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

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A β -SiH functionalized benzyl anion $[C(SiHMe_2)_2Ph]^-$ is obtained by deprotonation of $HC(SiHMe_2)_2Ph$ with KCH_2Ph or by reaction of $KOtBu$ and $(Me_2HSi)_3CPh$; $LnI_3(THF)_n$ and three equivalents of this carbanion combine to provide homoleptic tris(alkyl)lanthanide compounds $Ln[C(SiHMe_2)_2Ph]_3$ ($Ln = La, Ce, Pr, Nd$) 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.¹ Such homoleptic compounds should be valuable for the synthesis of new catalysts and new materials,² 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 $LaCl_3$ gives $Li_3[LaMe_6]$ as a TMEDA adduct.³ Three THF molecules coordinate to the labile tris(benzyl)lanthanum allowing isolation of $LaBn_3(THF)_3$,^{4,5} 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 $Ln(CH(NMe_2)Ph)_3$ ⁶ or $Ln(CH_2C_6H_4-2-NMe_2)_3$.⁷ An alternative approach combines bulky β -SiMe₃ with the benzyl group in $C(SiMe_3)_2Ph$,⁸ exemplified by a bis(alkyl)calcium compound possessing metal–aryl π -interactions. Coordinative unsaturation is important to the reactivity of organolanthanides, and donors such as TMEDA or THF can diminish reactivity,⁹ facilitate alkane elimination,¹⁰ or react by C–O bond cleavage.¹¹ While donor-free lanthanum and cerium compounds such as $Ln\{CH(SiMe_3)_2\}_3$ are known, they are inconveniently accessed through multistep synthesis *via* $Ln\{O(2,6-C_6H_3tBu_2)\}_3$.^{12,13}

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 $C(SiHMe_2)_3$ supports trivalent yttrium and divalent ytterbium and samarium homoleptic alkyls containing secondary $Ln-H-Si$ interactions.^{15,16} Recently, we reported $Ce\{C(SiHMe_2)_3\}_3$ as a precursor to a zwitterionic hydrosilylation catalyst.¹⁷ 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 $-C(SiHMe_2)_2Ph$, 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 $HCPHBr_2$ and $ClSiHMe_2$ affords $HC(SiHMe_2)_2Ph$ (**1**; eqn (1)) on preparative scale.

A diagnostic triplet in the ¹H NMR spectrum at 1.43 ppm (³J_{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, ¹J_{SiH} = 186 Hz). The two SiHMe₂ groups are magnetically inequivalent giving a virtual octet for the SiH resonance (a $M(AX_3Y_3)(AX_3Y_3)'$ spin system). Compound **1** is also characterized by an intense ν_{SiH} absorbance at 2115 cm⁻¹ in its IR spectrum.

While $HC(SiHMe_2)_3$ ¹⁸ reacts readily with lithium diisopropylamide,¹⁹ deprotonation of $HC(SiHMe_2)_2Ph$ is more challenging. Attempts to synthesize $[C(SiHMe_2)_2Ph]^-$ using $LiN(SiMe_3)_2$, *n*BuLi,

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KH, or $\text{KC}(\text{SiHMe}_2)_3$ as bases returned $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$. Potassium benzyl (KBN) gives Me_2SiBn_2 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 $\text{KC}(\text{SiHMe}_2)_2\text{Ph}$ (**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 $\text{Ph}(\text{Me}_2\text{HSi})_2\text{CK}(\text{TMEDA})$ (**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 ($J_{\text{SiH}} = 162$ Hz). This one-bond coupling constant was reduced compared to $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$ (186 Hz). In **2-TMEDA**, the SiMe_2 groups appeared as one doublet ($J_{\text{HH}} = 3.6$ Hz), unlike the diastereotopic methyls in $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$ noted above. In addition, the IR spectrum of **2-TMEDA** revealed two ν_{SiH} bands at 2115 and 1995 cm^{-1} .

A single-crystal X-ray diffraction study revealed a polymeric structure for **2-TMEDA**, $\ddagger$ with each K cation interacting with two $\text{C}(\text{SiHMe}_2)_2\text{Ph}$ groups (Fig. 1) through the H1s ($2.82(4)\text{ \AA}$), 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 ($3.565(4)\text{ \AA}$; *i.e.*, to the presumed carbanionic center) is exceedingly long and outside expected bonding range. For comparison, the K–C distance ($3.030(5)\text{ \AA}$) is much shorter in

dimeric $\{(\text{Me}_2\text{HSi})_3\text{CK}(\text{TMEDA})\}_2$ than in **2-TMEDA**.¹⁶ The SiH-free potassium alkyl $\{\text{KC}(\text{SiMe}_3)_2\text{Ph}\}_n$ ($3.007(2)\text{ \AA}$)⁸ and the compound $\{\text{KC}(\text{SiMe}_2\text{Ph})_2(\text{SiHMe}_2)\}_n$ ($3.167(8)\text{ \AA}$)²⁰ also have polymeric structures with π -coordinated arenes. While the central, carbanionic carbon adopts distorted, nearly planar geometries in these three examples ($\Sigma\text{angles} = 358.8^\circ$, 357.4° and 356.5°),^{8,16,20} C1 in **2-TMEDA** is perfectly planar ($\Sigma\text{angles} = 360.0(5)^\circ$).

The formation of Bn_2SiMe_2 in these reactions implies nucleophilic attack by KBN on a SiHMe_2 group and suggests an alternative route to the desired $\text{KC}(\text{SiHMe}_2)_2\text{Ph}$ (**2**) *via* Si–C cleavage. A related Si–Si bond cleavage provides $\text{MSi}(\text{SiMe}_3)_3$ from $\text{Si}(\text{SiMe}_3)_4$ and LiMe or KOtBu .²¹ This idea was tested by the reaction of $(\text{Me}_2\text{HSi})_3\text{CPh}$ and KOtBu to give the desired $\text{KC}(\text{SiHMe}_2)_2\text{Ph}$ (**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 $\text{LaI}_3(\text{THF})_4$, $\text{CeI}_3(\text{THF})_4$, $\text{PrI}_3(\text{THF})_3$, or $\text{NdI}_3(\text{THF})_3$ provide $\text{Ln}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$ ($\text{Ln} = \text{La}$ (**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 ν_{SiH} band ($2109 \pm 5\text{ cm}^{-1}$) assigned to non-bridging SiH and a broad, lower energy band ($1866 \pm 6\text{ cm}^{-1}$) attributed to a ν_{SiH} of the $\text{Ln}-\text{H}-\text{Si}$. In contrast, the cerium compound **4** showed only one ν_{SiH} band, which appeared at 2115 cm^{-1} . The solution IR spectra similarly showed two SiH absorbances for **3**, **5** and **6**. Although two ν_{SiH} bands were obtained for **4** in solution, the bands were low intensity and a number of the IR spectra were dominated by $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$. We attributed these observations to labile secondary $\text{Ln}-\text{H}-\text{Si}$ 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 SiHMe_2 groups with diastereotopic methyl moieties. A doublet resonance at 5.84 ppm, assigned to an *ortho*- C_6H_5 , appeared upfield compared to its chemical shift in the alkane starting material (6.97 ppm), suggesting a multihapto benzyl-Ln coordination. Evidence for $\text{La}-\text{H}-\text{Si}$ interactions were provided by the J_{SiH} of 144 Hz. The equivalence of the SiHMe_2 in the room

Fig. 1 Thermal ellipsoid plot of $\text{Ph}(\text{Me}_2\text{HSi})_2\text{CK}(\text{TMEDA})$ (**2-TMEDA**) at 50% probability. H1s and H2s were located objectively in the Fourier difference map and refined. 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, $3.844(2)$; K1–C6, $3.049(4)$; K1–C7, $3.389(5)$; K1–C8#, $3.359(5)$; K1–C9#, $3.085(5)$; K1–C10#, $3.038(4)$; 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 ($^\circ$): K1–H1s–Si1, $124(2)$; C6–C1–Si2, $119.8(3)$; Si2–C1–Si1, $121.6(2)$; Si1–C1–C6, $118.6(3)$.

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°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 $\text{Ln}-\text{H}-\text{Si}$ 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_6H_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_6H_5 were inequivalent. Thus, the alkyl ligands are equivalent in the low temperature solution-phase structure, with each ligand containing one $\text{La}-\text{H}-\text{Si}$ and a π -coordinated aryl group.

Single crystal X-ray diffraction reveals that the molecular structure of **3** ($P\bar{3}$) contains three, crystallographically related $\text{C}(\text{SiHMe}_2)_2\text{Ph}$ ligands, each of which interacts with the lanthanum center through the central carbon (C1), through a benzylic-type coordination of the C6, and also through one $\text{La}-\text{H}-\text{Si}$ (Fig. 2).§ The three ligands are arranged in a trigonal geometry around the lanthanum center ($\Sigma_{\text{C1-La1-C1}} = 357.15(6)^\circ$). This structure is consistent with the low temperature NMR and IR spectroscopic data. A few of the notable structural features include the sharp $\text{La1}-\text{C1}-\text{Si1}$ angle ($93.0(1)^\circ$), short $\text{La1}\cdots\text{Si1}$ and $\text{La1}\cdots\text{H1s}$ distances ($3.3141(9)$ and $2.69(4)\text{ \AA}$), and an unusually long $\text{La1}-\text{C1}$ distance ($2.674(3)\text{ \AA}$).

Fig. 2 Thermal ellipsoid plot of $\text{La}(\text{C}(\text{SiHMe}_2)_2\text{Ph})_3$ (**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 $\text{La}-\text{C}$ (green) and $\text{Ln}-\text{H}-\text{Si}$ (black) distances are highlighted with dashed lines. Selected interatomic distances ($\text{\AA}$): $\text{La1}-\text{C1}$, $2.674(3)$; $\text{La1}-\text{C6}$, $2.822(2)$; $\text{La1}-\text{Si1}$, $3.3141(9)$; $\text{La1}-\text{H1s}$, $2.69(4)$; $\text{C1}-\text{Si1}$, $1.821(3)$; $\text{Si1}-\text{H1s}$, $1.37(4)$; $\text{C1}-\text{Si2}$, $1.853(3)$; $\text{Si2}-\text{H2s}$, $1.45(4)$; $\text{C1}-\text{C6}$, $1.483(4)$; $\text{C6}-\text{C7}$, $1.415(5)$; $\text{C6}-\text{C11}$, $1.409(4)$. Selected interatomic angles ($^\circ$): $\text{C1}-\text{La1}-\text{C1}$, $119.05(2)$; $\text{La1}-\text{C1}-\text{C6}$, $80.0(1)$; $\text{La1}-\text{C1}-\text{Si1}$, $93.0(1)$; $\text{La1}-\text{C1}-\text{Si2}$, $128.3(1)$.

The corresponding $\text{La}-\text{C}$ distances in six-coordinate tris(benzyl)-lanthanum compounds, e.g., $\text{La}(\text{CH}_2\text{Ph})_3(\text{THF})_3$ ($2.648(2)\text{ \AA}$),⁵ are shorter, and the distance in $\text{La}(\text{CH}(\text{SiMe}_3)_2)_3$ ($2.515(9)\text{ \AA}$) is much shorter.¹² These trends extend to the comparisons of structures of **4–6** to the analogous benzyl lanthanide species. Moreover, the close contacts in the series (*i.e.*, $\text{Ln}-\text{C}$, $\text{Ln}\cdots\text{Si}$, and $\text{Ln}\cdots\text{H}$) follow the expected trend based on ionic radius ($\text{La} > \text{Ce} > \text{Pr} > \text{Nd}$).

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 $\text{Ln}-\text{H}-\text{Si}$ bridging moieties (Fig. 3).¶ The $\text{Ce}-\text{C}$ distances for the five ligands that contain bridging $\text{Ce}-\text{H}-\text{Si}$ interactions average $2.65 \pm 0.02\text{ \AA}$, whereas the η^2 -benzyl-only ligand ($\text{Ce2}-\text{C56}$, $2.587(3)\text{ \AA}$) distance is shorter. This distinction is also apparent in compounds **5** ($\text{Pr}-\text{C}_{\text{ave}}$, 2.63 ± 0.02 ; $\text{Pr2}-\text{C56}$, $2.556(5)\text{ \AA}$) and **6** ($\text{Nd}-\text{C}_{\text{ave}}$, 2.61 ± 0.02 ; $\text{Nd2}-\text{C56}$, $2.541(4)\text{ \AA}$).

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 $\text{Ln}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$ 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.*, $\text{Ln}-\text{C}$, $\text{Si}-\text{H}$, $\text{Si}-\text{C}$ distances) for moieties involved in

Fig. 3 Thermal ellipsoid plot of one of two crystallographically distinct molecules of $\text{Ce}(\text{C}(\text{SiHMe}_2)_2\text{Ph})_3$ (**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 $\text{Ce}-\text{C}$ (green) and $\text{Ln}-\text{H}-\text{Si}$ (black) distances are highlighted with dashed lines. Selected interatomic distances ($\text{\AA}$): $\text{Ce2}-\text{C34}$, $2.613(3)$; $\text{Ce2}-\text{C45}$, $2.671(2)$; $\text{Ce2}-\text{C56}$, $2.587(3)$; $\text{Ce2}-\text{Si7}$, $3.1947(9)$; $\text{Ce2}-\text{H7s}$, $2.47(2)$; $\text{C34}-\text{Si7}$, $1.829(2)$; $\text{Si7}-\text{H7s}$, $1.48(3)$; $\text{Ce2}-\text{Si9}$, $3.2379(9)$; $\text{Ce2}-\text{H9s}$, $2.46(3)$; $\text{C45}-\text{Si9}$, $1.829(3)$; $\text{Si9}-\text{H9s}$, $1.48(3)$; Selected interatomic angles ($^\circ$): $\text{C34}-\text{Ce2}-\text{C45}$, $118.57(9)$; $\text{Ce2}-\text{C34}-\text{C39}$, $83.8(2)$; $\text{Ce2}-\text{C34}-\text{Si7}$, $90.1(1)$.

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(SiHMe₂)₂Ph with KBn, but Me₂SiBn₂ and other side products in reactions of HC(SiHMe₂)₂Ph and KBn 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^tBu 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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- ‡ X-ray data for 2-TMEDA (CCDC 1517682): C₁₇H₃₅KN₂Si₂; FW 362.75; monoclinic; *a*: 8.7354(6), *b*: 23.003(1), *c*: 11.6433(7), β : 100.207(4), volume: 2302.5(3); *P*121/*c*1; *Z* = 4; temp. 173 K; reflections: collected, 20 907; independent, 3284; *R*_{int} 0.1552; 2217 data *I* > 2 σ (*I*): *R*₁ 0.0705, *wR*₂ 0.1845; *R*_{all}: *R*₁ 0.0996, *wR*₂ 0.2145.
- § X-ray data for 3 (CCDC: 1517683): C₃₃H₅₇LaSi₆(C₅H₁₂)_{1/2}; FW 797.31; trigonal; *a*: 12.4380(6), *c*: 16.157(1), volume, 2164.7(3); *P*3; *Z* = 2; temp. 173 K; reflections: collected, 23 107; independent, 3715; *R*_{int} 0.0345; 3439 data *I* > 2 σ (*I*): *R*₁ 0.0309, *wR*₂ 0.0828; *R*_{all}: *R*₁ 0.0351, *wR*₂ 0.0928.
- ¶ X-ray data for 4 (CCDC: 1517684): C₃₃H₅₇CeSi₆; FW 762.44; monoclinic; *a*: 22.324(2), *b*: 19.841(1), *c*: 19.921(1), β : 116.076(1), volume: 7925.5(9); *P*121/*c*1; *Z* = 8; temp. 173 K; reflections: collected, 79 198; independent, 18 762; *R*_{int} 0.0485; 14 549 data *I* > 2 σ (*I*): *R*₁ 0.0315, *wR*₂ 0.0698; *R*_{all}: *R*₁ 0.0515, *wR*₂ 0.0836; X-ray data for 5 (CCDC 1517686): C₃₃H₅₇PrSi₆; FW 763.23; monoclinic; *a*: 22.3310(6), *b*: 19.8399(5), *c*: 19.8802(5), β : 116.047(1), volume: 7913.2(4); *P*121/*c*1; *Z* = 8; temp. 173 K; reflections: collected, 79 681; independent, 15 456; *R*_{int} 0.0653; 14 828 data *I* > 2 σ (*I*): *R*₁ 0.0695, *wR*₂ 0.1909; *R*_{all}: *R*₁ 0.0710, *wR*₂ 0.1931; X-ray data for 6 (CCDC: 1517685): C₃₃H₅₇NdSi₆; monoclinic; *a*: 22.335(2), *b*: 19.843(2), *c*: 19.855(2), β : 116.017(1), volume: 7908(1); *P*121/*c*1; *Z* = 8; temp. 173 K; reflections: collected, 113 017; independent, 20 627; *R*_{int} 0.0711; 15 075 data *I* > 2 σ (*I*): *R*₁ 0.0346, *wR*₂ 0.0623; *R*_{all}: *R*₁ 0.0624, *wR*₂ 0.0768.
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