Homoleptic organolanthanide compounds supported by the bis(dimethylsilyl)benzyl ligand

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Abstract
A β-SiH functionalized benzyl anion [C(SiHMe2)2Ph]− is obtained by deprotonation of HC(SiHMe2)2Ph with KCH2Ph or by reaction of KOtBu and (Me2HSi)3CPh; LnI3(THF)n and three equivalents of this carbanion combine to provide homoleptic tris(alkyl)lanthanide compounds Ln{C(SiHMe2)2Ph}3 (Ln = La, Ce, Pr, Nd) containing secondary metal–ligand interactions.

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Homoleptic organolanthanide compounds supported by the bis(dimethylsilyl)benzyl ligand†

Kasuni C. Boteju, Arkady Ellern and Aaron D. Sadow*

A strategy for stabilizing coordinatively unsaturated rare earth amides has involved the incorporation of SiH groups, which form labile secondary interactions with the lanthanide center.14 Furthermore, the SiH moiety provides a powerful signature in ¹H and ²⁹Si NMR and IR spectra. This β-SiH strategy may also be applied to alkyls, and the ligand C(SiMe₃)₂ supports trivalent yttrium and divalent ytterbium and samarium homoleptic alkyls containing secondary Ln—H–Si interactions.15,16 Recently, we reported Ce[C(SiMe₃)₂]₁₂ as a precursor to a zwitterionic hydro-silylation catalyst.17 New chemistry might be accessed with alkyl ligand variations that include both β-SiH and benzyl functionalities, and these groups could compete to enhance the homoleptic compounds’ resistance to undesired ligand elimination pathways. Both SiH and benzyl groups may have significant charge delocalization and secondary interactions that might stabilize homoleptic compounds. A single ligand containing both elements, namely –C(SiMe₃)₂Ph, would test these ideas. Here we report the synthesis of allene precursors, two routes to potassium alkyl reagents, and isolation and characterization of a series of homoleptic organolanthanide complexes.

Reductive coupling of HCPhBr₂ and ClSiHMe₂ affords HClSiMe₂Br (1; eqn (1)) on preparative scale.

H–C

\frac{1}{2} {\text{SiHMe}}_2 \rightarrow \frac{1}{2} \text{ClSiHMe}_2 \rightarrow \frac{1}{2} \text{Ph}

H–C

\text{THF, reflux, 2 h}

H–C

\text{SiHMe}_2 \rightleftharpoons \text{SiHMe}_2

Ph

\text{Mg}

H–C

\text{SiHMe}_2

\text{SiHMe}_2

1, 70.9%

A diagnostic triplet in the ¹H NMR spectrum at 1.43 ppm (δH = 4 Hz, 1 H) for the H on the central carbon is coupled to a signal at 4.34 ppm assigned to the SiH (2 H, δSiH = 186 Hz). The two SiHMe₂ groups are magnetically inequivalent giving a virtual octet for the SiH resonance (a M(AX₂Y₃)(AX₃Y₃) spin system). Compound 1 is also characterized by an intense νSiH absorbance at 2115 cm⁻¹ in its IR spectrum.

While HClSiMe₂Br₁₈ reacts readily with lithium diisopropylamide,¹⁹ deprotonation of HClSiMe₂Brₚ is more challenging. Attempts to synthesize [C(SiMe₃)₂]₂Ph⁺ using LiN(SiMe₃)₂₂, nBuLi,
KH, or KC(SiMe2)3 as bases returned HC(SiMe2)2Ph. Potassium benzyl (KBN) gives Me2SiBu as the major product in its reaction with 1 at room temperature. Fortunately, reactions with KBN performed at –78 °C yielded a mixture now dominated by KC(SiMe2)2Ph (2), assigned to a doublet at 0.47 ppm in the 1H NMR spectrum. This signal was affected by addition of TMEDA, which gave a new doublet at 0.57 ppm. In preparative scale reactions, the desired potassium alkyl is crystallized from pentane at –30 °C to provide Ph[Me2HSi]2CK(TMEDA) (2 TMEDA) as dark red crystals (eqn (2)), albeit in low isolated yield.

The 1H NMR spectrum of isolated 2 TMEDA contained a septet at 4.78 ppm (JHH = 162 Hz). This one-bond coupling constant was reduced compared to HC(SiMe2)2Ph (186 Hz). In 2 TMEDA, the SiMe2 groups appeared as one doublet (JHH = 3.6 Hz), unlike the diastereotopic methyls in HC(SiMe2)2Ph noted above. In addition, the IR spectrum of 2 TMEDA revealed two νSiH bands at 2115 and 1995 cm⁻¹.

A single-crystal X-ray diffraction study revealed a polymeric structure for 2 TMEDA,⁴ with each K cation interacting with two C(SiMe2)2Ph groups (Fig. 1) through the H11s (2.82(4) Å), the C6 and C11 (from a phenyl group) of one ligand, and the C9 and C10 from a phenyl of the second. Notably, the K1–C1 distance (3.565(4) Å; i.e., to the presumed carbanionic center) is exceedingly long and outside expected bonding range. For comparison, the K–C distance (3.030(5) Å) is much shorter in dimeric {Me2HSi}2CK(TMEDA)₂ than in 2 TMEDA.¹⁶ The SiH-free potassium alkyl {KC(SiMe2)₂}Phₙ (3.007(2) Å)²⁰ and the compound {KC(SiMe2)ₙPhₙ}[SiHMe₂]ₙ (3.167(8) Å)²⁰ also have polymeric structures with π-coordinated arenes. While the central, carbanionic carbon adopts distorted, nearly planar geometries in these three examples (∑angles = 358.8°, 357.4° and 356.5°),⁴,¹⁶,²⁰ C1 in 2 TMEDA is perfectly planar (∑angles = 360.0(5°)).

The formation of Bn₃SiMe₂ in these reactions implies nucleophilic attack by KBN on a SiMe₂ group and suggests an alternative route to the desired KC(SiMe2)2Ph (2) via Si–C cleavage. A related Si–Si bond cleavage provides MSi(SiMe2)₃ from Si(SiMe2)₄ and LiMe or KOtBu.¹¹ This idea was tested by the reaction of (Me2HSi)₂CPh and KOtBu to give the desired KC(SiMe2)2Ph (2) in excellent yield (eqn (3)).

![Thermal ellipsoid plot of Ph[Me2HSi]2CK(TMEDA) (2 TMEDA) at 50% probability. H atoms bonded to C are not illustrated for clarity. Selected interatomic distances (Å): K1–C1, 3.565(4); K1–H1s, 2.82(4); K1–Si1, 3.843(7); K1–C0, 3.038(4); K1–C11, 3.091(5); C1–C6, 1.446(6); C6–C7, 1.434(7); C7–C8, 1.376(7); C8–C9, 1.392(7); C9–C10, 1.383(7); C10–C11, 1.374(6); C11–C6, 1.422(6). Selected interatomic angles (∠): K1–H1s–Si1, 124(2); C6–C1–Si2, 119.8(3); Si2–C1–Si1, 121.6(2); Si1–C1–Si2, 118.6(3).](image-url)
temperature NMR spectrum contrasts the two types of SiH groups observed in the IR spectra, suggesting fluxional process(es). A $^1$H NMR spectrum collected at −73 °C in toluene-$d_8$ revealed that two SiHMe$_2$ groups were inequivalent: signals at 4.67 ($J_{SiH}$ ~ 180 Hz) and 3.82 ($J_{SiH}$ ~ 120 Hz) ppm were assigned to nonbridging SiH and bridging La−H−Si moieties, respectively. These resonances correlated in a COSY experiment to signals at 0.35 and 0.08 ppm (with the downfield SiH) and 0.77 and 0.67 ppm (with the upfield SiH) of the now inequivalent methyl groups. Notably, one of the ortho-C$_6$H$_5$, whose resonance appeared unusually upfield at 4.15 ppm, was even more shielded than the nonbridging SiH. Moreover, all five H in

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0.77 and 0.67 ppm (with the upfield SiH) of the now inequivalent

tively. These resonances correlated in a COSY experiment

each ligand containing one La

A few of the notable structural features include the sharp La1–C1–Si1

equal in the low temperature solution-phase structure, with

lanthanum center (Fig. 2). This structure is con-

The three ligands are arranged in a trigonal geometry around the

coordination of the C$_6$, and also through one La–C–

centert h r o u g hab e n z y l i c - t y p e

aryl group.

Fig. 2 Thermal ellipsoid plot of La(C(SiHMe$_2$)$_2$Ph)$_3$ (3). La1 is located on a

crystallographic 3-fold axis. H atoms bonded to Si are located in the Fourier
difference map, their positions are refined and are illustrated. All other H

atoms and a disordered pentane molecule (0.5) are not shown for clarity.

Short La–C (green) and Ln–H–Si (black) distances are highlighted with
dashed lines. Selected interatomic distances (Å): La1–C1, 2.674(3); La1–C6, 2.822(2); La1–Si1, 3.3141(9); La1–H1s, 2.694(4); C1–Si1, 1.821(3); Si1–H1s, 1.37(4); C1–Si2, 1.853(3); Si2–H2s, 1.45(4); C1–C6, 1.483(4); C6–C7, 1.415(5); C6–C11, 1.409(4). Selected interatomic angles (°): C1–La1–C1, 82.0(1); C1–La1–Si1, 93.0(1); La1–C1–Si2, 128.3(1).

Fig. 3 Thermal ellipsoid plot of one of two crystallographically distinct

molecules of Ce(C(SiHMe$_2$)$_2$Ph)$_3$ (4). H atoms bonded to Si are located in

the Fourier difference map, their positions are refined and are illustrated. All other H atoms are not shown for clarity. Short Ce–C (green) and

Ln–H–Si (black) distances are highlighted with dashed lines. Selected

interatomic distances (Å): Ce2–C34, 2.613(3); Ce2–C45, 2.671(2); Ce2–C56, 2.587(3); Ce2–Si7, 3.1947(9); Ce2–H7s, 2.47(2); C34–Si7, 1.829(2); Si7–H7s, 1.48(3); Ce2–Si9, 3.2379(9); Ce2–H9s, 2.46(3); C45–Si9, 1.829(3); Si9–H9s, 1.48(3); Selected interatomic angles (°): C34–Ce2–C45, 118.57(9); Ce2–C34–C39, 83.8(2); Ce2–C34–Si7, 90.1(1).
secondary Ln—H–Si interactions are different than those with nonbridging SiH groups, and the Ln–C distances are also affected by the presence or lack of secondary Ln—H–Si interactions. The ligand itself is synthesized by deprotonation of the new alkane HC(SiMe₂)₂Ph with KBr, but Me₅SiNa₃ and other side products in reactions of HC(SiMe₂)₃Ph and KBr suggested a competing reaction involving nucleophilic attack on a Si center to cleave the C–Si bond. Therefore we developed an alternative route to KC(SiMe₂)₂Ph by reacting PhC(SiMe₂)₃ with KOBu that affords the desired product in excellent yield. This straightforward two-step synthesis to homoleptic organolanthanides may allow their application in the preparation of heteroleptic lanthanide complexes and as precursors for new catalytic chemistry.

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References

‡ X-ray data for 2-TMEDA (CCDC 1517682): C₁₃H₂₂KN₂Si₂; FW 362.75; monoclinic; α: 8.7354(6), β: 23.003(1), γ: 11.6433(7); β: 100.207(4), volume: 2302.5(3); P12₁/c1; Z = 4; temp. 173 K; reflections: collected, 20407; independent, 3284; Rint 0.1552; 2217 data I > 2σ(I); R1 0.0705, wR2 0.1845; R1 = 0.0996, wR2 = 0.2145.

§ X-ray data for 3 (CCDC: 1517683): C₁₃H₂₆LaSi₆(C₃H₅)₂; FW 797.31; trigonal; α: 12.4380(6), c: 16.157(1), volume, 2164.7(3); P3; Z = 2; temp. 173 K; reflections: collected, 23107; independent, 3715; Rint 0.0345; 3439 data I > 2σ(I); R1 0.0309, wR2 0.0828; R1 = 0.0351, wR2 = 0.0928.

¶ X-ray data for 4 (CCDC: 1517684): C₁₃H₂₆CeSi₆; FW 762.44; monoclinic; a: 22.324(2), b: 19.841(4), c: 19.921(5), β: 116.076(1), volume: 7925.5(9); P12₁/c1; Z = 8; temp. 173 K; reflections: collected, 79198; independent, 18762; Rint 0.0485; 14549 data I > 2σ(I); R1 0.0315, wR2 0.0698; R1 = 0.0515, wR2 = 0.0836; X-ray data for 5 (CCDC 1517685): C₁₃H₂₆PrSi₆; FW 763.23; monoclinic; a: 22.3310(6), b: 19.8399(5), c: 19.8802(5), β: 116.047(1), volume 7913.2(4); P12₁/c1; Z = 8; temp. 173 K; reflections: collected, 79681; independent, 15456; Rint 0.0653; 14828 data I > 2σ(I); R1 0.0695, wR2 0.1909; R1 = 0.0710, wR2 = 0.1931; X-ray data for 6 (CCDC: 1517686): C₁₃H₂₆NdSi₆; monoclinic; a: 22.3315(2), b: 19.843(2), c: 19.853(2), β: 116.017(1), volume: 7908(1); P12₁/c1; Z = 8; temp. 173 K; reflections: collected, 11307; independent, 20627; Rint = 0.0711; 15075 data I > 2σ(I); R1 0.0346, wR2 0.0623; R1 = 0.0624, wR2 = 0.0768.

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