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

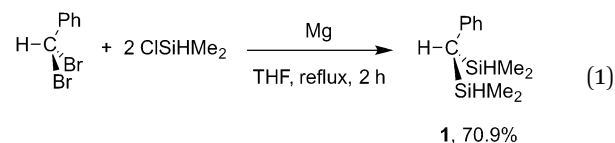
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**A  $\beta$ -SiH functionalized benzyl anion  $[\text{C}(\text{SiHMe}_2)_2\text{Ph}]^-$  is obtained by deprotonation of  $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$  with  $\text{KCH}_2\text{Ph}$  or by reaction of  $\text{KOtBu}$  and  $(\text{Me}_2\text{HSi})_3\text{CPh}$ ;  $\text{LnI}_3(\text{THF})_n$  and three equivalents of this carbanion combine to provide homoleptic tris(alkyl)lanthanide compounds  $\text{Ln}[\text{C}(\text{SiHMe}_2)_2\text{Ph}]_3$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$ ) containing secondary metal–ligand interactions.**

Synthesis of homoleptic organolanthanide complexes, particularly those of the early trivalent lanthanides ( $\text{La}$ – $\text{Nd}$ ), is challenging due to the large radii of these elements, polar bonding, high charge, and high Lewis acidity.<sup>1</sup> Such homoleptic compounds should be valuable for the synthesis of new catalysts and new materials,<sup>2</sup> 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  $\text{MeLi}$  and  $\text{LaCl}_3$  gives  $\text{Li}_3[\text{LaMe}_6]$  as a TMEDA adduct.<sup>3</sup> Three THF molecules coordinate to the labile tris(benzyl)lanthanum allowing isolation of  $\text{LaBn}_3(\text{THF})_3$ ,<sup>4,5</sup> 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  $\text{Ln}(\text{CH}(\text{NMe}_2)\text{Ph})_3$ <sup>6</sup> or  $\text{Ln}(\text{CH}_2\text{C}_6\text{H}_4\text{-2-NMe}_2)_3$ .<sup>7</sup> An alternative approach combines bulky  $\beta$ - $\text{SiMe}_3$  with the benzyl group in  $\text{C}(\text{SiMe}_3)_2\text{Ph}$ ,<sup>8</sup> exemplified by a bis(alkyl)calcium compound possessing metal–aryl  $\pi$ -interactions. Coordinative unsaturation is important to the reactivity of organolanthanides, and donors such as TMEDA or THF can diminish reactivity,<sup>9</sup> facilitate alkane elimination,<sup>10</sup> or react by C–O bond cleavage.<sup>11</sup> While donor-free lanthanum and cerium compounds such as  $\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}_3$  are known, they are inconveniently accessed through multistep synthesis *via*  $\text{Ln}\{\text{O}(\text{2,6-C}_6\text{H}_3\text{tBu}_2)\}_3$ .<sup>12,13</sup>

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.<sup>14</sup> Furthermore, the SiH moiety provides a powerful signature in  $^1\text{H}$  and  $^{29}\text{Si}$  NMR and IR spectra. This  $\beta$ -SiH strategy may also be applied to alkyls, and the ligand  $\text{C}(\text{SiHMe}_2)_3$  supports trivalent yttrium and divalent ytterbium and samarium homoleptic alkyls containing secondary  $\text{Ln}–\text{H}–\text{Si}$  interactions.<sup>15,16</sup> Recently, we reported  $\text{Ce}\{\text{C}(\text{SiHMe}_2)_2\}_3$  as a precursor to a zwitterionic hydrosilylation catalyst.<sup>17</sup> New chemistry might be accessed with alkyl ligand variations that include both  $\beta$ -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  $-\text{C}(\text{SiHMe}_2)_2\text{Ph}$ , 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  $\text{HCPPhBr}_2$  and  $\text{ClSiHMe}_2$  affords  $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$  (**1**; eqn (1)) on preparative scale.



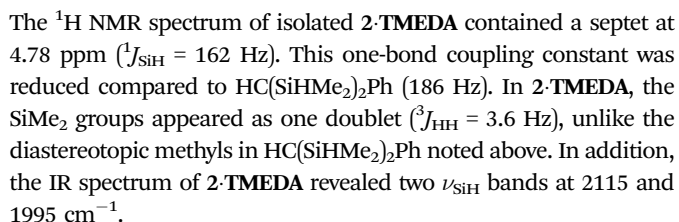
A diagnostic triplet in the  $^1\text{H}$  NMR spectrum at 1.43 ppm ( $^3J_{\text{HH}} = 4 \text{ Hz}$ , 1 H) for the H on the central carbon is coupled to a signal at 4.34 ppm assigned to the SiH (2 H,  $^1J_{\text{SiH}} = 186 \text{ Hz}$ ). The two  $\text{SiHMe}_2$  groups are magnetically inequivalent giving a virtual octet for the SiH resonance (a  $\text{M}(\text{AX}_3\text{Y}_3)(\text{AX}_3\text{Y}_3)'$  spin system). Compound **1** is also characterized by an intense  $\nu_{\text{SiH}}$  absorbance at  $2115 \text{ cm}^{-1}$  in its IR spectrum.

While  $\text{HC}(\text{SiHMe}_2)_3$ <sup>18</sup> reacts readily with lithium diisopropylamide,<sup>19</sup> deprotonation of  $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$  is more challenging. Attempts to synthesize  $[\text{C}(\text{SiHMe}_2)_2\text{Ph}]^-$  using  $\text{LiN}(\text{SiMe}_3)_2$ ,  $n\text{BuLi}$ ,

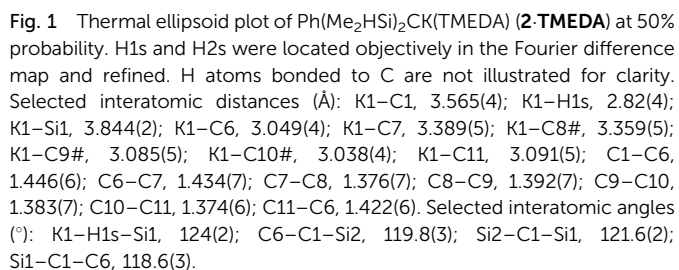
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† Electronic supplementary information (ESI) available: Experimental procedures, and characterization for compounds **1**, **2**, **2-TMEDA**, **3–6**. CCDC 1517682–1517686. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc09304c



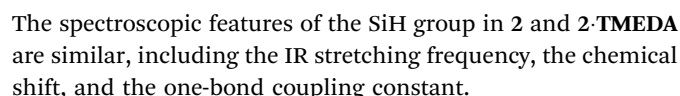


A single-crystal X-ray diffraction study revealed a polymeric structure for **2-TMEDA**,<sup>‡</sup> with each K cation interacting with two C(SiHMe<sub>2</sub>)<sub>2</sub>Ph groups (Fig. 1) through the H1s (2.82(4) Å), the C6 and C11 (from a phenyl group) of one ligand, and the C9 and C10 from a phenyl 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

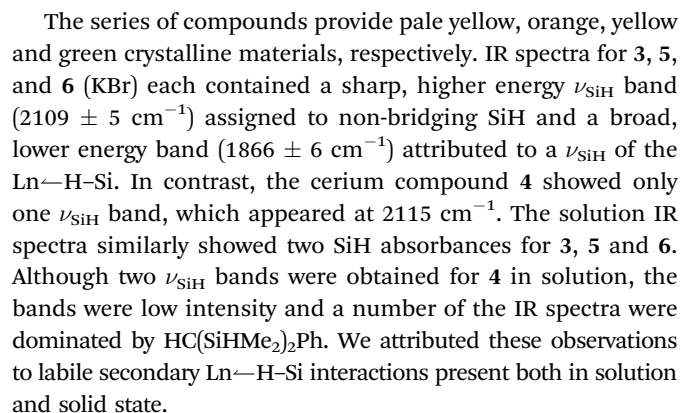


dimeric  $\{(\text{Me}_2\text{HSi})_3\text{CK}(\text{TMEDA})\}_2$  than in **2-TMEDA**.<sup>16</sup> The SiH-free potassium alkyl  $\{\text{KC}(\text{SiMe}_3)_2\text{Ph}\}_n$  (3.007(2) Å)<sup>8</sup> and the compound  $\{\text{KC}(\text{SiMe}_2\text{Ph})_2(\text{SiHMe}_2)\}_n$  (3.167(8) Å)<sup>20</sup>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

The formation of  $\text{Bn}_2\text{SiMe}_2$  in these reactions implies nucleophilic attack by  $\text{KBn}$  on a  $\text{SiHMe}_2$  group and suggests an alternative route to the desired  $\text{KC}(\text{SiHMe}_2)_2\text{Ph}$  (**2**) *via*  $\text{Si-C}$  cleavage. A related  $\text{Si-Si}$  bond cleavage provides  $\text{MSi}(\text{SiMe}_3)_3$  from  $\text{Si}(\text{SiMe}_3)_4$  and  $\text{LiMe}$  or  $\text{KOtBu}$ .<sup>21</sup> This idea was tested by the reaction of  $(\text{Me}_2\text{HSi})_3\text{CPh}$  and  $\text{KOtBu}$  to give the desired  $\text{KC}(\text{SiHMe}_2)_2\text{Ph}$  (**2**) in excellent yield (eqn (3)).



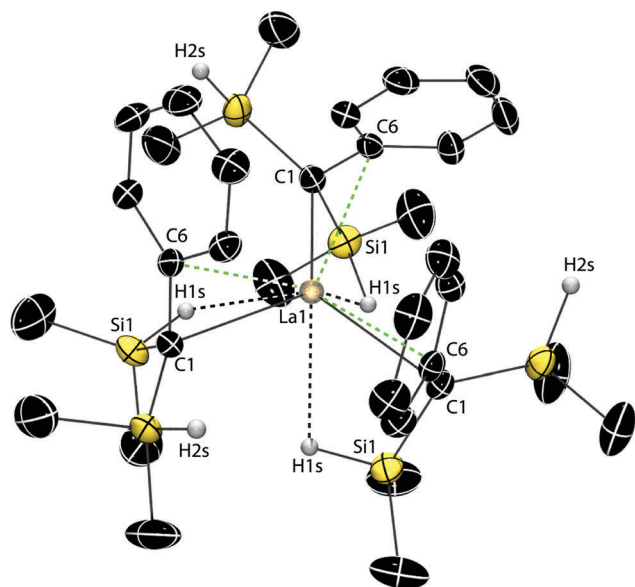
Reactions of three equiv. of 2 or 2-**TMEDA** and  $\text{LaI}_3(\text{THF})_4$ ,  $\text{CeI}_3(\text{THF})_4$ ,  $\text{PrI}_3(\text{THF})_3$ , or  $\text{NdI}_3(\text{THF})_3$  provide  $\text{Ln}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$  ( $\text{Ln} = \text{La}$  (**3**),  $\text{Ce}$  (**4**),  $\text{Pr}$  (**5**),  $\text{Nd}$  (**6**)) in excellent yields (eqn (4)).



The  $^1\text{H}$  NMR spectrum of diamagnetic **3** revealed signals at 4.24, 0.43, and 0.32 ppm attributed to equivalent  $\text{SiHMe}_2$  groups with diastereotopic methyl moieties. A doublet resonance at 5.84 ppm, assigned to an *ortho*- $\text{C}_6\text{H}_5$ , 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  $^1J_{\text{SiH}}$  of 144 Hz. The equivalence of the  $\text{SiHMe}_2$  in the room

temperature NMR spectrum contrasts the two types of SiH groups observed in the IR spectra, suggesting fluxional process(es). A  $^1\text{H}$  NMR spectrum collected at  $-73^\circ\text{C}$  in toluene- $d_8$  revealed that two  $\text{SiHMe}_2$  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*- $\text{C}_6\text{H}_5$ , whose resonance appeared unusually upfield at 4.15 ppm, was even more shielded than the nonbridging SiH. Moreover, all five H in the  $\text{C}_6\text{H}_5$  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  $\pi$ -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 ( $2.674(3)\text{ \AA}$ ).

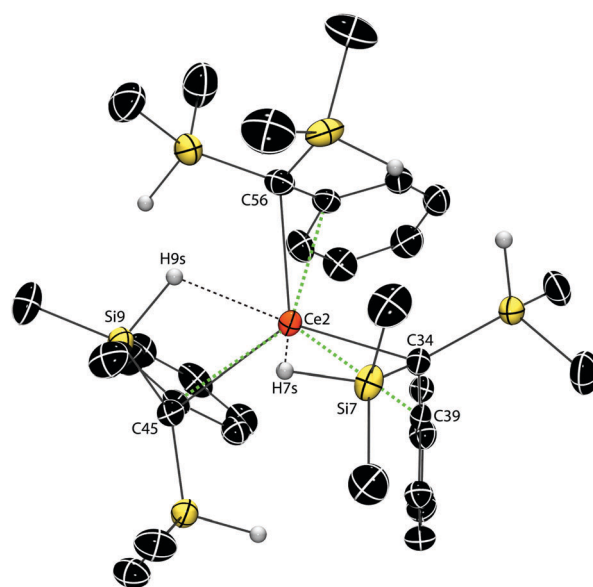


**Fig. 2** Thermal ellipsoid plot of  $\text{La}(\text{C}(\text{SiHMe}_2)_2\text{Ph})_3$  (**3**). La1 is located on a crystallographic 3-fold axis. H atoms bonded to Si are located in the Fourier difference map, their positions are refined and are illustrated. All other H atoms and a disordered pentane 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.,  $\text{La}(\text{CH}_2\text{Ph})_3(\text{THF})_3$  ( $2.648(2)\text{ \AA}$ ),<sup>5</sup> are shorter, and the distance in  $\text{La}(\text{CH}(\text{SiMe}_3)_2)_3$  ( $2.515(9)\text{ \AA}$ ) is much shorter.<sup>12</sup> 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  $\eta^2$ -benzyl-only ligand ( $\text{Ce2}-\text{C56}$ ,  $2.587(3)\text{ \AA}$ ) distance is shorter. This distinction is also apparent in compounds **5** ( $\text{Pr}-\text{C}_{\text{ave}}$ ,  $2.63 \pm 0.02$ ;  $\text{Pr2}-\text{C56}$ ,  $2.556(5)\text{ \AA}$ ) and **6** ( $\text{Nd}-\text{C}_{\text{ave}}$ ,  $2.61 \pm 0.02$ ;  $\text{Nd2}-\text{C56}$ ,  $2.541(4)\text{ \AA}$ ).

This work extends the idea that the  $\beta$ -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  $\beta$ -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(SiHMe<sub>2</sub>)<sub>2</sub>Ph with KBn, but Me<sub>2</sub>SiBn<sub>2</sub> and other side products in reactions of HC(SiHMe<sub>2</sub>)<sub>2</sub>Ph 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(SiHMe<sub>2</sub>)<sub>2</sub>Ph by reacting PhC(SiHMe<sub>2</sub>)<sub>3</sub> with KO<sup>t</sup>Bu 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): C<sub>17</sub>H<sub>35</sub>KN<sub>2</sub>Si<sub>2</sub>; FW 362.75; monoclinic; *a*: 8.7354(6), *b*: 23.003(1), *c*: 11.6433(7),  $\beta$ : 100.207(4), volume: 2302.5(3); *P*121/*c*1; *Z* = 4; temp. 173 K; reflections: collected, 20 907; independent, 3284; *R*<sub>int</sub> 0.1552; 2217 data *I* > 2 $\sigma$ (*I*): *R*<sub>1</sub> 0.0705, *wR*<sub>2</sub> 0.1845; *R*<sub>all</sub>: *R*<sub>1</sub> 0.0996, *wR*<sub>2</sub> 0.2145.

§ X-ray data for 3 (CCDC: 1517683): C<sub>33</sub>H<sub>57</sub>LaSi<sub>6</sub>(C<sub>5</sub>H<sub>12</sub>)<sub>1/2</sub>; 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*<sub>int</sub> 0.0345; 3439 data *I* > 2 $\sigma$ (*I*): *R*<sub>1</sub> 0.0309, *wR*<sub>2</sub> 0.0828; *R*<sub>all</sub>: *R*<sub>1</sub> 0.0351, *wR*<sub>2</sub> 0.0928.

¶ X-ray data for 4 (CCDC: 1517684): C<sub>33</sub>H<sub>57</sub>CeSi<sub>6</sub>; FW 762.44; monoclinic; *a*: 22.324(2), *b*: 19.841(1), *c*: 19.921(1),  $\beta$ : 116.076(1), volume: 7925.5(9); *P*121/*c*1; *Z* = 8; temp. 173 K; reflections: collected, 79 198; independent, 18 762; *R*<sub>int</sub> 0.0485; 14 549 data *I* > 2 $\sigma$ (*I*): *R*<sub>1</sub> 0.0315, *wR*<sub>2</sub> 0.0698; *R*<sub>all</sub>: *R*<sub>1</sub> 0.0515, *wR*<sub>2</sub> 0.0836; X-ray data for 5 (CCDC 1517686): C<sub>33</sub>H<sub>57</sub>PrSi<sub>6</sub>; FW 763.23; monoclinic; *a*: 22.3310(6), *b*: 19.8399(5), *c*: 19.8802(5),  $\beta$ : 116.047(1), volume: 7913.2(4); *P*121/*c*1; *Z* = 8; temp. 173 K; reflections: collected, 79 681; independent, 15 456; *R*<sub>int</sub> 0.0653; 14 828 data *I* > 2 $\sigma$ (*I*): *R*<sub>1</sub> 0.0695, *wR*<sub>2</sub> 0.1909; *R*<sub>all</sub>: *R*<sub>1</sub> 0.0710, *wR*<sub>2</sub> 0.1931; X-ray data for 6 (CCDC: 1517685): C<sub>33</sub>H<sub>57</sub>NdSi<sub>6</sub>; monoclinic; *a*: 22.335(2), *b*: 19.843(2), *c*: 19.855(2),  $\beta$ : 116.017(1), volume: 7908(1); *P*121/*c*1; *Z* = 8; temp. 173 K; reflections: collected, 113 017; independent, 20 627; *R*<sub>int</sub> 0.0711; 15 075 data *I* > 2 $\sigma$ (*I*): *R*<sub>1</sub> 0.0346, *wR*<sub>2</sub> 0.0623; *R*<sub>all</sub>: *R*<sub>1</sub> 0.0624, *wR*<sub>2</sub> 0.0768.

