

## Solution Interaction of Potassium and Calcium Bis(trimethylsilyl)amides; Preparation of $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ from Dibenzylcalcium

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$\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$  (**1**) is isolated in nearly quantitative yield from the room temperature reaction of  $\text{Ca}(\text{CH}_2\text{Ph})_2(\text{THF})$  and  $\text{HN}(\text{SiMe}_3)_2$  in toluene. A commonly used preparation of **1** involving the reaction of potassium bis(trimethylsilyl)amide,  $\text{K}[\text{N}(\text{SiMe}_3)_2]$  (**2**), with  $\text{CaI}_2$  can produce material that contains substantial amounts of potassium, probably in the form of a calciate such as  $\text{K}[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_3]$ . The favorable formation of  $\text{K}[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_3]$  from **1** and **2** was confirmed with density functional theory calculations. Deliberate doping of solutions of **1** with **2** initially causes only an upfield shift in the single  $^1\text{H}$  NMR resonance observed for **1**; not until K/Ca ratios exceed 1:1 is the presence of the added potassium obvious by the appearance of an additional peak in the spectrum.

### Introduction

The bis(trimethylsilylamides) of the alkaline-earth metals calcium, strontium, and barium have found expanding use as reagents in synthetic and materials chemistry.<sup>1</sup> Befitting their importance, multiple preparative routes have been developed for these silylamides. The THF-solvated calcium complex  $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$ , for example, was originally obtained from the direct reaction of activated elemental calcium and  $\text{HN}(\text{SiMe}_3)_2$  in refluxing THF,<sup>2</sup> by the reaction of  $\text{Ca}(\text{BHT})_2(\text{THF})_3$  (BHT = 2,6-di-*tert*-butyl-4-methylphenoxide) and  $\text{Li}[\text{N}(\text{SiMe}_3)_2]$  in hexane,<sup>2</sup> and by the transmetalation of  $\text{Hg}[\text{N}(\text{SiMe}_3)_2]_2$  with calcium in THF.<sup>3</sup> Westerhausen prepared the unsolvated complex from the reaction of distilled calcium with  $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ .<sup>4</sup> Subsequently reported preparations include the reaction of calcium metal

and  $\text{HN}(\text{SiMe}_3)_2$  in the presence of ammonia,<sup>5</sup> the redox transmetalation/ligand exchange reaction of calcium and  $\text{HN}(\text{SiMe}_3)_2$  in the presence of  $\text{HgPh}_2$  or  $\text{BiPh}_3$  under ultrasonication,<sup>6</sup> and the reaction of  $\text{K}[\text{N}(\text{SiMe}_3)_2]$  with  $\text{CaI}_2$  in diethyl ether<sup>7,8</sup> or toluene.<sup>9</sup> The product obtained from the halide metathesis route has been used to synthesize a wide variety of organometallic and inorganic compounds, including metallocenes,<sup>7,10</sup> heterobimetallic alkoxides,<sup>11</sup> aminotroponate and aminotroponimate calcium amides,<sup>12</sup> heterobimetallic amides,<sup>13</sup> and *N*-heterocyclic carbene adducts.<sup>14</sup> It has also been used in the study of enolization reactions of ketones.<sup>8,15</sup>

There have been no specific difficulties mentioned in the literature with the synthesis or subsequent use of  $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$  (**1**) obtained by halide metathesis. Given the

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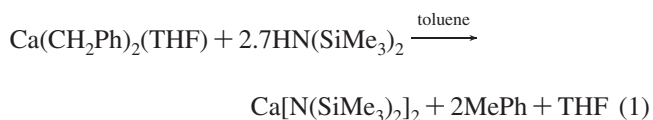
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importance of **1** as a reagent, however, and the ease of calcate formation during the formation of other calcium amides (e.g.,  $\text{K}[\text{Ca}\{\text{N}(\text{Ph})\text{R}\}_3]$ ;  $\text{R} = \text{Me}, i\text{Pr}$ ),<sup>16</sup> we have been investigating alternative synthetic preparations for it. In the course of this study, we have found that **1** prepared from  $\text{CaI}_2$  and  $\text{K}[\text{N}(\text{SiMe}_3)_2]$  (**2**) can be contaminated with potassium in a manner that can be difficult to detect with NMR spectroscopy. We report details of these findings here.

## Results and Discussion

**Preparation of  $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$  (**1**) from  $\text{Ca}(\text{CH}_2\text{Ph})_2$ - $(\text{THF})$  and  $\text{HN}(\text{SiMe}_3)_2$ .** Monosolvated dibenzylcalcium can be prepared via the reaction of benzylpotassium and calcium iodide in THF, followed by trituration in benzene and pentane. Unlike the similarly prepared tetrasolvated complex  $\text{Ca}(\text{CH}_2\text{Ph})_2(\text{THF})_4$ ,<sup>17</sup> the orange monosolvate is insoluble in hydrocarbon solvents and is probably extensively aggregated. Although THF can be difficult to remove from organocalcium species,<sup>18</sup> the extra metal coordination made possible by aggregation probably assists in the partial desolvation.

Harder has mentioned the reaction of the unsolvated complex  $(p\text{-}t\text{Bu-benzyl})_2\text{Ca}$  with  $\text{HN}(\text{SiMe}_3)_2$  in refluxing benzene to prepare  $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ .<sup>17</sup> We have found that desolvation of  $\text{Ca}(\text{CH}_2\text{Ph})_2(\text{THF})$  is not necessary prior to its reaction with an excess of hexamethyldisilazane in toluene at room temperature to yield the corresponding calcium amide and toluene (eq 1).



After removing all volatile species, **1** was recrystallized from cold hexane. Its composition was confirmed with elemental analysis, and its structure verified with X-ray diffraction.<sup>19</sup> In  $\text{C}_6\text{D}_6$ , the complex displays only a *single* peak in its  $^1\text{H}$  NMR spectrum at  $\delta$  0.31 ppm at room temperature (22 °C) and two broad singlets in its  $^{13}\text{C}$  NMR spectrum at  $\delta$  6.91 and 6.47.

If the tetrasolvated complex  $\text{Ca}(\text{CH}_2\text{Ph})_2(\text{THF})_4$ <sup>17</sup> is treated with excess  $\text{HN}(\text{SiMe}_3)_2$ , the corresponding  $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$  is isolated in 74% yield. It was identified by comparison with the known NMR spectrum.<sup>3</sup> It can be partially desolvated by drying under vacuum (roughly 0.3 THF per calcium center remains after 8 h).

**Preparation of **1** via Halide Metathesis.** The original procedure for the preparation of **1** via halide metathesis involved the reaction of **2** with  $\text{CaI}_2$  in  $\text{Et}_2\text{O}$ ; precipitated KI was removed by filtration.<sup>7,8</sup> The same reaction was subsequently conducted in toluene, generating **1** in 80% yield.<sup>9</sup> As noticed by us<sup>9</sup> and others,<sup>13</sup> the as-prepared material displays *two* peaks in both its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in benzene- $d_6$  or toluene- $d_8$  at room temperature. The two resonances were assigned to the bridging and terminal  $\text{-N}(\text{SiMe}_3)_2$  groups in the dimeric  $\{\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2\}_2$  and are comparable to those reported by Westerhausen (i.e., two peaks at  $\delta$  0.33 and 0.21 ppm in toluene- $d_8$  at  $-63$  °C).<sup>4,20</sup>

The discrepancy in the NMR spectra between the analytically clean  $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$  prepared from dibenzylcalcium and that synthesized through halide metathesis led us to conduct a series of systematic doping experiments that mixed discrete amounts of **2** with **1** (Figure 1). The addition of one-half equivalent of **2** to **1** does not produce a second peak in the  $^1\text{H}$  NMR spectrum but rather causes a shift in the single trimethylsilyl resonance from  $\delta$  0.31 to 0.25 (Figure 1, spectrum b). The resonance is unchanged when the K/Ca ratio is raised to 1:1 (Figure 1, spectrum c). Only when the K/Ca ratio is greater than 1:1 does clear evidence of the added potassium appear in the form of a second peak near  $\delta$  0.12 (Figure 1, spectrum d), matching the value of  $\delta$  0.12 observed for **2** in benzene- $d_6$  (22 °C) (Figure 1, spectrum e).

The spectra suggest that some species of calcate, i.e.,  $\text{K}_x\text{Ca}_y[\text{N}(\text{SiMe}_3)_2]_{x+2y}$ , forms with even substoichiometric amounts of **2**.<sup>21</sup> This is an interesting complement to Westerhausen's observation that calcates of the type  $[\text{L}_x\text{K}_2\text{Ca}\{\text{N}(\text{Ph})\text{R}\}_4]$  ( $\text{L} =$  neutral coligands) form during the metathesis reaction of  $\text{K}[\text{N}(\text{Ph})\text{R}]$  with  $\text{CaI}_2$  if any excess of the potassium amide is present, even if not in exact stoichiometric ratios.<sup>16</sup>

We have specifically reexamined the halide metathetical preparation of **1** in toluene, using 1:2 molar ratios of  $\text{CaI}_2$  and **2**. Two peaks near  $\delta$  0.25 and 0.12 are observed in the  $^1\text{H}$  NMR spectrum of the isolated product, although their ratio varies with the time and temperature of the reaction. A  $\delta$  0.25:0.12 peak ratio of 1.0:16.5 is found in material prepared at room temperature and with a 1 h reaction time, reflecting large amounts of unreacted **2**. The peak ratio changes to 1.0:0.3 if the reaction time is increased to 48 h, and if the time is extended to 4 days at reflux temperature, the  $\delta$  0.12 peak disappears entirely. Conversion to a calcate,

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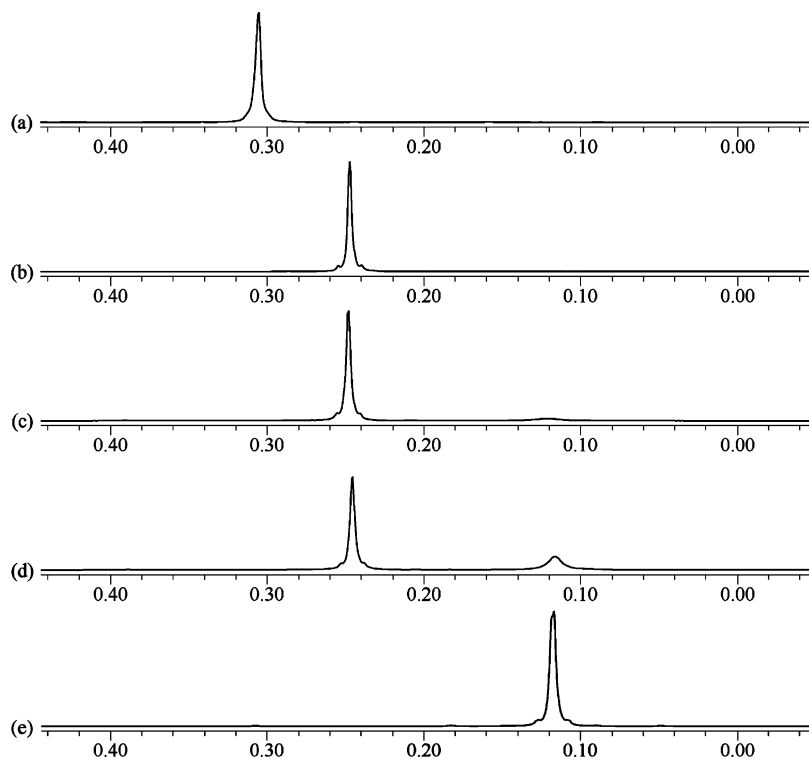
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(20) Although the paper states that  $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$  is fluxional in solution, and that the low temperature spectrum reflects separate resonances from the bridging and terminal resonances of dimeric  $\{\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2\}_2$ , there is no explicit mention of the value of the shift(s) in the room temperature  $^1\text{H}$  NMR spectrum. In the  $^{13}\text{C}$  NMR spectrum (tol- $d_8$ ), coalescence of the two peaks observed at room temperature (29 °C) is not achieved until 67 °C.

(21) The compound when  $x = y = 1$  has been prepared from the reaction of **1** and **2** in hexanes/THF and crystallographically characterized as its THF adduct (ref 8). Four resonances corresponding to trimethylsilyl groups are observed for  $(\text{THF})\text{K}[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_3]$  in pyridine- $d_5$ . The presence of the coordinated THF ligand and the potentially coordinated solvent have obviously reduced the symmetry of the complex in solution, and its spectrum cannot be directly compared with that of unsolvated  $\text{K}[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_3]$  in aromatic solvents.



**Figure 1.** Effect on the  $^1\text{H}$  NMR spectrum of doping a solution of **1** with **2** in  $\text{C}_6\text{D}_6$  at  $22^\circ\text{C}$ . (a) **1** prepared from dibenzylcalcium; (b) **1** + 0.5 equiv **2**; (c) **1** + 1.0 equiv **2**; (d) **1** + 2.0 equiv **2**; (e) **2** only.

for example,  $\text{K}[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_3]$ , must be the thermodynamically favored process, even if sufficient  $\text{CaI}_2$  is present to form **1**. The gradual consumption of **2** and its incorporation into a heterometallic species is supported by elemental analysis of material isolated at an intermediate stage of the reaction (ca. 16 h at room temperature, solids removed by filtration). The material was found to be iodide free ( $<0.1\%$ ) but contained potassium in a Ca/K ratio of 1.0:1.3.

The very low solubility of  $\text{CaI}_2$  in aromatic solvents ensures that  $\text{K}[\text{N}(\text{SiMe}_3)_2]$  will always be in excess in solution in a reaction conducted in toluene, thus contributing to calciate formation. Calcium iodide is more soluble in ethers,<sup>22</sup> but it is still likely that the potassium compound will be in excess in the early stages of the reaction.<sup>23</sup>

**Computational Study.** The structures of **1**, **2**, and  $\text{K}[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_3]$  were optimized at the B3PW91/cc-pVDZ level (triple- $\zeta$  on the metals). The potassium calciate was derived from the known structure of  $(\text{THF})\text{K}[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_3]$  by removing the coordinated THF ligand;<sup>8</sup> the other two used the crystal structures of the compounds as starting geometries.<sup>19,24</sup> The bond lengths and angles for  $\text{K}[\text{N}(\text{SiMe}_3)_2]$  and  $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$  are within  $0.05 \text{ \AA}$  and  $2^\circ$ ,

respectively, of the experimentally determined values. Even given that these are gas-phase energies and that solvation effects may play an important role, the proposed aggregation reaction (Scheme 1) is exothermic by  $7 \text{ kcal mol}^{-1}$  ( $\Delta H^\circ$ ) and has a free energy of approximately  $-8 \text{ kcal mol}^{-1}$ . The ease of aggregation could explain why separate resonances from **1** and **2** are not observed in NMR spectra until the amount of **2** becomes quite high. In this context, it is interesting that at a comparable level of theory the reaction of  $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$  and **1** to produce  $\text{CaMg}[\text{N}(\text{SiMe}_3)_2]_4$  was found to be essentially thermoneutral, helping to explain the appearance of all three species in NMR spectra of  $\text{CaMg}[\text{N}(\text{SiMe}_3)_2]_4$ .<sup>13</sup>

In summary, essentially potassium-free **1** is isolated in high yield from the room temperature reaction of  $\text{Ca}(\text{CH}_2\text{Ph})_2$  (THF) and  $\text{HN}(\text{SiMe}_3)_2$  in toluene. In contrast, we have no evidence that the reaction of  $\text{CaI}_2$  and **2** in toluene ever yields pure **1**; the formation of potassium calciates appears to be unavoidable in this solvent. That this fact has gone undetected for as long as it has indicates that for many synthetic purposes a species such as  $\text{K}[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_3]$  is an effective replacement for **1**, but this can hardly be assumed to be always the case. The use of ethers as reaction solvents for the metathetical preparation of **2** may be less problematic but still should be approached with caution. It might be noted that related halide metathetical preparations have been described for the analogous barium<sup>25</sup> and strontium<sup>9,26</sup> amides. They should

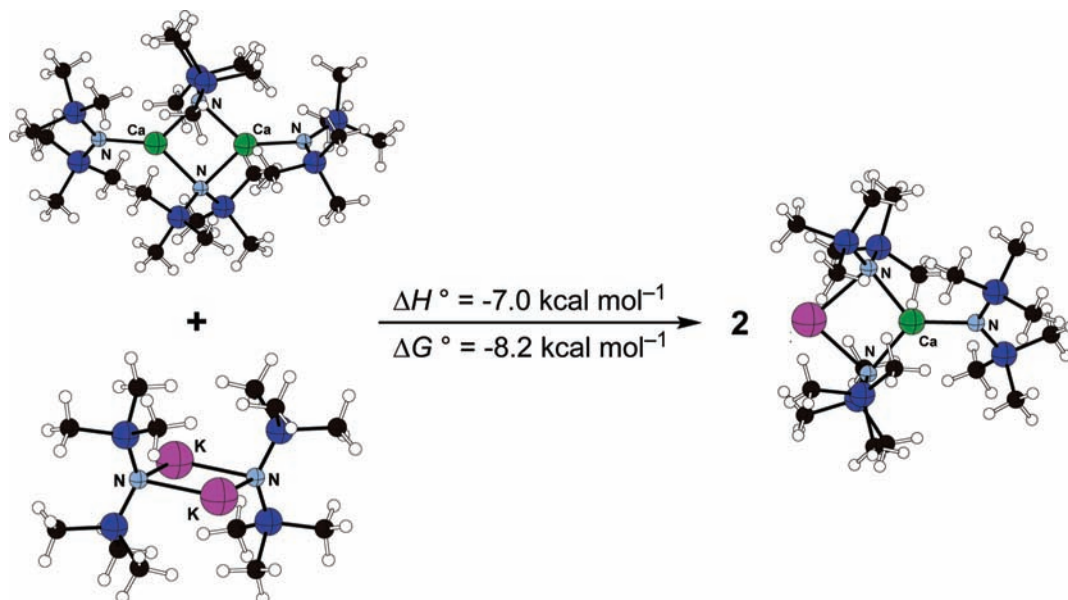
(22) The solubility of  $\text{CaI}_2$  in THF at room temperature is  $12.4 \text{ g L}^{-1}$  (McCormick, M. J.; Sockwell, S. C.; Davies, C. E. H.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1989**, *8*, 2044–2049).

(23) After recrystallization from toluene and then hexane, the product isolated from the metathesis of  $\text{CaI}_2$  and  $\text{K}[\text{N}(\text{SiMe}_3)_2]$  in  $\text{Et}_2\text{O}$  was ostensibly pure by ICP analysis (ref 8 Supplementary Material). Nevertheless, a sample prepared by the same method displays two peaks in its  $^1\text{H}$  NMR spectrum in toluene- $d_8$  at  $22^\circ\text{C}$  ( $\delta$  0.27, 0.31 ppm) (ref 13 Table 1). We currently have no simple explanation for the apparent discrepancy with the results reported here.

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**Scheme 1.** Optimized Structures and Reaction of **1** and **2** to Produce  $\text{K}[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_3]$ 

be used with care until the purity of the products is reconfirmed.

## Experimental Procedures

**General Considerations.** All manipulations were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or glovebox techniques.  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were obtained at 22 °C at 300 MHz (Bruker DPX-300) and 101 MHz (Bruker AV-I), respectively, and were referenced to residual solvent resonances. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ, or Desert Analytics, Tucson, AZ; metal analysis was conducted with ICP-OES.

**Materials.** Anhydrous calcium iodide and  $\text{K}[\text{N}(\text{SiMe}_3)_2]$  were obtained commercially (Aldrich, 99% and 95%, respectively) and used as received. Benzylpotassium was prepared using a reported procedure.<sup>25</sup> Reaction solvents (THF, toluene, benzene, hexanes, pentane) were sparged with nitrogen for 30 min and dried over type 4A molecular sieves prior to use.  $\text{C}_6\text{D}_6$  and toluene- $d_8$  were vacuum-distilled from Na/K (22/78) alloy and stored over type 4A molecular sieves.

**Preparation of  $\text{Ca}(\text{CH}_2\text{Ph})_2(\text{THF})$ .** To a 250 mL round-bottom flask equipped with a magnetic stir bar was added benzylpotassium (2.66 g, 20.4 mmol) and THF (50 mL).  $\text{CaI}_2$  (3.00 g, 10.2 mmol) was added in small portions, and the resulting suspension was stirred overnight. The reaction mixture was then filtered through Celite to remove KI and any unreacted  $\text{CaI}_2$ . Removal of solvent from the resulting orange filtrate left a dark red viscous oil. Subsequent trituration with benzene (50 mL) for 30 min followed by the addition of pentane (50 mL) resulted in a fine orange precipitate. The orange precipitate was isolated by filtration, washed with pentane (2 × 30 mL), and dried under vacuum to afford 2.07 g (69%) of  $\text{Ca}(\text{CH}_2\text{Ph})_2(\text{THF})$ . Anal. Calcd for  $\text{C}_{18}\text{CaH}_{22}\text{O}$ : Ca, 13.6; K, 0.0. Found: Ca, 13.4; K, 0.68. The complex is insoluble in common hydrocarbon solvents.  $^1\text{H}$  NMR (THF- $d_8$ , 22 °C,  $\delta$ ): 1.50 (s, 2H,  $\text{CH}_2$ ), 5.74 (t, 2H,  $^3J(\text{H},\text{H}) = 7.2 \text{ Hz}$ , *m*-H), 6.32 (d, 2H,  $^3J(\text{H},\text{H}) = 7.2 \text{ Hz}$ , *o*-H), 6.48 (t, 1H,  $^3J(\text{H},\text{H}) = 7.4 \text{ Hz}$ , *p*-H).

**Preparation of  $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$  (**1**).** To a 20 mL scintillation vial equipped with a magnetic stir bar was added  $\text{Ca}(\text{CH}_2\text{Ph})_2(\text{THF})$  (0.500 g, 1.70 mmol), toluene (5 mL), and hexamethyldisilazane (0.961 mL, 4.61 mmol, 2.7 equiv). The suspension was heated to 60 °C for 4 h then allowed to cool to room temperature. Filtration through Celite yielded a clear solution, which was dried under reduced pressure, and the resulting residue was recrystallized from hexanes at -40 °C over 16 h. The resulting X-ray quality crystals were isolated from the supernatant, washed with cold hexanes (2 × 5 mL), and dried under vacuum to afford 601 mg (98%) of **1**. Anal. Calcd for  $\text{C}_{12}\text{H}_{36}\text{CaN}_2\text{Si}_4$ : C, 39.94; H, 10.06; N, 7.76; Ca, 11.11; K, 0.0. Found: C, 39.25; H, 10.40; N, 7.39; Ca and K (average of two determinations each), 10.78 and 0.11, respectively.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 22 °C,  $\delta$ ) 0.31;  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 22 °C,  $\delta$ ) 6.91 and 6.47.

## Computational Details

All calculations were performed with the Gaussian 03W suite of programs.<sup>27</sup> For geometry optimization and energy calculations, the B3PW91 functional, which incorporates Becke's three-parameter exchange functional<sup>28</sup> with the 1991 gradient-corrected

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correlation functional of Perdew and Wang,<sup>29</sup> was used. For all atoms except K and Ca, the polarized double- $\zeta$  cc-pVDZ basis sets were used.<sup>30</sup> The cc-pCVTZ basis set was used on Ca ((14s,12p,6d)/[6s,5p,3d]) and the corresponding “Feller Misc. CVTZ” on potassium ((15s,12p,2d)/[6s,5p,2d]) ((*s,p*) exponents from Ahlrichs;<sup>31</sup> polarization and core/valence exponents from Feller<sup>32</sup>). The molecules displayed no imaginary frequencies; all geometries were minima on their potential energy surfaces.

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