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 (Me2H)SiH2CPH; LnI3(THF)n and three equivalents of this carbanion combine to provide homoleptic tris(alkyl)lanthanide compounds Ln[C(SiHMe2)2]3 (Ln = La, Ce, Pr, Nd) containing secondary metal–ligand interactions.

Synthesis of homoleptic organolanthanide complexes, particularly those of the early trivalent lanthanides (La–Nd), is challenging due to the large radii of these elements, polar bonding, high charge, and high Lewis acidity. Such homoleptic compounds should be valuable for the synthesis of new catalysts and new materials; yet solvent- or donor-group-free, salt-free, and thermally robust organolanthanide compounds are not readily accessed for the larger metal centers. For example, the reaction of MeLi and LaCl3 gives Li3[LaMe6] as a TMEDA adduct. Three THF molecules coordinate to the labile tris(benzyl)lanthanum allowing isolation of LaBn3(THF)3, however, even this adduct eliminates toluene at room temperature with a half-life of ca. 2 h. The persistence of related compounds may be enhanced by chelating benzylic ligands, for example Ln(CH(NMe2)Ph)3, which are conveniently accessed via multistep synthesis via Ln[O(2,6-C6H3–H2–NMe2)]3. A diagnostic triplet in the 1H NMR spectrum at 1.43 ppm (JHH = 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, 1 β-SiH) and the H on the benzylic group. The two SiHMe2 groups are magnetically inequivalent giving a different triplet at 2.38 ppm (2 H, 1 JHH = 4 Hz) and 2.25 ppm (2 H, 1 β-SiH). The two SiHMe2 groups are magnetically inequivalent giving a different triplet at 2.38 ppm (2 H, 1 JHH = 4 Hz) and 2.25 ppm (2 H, 1 β-SiH). The 29Si NMR and IR spectra. This β-SiH strategy may also be applied to alkyls, and the ligand C(SiHMe2)3 supports trivalent yttrium and divalent ytterbium and samarium homoleptic alkyls containing secondary Ln—H–Si interactions. Recently, we reported Ce[C(SiHMe2)3]3 as a precursor to a zwitterionic hydro-silylation catalyst. New chemistry might be accessed with alkyl ligand variations that include both β-SiH and benzylic 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(SiHMe2)2Ph, would test these ideas. Here we report the synthesis of alkane precursors, two routes to potassium alkyl reagents, and isolation and characterization of a series of homoleptic organolanthanide complexes.

Reductive coupling of HCPhBr2 and CeSiHMe2 affords HC(SiHMe2)2Ph (1; eqn (1)) on preparative scale.

A diagnostic triplet in the 1H NMR spectrum at 1.43 ppm (JHH = 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, JHH = 186 Hz). The two SiHMe2 groups are magnetically inequivalent giving a virtual octet for the SiH resonance (a M(AX3)(AY3) spin system). Compound 1 is also characterized by an intense νSiH absorbance at 2115 cm−1 in its IR spectrum.

While HC(SiHMe2)3 reacts readily with lithium diisopropylamide, deprotonation of HC(SiHMe2)2Ph is more challenging. Attempts to synthesize [C(SiHMe2)2Ph]+ using LiN(SiMe3)2, nBuLi,
KH, or KC(SiMe₂)₃, as bases returned HC(SiMe₂)₀Ph. Potassium benzyl (KBN) gives Me₂SiBn₂ 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)₀Ph (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]₀CK(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)₀Ph (186 Hz). In 2 TMEDA, the SiMe₂ groups appeared as one doublet (JHH = 3.6 Hz), unlike the diastereotopic methyls in HC(SiMe₂)₀Ph 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,² with each K cation interacting with two C(SiMe₂)₀Ph groups (Fig. 1) through the H1s (2.82(4) Å; i.e., to the presumed carbanionic center) and C10 from a phenyl of the second. Notably, the K1–C 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 the IR spectrum of 1. The solution IR spectra similarly showed two SiH bands were low intensity and a number of the IR spectra were polymeric structures with π-coordinated arenes. While the central, carbanionic carbon adopts distorted, nearly planar geometries in these three examples, Σangles = 358.8°, 357.4° and 356.5°,⁸,¹⁶,²⁰ C1 in 2 TMEDA is perfectly planar (Σangles = 360.0(5)°).

The formation of Bn₂SiMe₂ in these reactions implies nucleophilic attack by KBN on a SiMe₂ group and suggests an alternative route to the desired KC(SiMe₂)₀Ph (2) via Si–C cleavage. A related Si–Si bond cleavage provides MSi(SiMe₂)₃ from Si(SiMe₂)₄ and LiMe or KOBu.²¹ This idea was tested by the reaction of (Me₂HSi)₂CPh and KOtBu to give the desired KC(SiMe₂)₀Ph (2) in excellent yield [eqn (3)].

The spectroscopic features of the SiH group in 2 and 2 TMEDA are similar, including the IR stretching frequency, the chemical shift, and the one-bond coupling constant.

Reactions of three equiv. of 2 or 2 TMEDA and LaI₃(THF)₄, CeI₃(THF)₄, PrI₃(THF)₃, or NdI₃(THF)₃ provide Ln(C(SiMe₂)₀Ph)₃ (Ln = La (3), Ce (4), Pr (5), Nd (6)) in excellent yields [eqn (4)].

The series of compounds provide pale yellow, orange, yellow and green crystalline materials, respectively. IR spectra for 3, 5, and 6 (KBr) each contained a sharp, higher energy νSiH band (2109 ± 5 cm⁻¹) assigned to non-bridging SiH and a broad, lower energy band (1866 ± 6 cm⁻¹) attributed to a νSiH of the Ln–H–Si. In contrast, the cerium compound 4 showed only one νSiH band, which appeared at 2115 cm⁻¹. The solution IR spectra similarly showed two SiH absorbances for 3 and 5. Although two νSiH bands were obtained for 4 in solution, the bands were low intensity and a number of the IR spectra were dominated by HC(SiMe₂)₀Ph. We attributed these observations to labile secondary Ln–H–Si interactions present both in solution and solid state.

The ¹H NMR spectrum of diamagnetic 3 revealed signals at 4.24, 0.43, and 0.32 ppm attributed to equivalent SiMe₂ groups with diastereotopic methyl moieties. A doublet resonance at 5.84 ppm, assigned to an ortho-C₆H₅, appeared upfield compared to its chemical shift in the alkane starting material (6.97 ppm), suggesting a multihapto benzyl-Ln coordination. Evidence for La–H–Si interactions were provided by the JHH of 144 Hz. The equivalence of the SiMe₂ in the room
temperature NMR spectrum contrasts the two types of SiH groups observed in the IR spectra, suggesting fluxional process(es). A $^1H$ NMR spectrum collected at $-73^\circ\text{C}$ in toluene-$d_8$ revealed that two SiHMe$_2$ groups were inequivalent: signals at 4.67 ($J_{\text{SiH}} \sim 180\text{ Hz}$) and 3.82 ($J_{\text{SiH}} \sim 120\text{ Hz}$) ppm were assigned to nonbridging SiH and bridging Ln–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 the C$_6$H$_5$ were inequivalent. Thus, the alkyl ligands are equivalently shielded than the nonbridging SiH.

Interestingly, isomorphous cerium 4, praseodymium 5 and neodymium 6 compounds’ structures (P2$_1$/c) are inequivalent with that of La 3. The two molecules in the unit cells for 4, 5 and 6 have inequivalent configurations, with one of the molecules containing only two Ln–H–Si bridging moieties (Fig. 3). The Ce–C distances for the five ligands that contain bridging Ce–H–Si interactions average 2.65 ± 0.02 Å, whereas the $\eta^3$-benzyl-only ligand (Ce–C, 2.587(3) Å) distance is shorter. This distinction is also apparent in compounds 5 (Pr–C$_{\text{ave}}$, 2.63 ± 0.02; Pr2–C56, 2.556(5) Å) and 6 (Nd–C$_{\text{ave}}$, 2.61 ± 0.02; Nd2–C56, 2.541(4) Å).

This work extends the idea that the β-SiH group supports large, coordinatively unsaturated rare earth centers in homoleptic, solvent-free compounds to include a new mixed benzyl dimethylsilyl ligand. Tris[alkyl]lanthanides Ln[C(SiHMe$_2$)$_2$Ph]$_3$, are synthesized in good yields, and the secondary interactions involving β-SiH and aryl moieties are likely important to the facile isolation of these compounds. The structural parameters (e.g., Ln–C, Si–H, Si–C distances) for moieties involved in 

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**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, 2.67(4); La1–C6, 2.82(2); La1–Si1, 3.31(19); La1–H1s, 2.69(4); C1–Si1, 1.82(13); Si1–H1s, 1.37(4); C1–Si2, 1.85(3); Si2–H2s, 1.45(4); C1–C6, 1.48(3); C6–C7, 1.41(5); C6–C11, 1.40(9). Selected interatomic angles (°): C1–La1–C1, 119.0(5); La1–C1–C6, 80.0(1); La1–C1–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, 2.61(3); Ce2–C45, 2.67(2); Ce2–C56, 2.58(3); Ce2–Si7, 3.19(7); Ce2–H7s, 1.82(9); Si7–H7s, 1.48(3); Ce2–Si9, 3.23(9); Ce2–H9s, 2.46(3); C45–Si9, 1.82(9); Si9–H9s, 1.48(3). Selected interatomic angles (°): C34–Ce2–C45, 118.5(9); C24–C34–C39, 83.8(2); C24–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(SiMe3)2Ph with KBr, then Me2SiBr2 and other side products in reactions of HC(SiMe3)2Ph 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(SiMe3)2Ph by reacting PhC(SiMe3)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): C15H13KN5Si2; FW 362.75; monoclinic; α: 8.7354(6), β: 23.003(1), γ: 11.6433(7), β: 100.207(4), volume: 2302.5(3), P21/c1; Z = 4; temp. 173 K; reflections: collected, 21 187; independent, 3284; Rint 0.0485; 14 549 data R1 0.0698, wR2 0.1845; Rrel 0.0996, wR2 0.2145.

§ X-ray data for 3 (CCDC: 1517683): C16H12LaSi6(CH3)2; FW 797.31; trigonal; α: 12.4380(6), β: 16.157(1), γ: 2164.7(3); P31; Z = 2; temp. 173 K; reflections: collected, 23 107; independent, 3715; Rint 0.0345; 3439 data I > 2σ(I); R1 0.0309, wR2 0.0828; Rrel 0.0351, wR2 0.0928.

# X-ray data for 4 (CCDC: 1517684): C33H57NdSi6; monoclinic; α: 22.324(2), β: 19.841(1), γ: 116.921(1), β: 116.076(1), volume: 7925.5(9); P21/c1; Z = 8; temp. 173 K; reflections: collected, 79 198; independent, 18 762; Rint 0.0485; 14 549 data I > 2σ(I); R1 0.0315, wR2 0.0698; Rrel 0.0515, wR2 0.0836; X-ray data for 5 (CCDC: 1517685): C33H57CeSi6; FW 762.44; monoclinic; α: 22.324(2), β: 19.841(1), γ: 116.921(1), β: 116.076(1), volume: 7925.5(9); P21/c1; Z = 8; temp. 173 K; reflections: collected, 79 198; independent, 17 762; Rint 0.0485; 14 549 data I > 2σ(I); R1 0.0315, wR2 0.0698; Rrel 0.0515, wR2 0.0836; X-ray data for 6 (CCDC: 1517686): C33H57NdSi6; monoclinic; α: 22.324(2), β: 19.841(1), γ: 116.921(1), β: 116.076(1), volume: 7925.5(9); P21/c1; Z = 8; temp. 173 K; reflections: collected, 113 017; independent, 20 672; R1 0.0711, wR2 0.0768.


