (**2**) and LSm[N(SiMe₃)₂]₂ (**3**), respectively. Reaction of **1** with the amide KNHAr followed by addition of KBHET₃ generated LSm(NHAr)(HBET₃) (**4**, Ar = 2,4,6-*t*-Bu₃C₆H₂). Compound **1** also reacts with two eq of KNHAr at elevated temperature to afford LSm(NHAr)₂ (**5**). A single chloride ligand can also be replaced by Cp* *via* treatment of **1** with Cp*K, which affords LSmCp*Cl (**6**) in high yield (Scheme 2).

Attempts to prepare mono- or di-alkyl complexes by reacting **1** with various alkyl reagents have been unsuccessful to date.

The ¹H NMR spectrum of **2** is resolvable (although the resonances are broad and shifted due to its paramagnetic nature), while that of **3** appears very broad. The latter is thermally stable in refluxing toluene over several days. In contrast, **4** is thermally unstable and very air- and moisture-sensitive at room temperature in solution; nonetheless it can be stored as a solid for one week without noticeable decomposition.

The ¹H NMR spectrum of **4** shows a high field, broad singlet (δ –20.15 ppm in C₇D₈; –18.95 ppm in C₆D₆) assigned to the proton in the HBET₃, indicating a Sm–H–B interaction in this molecule. Similar high field resonances have been reported for the metallocenes [C₅H₄(CMe₃)₂SmHBET₃(THF)_x (δ –23 ppm) and [C₅H₄(CH₂)₂OCH₃]₂SmHBET₃ (δ –23.4 ppm).^{29,30} A strong band for the B–H stretch occurs at 1880 cm^{–1} (KBr) in the IR spectrum, in the region associated with μ-HB bonds (*cf.* ν(BH) in M(HBET₃) salts at 1870, 1835, and 1950 cm^{–1} for M = Li, Na, K, respectively).³¹ Addition of PMe₃, pyridine or triethylamine to **4** in THF or toluene led to unidentified products rather than the anticipated terminal hydride. There are few examples of structurally characterized metal triethylborohydride complexes,³² although several lanthanide complexes of this type have been spectroscopically characterized.^{29,30,33} An X-ray dataset was obtained on **4**, solution of which established the

proposed connectivity; however, the data is of relatively poor quality and will not be discussed further.

Reaction of **1** with a 1 : 1 ratio of KNHAr and KN(SiMe₃)₂ in toluene at 80 °C did not yield mixed amide or deprotonated imide species, but instead gave a 1 : 1 mixture of **3** and **5**. When the reaction was carried out stepwise (first, addition of KNHAr and stirred overnight, then KN(SiMe₃)₂), the same 1 : 1 mixture of **3** and **5** was still obtained.

The molecular structures of **2**, **3**, **5**, and **6** are shown in Figs. 2–5, respectively. All of these complexes have a monomeric structure in the solid state with the β-diketiminato ligand coordinated to the samarium atom in a chelating mode with a relatively acute angle. Single crystals of **2** suitable for X-ray diffraction were obtained from toluene at –40 °C. The compound crystallizes in monoclinic space group *P*2₁/*c*. The structure is pseudo-tetrahedral (Fig. 2), with three nitrogen atoms and one chlorine atom coordinated to the central atom. The Sm–Cl distance (2.615(1) Å) is in line with that found in **1**. The Sm1–N1 (amide) bond is shorter (2.276(3) Å) than Sm–N bonds to the diketiminato ligand (Sm1–N2 (2.334(3) Å) and Sm1–N3 (2.354(3) Å)). The typical ‘enveloping’ of the

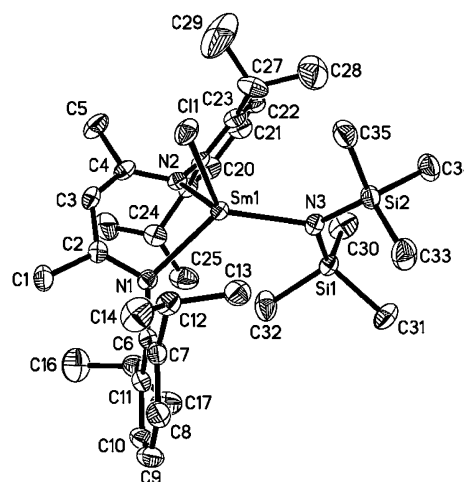
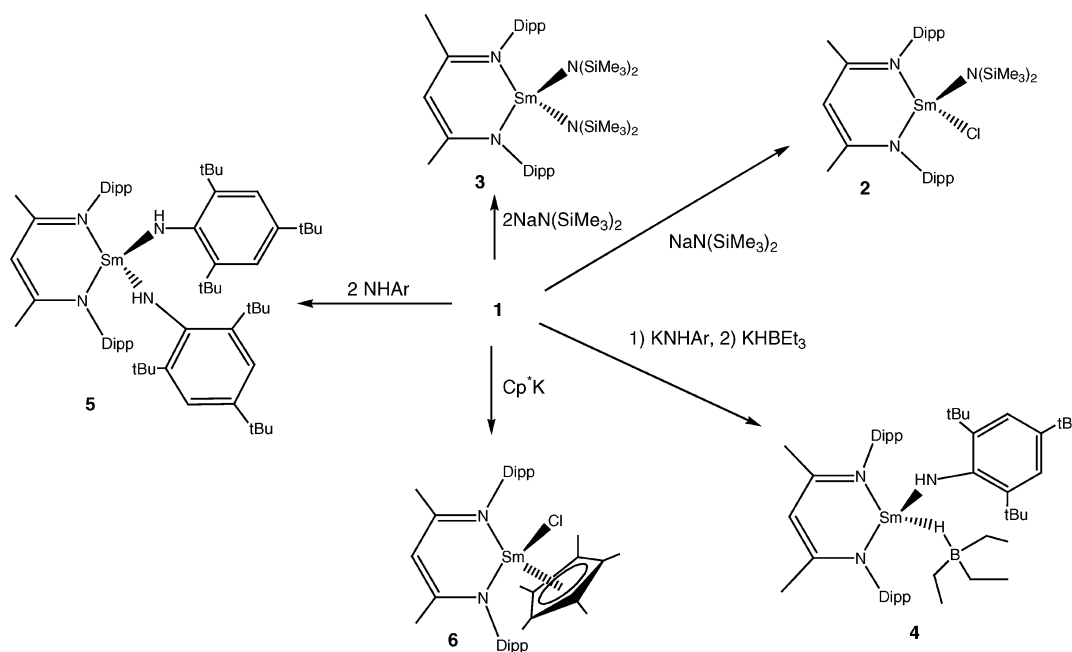


Fig. 2 Ortep drawing of complex **2** (50% probability). Hydrogen atoms have been omitted for clarity.



Scheme 2

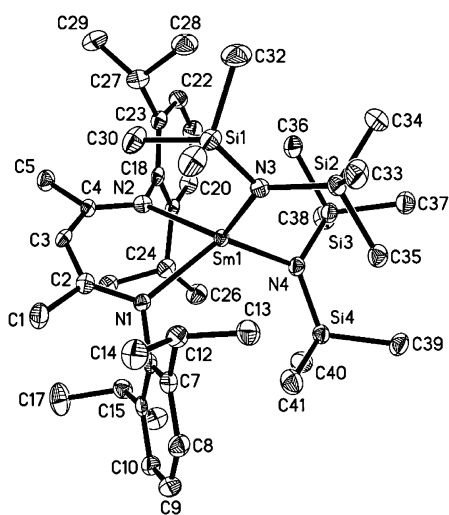


Fig. 3 Ortep drawing of complex **3** (50% probability). Hydrogen atoms have been omitted for clarity.

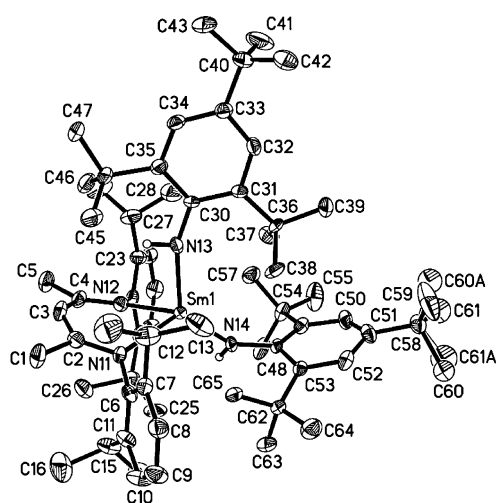


Fig. 4 Ortep drawing of complex **5** (50% probability). Hydrogen atoms have been omitted for clarity.

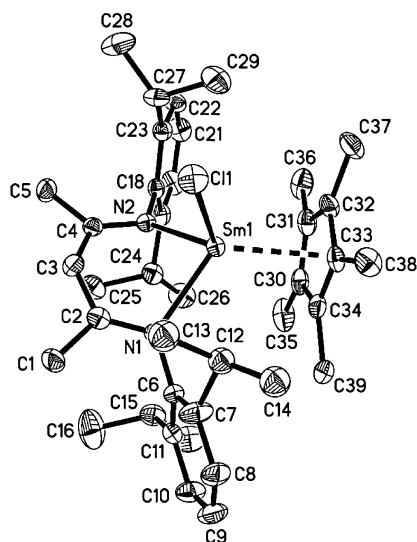


Fig. 5 Ortep drawing of complex **6** (50% probability). Hydrogen atoms have been omitted for clarity.

diketiminato ligand is observed in which the carbon atoms are folded down *ca.* 43° from the N–Sm–N plane.

The structure of closely related **3** is also four-coordinate (Fig. 3). The two amides display shorter bonds to Sm (2.299(3)

and 2.324(3) Å) than does the diketiminato ligand (2.503(3), 2.427(3) Å). All four Sm–N bonds are longer than the corresponding metrics found in **2** due no doubt to the more crowded coordination environment. Correspondingly, the N–Sm–N angle to the diketiminato ligand (79.100(2)°) is smaller than that (81.6(1)°) in **2**.

Compound **5** crystallizes in monoclinic space group $P2_1/c$ with two molecules of **5** and 1.5 eq of pentane in the asymmetric unit (Fig. 4). One of the molecules is shown in Fig. 4. The overall structure is very similar to that of **3** with four nitrogen atoms coordinated to the samarium atom. Again, the two Sm–N (amide) distances (2.311(5) and 2.260(5) Å) are similar and are close to those seen in **4**. The N13–Sm–N14 angle (133.6(2)°) is large due to the bulkiness of the Ar group while the N12–Sm–N11 (79.6(2)°) of the chelating ring is still acute, similar to those in compounds **2** and **3**.

The X-ray structure of **6** (Fig. 5) shows it to be a solvent-free “half-metallocene” complex. Samarium compounds involving Cp ligands are well-known, with the work of Evans and co-workers dominating the literature in this area.^{34–37} By far the vast majority of complexes entail bis-Cp* ligand sets, although in recent years a number of mono-Cp* derivatives have been prepared.^{38–40} The β -diketiminato ligand is coordinated to the central atom in a chelating fashion and Cp* is bound in the normal η^5 fashion. The overall geometry can be described as tetrahedral. The Sm–Cl bond length (2.610(1) Å) is very close to that in **2** and Sm(Tp^{Me2})₂Cl (2.637(3) Å),⁴¹ and is noticeably shorter than that found in (C₅Me₅)₂SmCl(THF) (ave 2.73(1) Å).⁴²

Upon treatment of yellow compound **1** with one eq of NaN(SiMe₃)₂, followed by an excess of AlMe₃ in toluene, a deep red color was developed in 2 h, and an interesting samarium aluminate tetramer Cl₃L₂Sm₂(AlMe₄)₂Sm₂L₂Cl₃ (**7**) could be crystallized in low yield (*ca.* 20%) after careful work-up. We note that direct reaction of **1** with AlMe₃ did not yield identified products. One possible mechanism for the formation of **7** proceeds *via* substitution of the terminal chlorine atom in **1** by an [N(SiMe₃)₂][−] group, followed by exchange of the [N(SiMe₃)₂][−] with [AlMe₄][−] and displacement of THF.

The structure of **7** is shown in Fig. 6, the geometry of the Sm atoms being distorted octahedral while that of aluminium is tetrahedral. The most interesting feature of this molecule is the distorted square geometry formed by Al1–C5–Sm2–C11–Sm1–C1–Al2–C2–Sm4–C14–Sm3–C6 atoms, with methyl groups bridging the Al and Sm atoms and Cl and Al atoms at the corners. The Sm1–C11–Sm2 angle is 89.43° whereas the C5–Al1–C6 angle is rather more obtuse (107.1(2)°). The angle at Sm (*i.e.* C11–Sm2–C5) is far from linear (159.1(1)°) while that seen at the bridging methyl groups is much closer (Sm2–C5–Al1

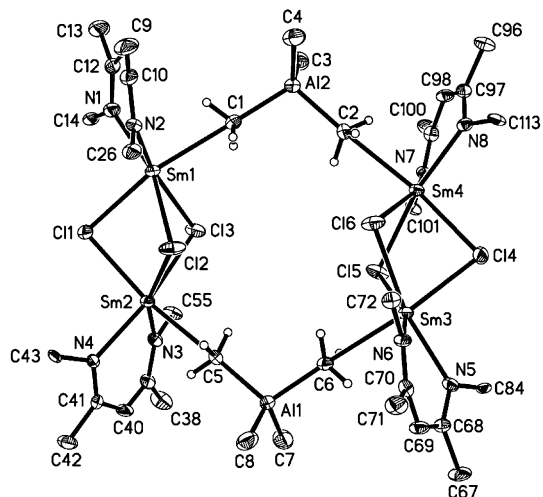
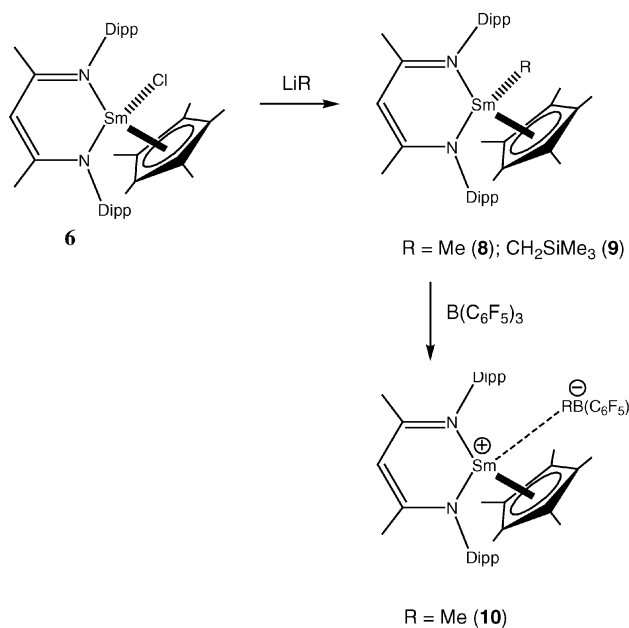


Fig. 6 Ortep drawing of complex **7** (50% probability). Hydrogen atoms and the two Dipp groups have been omitted for clarity.

(177.5(3)°). The N–Sm–N angles are all acute (77.8–78.7°) and the Sm–Cl bond lengths (2.750(2)–2.783(2) Å) are comparable to those found in **1** (2.720–2.835 Å). The Sm–N distances (2.354(4)–2.397(5) Å) are also in the range found in all compounds in this paper. The Sm–C bond lengths (2.720(6)–2.759(6) Å) and the Al–C (bridging) distances (2.034–2.037 Å) are very close to those found in [Cp*₂Sm(AlMe₄)₂] (2.743–2.750 Å, 2.003–2.051 Å).⁴² The overall structural features of the AlMe₄[−] units are similar to normal AlMe₄[−] anions.⁴³

Compound **6** cleanly reacted with lithium alkyl reagents LiR to give mono-alkyls LSmCp*R (R = Me (**8**), CH₂SiMe₃ (**9**); Scheme 3) in excellent yield.



Scheme 3

Formation of the Sm–C bond is indicated by the ¹H NMR spectra of paramagnetic compounds **8** and **9**, which showed the low field alkyl resonances at 10.20 (Sm–Me) and 11.98 ppm (Sm–CH₂SiMe₃), respectively. A singlet (δ 1.15 for **8** and 1.30 ppm for **9**) in the ¹H NMR spectra could be assigned to the Cp*methyl groups.

Compounds **8** and **9** are not active catalysts for ethylene or methyl methacrylate (MMA) polymerization. Attempts to prepare hydrides by the reaction of **8** and **9** with H₂ or PhSiH₃ led to the formation of complicated mixtures according to NMR analysis, and no pure products have yet been isolated from preparative scale reactions.

Reaction of **8** with B(C₆F₅)₃ in an attempt to effect methyl abstraction afforded the species (LSmCp*⁺)[MeB(C₆F₅)₃[−]] (**10**) as judged by NMR spectroscopy and elemental analysis. The ¹H NMR spectrum showed a broad singlet (δ −15.47 ppm) attributable to the methyl group, indicating its proximity to the paramagnetic samarium center in solution. A singlet attributable to the Cp* methyl groups at δ 0.13 ppm in **10** is shifted upfield by 1 ppm compared to that (δ 1.15 ppm) of the parent compound **8**. Compound **10** is remarkably stable under CO atmosphere in toluene and does not react with ethylene or MMA at room temperature. It is air and moisture sensitive, but appears to be quite thermally stable in aromatic solvents. The relatively low solubility in toluene compared to parent compound **8** lends further support to its ionic formulation. X-Ray quality crystals have not been obtained thus far.

The molecular structure of compound **9** was determined by X-ray single crystal analysis, as shown in Fig. 7. The overall structure of **9** may be viewed as being typical of a distorted tetrahedron, with the central samarium atom coordinated to two ni-

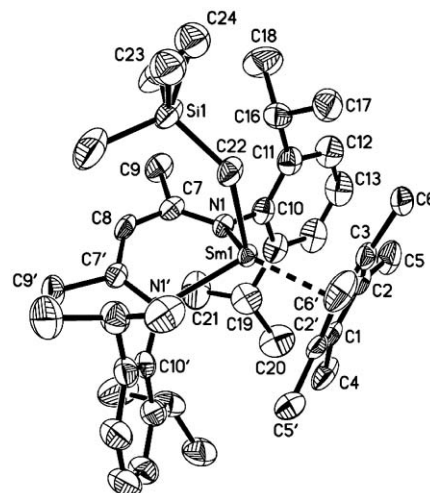
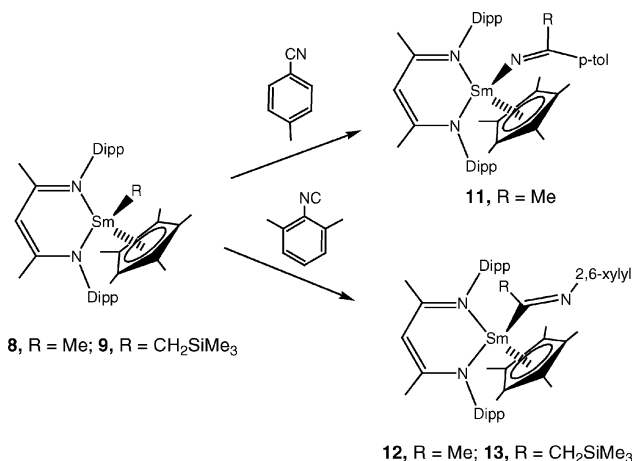


Fig. 7 Ortep drawing of complex **9** (50% probability). Hydrogen atoms have been omitted for clarity.

trogen atoms, one carbon atom from the alkyl ligand and the Cp* ring. The Sm–C distances (C₅Me₃ ring) (2.695–2.776 Å) are similar to those in the bis-metalloocene compounds Cp*₂SmCl(THF) (2.72(3) Å), Cp*₂SmMe(THF) (2.711(6) Å), and Cp*₂SmCH₂-C₆H₅(THF) (2.755(2) Å).⁴² The Sm–C (CH₂SiMe₃) distance (2.458(9) Å) is similar to related bonds in Cp*₂SmMe(THF) (2.48(1) Å), Cp*₂SmCH₂C₆H₅(THF) (2.498(5) Å), and Cp*₂C₆H₅(THF) (2.511(5) Å), and [2-(CH=NC₆H₃-2,6-*i*Pr₂)-5-*t*BuC₄N]₂SmCH₂SiMe₃(THF) (2.455(4) Å). The Sm–N distances (2.399(4) Å) are close to those seen in **6** (2.381(3) Å), whereas the N–Sm–N angle (79.7(2)°) is more acute (by ca. 2.4°) due presumably to the bulk of CH₂SiMe₃ relative to the chloride in **6**.

Nitriles and isocyanides insert into the Sm–C bond in alkyls **8** and **9** to afford mono-insertion products (Scheme 4). Under ambient conditions, they display no further tendency toward reaction with excess substrate.



Scheme 4

The products LSmCp*[N=C(Me)(C₆H₄-4-Me)] (**11**), LSmCp*[C(Me)=N–C₆H₃-2,6-Me₂] (**12**), and LSmCp*[C(CH₂-SiMe₃)=N–C₆H₃-2,6-Me₂] (**13**) have been characterized by ¹H NMR, IR spectroscopy, and elemental analysis.

Orange complex **11** is soluble in toluene and benzene, but is sparingly soluble in hexane. Its ¹H NMR spectrum showed a resonance attributable to NCM_e at δ 6.19 ppm, while a strong absorption at 1640 cm^{−1} can be attributed to the C=N stretch. Compounds **12** and **13** were obtained as yellow crystals from toluene/pentane. Their ¹H NMR spectra are similar, showing alkyl resonances (Me and CH₂SiMe₃) in SmC(R)N at δ 4.51 and

5.12 ppm, respectively. A singlet for the C₅Me₃ methyl groups appears at δ 1.04 for **12** and 0.96 ppm for **13**.

Experimental

General

Standard Schlenk-line and glovebox techniques were used unless stated otherwise. Toluene and pentane were purified by passage through a column of activated alumina and degassed with argon. THF was dried by passage through a column of 4 Å molecular sieves and degassed under vacuum. C₆D₆ was vacuum transferred from sodium/benzophenone. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected. ¹H and ¹³C NMR spectra were recorded at ambient temperature on a Bruker AM-300 spectrometer. ¹H NMR chemical shifts are given relative to C₆D₅H (7.15 ppm) or C₇D₇H (2.09 ppm). ¹³C NMR spectra are relative to C₆D₆ (128.39 ppm). IR samples were prepared as Nujol mulls and taken between KBr plates. Elemental analyses were determined at the College of Chemistry, University of California, Berkeley. Single-crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley.

Syntheses

LSmCl₂(THF)Cl₂SmL (1). THF (50 mL) was condensed onto a mixture of SmCl₃ (1.28 g, 5.0 mmol) and KL (2.28 g, 5.0 mmol) at -78 °C. The suspension was allowed to warm to room temperature and stirred overnight. The solvent was removed under vacuum and the remaining solid was extracted with toluene (50 mL). After filtration, the filtrate was concentrated and stored at -40 °C overnight to afford orange yellow crystals of **1** (2.93 g, 87%). Mp: 147 °C (decomp.). Anal. calcd for C₆₂H₉₀Cl₄N₄OSm₂: C, 55.17; H, 6.72; N, 4.15. Found: C, 55.66; H, 7.01; N, 3.90%. IR (Nujol, KBr): 3057 (m), 2724 (w), 2669 (w), 1841 (w), 1623 (m), 1317 (s), 1261 (s), 1166 (s), 1097 (m), 1074 (m), 1020 (s), 965 (w), 926 (s), 862 (m), 839 (m), 791 (s), 757 (m), 722 (w), 667 (m), 633 (m), 585 (w), 555 (m), 509 (m).

LSmClN(SiMe₃)₂ (2). To a solution of **1** (0.67 g, 0.5 mmol) in toluene (25 mL) was added a solution of NaN(SiMe₃)₂ (0.18 g, 1 mmol) in toluene (10 mL) at room temperature. The mixture was stirred for 12 h and filtered. The filtrate was concentrated and stored at -40 °C for 2 d to give yellow crystals of **2** (0.57 g, 75%). Mp: 234 °C. Anal. calcd for C₃₅H₅₉ClN₃Si₂Sm: C, 55.05; H, 7.79; N, 5.50. Found: C, 54.95; H, 7.87; N, 5.22%. ¹H NMR (C₆D₆): δ -2.30 (br, 6H, CHMe₂), -1.32 (br, 6H, CHMe₂), 0.80 (s, 18H, SiMe₃), 1.21 (d, 6H, CHMe₂), 2.23 (d, 6H, CHMe₂), 3.21 (s, 6H, Me), 5.09 (d, 2H, Ar-H), 5.96 (br m, 2H, CHMe₂), 6.27 (m, 2H, Ar-H), 6.53 (d, 2H, Ar-H), 11.78 (s, 1H, CH).

LSm[N(SiMe₃)₂]₂ (3). The compound was prepared similarly to **2** except 4 mole eq of NaN(SiMe₃)₂ (0.36 g, 2.0 mmol) was employed. The product was crystallized from pentane to give yellow crystals of **3** (0.67 g, 52%). Mp: 275 °C. Anal. calcd for C₄₁H₇₇N₄Si₄Sm: C, 55.43; H, 8.74; N, 6.30. Found: C, 55.27; H, 9.03; N, 5.96%. IR (Nujol, KBr): 3060 (w), 2361 (m), 2339 (m), 1623 (w), 1578 (w), 1306 (s), 1251 (s), 1165 (m), 1093 (m), 1020 (s), 948 (s), 924 (s), 877 (m), 831 (s), 791 (m), 771 (m), 731 (m), 667 (s), 605 (m).

LSm(NHAr)(BHET₃) (4, Ar = 2,4,6-*t*-Bu₃C₆H₂). Toluene was added to a mixture of **1** (0.67 g, 0.5 mmol) and KNHAr (0.30 g, 1.0 mmol) at room temperature. The mixture was stirred overnight, then a solution of KBHET₃ in THF was added. The solution was stirred for an additional 12 h, the solvent was then removed under vacuum, and the remaining red residue was extracted with pentane. It was filtered, and the filtrate was concentrated and stored at -40 °C for 2 d to afford red crystals of **4** (0.73 g, 79%). Mp: 120 °C (decomp.). Anal. calcd for C₅₃H₈₇BN₃Sm: C, 68.64; H, 9.45; N, 4.53. Found: C,

68.43; H, 9.79; N, 4.47%. ¹H NMR (C₆D₆): δ -18.95 (br s, 1H, HBET₃), -5.08 (br, 2H, CHMe₂), -1.45 (m, 6H, B(CH₂CH₃)₃), -0.80 (d, 6H, CHMe₂), -0.28 (s, 6H, CHMe₂), 0.36 (br, 9H, B(CH₂CH₃)₃), 0.84 (s, 6H, Me), 1.65 (d, 6H, CHMe₂), 1.71 (s, 9H, CMe₃), 1.74 (s, 9H, CMe₃), 2.70 (d, 6H, CHMe₂), 3.08 (s, 9H, CMe₃), 4.42 (s, 1H, NH), 5.67 (d, 2H, Ar-H), 6.65 (m, 2H, Ar-H), 6.92 (sept, 2H, CHMe₂), 7.85 (s, 1H, Ar-H), 8.52 (s, 1H, Ar-H), 16.95 (s, 1H, CH). IR (Nujol, KBr): 3283 (w), 3059 (w), 2765 (w), 2363 (m), 2027 (m), 1880 (s), 1766 (w), 1622 (w), 1583 (m), 1505 (w), 1293 (w), 1253 (w), 1230 (m), 1197 (m), 1167 (m), 1108 (s), 1046 (s), 1016 (m), 926 (m), 888 (s), 827 (m), 797 (m), 757 (s), 740 (m), 599 (s), 524 (m).

LSm(NHAr)₂ (5, Ar = 2,4,6-*t*-Bu₃C₆H₂). Toluene (30 mmol) was added to a mixture of **1** (0.67 g, 0.5 mmol) and KNHAr (0.60 g, 2 mmol). The mixture was heated to 80 °C and was stirred for 4 h before being allowed to cool to room temperature. The solution was filtered, the filtrate was reduced to 5 mL then stored at -40 °C for one week. Red crystals of **5** were obtained in 80% yield (0.87 g). Mp: 225 °C. Anal. calcd for C₆₅H₁₀₁N₄Sm: C, 71.70; H, 9.35; N, 5.14. Found: C, 71.43; H, 9.02; N, 4.96%. ¹H NMR (C₆D₆): δ -4.05 (sept, 2H, CHMe₂), -3.20 (d, 6H, CHMe₂), -1.23 (s, 18H, CMe₃), -0.16 (d, 6H, CHMe₂), 1.39 (d, 9H, CMe₃), 1.66 (s, 2H, NH), 1.73 (d, 9H, CMe₃), 1.78 (d, 6H, CHMe₂), 1.89 (s, 6H, Me), 2.12 (s, 9H, CMe₃), 3.11 (d, 6H, CHMe₂), 3.62 (s, 9H, CMe₃), 4.34 (d, 2H, Ar-H), 5.82 (m, 2H, Ar-H), 6.50 (d, 2H, Ar-H), 7.15 (s, 1H, Ar-H), 7.31 (s, 2H, Ar-H), 7.55 (s, 1H, Ar-H), 7.69 (sept, 2H, CHMe₂), 8.00 (s, 1H, CH). IR (Nujol, KBr): 3693 (w), 3504 (w), 2364 (w), 1720 (w), 1312 (m), 1235 (s), 1199 (m), 1165 (m), 1091 (m), 1020 (s), 926 (m), 867 (m), 829 (m), 794 (s), 776 (s), 729 (m), 594 (m), 565 (m).

LSmCp*Cl (6). Toluene (20 mL) was transferred to a solid mixture of **1** (1.35 g, 1 mmol) and Cp*K (0.35 g, 2 mmol). After the mixture was stirred at room temperature for 15 h, it was filtered. The orange filtrate was concentrated and stored at -40 °C overnight to afford orange crystals of **7** (1.12 g, 76%). Mp: 186 °C (decomp.). Anal. calcd for C₃₉H₅₆ClN₂Sm (738.73): C, 63.41; H, 7.64; N, 3.79. Found: C, 63.29; H, 7.78; N, 3.69%. ¹H NMR (C₆D₆): δ -9.51 (sept, 2H, CHMe₂), 3.92 (d, 6H, CHMe₂), -0.87 (d, 6H, CHMe₂), 0.98 (s, 15H, C₅Me₅), 1.62 (d, 6H, CHMe₂), 2.38 (d, 6H, CHMe₂), 2.98 (s, 6H, Me), 4.35 (d, 2H, Ar-H), 5.77 (t, 2H, Ar-H), 6.19 (d, 2H, Ar-H), 6.57 (sept, 2H, CHMe₂), 10.82 (s, 1H, CH). IR (Nujol, KBr): 2726 (m), 1925 (w), 1863 (w), 1579 (w), 1513 (s), 1313 (s), 1271 (m), 1253 (m), 1232 (s), 1170 (s), 1108 (m), 1020 (s), 926 (s), 859 (s), 787 (s), 742 (m), 711 (m), 668 (m), 635 (w), 507 (m).

Cl₂L₂Sm₂(AlMe₄)₂Sm₂L₂Cl₃ (7). To a solution of **2** (0.76 g, 1.0 mmol) in toluene was added AlMe₃ (1 mL, 2 M in heptane, 2.0 mmol) at room temperature. The yellow solution immediately turned to red. The mixture was stirred for 12 h, and it was filtered to give a clear solution. The solution was concentrated and stored at -40 °C for 3 d to give red crystals of **7** (0.17 g, 20%). Mp: 127 °C (decomp.). Anal. calcd for C₁₂₄H₁₈₈Al₂Cl₆N₈Sm₄: C, 56.02; H, 7.13; N, 4.21. Found: 55.71; H, 7.24; N, 4.60%. IR (Nujol, KBr): 3057 (m), 2729 (m), 1929 (w), 1867 (w), 1604 (m), 1516 (s), 1310 (m), 1259 (m), 1165 (m), 1097 (s), 1021 (s), 928 (m), 893 (w), 842 (m), 791 (s), 755 (m), 727 (s), 694 (s), 638 (m), 616 (m), 564 (w), 543 (m), 512 (m).

LSmCp*Me (8). To a solution of **6** (0.74 g, 1 mmol) in toluene (15 mL) was added MeLi (0.72 mL, 1.4 M in ether, 1 mmol) at room temperature. After stirring overnight, the solution was filtered. The solvent was evaporated and the remaining solid was washed with a small amount of cold pentane to afford pure **8** as an orange microcrystalline solid (0.65 g, 90%). Mp: 132 °C (decomp.). Anal. calcd for C₄₀H₅₉N₂Sm (718.32): C, 66.88; H, 8.28; N, 3.90. Found: C, 66.59; H, 8.34; N, 3.96%. ¹H NMR (C₆D₆): δ -10.65 (br, 2H, CHMe₂), -5.40 (d, 6H, CHMe₂), -1.15 (d, 6H, CHMe₂), 1.15 (s, 15H, C₅Me₅), 2.32 (d, 6H, CHMe₂), 2.60 (s, 6H, Me), 2.76 (d, 6H, CHMe₂), 3.32 (d, 2H,

Ar–H), 5.17 (m, 2H, Ar–H), 5.94 (d, 2H, Ar–H), 9.13 (br, 2H, CHMe₂), 10.2 (br s, 3H, Sm–Me), 10.51 (s, 1H, CH). IR (Nujol, KBr): 3057 (w), 2720 (w), 1721 (w), 1515 (s), 1309 (s), 1269 (m), 1236 (w), 1167 (m), 1108 (m), 1090 (m), 1019 (s), 928 (m), 835 (m), 783 (s), 742 (m), 504 (m).

LSmCp*CH₂SiMe₃ (9). To a solid mixture of **6** (0.74 g, 1 mmol) and LiCH₂SiMe₃ (0.094 g, 1 mmol) was added toluene (15 mL) at room temperature. The mixture was stirred at room temperature for 15 h. All volatiles were removed under vacuum, and the residue was extracted with pentane. It was filtered, and the filtrate was stored at –40 °C overnight to give orange crystals of **9** (0.70 g, 89%). Mp: 142 °C (decomp.). Anal. calcd for C₄₃H₆₇N₃SiSm: C, 65.33; H, 8.54; N, 3.54. Found: C, 65.03; H, 8.88; N, 3.29%. ¹H NMR (C₆D₆): δ –8.75 (br, 2H, CHMe₂), –5.48 (d, 6H, CHMe₂), –0.98 (d, 6H, CHMe₂), 1.25 (s, 9H, SiMe₃), 1.30 (s, 15H, C₅Me₅), 2.26 (s, 6H, Me), 2.37 (d, 6H, CHMe₂), 2.62 (d, 6H, CHMe₂), 3.93 (d, 2H, Ar–H), 5.62 (m, 2H, Ar–H), 6.40 (d, 2H, Ar–H), 8.96 (br, 2H, CHMe₂), 9.90 (s, 1H, CH), 11.98 (s, 2H, SmCH₂). IR (Nujol, KBr): 3059 (m), 2726 (m), 1924 (w), 1863 (w), 1579 (w), 1313 (s), 1271 (s), 1252 (s), 1232 (s), 1170 (s), 1108 (s), 1020 (s), 926 (s), 859 (s), 786 (m), 742 (s), 710 (m), 668 (m), 636 (m), 507 (m).

(LSmCp*)[MeB(C₆F₅)₃] (10). Toluene (20 mL) was added to a mixture of **8** (0.30 g, 0.42 mmol) and B(C₆F₅)₃ (0.21 g, 0.42 mmol) at 0 °C. The mixture immediately turned red. The ice bath was removed, and the mixture was stirred at room temperature for 4 h. After removal of solvent *in vacuo*, the red solid was washed twice with pentane and dried under vacuum to give **10** as a deep red powder (0.42 g, 81%). Mp: 340 °C (decomp.). Anal. calcd for C₃₈H₅₉BF₁₅N₂Sm (1230.18): C, 56.63; H, 4.83; N, 2.28. Found: C, 56.87; H, 5.18, N, 2.40%. ¹H NMR (C₇D₈): δ –15.78 (br s, 3H, MeB), –2.08 (br, 2H, CHMe₂), –0.82 (br, 6H, CHMe₂), –0.18 (br, 6H, CHMe₂), 0.13 (s, 15H, C₅Me₅), 0.18 (br, 6H, CHMe₂), 0.73 (br, 2H, CHMe₂), 1.49 (br, 6H, CHMe₂), 4.17 (s, 6H, Me), 6.24 (d, 4H, Ar–H), 6.68 (m, 2H, Ar–H), 12.50 (s, 1H, CH).

LSmCp*[N=C(Me)(C₆H₄-4-Me)] (11). To a solution of **8** (0.50 g, 0.7 mmol) in toluene (10 mL) was added 4-MeC₆H₄CN (0.082 g, 0.7 mmol). The orange solution was stirred at room temperature for 2 h. All volatiles were removed under vacuum, and the residue was crystallized from toluene to give orange crystals of **11** (380 mg, 65%). Mp: 124 °C (decomp.). Anal. calcd for C₄₈H₆₆N₃Sm (835.45): C, 69.01; H, 7.96; N, 5.03. Found: C, 69.01; H, 8.12; N, 4.96%. ¹H NMR (C₆D₆): δ –12.01 (br, 2H, CHMe₂), –6.32 (br, 6H, CHMe₂), –1.65 (br, 6H, CHMe₂), 1.08 (s, 15H, C₅Me₅), 2.41 (s, 6H, Me), 2.56 (d, 6H, CHMe₂), 2.62 (s, 3H, Ar–Me), 2.68 (d, 6H, CHMe₂), 3.12 (d, 2H, Ar–H), 5.13 (m, 2H, Ar–H), 6.02 (d, 2H, Ar–H), 6.19 (s, 3H, NCMe), 7.98 (d, 2H, Ar–H), 9.02 (sept, 2H, CHMe₂), 10.34 (s, 1H, CH), 11.43 (d, 2H, Ar–H). IR (Nujol, KBr): 3059 (w), 2720 (w), 1640 (s), 1602 (w), 1566 (w), 1518 (s), 1315 (s), 1261 (s), 1228 (m), 1173 (m), 1096 (m), 1020 (m), 956 (w), 926 (m), 815 (m), 787 (s), 755 (m), 722 (m), 579 (w).

LSmCp*[C(Me)=N–C₆H₃-2,6-Me₂] (12). To an orange solution of **8** (0.50 g, 0.7 mmol) in toluene was added 2,6-Me₂C₆H₃NC (0.092 g, 0.7 mmol). The mixture was stirred at room temperature for 4 h. After removal of solvent under vacuum, the remaining orange solid was washed with cold pentane to give yellow **12** (0.42 g, 71%). Mp: 131 °C (decomp.). Anal. calcd for C₄₉H₆₈N₃Sm: C, 69.28; H, 8.07; N, 4.94. Found: C, 69.21, H, 8.23; N, 4.87%. ¹H NMR (C₆D₆): δ 0.45 (s, 6H, Me), 0.52 (br, 6H, CHMe₂), 0.58 (d, 6H, CHMe₂), 1.04 (s, 15H, C₅Me₅), 1.29 (d, 6H, CHMe₂), 2.20 (s, 6H, Me), 2.40 (s, 1H, CH), 2.59 (d, 6H, CHMe₂), 4.51 (s, 3H, β-Me), 6.60 (sept, 2H, CHMe₂), 6.67 (d, 2H, Ar–H), 7.35 (m, 2H, Ar–H), 7.50 (d, 2H, Ar–H). IR (Nujol, KBr): 3058 (m), 2725 (m), 1914 (w), 1845 (w), 1655 (w), 1621 (w), 1590 (w), 1510 (s), 1312 (s), 1274 (s), 1252

Table 1 Crystallographic data for **1–3**, **5–7** and **9**

	1-(C ₇ H ₈) _{3.5}	2	3	5 ₂ -(C ₅ H ₁₂) _{1.5}	6	7-(C ₇ H ₈) _{3.5}	9
Formula	C _{153.75} H ₂₀₄ Cl ₁₈ N ₈ O ₂ Sm ₄	C ₃₃ H ₅₉ CIN ₃ Si ₂ Sm	C _{44.5} H ₇₉ N ₄ Si ₄ Sm	C ₆₉ H _{100.75} N ₄ Sm	C ₃₉ H ₅₆ CIN ₂ Sm	C _{155.5} H ₂₃₆ Al ₂ Cl ₆ N ₈ Sm ₄	C ₄₉ H ₇₅ N ₅ SiSm
<i>M</i>	3081.25	763.83	932.83	1136.64	738.66	3085.58	870.55
Crystal size/mm	0.24 × 0.22 × 0.15	0.31 × 0.26 × 0.15	0.34 × 0.23 × 0.12	0.24 × 0.18 × 0.10	0.30 × 0.21 × 0.15	0.29 × 0.22 × 0.05	0.33 × 0.24 × 0.08
Color, habit	Yellow, block	Yellow, block	Yellow, block	Red, block	Orange, block	Red, block	Yellow, block
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
<i>a</i> /Å	23.766(1)	17.208(3)	11.686(2)	25.2973(6)	10.6492(4)	16.0730(3)	16.573(3)
<i>b</i> /Å	26.143(1)	18.256(4)	11.708(2)	13.4722(4)	12.0177(5)	28.2943(3)	22.284(5)
<i>c</i> /Å	26.765(1)	13.022(3)	20.510(4)	39.0529(9)	15.7839(6)	34.5779(6)	12.794(3)
<i>a</i> /°	90	90	75.55(3)	90	104.152(1)	90	90
<i>β</i> /°	110.844(1)	103.74(3)	79.49(3)	100.463(1)	97.114(1)	99.4430(10)	90
<i>γ</i> /°	90	90	68.51(3)	90	106.841(1)	90	90
<i>V</i> /Å ³	15541.1(12)	3973.8(14)	2515.4(9)	13088.3(6)	1832.99(1)	15512.1(4)	4725.0(2)
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>Prima</i> (no. 62)
<i>Z</i>	4	4	2	8	2	4	4
<i>D</i> _c /g cm ^{–3}	1.32	1.28	1.23	1.15	1.34	1.32	1.22
<i>μ</i> /cm ^{–1}	16.77	16.3	12.94	9.37	17.02	16.56	13.02
<i>R</i>	0.0615	0.0310	0.0417	0.0561	0.0332	0.0410	0.0379
<i>R</i> _w	0.1556	0.0744	0.1083	0.1162	0.0859	0.0801	0.901
<i>R</i> _{int}	0.1308	0.0408	0.0492	0.1163	0.0361	0.0829	0.0602
GOF	0.988	0.979	0.998	1.000	1.044	0.936	1.020

(s), 1228 (m), 1167 (s), 1109 (m), 1018 (s), 927 (m), 823 (m), 786 (s), 755 (m), 721 (m), 612 (m).

LSmCp*[C(CH₂SiMe₃)=N-C₆H₃-2,6-Me₂] (13). Compound **13** was obtained analogously to **12** above using **9**. Yellow crystals (0.53 g, 82%). Mp: 197 °C (decomp.). Anal. calcd for C₅₂H₇₆N₃SiSm: C, 67.76; H, 8.32; N, 4.56. Found: C, 67.23; H, 8.28; N, 4.27%. ¹H NMR (C₆D₆): δ 0.02 (s, 6H, Ar-Me), 0.36 (s, 9H, SiMe₃), 0.96 (s, 15H, C₅Me₅), 1.16 (d, 6H, CHMe₂), 1.23 (d, 6H, CHMe₂), 2.04 (s, 6H, Me), 2.42 (d, 6H, CHMe₂), 2.78 (d, 6H, CHMe₂), 5.12 (br s, 2H, CH₂SiMe₃), 6.58 (d, 2H, Ar-H), 6.86 (sept, 2H, CHMe₂), 7.03 (m, 3H, Ar-H), 7.33 (m, 2H, Ar-H), 7.43 (s, 1H, CH), 7.46 (sept, 2H, CHMe₂), 7.72 (d, 2H, Ar-H).

X-Ray structural determinations

Pertinent details for the individual compounds can be found in Table 1. A suitable crystal was mounted on a glass capillary using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART diffractometer/CCD area detector⁴⁴ with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), centered in the beam, and cooled by a nitrogen flow low temperature apparatus. Preliminary orientation matrix and cell constants were determined by collection of 60 10-second frames, followed by spot integration and least square refinement. An arbitrary hemisphere of data was collected and the raw data were integrated using SAINT.⁴⁵ Cell dimensions reported in Table 1 were calculated from all reflections with $I > 10\sigma(I)$. Data were analyzed for agreement and possible absorption using XPREP.⁴⁶ An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.⁴⁷ The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. The structures were solved and refined with the teXsan software package.⁴⁸

CCDC reference numbers 244217–244219, 244221–244223 and 245593 (there is no CCDC reference number for compound **4**).

See <http://www.rsc.org/suppdata/dt/b5/b501437a/> for crystallographic data in .cif or other electronic format.

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