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

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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. Furthermore, the SiH moiety provides a powerful signature in $^1$H and $^{29}$Si NMR and IR spectra. This β-SiH strategy may also be applied to alkyls, and the ligand Ce(SiHMe$_2$)$_3$ supports trivalent yttrium and divalent ytterbium and samarium homoleptic alkyls containing secondary Ln—H–Si interactions. Recently, we reported Ce[Ce(SiHMe)$_2$]$_3$ 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 Ce(C(SiHMe)$_2$)$_3$Ph, 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 HCPhBr$_2$ and ClSiHMe$_2$ affords HC(SiHMe)$_2$Br (1; eqn (1)) on preparative scale.

A diagnostic triplet in the $^1$H NMR spectrum at 1.43 ppm ($J_{HH} = 4$ 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, $J_{SiH} = 186$ Hz). The two SiHMe$_2$ groups are magnetically inequivalent giving a virtual octet for the SiH resonance (a M(AX$_3$Y$_3$)[AX$_3$Y] spin system). Compound 1 is also characterized by an intense $v_{SiH}$ absorbance at 2115 cm$^{-1}$ in its IR spectrum.

While HC(SiHMe)$_2$Br reacts readily with lithium diisopropylamide, deprotonation of HC(SiHMe)$_2$Ph is more challenging. Attempts to synthesize Ce(C(SiHMe)$_2$Ph) using LiN(SiMe)$_3$, nBuLi, and characterization for compounds 1, 2, 2 TMEDA, 3–6. CCDC 1517682–1517686. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc09304c
KH, or KC(SiMe₂)₃, as bases returned HC(SiMe₂)₂Ph. Potassium benzyl (KBN) gives Me₂SBn 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(SiHMe₂)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 set at 4.78 ppm (JHH = 162 Hz). This one-bond coupling constant was reduced compared to HC(SiHMe₂)₂Ph (186 Hz). In 2 TMEDA, the SiMe₂ groups appeared as one doublet (JHH = 3.6 Hz), unlike the diastereotopic methyls in HC(SiHMe₂)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, with each K cation interacting with two C(SiHMe₂)₂Ph groups (Fig. 1) through the H₁s (2.82(4) Å; i.e., to the presumed carbanionic center) and solid state. The geometries in these three examples (Σangles = 358.8°, 357.4° and 356.5°) 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(SiHMe₂)₂Ph)₃ (Ln = La (3), Ce (4), Pr (5), Nd (6)) in excellent yield (eqn (4)).

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.

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, 5, and 6. 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(SiHMe₂)₂Ph. We attributed these observations to labile secondary Ln−H−Si interactions present both in solution and solid state.

The ¹H NMR spectrum of 3 revealed signals at 4.24, 0.43, and 0.32 ppm attributed to equivalent SiHMe₂ 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 SiHMe₂ in the room
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 $-73\, ^\circ\mathrm{C}$ in toluene-$d_8$ revealed that two SiHMe$_2$ groups were inequivalent: signals at 4.67 ($J_{\mathrm{SiH}} \sim 180\, \mathrm{Hz}$) and 3.82 ($J_{\mathrm{SiH}} \sim 120\, \mathrm{Hz}$) 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 equivalent, and the close contacts in the series (i.e., Ln–C, Ln···Si, and Ln···H) follow the expected trend based on ionic radius (La > Ce > Pr > Nd).

Interestingly, isomorphous cerium 4, praseodymium 5 and neodymium 6 compounds' structures (P2i/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 $\eta^2$-benzyl-only ligand (Ce2–C56, 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, coordinately 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...
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(SiHMe2)2Ph with K&n, but Me6SiBn2 and other side products in reactions of HC(SiHMe2)2Ph and K&n 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(SiHMe2)2Ph by reacting PhC(SiHMe2)3 with KO&Bu that affords the desired product in excellent yield. This straightforward two-step synthesis to holoenzyme organolanthanides may allow their application in the preparation of heteroleptic lanthanide complexes and as precursors for new catalytic chemistry.

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