Synthesis, Experimental/Theoretical Characterization, and Thermolysis Chemistry of CpBe(SiMe$_3$), a Molecule Containing an Unprecedented Beryllium−Silicon Bond

Dovas A. Saulys* and Douglas R. Powell[†]

Department of Chemistry, University of Wisconsin−Madison, Madison, Wisconsin 53706

Received February 28, 2002

The synthesis, characterization, and thermal decomposition of CpBe(SiMe$_3$) are presented as part of an exploratory investigation designed to obtain more effective chemical vapor deposition precursors of metallic beryllium. The title compound provides the first example of a direct bond between beryllium and a non-carbenoid group 14 element. The base-free reaction of LiSiMe$_3$ with CpBeCl in pentane affords the air-sensitive, volatile solid CpBe(SiMe$_3$) (ca. 70% yield based on CpBeCl), which was characterized by single-crystal CCD X-ray diffraction, multinuclear NMR, and mass spectrometric studies, and theoretically by DFT/NBO analysis**.** The solid-state molecular geometry of CpBe(SiMe$_3$) ideally conforms to C_{3v} symmetry (under assumed cylindrical symmetry for the C$_5$H$_5$ ring); the Be−Si bond length of 2.185(2) Å is markedly longer than the sum of covalent radii (2.01 Å). The DFT-optimized molecular geometry closely conforms to that determined crystallographically. Total fragment charges (based upon atomic charge NBO calculations) of −0.79 e for C$_5$H$_5$, +1.26 e for Be, +0.81 e for Si, and −1.28 e for the three Me groups constitute a polarity pattern consistent with the Be−Cp bonding interaction being mainly ionic and with the Be−Si bonding pair being polarized toward the more electronegative SiMe$_3$ fragment. Beryllium-9 and ^{29}Si NMR spectra exhibit a large J(Be−Si) coupling constant of 51 Hz; the ^{9}Be chemical shift of δ −27.70 ppm, the highest field value recorded to date, is in accordance with the calculated bond-polarity pattern, as well as a bond to Si. Mass spectra (EI) exhibited peaks for the molecular ion and its isotopomers. Thermal decomposition of CpBe(SiMe$_3$) gives rise to trimethylsilane, CpBeMe, and CpBe(SiMe$_2$SiMe$_3$) as the major products, as determined by multinuclear NMR. The latter species is likewise formed by the reaction of CpBeCl with LiSiMe$_2$SiMe$_3$.

Introduction

Prior to the chemistry reported here, beryllium−silicon chemistry was virtually nonexistent. In fact, fully characterized examples of bonds between the group 2 elements and silicon are known only for magnesium, for which three (Me$_3$Si)$_2$Mg·Base adducts (viz., Base = dimethoxyethane,[1a,b] tetramethylenediamine,[1c] and tetramethyldiaminopropane[1d]) have been described. Characterization of other group 2 element−silicon linkages has been indirect. Bis(triphenylsilyl)barium was reportedly isolated from a liquid ammonia solution of Ba and Si$_2$Ph$_6$ and characterized by solvolysis reactions; however, experimental details were not provided.[2] Calcium−silicon bonds have been inferred from the derivatization of the products of metal−atom reactions of Ca with chlorosilanes.[3] In the case of beryllium, previous experimental work has been limited to the beryllium doping of silicon by means of the high-temperature evaporation and subsequent vapor deposition of Be metal onto Si wafers; the resultant structures were probed by means of absorption spectroscopy and electrical measurements.[4−6] The energies and structures of beryllium doped into bulk silicon were also calculated.[7] In addition, ab initio[8,9] and Hartree−Fock[10] calculations performed on hypothetical molecules containing covalent Be−Si linkages (e.g., HBe(SiH$_3$) and HBeSi(=O)H)

---

* Corresponding author. Current address: Materials Research Science and Engineering Center, University of Wisconsin, 1415 Engineering Dr., Madison, WI 53706. E-mail: dovas@amps.che.wisc.edu. Tel: (608) 263-0346. Fax: (608) 265-3782.

[†] Department of Chemistry, University of Kansas, Lawrence, KS 66045-7582.

(1) B = dimethoxyethane: (a) Rosch, L. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 247. (b) Claggett, A. R.; Ilsley, W. H.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Am. Soc.* **1977**, *99*, 1797. B = tetramethylethylenediamine: (c) Goebel, D. W., Jr.; Hencher, J. L.; Oliver, J. P. *Organometallics* **1983**, *2*, 746. B = tetramethyldiaminopropane: (d) Rosch, L.; Pickardt, J.; Imme, G.; Borner, U. *Z. Naturforsch., Teil B* **1986**, *41*, 1523.

(2) Wiberg, E.; Stecher, O.; Andrashek, H. J.; Kreuzbichler, L.; Staude, E. *Angew. Chem., Int. Ed.* **1963**, *2*, 507.

(3) Mochida, K.; Manishi, M. *Chem. Lett.* **1984**, 1077.

(4) Robertson, J. B.; Franks, R. K. *Solid State Commun.* **1968**, *6*, 825.

(5) Kleverman, M.; Grimmeiss, H. G. *Semicond. Sci. Technol.* **1986**, *1*, 45.

(6) Crouch, R. K.; Robertson, J. B.; Gilmer, T. E., Jr. *Phy. Rev. B* **1972**, *5*, 3111.

(7) Tarnow, E.; Zhang, S. B.; Chang, K. J.; Chadi, D. J. *Mater. Res. Soc. Symp. Proc.* **1991**, *209*, 119.

(8) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M. B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108* (8), 260.

(9) Coolidge, M. B.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 2299.

(10) Jennings, J. L.; Wright, D. W. *Main Group Met. Chem.* **1994**, *17*, 387.

10.1021/om0201720 CCC: $25.00
Publication on Web 12/31/2002

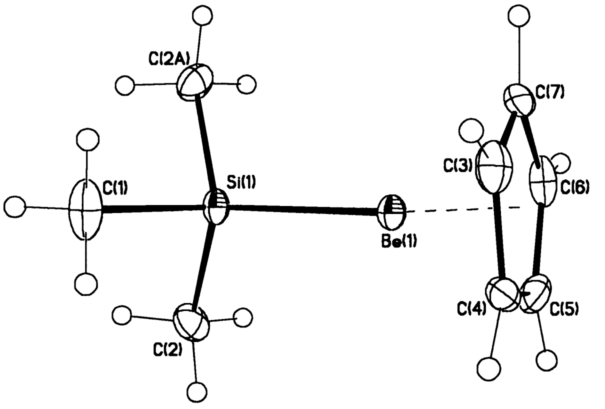


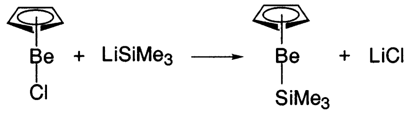
Figure 1. ORTEP drawing of $CpBe(SiMe_3)$, with ellipsoids shown at the 50% level.

have resulted in predictions of molecular bond lengths,[8] bond angles,[8] bond dissociation energies,[8,9] and NMR chemical shift derivatives.[10]

The research reported herein is a result of our interest in designing volatile, base-free group 2 compounds as dopants for chemical vapor deposition. In this context, the thermal stability and decomposition pathways of compounds containing beryllium−silicon bonds are of prime importance. This research was also motivated by the fact that there had been no previous report of any well-defined, discrete compounds containing a bond between beryllium and a non-carbenoid group 14 element.

Results and Discussion

$CpBe(SiMe_3)$. (a) Synthesis and Physical Properties. The reaction of high-purity $LiSiMe_3$ with CpBeCl yields the volatile, base-free species $CpBe(SiMe_3)$ (eq 1), the first fully characterized example of a beryllium−silicon bond. It is soluble in hydrocarbons and reacts spontaneously with aerial oxygen.



$$\underset{\text{Cl}}{\text{Be}} + \text{LiSiMe}_3 \longrightarrow \underset{\text{SiMe}_3}{\text{Be}} + \text{LiCl} \qquad (1)$$

(b) Molecular Structure from X-ray Diffraction Analysis. Cyclopentadienyl(trimethylsilyl)beryllium crystallizes under vacuum at ambient temperature as clear, colorless prisms that appear to be stable indefinitely under these conditions.

The molecular structure of $CpBe(SiMe_3)$ is shown in Figure 1, and selected distances and bond angles are shown in Table 1. Two molecules constitute the unit cell of symmetry $P2_1/m$, such that one-half molecule is crystallographically independent. Each molecule is bisected by a mirror plane through Be, Si, and C(1), with the entire cyclopentadienyl ligand disordered over two equivalent sites. The equivalent Be−C(Cp) distances (range 1.880(5)−1.927(7) Å, mean 1.904 Å), which are similar to the crystallographically determined Be−C(Cp) values for other CpBeX derivatives,[11−13] establish that Be is equally coordinated to the five ring carbons. The average value of 1.398(8) Å for the five C−C distances (Table 1) comprising the cyclopentadienyl ring is virtually identical to that of 1.401 Å found for the η^5-bonded Cp ring in the well-determined crystal structure of $BeCp_2$.[11] The (essentially) perpendicular distance from Be to the Cp ring centroid of 1.487 Å is also analogous to those for $BeCp_2$ (1.508 Å),[11] $CpBe(B_5H_8)$ (1.45 Å),[12] and CpBeCl (1.451 Å).[13] The two independent Si−C(methyl) distances of 1.891(2) and 1.892(1) Å are representative of the Si−C(Me) bond.[14] As is typical for bonds between silicon and other main-group metals,[14] the Si−Be distance (2.185(2) Å) is significantly longer than the sum of covalent radii (2.01 Å).

Table 1. Selected Bond Distances and Angles for $CpBe(SiMe_3)$ from X-ray Crystallographic Study

A. Bond Distances (Å)

Si−C(1)	1.891(2)	Si−C(2)	1.892(1)
Si−Be	2.185(2)	Be−C(5)	1.880(5)
Be−C(4)	1.894(13)	Be−C(6)	1.909(4)
Be−C(3)	1.909(14)	Be−C(7)	1.927(7)
C(3)−C(4)	1.393(7)	C(3)−C(7)	1.412(11)
C(4)−C(5)	1.398(10)	C(5)−C(6)	1.391(7)
C(6)−C(7)	1.395(5)	Be−CENT[a]	1.487

B. Bond Angles (deg)

C(1)−Si−C(2)	105.52(6)	C(2)−Si−C(2)#1	105.51(9)
C(1)−Si−Be	114.52(8)	C(2)−Si−Be	112.51(5)
C(5)−Be−Si	144.0(2)	C(4)−Be−Si	144.1(3)
C(6)−Be−Si	139.5(2)	C(3)−Be−Si	141.1(4)
C(7)−Be−Si	137.6(2)	C(4)−C(3)−C(7)	109.1(11)
C(3)−C(4)−C(5)	106.6(10)	C(6)−C(5)−C(4)	109.3(6)
C(5)−C(6)−C(7)	108.1(4)	C(6)−C(7)−C(3)	106.9(7)

[a] CENT = centroid of the five-membered ring.

The ligand coordination about the Si atom is trigonal pyramidal. The three Be−Si−C(methyl) bond angles (av 113.2°) exceed the ideal tetrahedral angle of 109.5°, while the three C(methyl)−Si−C(methyl) bond angles (av 105.5°) are correspondingly lower. As the molecular geometry offers no evidence for steric compression of the methyl groups, the deviations of the angles around Si from ideal tetrahedral values are consistent with a moderate polarization of the Be−Si bonding pair toward Si. Additional evidence regarding the polarity of the beryllium−silicon bond is provided by the ^{29}Si NMR chemical shift data and calculational results (vide infra).

(c) Theoretical Analysis and Resulting Implications.[15] Density functional theory (DFT) calculations, performed at the B3LYP/6-31+G* level with the Gaussian-98 package,[16] were utilized to obtain the optimal geometry of the $CpBe(SiMe_3)$ molecule. The calculated bond distances and bond angles essentially reproduce

---

(11) Nugent, K. W.; Beattie, J. K.; Hambley, T. W.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1601.

(12) Gaines, D. F.; Walsh, J. L.; Morris, J. H.; Hillenbrand, D. F. *Inorg. Chem.* **1978**, *17*, 1516.

(13) Goddard, R.; Akhtar, J.; Starowieyski, K. B. *J. Organomet. Chem.* **1985**, *282*, 149.

(14) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Part 1, Chapter 3, p 246.

(15) Saulys, D. A.; Weinhold, F. Unpublished results.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gausian 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

Table 2. Comparison between DFT-Optimized and X-ray-Determined Mean Bond Distances and Angles for CpBe(SiMe$_3$) under Pseudo-C_{3v} Symmetry[a]

distances (Å)/ angles (deg)	N^b	DFT-opt	X-ray detmn	difference
Si−C(Me)	3	1.917	1.892	0.025
Si−Be	1	2.197	2.185	0.012
Be−C(Cp)	5	1.928	1.904	0.024
Be−CENT[c]	1	1.501	1.487	0.014
C(Cp)−C(Cp)	5	1.422	1.398	0.024
C(Me)−Si−C(Me)	3	105.9	105.5	0.4
C(Me)−Si−Be	3	112.8	113.2	0.4
Si−C(Me)−H	15	111.3		

[a] Cp ligand is assumed to be cylindrically symmetric. [b] N denotes the number of symmetry-equivalent distances and angles under C_{3v} symmetry. [c] CENT = centroid of the five-membered ring.

Table 3. Natural Charges (e) in CpBe(SiMe$_3$) Obtained from NBO Analysis

Be	+1.258	Si	+0.809
C (Me)	−1.161	H (Me)	+0.245
C (Cp)	−0.432	H (Cp)	+0.273
C_5H_5	−0.794		

those determined crystallographically; the values of selected bond angles and distances are provided in Table 2. Differences between corresponding calculated and crystallographic values are in all cases less than 2% of the latter values.

The natural bond orbital (NBO) technique, developed by Weinhold and co-workers,[17,18] was used to describe the atomic charge distribution, geometry, and bonding in CpBe(SiMe$_3$). A key insight of NBO theory has been the recognition of the potential significance of donor−acceptor interactions (hyperconjugation) between localized valence bonds (σ, π) and unoccupied antibonds (σ^*,π^*). The energy lowering[19] provided by these delocalizations can contribute to the driving force for chemical reactions, as is described in the calculational analysis below.

Natural atomic charges are displayed in Table 3. Several important features of the NBO description merit comment. The NBO method does not describe a covalent bond between the Cp ring and the Be(SiMe$_3$) moiety. Instead, the analysis provides strong evidence that the Cp ring is nearly anionic (Q = −0.794 e) and interacts with the Be atom via a number of delocalization interactions[20] that channel small amounts of electron density from the Cp ring π bonds to the Be−Si antibond and the Be 2p atomic orbitals. The Be valence electrons are localized primarily in the Be 2s orbital (0.59 e), with much smaller amounts of electron density found in the $2p_x$ (0.072 e), $2p_y$ (0.036 e), and $2p_z$ (0.036 e) orbitals (the Be−Si bond lies on the x axis).

Figure 2. (a) Electron-pushing diagram denoting the NBO $\sigma_{\text{Be−Si}} \rightarrow \sigma^*_{\text{Si−C(Me)}}$ geminal donor−acceptor interaction. (b) One of the three resonance structures of CpBe(SiMe$_3$) at the ionic bonding limit.

The calculated natural atomic charge distribution in CpBe(SiMe$_3$) is unusual in that it includes sizable like charges on adjacent Be (Q = +1.258 e) and Si (Q = +0.809 e) atoms, while the periphery of the molecule, consisting of the Me (Q = −0.43 e) and Cp groups, is negatively charged. This polarity pattern is interesting in several respects. The juxtaposition of positive charges on Be and Si would be expected to facilitate homolysis of the Be−Si bond, a reaction that is indeed observed, although to a minor degree. This polarity pattern is also conducive to geminal hyperconjugation[21] (Figure 2a). While vicinal donor−acceptor interactions predominate in molecules comprised of first-row elements, the presence of second-row elements often enables geminal hyperconjugation.[21]

The calculated pattern of natural atomic charges and the geminal hyperconjugation centered on Si provides a rationale for the proposed role of dimethysilylene in the thermal decomposition mechanism of CpBe(SiMe$_3$). The formal transfer of the entire two-electron bonding pair from $\sigma_{\text{Be−Si}}$ to $\sigma^*_{\text{Si−C(Me)}}$ of one Me group is depicted in the resonance structure shown in Figure 2b.[21] This formulation is consistent with the presence of dimethysilylene intermediates in the thermal decomposition of CpBe(SiMe$_3$), as discussed below.

(d) Mass Spectrometric Analysis. The mass spectrum of CpBe(SiMe$_3$) is dominated by peaks due to the Cp and SiMe$_3$ ligands and fragments thereof. The major Be-containing peaks are those due to the molecular ion and its isotopomers. In particular, the [CpBe]$^+$ fragment peak is of minor intensity (8%), while that due to [SiMe$_3$]$^+$ is 77% as intense as the base peak, [HSiMe$_2$]$^+$. This is in sharp contrast to the fragmentation behavior exhibited by the organic derivatives CpBeR. In an in-depth electron ionization (EI) mass spectral study of CpBeR compounds (R = H, Me, Et, n-Bu, t-Bu), Bartke[22] found that the [CpBe]$^+$ fragment constitutes the base peak in all spectra run at 70 eV, while peaks due to the intact organic ligand, R$^+$, are minor or absent. While this difference in relative peak intensities is consistent with the lower ionization potential of the SiMe$_3$ radical (6.32 eV)[23] relative to that of the organic fragments (Me, 9.84; Et, 8.12; t-Bu, 6.70),[24] the differences in ionization potentials are probably not large enough to completely account for the relative differences in peak intensities. The decreased stability of the CpBe unit in CpBe(SiMe$_3$) is likely a contributing factor. The larger ionic character

---

(17) Weinhold, F. In *Encyclopedia of Computational Chemistry*; Wiley: New York, 1998; Vol. 3, p 1792.

(18) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO Version 4.0 in Gaussian 98*;[16] Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 1996.

(19) The second-order energy lowering that arises from the delocalization of electron density from a doubly occupied σ bond, σ_{AB}, into an empty antibond σ^*_{CD} can be approximated by means of a standard Rayleigh−Schrodinger perturbation treatment: $\Delta E^{(2)}_{\sigma\rightarrow\sigma^*} = -2\langle\sigma_{AB}|\boldsymbol{F}|\sigma^*_{CD}\rangle^2/(\epsilon_\sigma - \epsilon_{\sigma^*})$, where $\langle\sigma_{AB}|\boldsymbol{F}|\sigma^*_{CD}\rangle$ is the NBO Fock matrix element that describes the orbital interaction, and $\epsilon_\sigma = \langle\sigma_{AB}|\boldsymbol{F}|\sigma_{AB}\rangle$ and $\epsilon_{\sigma^*} = \langle\sigma^*_{CD}|\boldsymbol{F}|\sigma^*_{CD}\rangle$ are the orbital energies. (See ref 17, p 1799.)

(20) Typical calculated strengths, $\Delta E^{(2)}$, of relevant delocalizing interactions range from −4 to −9 kcal/mol.[15] The strength of the geminal delocalizations centered on Si (discussed below), $\sigma_{\text{Be−Si}} \rightarrow \sigma^*_{\text{Si−C(Me)}}$, is −4.45 kcal/mol.

(21) Glendening, E. D. Ph.D. Thesis, University of Wisconsin−Madison, Madison, WI, Chapter 6.

(22) Bartke, T. C. Ph.D. Dissertation, University of Wyoming, Laramie, Wyoming, 1975.

(23) Shin, S. K.; Corderman, R. R.; Beauchamp, J. L. *Int. J. Mass Spec. Ion Processes* **1990**, *101*, 257.

(24) Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 900.

Table 4. Chemical Shift Data (δ) for CpBe−Si Species[a]

compound	δ ^{9}Be: δ	δ ^{9}Be: $\Delta\omega_{1/2}$[b]	δ ^{29}Si: $SiMe_3$	δ ^{29}Si: $SiMe_2$	δ ^{13}C: Cp	δ ^{13}C: $SiMe_2$	δ ^{13}C: $SiMe_3$	^{1}H[c]: Cp	^{1}H[c]: $SiMe_2$	^{1}H[c]: $SiMe_3$
$CpBe(SiMe_3)$	−27.70	8.0	−27.31 q		103.10		3.51	5.54		0.21
$CpBe(SiMe_2SiMe_3)$	−27.20		−14.67	−61.90 q	103.33	−3.62	−1.14	5.62	0.205	0.17

[a] q = 1:1:1:1 quartet. [b] Peak width at half-height, in hertz. [c] Relative integration intensities are consistent with the molecular formulations.

Table 5. Coupling Constants[a] **(J) for CpBe−Si Species**[b]

compound	^1J(Be−Si)		^1J(Si−C) Be−SiMe$_n$	^2J(Si−H) Be−SiMe$_n$	^1J(C−H) Cp	^1J(C−H) Me
$CpBe(SiMe_3)$	51.4 q	50.2 d	36.0	5.4	177.7	117.8
$CpBe(SiMe_2SiMe_3)$	48.3 q		41.5	4.28	*c*	*c*

[a] In hertz. [b] q = 1:1:1:1 quartet, d = doublet. [c] Resonance not observed.

of the Be−Cp bond may, in turn, be attributed to the decreased electronegativity of the Be-attached trimethylsilyl group relative to that of the Be-attached alkyl groups. Proton NMR data (vide infra) support this interpretation.

(e) NMR Spectral Analysis. The NMR chemical shift range of ^{9}Be for previously known CpBeX species is from −18.5 to −22.1 ppm;[25] the title compound (X = $SiMe_3$) doubles this range and extends it in the high-field direction. To our knowledge, this ^{9}Be chemical shift, −27.70 ppm, is the highest field value recorded to date. While high-field chemical shifts of Be nuclei in cyclopentadienide derivatives are ascribed to ring-current effects, this extension can be qualitatively attributed to the electropositivity of silicon, by virtue of a simple inductive effect and/or the subsequent decrease in the [$1/r^3$] factor of the paramagnetic shielding term for the Be nucleus. The upfield shift, in part, is also consistent with a higher electron density at the Cp ring, resulting in a stronger ring-current effect. The chemical shifts of the Cp ring protons are also of interest in this regard. Proton chemical shifts of cyclic aromatic compounds in general,[26] and of metal cyclopentadienyls in particular,[27] have been shown to correlate roughly with the π electron density in the ring: a higher Cp electron density (i.e., a more ionic metal−Cp linkage) usually results in shifts to lower frequency. In CpBeX species, the Cp proton chemical shifts roughly track the electronegativity of the nonaromatic ligand (X, chemical shift in ppm): $SiMe_3$, 5.54; Me, 5.70; Cl, 5.75.[28] The resulting implication is that the relatively electropositive trimethylsilyl ligand gives rise to a somewhat more ionic Be−Cp linkage than that found in organic or halide derivatives, CpBeX. This hypothesis is consistent with the mass spectral results discussed above.

Silicon chemical shifts are thought to be dominated by the paramagnetic shielding term.[29] Empirically, however, it is commonly found that among similar compounds, for example within the series $XSiMe_3$ (e.g., X = Li, $SiMe_3$, O, Cl), shielding of the Si nucleus decreases with increasing electronegativity of X.[30] That is, shifts to lower field are associated with a decrease in electron density at the Si atom, and vice versa.[31] By this criterion, the electron density at Si in $CpBe(SiMe_3)$ (^{29}Si = −27.3 ppm) is intermediate to that found in $LiSiMe_3$ (−38.0 ppm) versus those observed in trimethylsilyl groups bound to a moiety of equivalent (Si_2Me_6, −19.7 ppm) or higher electronegativity (e.g., $[Me_3SiO]_4Si$, 7.6 ppm;[30] or Me_3SiCl, 29.4 ppm[30]).

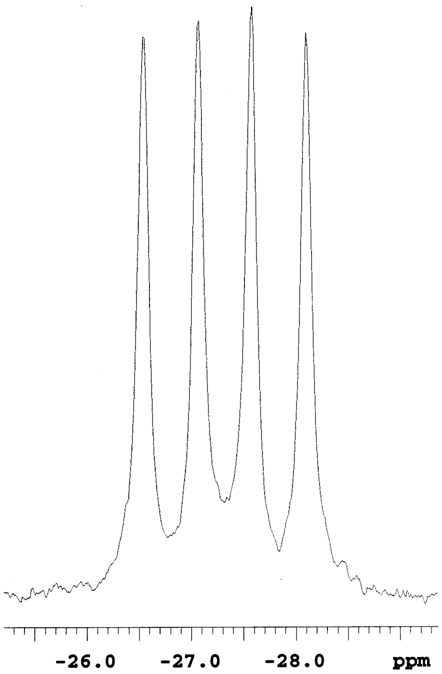


Figure 3. ^{29}Si NMR spectrum of $CpBe(SiMe_3)$ illustrating the 1:1:1:1 quartet with J_{Be-Si} = 51.4 Hz.

The large J_{Be-Si} coupling constant between beryllium and silicon, 50.15 Hz[32] (Table 5 and Figure 3), characterizes several features of this linkage. A significant degree of covalency, in accordance with a small electronegativity difference, $\Delta\chi(Si-Be) = 0.33$, as well as a high degree of s-orbital participation in the Be−Si bond are indicated. Consistent with the latter indication, the value of $^1J_{Si-C}$ observed (Table 5) is in the low end of

---

[25] Gaines, D. F.; Coleson, K. M.; Hillenbrand, D. F. *J. Magn. Reson.* **1981**, *44*, 84−88.

[26] Gunther, H. *NMR Spectroscopy*; John Wiley and Sons: New York, 1980; p 68.

[27] (a) Maddox, M. L.; Stafford, S. L.; Kaesz, H. D. *Adv. Organomet. Chem.* **1965**, *3*, 38. (b) Fraenkel, G.; Carter, R. E.; McLachlan, A.; Richards, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 5846.

[28] Samples run in cyclohexane as opposed to benzene exhibit a much greater chemical shift dispersion and thus demonstrate this effect more clearly: ref 22.

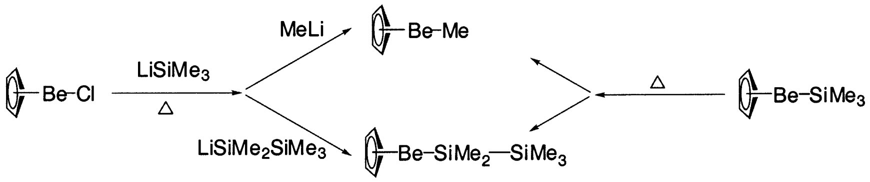
[29] (a) Williams, E. A.; Cargioli, J. D. *Annu. Rep. NMR Spectrosc.* **1979**, *5*, 221. (b)Williams, E. A. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 235.

[30] Harris, R. K.; Kimber, B. J. *J Magn. Reson.* **1975**, *17*, 174.

[31] Al-Hassan, M. I.; Al-Najjar, I. M.; Al-Oraify, I. M. *Magn. Reson. Chem.* **1989**, *27*, 1112.

[32] For purposes of comparison, note the reduced coupling constants K (10^{20} NA^{-2} m^{-3}) and J (Hz) for the following species: $CpBeSiMe_3$, $K(^{29}Si-^9Be) = 15.3$, $J = 51.4$; CpBeMe, $K(^{13}C-^9Be) = -7.4$, $J = 31.3$; $LiSiMe_3$, $K(^6Li-^{29}Si) = -6.0$, $J = 21.1$.[44a]

Scheme 1



the range for silicon–carbon couplings,[29] as would be predicted by Bent's rule,[33] which states that electronegative substituents (viz., Me groups) prefer hybrid orbitals with less valence s AO character.

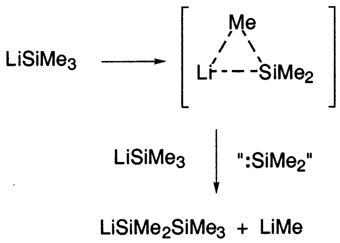
$CpBe(SiMe_2SiMe_3)$. An NMR tube-reaction mixture of CpBeCl and $LiSiMe_3$ that was briefly heated yielded $CpBe(SiMe_3)$, CpBeMe, and a species identified as $CpBe(SiMe_2SiMe_3)$: the high-field ^{9}Be chemical shift (Table 4) indicates a species bound to both a Cp ring and silicon; in the ^{29}Si NMR spectrum, the 1:1:1:1 splitting substantiates the bonding to Be ($I = 3/2$), while the high-field chemical shift is characteristic of a secondary silicon in permethylated silicon derivatives.[34] The reactive species methyllithium and pentamethyldisilyllithium are indicated as thermal decomposition products of $LiSiMe_3$ (Scheme 1).

As was the case for $CpBe(SiMe_3)$ in relation to $X(SiMe_3)$ species, the ^{29}Si chemical shifts for $CpBe(SiMe_2SiMe_3)$ conform to patterns exhibited by other $XSiMe_2SiMe_3$ compounds.[29a] The shielding of the Si bound to X increases with decreasing electronegativity of X (X, δ ppm): Cl, +22.8;[29a] $SiMe_3SiMe_2$, −44.7;[29b] CpBe, −61.9; Li −79.3. The trimethylsilyl resonances of $X(SiMe_2SiMe_3)$ compounds have been observed to exhibit the opposite relation with respect to the electronegativity of X, along with a significantly decreased chemical-shift dispersion. The resonance for $CpBe(SiMe_2\mathit{Si}Me_3)$ likewise fits this pattern (X, δ ppm): Cl, −18.2;[29a] $SiMe_3SiMe_2$, −15.2;[29b] CpBe, −14.7; Li, −12.5.

Heating $CpBe(SiMe_3)$ for long periods at 217–235 °C likewise generates CpBeMe and $CpBe(SiMe_2SiMe_3)$, along with Me_3SiH. These thermolysis products are compatible with at least two concurrent decomposition pathways. The generation of CpBeMe and $CpBe(SiMe_2SiMe_3)$ is consistent with the presence of dimethylsilylene intermediates, while the formation of Me_3SiH implies a homolytic process. Whether "free" silylenes or metal-complexed "silylenoids" are involved in the former pathway is unclear. In this respect, the presence or absence of particular side-products is instructive. Dimethylsilylene, $:SiMe_2$, readily inserts into the Si–hydrogen bond of Me_3SiH.[35] Despite the continual presence of Me_3SiH in the thermolysis reaction mixture, however, only minute amounts of the anticipated insertion product, Me_3SiMe_2SiH, are observed. Whether this indicates the absence of free silylene or is a testament to the relative silylene acceptor capabilities of Be–Si bonds is as yet unclear. (To our knowledge, the silylene insertion behavior of main-group metal–silicon bonds has not been systematically studied.) Kinetic studies as well as trapping experiments utilizing well-defined silylene acceptors are needed to precisely identify the nature of the intermediate(s).

The Me_3SiH observed is most likely the result of homolytic cleavage of the Be–Si bond to generate the $Me_3Si^\bullet$ radical, followed by hydrogen abstraction. In this context, the fact that little Si_2Me_5H is observed could be taken as an indication that the $Be–SiMe_2SiMe_3$ linkage is more thermally robust (for reasons noted below) than $Be–SiMe_3$. The fate of the Be-containing homolysis product is undetermined: it is apparently not possible to definitively characterize CpBeH by NMR.[22]

Thermal Decomposition of $LiSiMe_3$. Upon standing at room temperature for long periods, a sealed-tube solution of pure $LiSiMe_3$ in C_6D_6 develops ^{1}H, ^{13}C, and ^{29}Si NMR peaks due to $LiSiMe_2SiMe_3$. Heating at 65 °C accelerates this transformation. Formation of $LiSiMe_2SiMe_3$ from $LiSiMe_3$ with increasing temperature implies its higher thermal stability; apparently a trimethylsilyl group more effectively stabilizes the partial negative charge on the Li-bearing Si than does a methyl group. Derivatization experiments (vide supra) indicate MeLi as a decomposition product and also confirm the formation of $LiSiMe_2SiMe_3$. The formation of $LiSiMe_2SiMe_3$ from Si_2Me_6 in basic solution has been ascribed to the cleavage of a silicon–carbon bond with $LiSiMe_3$[36] or MeLi.[37] As none of the required byproducts (e.g., $SiMe_4$, C_2H_6) of nucleophilic attack on Si_2Me_6 is observed here, silylene intermediates, analogous to those invoked above in the decomposition of $CpBe(SiMe_3)$, may be operative in this case (eq 2):[2,38]



(2)

Although the mechanistic aspects of this reaction are still under investigation, the bridge-bonded transition state depicted in reaction 2 can account for the observed products.

Experimental Section

CAUTIONARY NOTE: Beryllium and its compounds are extremely toxic. Finely divided metal, the vapor of its compounds, and BeO (from aerial oxidation of Be compounds or

---

[33] Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

[34] Williams, E. A. NMR Spectroscopy of Organosilicon Compounds. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 8.

[35] Nefedov, O. M.; Skell, P. S. *Dokl. Akad. Nauk. SSSR* **1981**, *259*, 377

[36] Hudrlik, P. F.; Waugh, M. A.; Hudrlik, A. M. *J. Organomet. Chem.* **1984**, *271*, 69.

[37] Krohn, K.; Khanbabaee, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33* (1), 99.

[38] L. Rosch has implicated Me_2Si: species, polysilanes, and Me–Al bonds in the decomposition of $Al(SiMe_3)_3$: Rosch, L. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 7, 480.

ignition of the metal) are all extremely toxic to the lungs.[39] Physical exposure of any type, e.g., skin contact or inhalation, is to be rigorously avoided. Bis(trimethylsilyl)mercury is also hazardous, due both to its volatility and the facile formation of elemental Hg upon exposure to air. Strict laboratory hygiene is essential in dealing with these materials.[40]

General Considerations. All manipulations were carried out in the absence of air and moisture by use of a standard glass high-vacuum line or a nitrogen-filled glovebox. Five millimeter NMR tubes (Wilmad) were either flamed with a hand torch while under high vacuum or treated with liquid Me_3SiCl to remove residual water; glass reaction vessels were dried similarly. Solvents were purchased from Aldrich (anhydrous grade) and stored over sodium−potassium alloy. Fourier transform NMR spectra at 70.28 (^{9}Be), 500.13 (^{1}H), 99.36 (^{29}Si), and 125.76 (^{13}C) megahertz (MHz) were obtained on Bruker AM-500 or Varian Unity 500 instruments. Proton NMR spectra are referenced to the residual protons of C_6D_6 (7.15 ppm), and ^{13}C spectra to the center of the C_6D_6 triplet (128.0 ppm); positive chemical shifts are deshielded from the external standards: namely, aqueous $Be(NO_3)_2$, as $[Be(H_2O)_4]^{2+}$ (^{9}Be), and $(CH_3)_4Si$ (^{13}C, ^{1}H, and ^{29}Si). All NMR spectra were recorded at room temperature in sealed tubes with degassed C_6D_6 solvent. Low-resolution mass spectra were acquired by use of a Kratos MS-80 instrument operated at 70 eV, with the source at ∼150 °C.

Starting Materials. Be powder (10−20 μm, Alfa Johnson-Matthey) was heated in a quartz reactor at 400−470 °C for 2 h under high vacuum prior to use. Beryllium chloride was prepared by the passing of chlorine gas (AGA, 99.99%) over beryllium metal (99.9%, Aldrich) at 500−550 °C. Bis(trimethylsilyl)mercury[41] was prepared by reaction of mechanically stirred lithium amalgam and trimethylchlorosilane in a slurry of sodium chloride, sodium iodide, and diethyl ether for 3 days in the dark; the resulting mercurial was then extracted in pentane and sublimed under high vacuum. Base-free trimethylsilyllithium[42] was synthesized by addition of an excess of lithium powder (high sodium, 99%, Aldrich) to a stirred solution of $Hg(SiMe_3)_2$ in hexane. After being stirred for 3 days in the dark, the product was isolated by recrystallization from the filtered reaction solution. A solution of NaCp ($Cp = C_5H_5$) in ether was prepared by removal of the solvent from a commercial solution of NaCp in THF (2.0 M, Aldrich), after which the residual solid was redissolved in diethyl ether. Addition of the latter solution to a solution of $BeCl_2$ in diethyl ether afforded bis-cyclopentadienylberyllium, which was twice sublimed at temperatures up to 150 °C in high vacuum.[43] Mixing of a slight excess of $BeCl_2$ with $BeCp_2$ yielded CpBeCl, which was purified by vacuum transfer.

Reactions with $LiSiMe_3$. (a) Thermal Decomposition of $LiSiMe_3$. In a nitrogen-filled glovebox, a 5 mm NMR tube was charged with 40 mg (0.50 mmol) of recently twice-recrystallized $LiSiMe_3$. After deuterated benzene was added via condensation on a high-vacuum line, the tube was sealed. The resulting clear, light green solution was free of solids. The initial spectra exhibited resonances (ppm) consistent with the exclusive presence of pure $LiSiMe_3$ (literature values,[44a] ppm): ^{1}H 0.26 (0.21); ^{13}C 4.95 (5.1); ^{29}Si −37.97 (−38.0). The tube was maintained at room temperature and monitored by multinuclear NMR. After approximately 5 months, the initially clear light green solution contained light and dark colored solids; 59% of the integrated ^{1}H NMR intensity was due to $LiSiMe_3$ and 32% to $LiSiMe_2SiMe_3$: δ ppm (literature values)[44b] ^{1}H 0.28, (0.33), 6H, 0.19, (0.22), 9H; ^{13}C −0.77 (−0.56), −2.64 (−2.51); ^{29}Si −12.5 (−12.4), −79.3 (−79.6). Heating the tube in an oil bath at 55 °C for 20 h produced no major change in the ^{1}H spectrum; after further heating for an additional 115 h at 65 °C, approximately equimolar amounts of $LiSiMe_3$ and $LiSiMe_2SiMe_3$ (compromising ∼80% of the total integrated peak intensity) were detected. Only minor resonances due to hexamethyldisilane and no resonances indicative of methane, ethane, or tetramethylsilane were observed.

(b) $LiSiMe_3$ + CpBeCl. Synthesis and Characterization of $CpBe(SiMe_3)$. A glass reactor fitted with a Teflon high-vacuum stopcock was charged with 0.23 g (2.87 mmol) of freshly recrystallized $LiSiMe_3$ in a nitrogen-filled drybox, transferred to a high-vacuum line and evacuated; then CpBeCl (0.21 g, 1.92 mmol) and pentane (12 mL) were condensed in. After the mixture was magnetically stirred for 19 h, the reaction products were separated by means of fractional condensation. Material subsequently identified as $CpBe(SiMe_3)$ (0.19 g, 1.31 mmol, 68.2% yield based on CpBeCl) passed through a trap held at 0 °C and was retained in a trap held at −30 °C. NMR data are in Tables 4 and 5. MS (EI): m/z (I_{rel}) 37 (6%, C_3H^+), 38 (12%, $C_3H_2^+$), 39 (41%, $C_3H_3^+$), 58 (28.2%, $[SiC_2H_6]^+$), 59 (100%, $HSiMe_2^+$), 65 (51%, $C_5H_5^+$), 66 (93%, $C_5H_6^{+\bullet}$), 73 (77%, $SiMe_3^+$), 74 (8%, $C_5H_5Be^+$), 147 (18%, $M^{+\bullet}$), 148 (3%, $CpBe^{29}SiMe_3^{+\bullet}$), 149 (1%, $CpBe^{30}SiMe_3^{+\bullet}$).

X-ray Crystallography of $CpBe(SiMe_3)$. Capillaries of a thickness suitable for X-ray diffraction were pulled from flame-softened 5 mm Pyrex tubing, flame-sealed to standard tapered glass joints, and evacuated on a high-vacuum line. Small amounts of $CpBe(SiMe_3)$ were condensed in, and the capillaries sealed off. After some months at room temperature, single crystals appeared to form in all of the capillaries. Crystal structure analysis: Intensity data were collected at 133(2) K on a colorless prism-shaped crystal of dimensions 0.42 × 0.34 × 0.24 mm with a Bruker Smart CCD area detector mounted on a Bruker P4 goniometer with Mo Kα radiation (0.71073 Å). $C_8H_{14}BeSi$: $M = 147.29$, monoclinic, $a = 6.1881(5)$ Å, $b = 10.2775(9)$ Å, $c = 8.2346(6)$ Å, $\beta = 110.206(3)°$, $V = 491.48(7)$ Å^3; $P2_1/m$, $Z = 2$, $D_c = 0.995$ Mg/m^3; $F(000) = 160$ electrons. A total of 2178 reflections were collected by 0.4° ϕ oscillation frames (10 s/frame) over $2.64° \leq \theta \leq 28.24°$. An empirical absorption correction (SADABS) was applied ($\mu = 0.169$ mm^{-1} for Mo Kα radiation). The crystal structure was solved by direct methods and refined by full-matrix anisotropic least squares (based on F^2).[45] Refinement (1134 data/73 parameters/no restraints) converged at $wR_2(F^2) = 0.0871$ for all data; $R_1(F) = 0.0328$ for 982 observed data ($I > 2\sigma(I)$); GOF(on F^2) = 1.025; max./min. residual electron density, +2.26 /−0.28 e Å^{-3}.

Thermal Decomposition of $CpBe(SiMe_3)$. A sealed 5 mm NMR tube containing a clear, colorless solution of 0.65 M $CpBe(SiMe_3)$ in C_6D_6 was prepared on a high-vacuum line. Initial ^{1}H, ^{13}C, ^{29}Si, and ^{9}Be NMR spectra exhibited only resonances due to the metal silyl. The tube was heated in a silicon oil bath and monitored by multinuclear NMR. Proton and ^{9}Be NMR spectra indicated no change in the composition of the solution after prolonged (∼11 days) heating at temperatures up to 150 °C. After 26 h at 190 °C, a small doublet due to the methyl hydrogens of Me_3SiH became visible in the proton NMR. After an additional 177 h at 230−235 °C, the clear, colorless solution contained a small amount of finely divided black solid. Multinuclear NMR spectra revealed the

---

[39] For a concise discussion of Be toxicity see: Skilleter, D. N. *Chem. Br.* **1990**, *26*, 26.

[40] Laboratory handling, storage, and disposal procedures are described in (a) *Toxic and Hazardous Industrial Chemicals Safety Manual*; The International Technical Information Institute, 1975. and (b) *The Sigma-Aldrich Library of Chemical Safety Data*, ed. II, Vol. I; Lenga, R. E., Ed.; Sigma-Aldrich Corp.: Milwaukee, WI, 1988.

[41] Rosch, L.; Altnau, G.; Hahn, E.; Havemann H. *Z. Naturforsch.* **1981**, *36b*, 1234.

[42] Schaaf, T. F.; Oliver, J. P. *J. Am. Chem. Soc.* **1969**, *91*, 4327.

[43] Fischer, E. O.; Hofmann, H. P. *Chem. Ber.* **1959**, *92*, 482.

[44] (a) Nanjo, M.; Sekiguchi, A.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 741. (b) Nanjo, M.; Sekiguchi, A.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1387. (c) Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *Organometallics* **1995**, *14*, 2630.

[45] Sheldrick, G. M. *SHELXTL Version 5 Reference Manual*; Siemens Analytical X-ray Instruments: Madison, WI, 1994.

presence of small amounts of CpBeMe[46] (^{9}Be δ −20.54; ^{13}C δ 103.62, −25.46, 1:1:1:1 qt, $J_{\mathrm{Be-C}} = 31.3$ Hz; ^{1}H δ 5.70, 5H; −1.26, 3H) and CpBe(SiMe$_2$SiMe$_3$) (NMR data presented in Tables 4 and 5), along with increased amounts of Me$_3$SiH (literature values in parentheses):[30,47] ^{1}H δ 4.14 (4.20), decet, $^3J_{\mathrm{H-Si-CH}} = 3.5$ (3.8) Hz, $J_{\mathrm{Si-H}} = 182.5$ (183.8) Hz, 1H; δ 0.004 (0.20), d, $^3J_{\mathrm{H-Si-CH}} = 4.0$ Hz, 9H; ^{13}C δ −2.71 (−2.65); ^{29}Si δ −16.12 (−16.34). Resonances due to the three CpBeX species and Me$_3$SiH accounted for 97% of the total proton NMR intensity. The relative molar ratios based on the integrated intensities of the SiMe$_3$ resonances (or the Me resonance in the case of CpBeMe) were 37.5 (X = SiMe$_3$):3.1 (X = Me):2.4 (X = SiMe$_2$SiMe$_3$):1.0 (Me$_3$SiH). After an additional 25 days at 217−224 °C, ca. 85% of the total proton NMR intensity was due to the four aformentioned species. The molar ratios were 4.3:3.5:1.2:1.0. The remaining 15% of the 1H NMR intensity was distributed among numerous small resonances in the Cp, Si−Me, Si−H, and CpBe−*Me* δ regions. Also observed were resonances consistent with the presence of SiMe$_3$SiMe$_2$H: ^{1}H δ 3.90, septet, $^3J_{\mathrm{H-Si-CH}} = 4.5$ Hz, 1H, δ 0.10, d, $^3J_{\mathrm{H-Si-CH}} =$ 4.0 Hz, 6H, δ 0.078, s, 9H; ^{29}Si δ −18.9, −39.1. The ^{1}H NMR intensity of the Si−H multiplet was 14% of that of Me$_3$SiH. Beryllium-9 NMR spectra exhibited resonances due to the three beryllium species in question, along with a peak at −21.81 comprising ca. 4% of the total intensity.

Cyclopentadienyl(pentamethyldisilyl)beryllium. Bis(cyclopentadienyl)beryllium, 0.080 g (0.58 mmol), was condensed into a 5 mm NMR tube on a high-vacuum line, then removed to a nitrogen-filled drybox for addition of 0.060 g (0.75 mmol) of BeCl$_2$. The two solids began to liquefy upon contact, forming a viscous slush. After standing overnight, ∼20 mg (0.25 mmol) of twice-recrystallized LiSiMe$_3$ was added, and the contents of the tube were heated momentarily with a heat gun. The tube was then fitted with a high-vaccum stopcock and removed to a glass high-vacuum line, where ∼0.5 mL of dry C$_6$D$_6$ was condensed in and the tube flame-sealed under vacuum. Species identified by means of multinuclear NMR included CpBeCl[46] (^{9}Be δ −18.79; ^{13}C δ 105.11; ^{1}H δ 5.75); CpBeMe;[46] CpBe(SiMe$_3$); and CpBe(SiMe$_2$SiMe$_3$) (NMR data are presented in Tables 4 and 5). Cyclopentadienylberyllium chloride remained in excess, while approximately equivalent amounts of the other CpBeX (X = SiMe$_3$, Me, SiMe$_2$SiMe$_3$) species were formed (^{9}Be NMR integration).

Acknowledgment. This work was financially supported by the Materials Research Science and Engineering Center at the University of Wisconsin, Madison. NMR instrumentation was supported by the National Science Foundation (CHE-8306121, CHE-8813550, CHE-9629688) and the National Institutes of Health (ISI-ORRO2388-01). We are indebted to Professor Frank Weinhold for the theoretical results and insights therein, and Professors Don Gaines and Larry Dahl for advice and helpful discussions.

Supporting Information Available: Tables listing crystallographic data for CpBe(SiMe$_3$). This material is available free of charge via the Internet at http://pubs.acs.org.

OM0201720

---

[46] Proton, ^{13}C, and ^{9}Be NMR chemical shift data for CpBeMe and CpBeCl were essentially identical to those of authentic samples. Proton and ^{9}Be data are also available in the literature: Drew, D. A.; Morgan, G. L. *Inorg. Chem.* **1977**, *16*, 1704.

[47] Hunter, B. K.; Reeves. L. W. *Can. J. Chem.* **1968**, *46*, 1399.