Syntheses and Structures of the First Heavy Alkaline Earth Metal Bis(tris(trimethylsilyl))silanides

Weijie Teng and Karin Ruhlandt-Senge*

Department of Chemistry, 1-014 Center for Science and Technology, Syracuse University, Syracuse, New York 13244-4100

The first heavy alkaline earth metal bis(tris(trimethylsilyl))silanides were obtained in high yield and purity by a straightforward metathesis reaction involving the treatment of potassium tris(trimethylsilyl)silanide, $K(THF)_n Si(SiMe_3)_3$, with calcium, strontium, and barium iodides. The addition of specific donors provided either contact or separated species in the solid state, whereas in aromatic solvents the compounds dissociate into separated ions, as shown by ^{29}Si NMR spectroscopic studies. We here report on the syntheses and characterization of compounds displaying M–Si bonds in the solid state with the general formula of $M(THF)_n(Si(SiMe_3)_3)_2$ (M = Ca, n = 3, **1**; Sr, n = 3, **2**; and Ba, n = 4, **3**) and $Sr(TMEDA)(THF)(Si(SiMe_3)_3)_2$, **4** (TMEDA = N,N,N',N'-tetramethylethylenediamine). Compound **5**, $[Ba(HMPA)_6][(Si(SiMe_3)_3)_2]$, displays separated ions, while **6**, $[Ba(18\text{-crown-}6)(Si(SiMe_3)_3)_2][Ba(HMPA)_6][(Si(SiMe_3)_3)_2]$, is a rare example containing both contact and separated ions in the asymmetric unit. All compounds were characterized using X-ray crystallography, ^1H, ^{13}C, and ^{29}Si NMR, and IR spectroscopy.

Introduction

The organometallic chemistry of the heavy alkaline earth metals is slowly emerging from obscurity with a small but increasing number of well-characterized compounds, as summarized in some recent review articles.[1] Progress in this area of chemistry has been held back by the high reactivity, lability, and often low solubility of the target compounds.[2]

A critical task in the further development of the organometallic chemistry of calcium, strontium, and barium remains the identification of straightforward synthetic access routes and viable ligand, donor, and solvent systems. As such, model studies on less reactive, but closely related systems, such as the heavier group 14 ligand systems are an important tool to promote the further development of this emerging area of organometallic chemistry.

Alkaline earth metal silanides not only serve as model compounds for the more reactive organometallic congeners but also have been recognized in a patent application as effective initiators in the polymerization of acrylonitrile.[3] Specifically, $Ca(SiMe_3)_2$, $(i\text{-}Pr_3)SiSrSiMe_3$, and $(i\text{-}Pr)_3SiBaSiMe_3$ have been mentioned, but no information on synthetic access and spectroscopic and structural details or even exact molecular composition

is available, thus eluding the further advancement of this application.

Examples of well-characterized alkaline earth metal derivatives bearing heavy group 14 ligands are scarce and are mainly limited to magnesium. Examples include $Mg(DME)(SiMe_3)_2$ (DME = 1,2-dimethyloxyethane),[4] $Mg(THF)_2Br(Si(SiMe_3)_3)$,[5] $Mg(THF)_2(Si(SiMe_3)_3)_2$,[5] $Mg((CH_3)_2NCH_2CH_2CH_2N(CH_3)_2)(SiMe_3)_2$,[6] $[Mg(TMEDA)Br(SiMe_3)]_2$,[7] $Mg(TMEDA)(SiMe_3)_2$,[8] and $Mg(DME)_2(GeMe_3)_2$.[9] Examples of heavier alkaline earth metal derivatives exhibiting metal–ligand bonds are limited to a small number of germanides, namely, $M(THF)_n(Ge(SiMe_3)_3)_2$ (M = Ca, Sr, n = 3; M = Ba, n = 4), prepared by this group,[10] and stannides, including $Ca(THF)_4(SnMe_3)_2$[11] and $Ba(Sn(O^tBu)_3)_2(Cr(CO)_5)_2$.[12] Compounds containing both alkaline earth metal and silicon, germanium, or tin fragments in one structure include $Ba[(Pz^*)_3Ge]_2 \cdot 0.5$dioxane ($Pz^*$ = 3,5-dimethylpyrazol-1-yl),[13] $[Ba(HMPA)_2(18\text{-crown-}6)][(SnPh_3)_2]$, and $[M(HMPA)_2(18\text{-crown-}6)][(Sn(SnPh_3)_3)_2]$, M = Ca, Sr (HMPA = hexamethylphosphoramide), but no contacts between metal and group 14 element were detected in

* Corresponding author. Phone: 315-443-1306. Fax: 315-443-4070. E-mail: kruhland@syr.edu.

(1) For recent review see: (a) Hanusa, T. P. *Coord. Chem. Rev.* **2000**, *210*, 329. (b) Alexander, J. S.; Ruhlandt-Senge, K. *Eur. J. Inorg. Chem.* **2002**, *11*, 2761, and references therein.
(2) See for example: (a) Coles, M. A.; Hart, F. A. *J. Organomet. Chem.* **1971**, *32*, 279. (b) Weeber, A.; Harder, S.; Brintzinger, H. H. *Organometallics* **2000**, *19*, 1325. (c) Alexander, J. S.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2658.
(3) Shizuka, O.; Kunio, H. (Jpn. Kokai Tokkyo Koho). Preparation of high-molecular weight stereoregular polyacrlonitrile. Patent No. JP 0306806, 1991.

(4) (a) Rösch, 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. Chem. Soc.* **1977**, *99*, 1797.
(5) Farwell, J. D.; Lappert, M. F.; Marschner, C.; Strissel, C.; Tilley, T. D. *J. Organomet. Chem.* **2000**, *603*, 185.
(6) Rösch, L.; Pickardt, J.; Imme, S.; Börner, U. *Z. Naturforsch. B* **1986**, *41*, 1523.
(7) Goddard, R.; Krüger, C.; Ramadan, N. A.; Ritter, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1030.
(8) Goebel, D. W., Jr.; Hencher, J. L.; Oliver, J. P. *Organometallics* **1983**, *2*, 746.
(9) Rösch, L.; Krüger, C.; Chiang, A.-P. *Z. Naturforsch. B* **1984**, *39*, 855.
(10) Teng, W.; Ruhlandt-Senge, K. *Organometallics* **2004**, *23*, 952.
(11) Westerhausen, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1493.
(12) Veith, M.; Weidner, S.; Kunze, K.; Kafer, D.; Hans, J.; Huch, V. *Coord. Chem. Rev.* **1994**, *137*, 297.
(13) Steiner, A.; Stalke, D. *Inorg. Chem.* **1995**, *34*, 4846.

the solid state.[14] Recently, our group communicated the synthesis of a family of barium silanides where the addition of specific donors afforded contact or separated species in the solid state.[15] These compounds have been included in this publication as compounds **3**, **5**, and **6** together with a group of novel calcium and strontium silanides to afford a detailed view of alkaline earth metal silanides chemistry.

The $Si(SiMe_3)_3^-$ ligand, commonly called hypersilanide, has been widely recognized in connection with numerous transition and main group elements.[16,17] Advantages of this ligand system are based on the ease of preparation, the high solubility of products even in hydrocarbon solvents, and large steric demand, providing the critical kinetic stabilization to allow the formation of the resulting metal complexes.[18] This was shown impressively by Klinkhammer with a series of dimeric alkali metal hypersilanides $[MSi(SiMe_3)_3]_2$ (M = Li, Na, K, Rb, Cs).[19] While highly reactive, the alkali metal derivatives displayed good solubility properties in a wide range of solvent systems and tolerated the use of ethereal solvents without indication of ether cleavage reactions. As such, the hypersilanides seemed perfectly suited for the preparation of heavy alkaline earth metal silanides.

We here report the first family of heavy alkaline earth metal hypersilanides with the general formula $M(THF)_n(Si(SiMe_3)_3)_2$ (M = Ca, $n = 3$, **1**; Sr, $n = 3$, **2**; and Ba, $n = 4$, **3**). To investigate the effect of different donors on solution and solid-state structures, several different donor systems were introduced. Use of TMEDA resulted in the formation of $Sr(TMEDA)(THF)(Si(SiMe_3)_3)_2$, **4**, which displays together with compounds **1**−**3** contact molecules with M−Si bonds in the solid state. In contrast, compound **5**, $[Ba(HMPA)_6][(Si(SiMe_3)_3)_2]$, obtained by the addition of HMPA, exhibits separated ions. We also report on $[Ba(18\text{-crown-}6)(Si(SiMe_3)_3)_2][Ba(HMPA)_6][(Si(SiMe_3)_3)_2]$, **6**, a rare example with both contact molecules and separated ions in the solid state. In aromatic solvents, all compounds dissociate into separated ions, as shown by extensive NMR studies.

Results and Discussion

Synthetic Aspects/Reactivity. All compounds were prepared in high yields and purity by straightforward metathesis chemistry involving treatment of the appropriate alkaline earth metal iodides with 2 equiv of potassium hypersilanide $K(THF)_nSi(SiMe_3)_3$ in THF (eq 1). The synthetic routes differed only by the choice of specific donors that were introduced into the reaction mixture.

$$MI_2 + 2KSi(SiMe_3)_3 \xrightarrow{\text{donor}}$$
$$M(\text{donor})_n(Si(SiMe_3)_3)_2 + 2KI \quad (1)$$
$$M = Ca, Sr, Ba$$
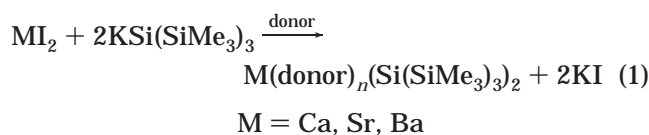
The potassium silanide reagent was prepared in situ by treating $Si(SiMe_3)_4$ with potassium *tert*-butoxide, affording the reagent in good yield and purity.[20] The quality of potassium silanide is dependent on the purity of potassium *tert*-butoxide. If lower quality reagent is employed, only an incomplete reaction under formation of a mixed complex between potassium silanide and potassium *tert*-butoxide is observed. This complex precipitates out of the reaction mixture.[18] A large quantity of potassium silanide was prepared and stored under inert gas. An appropriate amount was dissolved in THF and combined with alkaline earth metal iodides dissolved in THF. The target compounds formed immediately, as evidenced through the formation of a white precipitate, identified as KI. In the presence of THF the target compounds decomposed rapidly involving $SiMe_3$ group migration under formation of $Si(SiMe_3)_4$, as evidenced by ^1H NMR studies (δ (C_6D_6) = 0.27 ppm). Also observed was a black powder, presumably elemental silicon. Since a homogeneous metathesis reaction requires the presence of THF, due to the limited solubility of the alkaline earth metal iodides in hydrocarbons and diethyl ether, the necessary contact to THF was limited to the minimum time needed for the reaction to proceed in acceptable yields. THF was then removed in a vacuum, and the reaction mixtures extracted with hexanes.

Similar chemistry has been observed previously. $SiMe_3$ migration in the presence of THF is responsible for the decomposition of the germanides $M(THF)_n(Ge(SiMe_3)_3)_3$ (M = Ca, Sr, Ba) into $Ge(SiMe_3)_4$, elemental germanium, and unidentified products.[10] Similarly SiR_3 group (R = Ph, Me) migration was responsible for the formation of complex product mixtures in the reaction of R_3SiSiR_3 with elemental calcium, strontium, and barium in THF/NH_3 mixtures.[21] Analogously, $SnPh_3$ group migration was identified in the decomposition of $M(SnPh_3)_2$ (M = Ca, Sr) under concurrent formation of $M(Sn(SnPh_3)_3)_2$, $Sn(SnPh_3)_4$, $SnPh_4$, and elemental Sn.[14] Likewise, $Li(PMDTA)PbPh_3$ (PMDTA = N,N,N,N',N'-pentamethyldiethylenetriamine) decomposes rapidly under formation of a black powder, presumably elemental lead and other unidentified reaction products.[22]

The preparation of the target molecules by metathesis chemistry affords a clean, straightforward route toward the target compounds, without the need to handle mercury and its compounds, as used in the preparation of the related alkali metal hypersilanides.[19] This transmetalation method proceeds smoothly due to the low melting points of the alkali metals; however, the higher melting points of the alkaline earth metals make analogous alkaline earth metal chemistry difficult. An alternative route to alkali metal silanides is metal exchange involving the treatment of lithium silanides with the appropriate alkali metal *tert*-butoxides.[18] This route has been established for the preparation of heavy

(14) Englich, U.; Ruhlandt-Senge, K.; Uhlig, F. *J. Organomet. Chem.* **2000**, *613*, 139.

(15) Teng, W.; Englich, U.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3661.

(16) See for example: (a) Klinkhammer, K. W.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1209. (b). Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1334.

(17) See for example: (a) Wochele, R.; Schwarz, W.; Klinkhammer, K. W.; Weidlein, J. *Z. Anorg. Allg. Chem.* **2000**, *626*, 833. (b) Henkel, S.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 681.

(18) Jenkins, D. M.; Teng, W.; Englich, U.; Stone, D.; Ruhlandt-Senge, K. *Organometallics* **2001**, *20*, 4600.

(19) Klinkhammer, K. W. *Chem. Eur. J.* **1997**, *3*, 1418.

(20) Marschner, C. *Eur. J. Inorg. Chem.* **1998**, 221.

(21) Jenkins, D. M.; Ruhlandt-Senge, K. Unpublished results.

(22) Armstrong, D. R.; Davidson, M. G.; Moncrieff, D.; Stalke, D.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1992**, 1413.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Alkaline Earth Metal Hypersilanides 1−6

compound	M−Si (Å)	M−donor (Å)	Si−Si (Å) (av)	Si−Si−Si (deg) (av)	Si−M−Si (deg)
Ca(THF)$_3$(Si(SiMe$_3$)$_3$)$_2$, **1**	3.042(9), 3.086(9)	2.348(2)^a, 2.355(2)^a, 2.389(2)^a	2.344	101.75	125.53(3)
Sr(THF)$_3$(Si(SiMe$_3$)$_3$)$_2$, **2**	3.167(1), 3.224(1)	2.507(3)^a, 2.512(4)^a, 2.541(4)^a	2.317	102.59	122.23(4)
Ba(THF)$_4$(Si(SiMe$_3$)$_3$)$_2$, **3**	3.419(1), 3.462(1)	2.717(3)^a, 2.743(3)^a, 2.746(3)^a	2.339	102.59	140.62(3)
Sr(TMEDA)(THF)(Si(SiMe$_3$)$_3$)$_2$, **4**	3.195(1), 3.251(1)	2.536(3)^a, 2.696(3)^b, 2.709(3)^b	2.348	104.12	123.51(3)
[Ba(HMPA)$_6$][Si(SiMe$_3$)$_3$)$_2$], **5**	NA	2.647^d (av)	2.326	99.01	NA
[Ba(18-crown-6)Si(SiMe$_3$)$_3$)$_2$]· [Ba(HMPA)$_6$][Si(SiMe$_3$)$_3$)$_2$], **6**	3.644(4)	2.779(4)^c, 2.621(4)^d	2.399(3)^e, 2.322(2)^f	103.39(1)^e, 100.53(7)^f	180.0

^{a} THF. ^{b} TMEDA. ^{c} 18-Crown-6. ^{d} HMPA. ^{e} Contact molecule. ^{f} Separated ions.

Table 2. Crystallographic Data for Compounds 1−6

	1	2	3	4	5	6
formula	C$_{30}$H$_{78}$CaO$_3$Si$_8$	C$_{30}$H$_{78}$O$_3$Si$_8$Sr	C$_{34}$H$_{86}$BaO$_4$Si$_8$	C$_{28}$H$_{78}$N$_2$OSi$_8$Sr	C$_{54}$H$_{162}$BaN$_{18}$O$_6$-P$_6$Si$_8$	C$_{84}$H$_{240}$Ba$_2$N$_{18}$O$_{12}$-P$_6$Si$_{16}$
fw	751.72	799.26	921.09	771.26	1707.90	2604.88
a (Å)	18.7358(9)	18.7185(8)	19.157(3)	18.9384(11)	19.1916(15)	17.4605(6)
b (Å)	14.9665(7)	15.1465(6)	17.219(3)	15.0194(9)	19.6364(15)	17.4605(6)
c (Å)	16.9897(9)	17.1385(7)	31.602(5)	16.7505(10)	14.3466(11)	84.697(5)
α (deg)					71.4910(10)	
β (deg)					71.2320(10)	
γ (deg)					81.048(2)	
V (Å^3)	4764.1(4)	4859.1(3)	10424(3)	4764.6(5)	4845.7(6)	22362.1(16)
Z	4	4	8	4	2	6
space group	$Pna2(1)$	$Pna2(1)$	$Pbca$	$Pna2(1)$	$P\bar{1}$	$R\bar{3}c$
d_{calc} (g/cm^3)	1.048	1.093	1.174	1.075	1.171	1.161
linear abs coeff (mm^{-1})	0.358	1.331	0.975	1.354	0.655	0.767
T (K)	94	88	98	86	91	85
2θ range (deg)	4.22−66.32	3.58−56.00	3.34−56.60	3.64−56.00	3.26−50.30	2.88−50.48
no. of indep reflns	16 901	11 680	12 693	11 502	17 241	4313
no. of params	380	379	442	363	1420	219
R1, wR2 (all data)	0.0628, 0.1162	0.0571, 0.1341	0.0522, 0.0891	0.0414, 0.0926	0.0693, 0.1740	0.0541, 0.1290
R1, wR2 (>2σ)	0.1029, 0.1315	0.0735, 0.1438	0.0978, 0.1011	0.0617, 0.1025	0.1086, 0.1991	0.1062, 0.1416

alkali metal silanides due to the availability of the metal *tert*-butoxides, but similar chemistry has not yet been successfully applied for the alkaline earth metals, due to difficulties obtaining good quality alkaline earth metal *tert*-butoxides devoid of free alcohol, hydroxide, or oxide.[23] As such, metathesis remains the most attractive option for the preparation of the target compounds.

Compounds **1**−**6** are highly sensitive to oxygen and moisture. Generally, reactivity increases upon descending group 2, making the barium compound **3** significantly more reactive than the calcium analogue **1**. In addition, the reactivity of the separated ions is higher than that of the contact molecules, rendering compound **5** the most reactive of the series. In fact, **5** decomposes violently upon contact with air, requiring extremely careful handling conditions.

Spectroscopic Studies. All compounds were characterized using ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectroscopy, confirming the identity of all compounds. The low solubility of the barium species **3**, **5**, and **6** did not allow the observation of the signals for the quaternary silicon atom *Si*(SiMe$_3$)$_3$ in the ^{29}Si NMR spectra, which would provide the most direct information on solvation and ligation. We were unable to observe these signals even after extended run times (24 h) on a 500 MHz spectrometer using a wide bore probe (10 mm) applying DEPT or ZG techniques. This might be due to the low sensitivity of the quaternary silicon atom paired with

the low solubility of the target compounds in [D$_6$]-benzene or [D$_8$]toluene. Use of THF, in which the solubility of the compounds is higher, results in rapid decomposition under SiMe$_3$ group migration and formation of Si(SiMe$_3$)$_4$, as confirmed by ^{1}H and ^{29}Si NMR spectroscopic studies in [D$_8$]THF.

^{29}Si NMR studies show the chemical shifts of [Si(*Si*Me$_3$)]$^-$ signals in close proximity, indicating the formation of identical species upon dissolution, independent of the ion association in the solid state. Moreover, the chemical shifts for the SiMe$_3$ groups in **1**−**6** are in close proximity to those for the alkali metal hypersilanides, where the formation of separated species upon dissolution in aromatic solvents was proposed.[18] Considering the proximity of chemical shifts and the effective coordination of the heavy alkaline earth metals to aromatic solvents,[24] the formation of separated ions upon dissolution in [D$_6$]benzene is proposed. This view is further supported by the similar solid-state anion geometries in all silanides (see Table 1) regardless of their nature as contact molecules or separated ions. The pyramidal nature of the central silicon atom suggests a significant transfer of charge from the cation to the anion, thus facilitating dissociation upon dissolution.

Structural Aspects. Crystallographic information and data collection parameters for compounds **1**−**6** are summarized in Table 2 and the Experimental Section. A compilation of selected geometrical parameters for all

(23) Gomez, E.; Guino-o M.; Newlon, A.; Taylor, J.; Teng, W.; Vargas, W.; Zuniga, M.; Ruhlandt-Senge, K. In preparation.

(24) (a) Deacon, G. B.; Forsyth, C. M.; Junk, P. C. *J. Organomet. Chem.* **2000**, *607*, 112. (b) Chadwick, S.; Englich, U.; Ruhlandt-Senge, K. *Organometallics* **1997**, *16*, 5792.
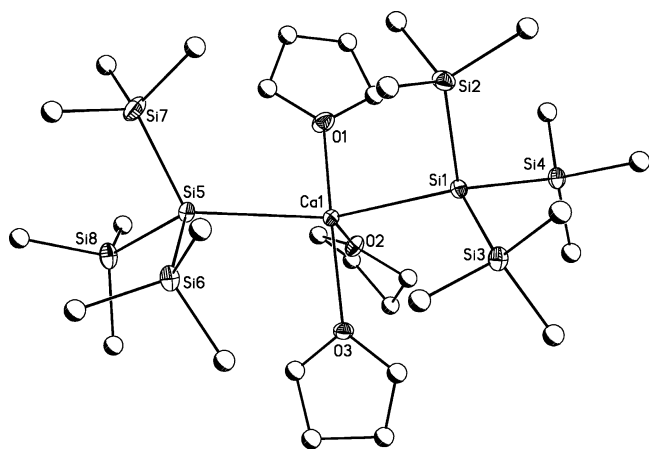
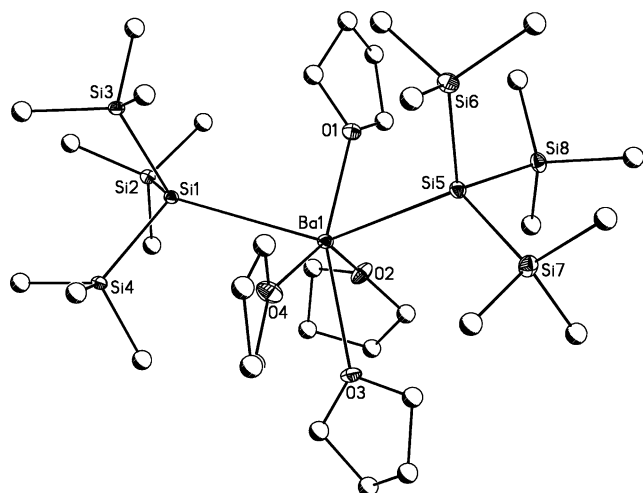**Figure 1.** Crystal structure of compound **1**. Hydrogen atoms have been omitted for clarity.

Figure 2. Crystal structure of compound **3**. Hydrogen atoms have been omitted for clarity.
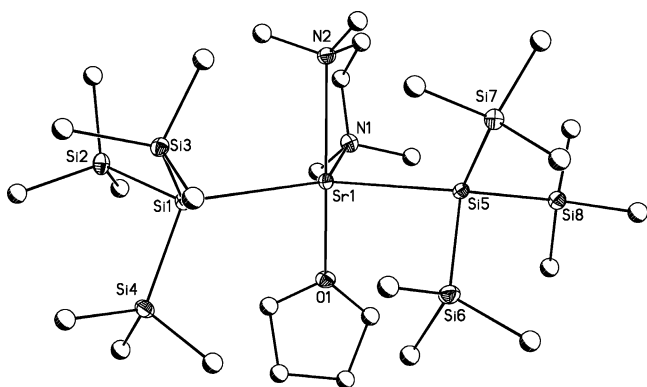

Figure 3. Crystal structure of compound **4**. Hydrogen atoms have been omitted for clarity.

compounds is given in Table 1. Compounds **1**, **3**, **4**, and **5** are shown in Figures 1−4, respectively; an illustration of compound **6** can be found on the table of contents page.

Compounds **1**−**4** all display metal−silicon bonds in the solid state. Of those, compounds **1** (Figure 1), **2**, and **4** (Figure 3) are five-coordinate, while the barium derivative **3** (Figure 2) is six-coordinate by addition of an extra donor to saturate the metal coordination sphere. Compounds **1**, **2**, and **4** display very similar coordination geometries and will be described together.
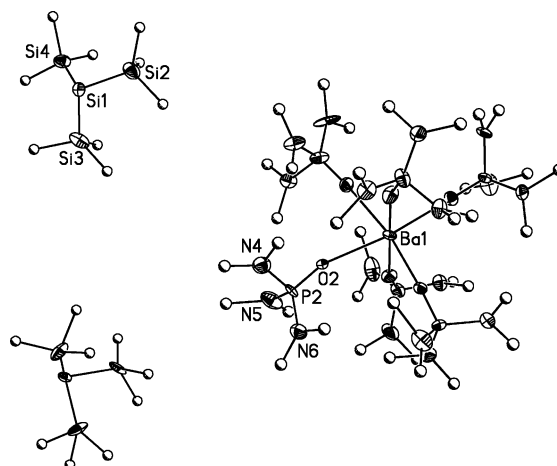

Figure 4. Crystal structure of compound **5**. Hydrogen atoms and disordered positions have been omitted for clarity.

The metal coordination environment is a distorted trigonal bipyramid with the sterically demanding silanides in the equatorial plane and the less bulky donors in the third equatorial and the two axial positions. In compound **4** the bidentate TMEDA spans to occupy one equatorial and one axial position. The trans angles reflect the degree of distortion from ideal trigonal bipyramidal geometry with 154.59(8)° in **1**, 149.52(1)° in **2**, and 145.00(9)° in **4**. The large distortion from ideal geometry in **4** is due to the TMEDA bridging axial and equatorial positions, as expressed by the narrow N−Sr−N angle of 67.12(1)°. Metal−silicon and −oxygen distances are 3.064(2) Å (av) and 2.364(6) Å (av) for **1** and 3.195(3) Å (av) and 2.520(1) Å (av) for **2**. The strontium−silicon, −oxygen, and −nitrogen distances in **4** are 3.223(1) Å (av), 2.536(3) Å, and 2.703(3) Å (av), respectively. The Si−M−Si angles reflect their position in the equatorial plane with 125.53(3)° for **1**, 122.23(4)° for **2**, and 123.51(3)° for **4**. The angle sums of the central silicon atoms indicate their considerable pyramidal character with 305.25° (av) for **1**, 307.77° (av) for **2**, and 304.98° (av) for **4**.

Compound **3**, shown in Figure 2, displays a distorted octahedral geometry with Ba−Si and Ba−O bond lengths of 3.440(2) Å (av) and 2.738(1) Å (av). The deviation from ideal octahedral geometry is significant, with a Si−Ba−Si angle of 140.62(3)° and O−Ba−O angles as small as 71.69(9)°. The Si−Si−Si angle sums represent the pyramidal character of the central silicon atom.

The alkaline earth metal silanides **1**−**4** and germanides $M(THF)_n(E(SiMe_3)_2)_2$ (M = Ca, E = Si, Ge, n = 3; M = Sr, E = Si, Ge, n = 3; M = Ba, E = Si, Ge, n = 4)[10] display very similar structural features. Especially striking are the almost identical metal−silicon and −germanium distances (see Table 3). The initially surprising fact that the metal−silicon distances are slightly longer than the metal−germanium bond lengths, despite the smaller silicon radius (ionic radius Si^{4+} (CN = 4) = 0.40 Å, Ge^{4+} (CN = 4) = 0.53 Å),[25] can be explained by the increased polar character in the alkaline earth metal germanium bond, as reflected by the higher electronegativity of germanium (Allred Roch-

(25) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

**Table 3. Selected Bond Distances (Å) for
Compounds 1−3 and the Corresponding
Germanides**

compound	M−Si/M−Ge (Å)
Ca(THF)$_3$(Si(SiMe$_3$)$_3$)$_2$, **1**	3.042(9), 3.086(9)
Ca(THF)$_3$(Ge(SiMe$_3$)$_3$)$_2$	3.022(2), 3.067(2)
Sr(THF)$_3$(Si(SiMe$_3$)$_3$)$_2$, **2**	3.167(1), 3.224(1)
Sr(THF)$_3$(Ge(SiMe$_3$)$_3$)$_2$	3.147(5), 3.198(5)
Ba(THF)$_4$(Si(SiMe$_3$)$_3$)$_2$, **3**	3.419(1), 3.462(1)
Ba(THF)$_4$(Ge(SiMe$_3$)$_3$)$_2$	3.398(9), 3.431(9)

ow electronegativity Si = 1.74, Ge = 2.02).[26] Due to the almost identical metal−silicon and −germanium bond lengths and consequent similar ligand steric requirements, it is not surprising that the overall structural features in the silanides and germanides are very similar. For example, the E−M−E (E = Si, Ge) angles are almost identical with 125.53(3)° for **1** and 125.43(6)° for the corresponding germanide. This trend continues for the strontium and barium derivative with Si−M−Si angles of 122.23(4)° for **2** and 140.62(3)° for **3** and values for the germanides at 122.11(2)° and 140.52-(2)°. Similar trends are also found in earlier work by Mallela and Geanangel, who compared cone angles in a series of Sn-E(SiMe$_3$)$_3$ (E = Si, Ge) compounds. They concluded that despite the larger germanium radius, the cone angles of the silanides and germanides are essentially similar, and thus the steric influence of both ligands is not significantly different.[27] This argument is further supported by comparing the structural features of a series of lithium silanides and germanides Li(THF)$_3$E(SiMe$_3$)$_3$ (E = Si,[28,29] E = Ge[30]), where essentially similar Li−Si (2.669(1) Å[28] and 2.644(1) Å[29]) and Li−Ge distances (2.666(6) Å) were observed.

The trans angles in compounds **1−3** are in good agreement with those for the isomorphous germanides with 155.1(2)° and 150.13(1)° for the distorted trigonal bipyramidal   Ca(THF)$_3$(Ge(SiMe$_3$)$_3$)$_2$ and Sr(THF)$_3$(Ge(SiMe$_3$)$_3$)$_2$ and the distorted octahedral Ba(THF)$_4$(Ge(SiMe$_3$)$_3$)$_2$ (140.52(2)°).[10] Interestingly, the angle decreases when descending group 2. Analogous structural trends in regards to trans angle compression have been observed previously in alkaline earth metal chemistry, and routinely, trans angles as low as 132° are observed.[31]

Compound **5**, shown in Figure 4, consists of separated ions. The cation displays a slightly distorted octahedral environment with O−Ba−O angles ranging from 82.4(4)° to 98.2(3)° and trans angles from 169.1(3)° to 176.82(2)°. The separated silanide anions display significant pyramidal geometry with the angle sums at the central Si of 297.02° (av).

Due to severe crystallographic disorder in **5**, the reaction was repeated, and 18-crown-6 and HMPA were added to the reaction mixture with the intent to form the previously observed, stable [Ba(18-crown-6)(HM-

PA)$_2$]$^{2+}$ cation in conjunction with separated silanide anions.[14] Past research has shown that the combination of crown ether and HMPA ensures the formation of separated ions even in the large barium cations. Examples for this motif are thiolates and selenolates,[32] stannides   [M(HMPA)$_2$(18-crown-6)][(Sn(SnPh$_3$)$_3$)$_2$], (M = Ca, Sr) or [Ba(HMPA)$_2$(18-crown-6)][(SnPh$_3$)$_2$],[14] and organometallics [M(HMPA)$_2$(18-crown-6)][CPh$_3$]$_2$ (M = Sr, Ba).[2c,33]

Remarkably, compound **6**, containing both separated ions [Ba(HMPA)$_6$][Si(SiMe$_3$)$_3$]$_2$ and contact molecules Ba(18-crown-6)(Si(SiMe$_3$)$_3$)$_2$, was obtained. After the initial isolation of compound **6** in low yields, the reaction was repeated using the exact equivalent amount of donors to verify the reproducible formation of compound **6**.

The separated ion in **6** essentially displays the same geometry as described for compound **5**. In the contact species, the barium is situated on a 6-fold rotation axis and is coordinated by an 18-crown-6 macrocycle and two silanides, of which the space group symmetry demands occupancy of barium at one-sixth and one-third for the anion. Consequently, one-sixth of the crown ether is crystallographically independent. The 6-fold rotation axis is also responsible for the Si−Ba−Si angle of 180°. The Ba−Si and Ba−O distances are 3.644(4) and 2.779(4) Å. The sum of angles at the central Si is 310.17° (av).

The formation of contact molecules or separated ions in the solid state can be rationalized by the coordination of different donors to the metal. If THF is used, as seen in compounds **1−3**, contact molecules are obtained. To map the preferred metal coordination environment, various amounts of TMEDA were added to a solution containing compound **2**. As expected, the bidentate TMEDA coordinates to the metal center. Curiously though, only one TMEDA replaces two THF molecules under retention of the five-coordinate distorted trigonal bipyramidal geometry, yielding compound **4**. This situation does not change, even if a large excess of TMEDA is utilized, and a hypothetical six-coordinate Sr(TMEDA)$_2$-(Si(SiMe$_3$)$_3$)$_2$ is not identified. This result confirms the large steric demand of the silanide ligand, preventing an increase in coordination number. In contrast, addition of the strong, sterically demanding donor HMPA affects the separation of ions, under formation of the stable [Ba(HMPA)$_6$]$^{2+}$ cation, as demonstrated in compound **5** and the separated ion in **6**.

The observation of both contact molecules and separated ions in compound **6** was unexpected. It was believed that the large steric demand of the silanide anion in combination with crown ether would prevent the formation of a contact molecule due to steric arguments. Apparently though, a weak Ba−Si bond is formed, as evidenced by the long Ba−Si contacts (3.645-(4) Å). A comparison with compound **3**, where four THFs fill the equatorial plane, indicated a stronger, shorter Ba−Si bond (3.440(9) Å (av)), probably due to a reduced amount of steric repulsion. A comparison of barium thiolates and selenolates with either four THF or one crown ether occupying the equatorial plane of the

(26) Allred, A. L.; Rochow, E. G. *Inorg. Nucl. Chem.* **1958**, *5*, 264.
(27) Schwan, F.; Mallela, S. P.; Geanangel, R. A. *J. Chem. Soc., Dalton Trans.* **1996**, 4183.
(28) Dias, H. V. R.; Olmstead, M. M.; Ruhlandt-Senge, K.; Power, P. P. *J. Organomet. Chem.* **1993**, *462*, 1.
(29) Heine, A.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *Inorg. Chem.* **1993**, *32*, 1694.
(30) Freitag, S.; Herbst-Irmer, R.; Lameyer, L.; Stalke, D. *Organometallics* **1996**, *15*, 2839.
(31) Green, D. C.; Englich, U.; Alexander, J. S.; Ruhlandt-Senge, K. Unpublished results.

(32) Ruhlandt-Senge, K.; Englich, U. *Chem. Eur. J.* **2000**, *6*, 4063.
(33) Alexander, J. S.; Ruhlandt-Senge, K. *Organometallics* **2003**, *22*, 4933.

molecule showed only a minor bond elongation upon replacing the four THF donors by one crown ether.[32] The influence of the increased coordination number (six vs eight) seems to be minor, and the space requirement of four THF donors and one crown ether seems fairly comparable. However, if the metal size is reduced, the difference between the steric demand of the crown ether or THF donors becomes significant, and in the presence of 18-crown-6 typically separated ions are observed. An apparent exception is the crown ether encapsulated calcium thiolate Ca(18-crown-6)(S-2,4,6-^{t}Bu$_3$C$_6$H$_2$)$_2$, displaying weak Ca−S bonds due to significant steric repulsion between the crown and the ligands, as expressed by Ca−S bonds of quite different lengths (2.775(3) and 2.851(2) Å) and significantly different Ca−S−C angles, of which one is unusually large (119.1(2)° and 154.0(3)°).[34] However, if the less sterically demanding chalcogenolates are replaced by the larger hypersilanide ligand, the more conformationally flexible THF donors reduce the steric repulsion between donor and ligand.

The barium and crown ether oxygen bonds in the contact molecule in **6** are very short (2.779(4) Å (av)). In fact, the Ba−O (crown) bonds are very similar to those in any of the previously reported [Ba(HMPA)$_2$(18-crown-6)]$^{2+}$ dications, where Ba−O contact bonds between 2.770(2) and 2.810(1) Å were observed.[14] In the [Ba(HMPA)$_6$]$^{2+}$ cation, as observed in compounds **5** and **6**, the Ba−O bonds are also short (2.621(4) Å (av) **6**; 2.641(6) Å (av) **5**), but slightly elongated as compared to the barium−oxygen(HMPA) distances in the [Ba(HMPA)$_2$(18-crown-6)][(SnPh$_3$)$_2$] cation, where typically Ba−O bond lengths of 2.5−2.6 Å are found.[14] Apparently, the steric demand of a 18-crown-6 macrocycle is smaller than that of four HMPA donors.

Compounds **1**−**6** exhibit significant pyramidicity at the central silicon atom, with Si−Si−Si angles around 100° (see Table 1). No discernible trend could be identified, differentiating either contact molecules or separated ions or within the group of alkaline earth metals. Klinkhammer discussed a slight Si−Si−Si angle compression upon descending the group of alkali metal hypersilanides, interpreted as increased metal−ligand charge transfer. With very similar values for contact molecules or separated ions, the charge transfer between cation and anion must be substantial in all cases. The separation of cation and anion, the extreme form of charge transfer, results in only minor further angle compression. This interpretation is also supported by the formation of separated ions upon dissolution in aromatic solvents, facilitated by the favorable coordination of the alkaline earth metals to aromatic solvents.[24]

The significant pyramidal nature of the anions has been observed in a range of silanides, germanides, stannides, and plumbides attached to electropositive metals. A significant bond polarization results in increased s-character at the lone pair, and consequently higher p-character in the Si−Si bond, responsible for the considerable pyramidicity. The trend becomes more significant upon descending group 14. For example, Li-(PMDTA)PbPh$_3$ displays a C−Pb−C angle of 94.3° (av),[22] Li(PMDTA)SnPh$_3$ shows a C−Sn−C angle of

96.1° (av),[35] and Li(THF)$_3$SiPh$_3$ displays a C−Si−C angle of 101.3° (av).[28]

Only few examples exist with both contact and separated ions in one crystal. Selected examples include a tetraphenyl butadiene disodium derivative[36] and a rubidium hypersilanide ([Rb(18-crown-6)$_2$][(Si(SiMe$_3$)$_3$)$_2$]-[Rb(18-crown-6)Si(SiMe$_3$)$_3$]$_2$),[18] both displaying weak, highly polar metal−ligand bonds, with a high potential for dissociation upon dissolution. Compounds **1**−**6** also display highly polar, weak metal−silicon bonds, and in the presence of an effectively coordinating donor such as benzene dissociation into separated ions occurs, as verified by NMR spectroscopic studies.

Conclusion

In summary, a family of novel heavy alkaline earth metal hypersilanides has been synthesized and characterized. It is critical to limit the exposure of the target compounds to THF since rapid decomposition under formation of Si(SiMe$_3$)$_4$ is observed. This has significant implications on their use of polymerization initiators and partly explains why only little information in regards to chemical properties and structural data was disseminated in the earlier patent application. Depending on the donor, either contact or separated ions were obtained in the solid state. We also obtained a rare compound containing both contact molecules and separated ions in the asymmetric unit. The compounds exhibit a distinct pyramidal environment at the central silicon atom, suggesting significant charge transfer from cation to anion, coinciding with a highly polar bond. This interpretation is also manifested using ^{29}Si NMR spectroscopy. Upon dissolution in C$_6$D$_6$, all compounds dissociate into separated ions. The compounds exhibit very close structural similarities to the isomorphous germanides.

Experimental Section

General Procedure. All reactions were performed under purified nitrogen atmosphere by using modified Schlenk techniques and/or a Braun Labmaster 100 drybox. Tetrahydrofuran and *n*-hexane were distilled prior to use from a Na/K alloy and freshly degassed using two freeze−pump−thaw cycles. Alkaline earth metal iodides were obtained commercially and used as received. 18-Crown-6, HMPA, and TMEDA were obtained commercially. 18-Crown-6 was purified by solvation in freshly distilled diethyl ether and stirred with finely cut sodium metal for 1 day. After filtration from excess metal, the crown was recrystallized at −20 °C from hexanes. HMPA and TMEDA were stirred over CaH$_2$ and distilled prior to use. K(THF)$_n$Si(SiMe$_3$)$_3$ was prepared following literature procedures.[20] All ^{1}H NMR and ^{13}C NMR were recorded on a Bruker DPX-300 spectrometer. ^{29}Si NMR data were recorded on a Bruker DPX-500 instrument using a wide bore probe. All NMR spectra were recorded in C$_6$D$_6$. Limited solubility of some compounds resulted in unobserved [*Si*(SiMe$_3$)$_3$]$^-$ signals in the ^{29}Si NMR spectra. Use of THF in which the compounds display higher solubility was not possible due to immediate redox reaction under formation of Si(SiMe$_3$)$_4$. Attempts to obtain elemental analysis of freshly prepared samples with clean NMR spectra failed even when expedited service was requested

(34) Chadwick, S.; Englich, U.; Noll, B.; Ruhlandt-Senge, K. *Inorg. Chem.* **1998**, *37*, 4718.

(35) Reed, D.; Stalke, D.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1459.

(36) Bock, H.; Näther, C.; Ruppert, K.; Havlas, Z. *J. Am. Chem. Soc.* **1992**, *114*, 6907.

and the samples were shipped next day. Multiple analyses were performed, but afforded significant deviations between the runs. There was no systematic deviation from theoretical values.

General Procedure for the Synthesis of Compounds 1−6. A fresh, in situ prepared solution containing 2 mmol (0.72 g) of $K(THF)_n Si(SiMe_3)_3$ in 15 mL of THF was added to 1 mmol of alkaline earth metal iodide (0.29 g of CaI_2, 0.34 g of SrI_2, and 0.39 g of BaI_2, respectively) dissolved in 25 mL of THF at room temperature. The mixture was stirred for about 45 min, upon which the solvent was removed under reduced pressure. The residue was extracted with 80 mL of hexane and filtered through a Celite-layered filter frit. The resulting clear, yellow solution was then reduced in volume to about 40 mL. To obtain compound **1−3**, the solution was then stored at −20 °C and crystals of compound **1−3** were obtained within 4 days. To obtain compound **4**, 1.33 mmol (0.20 mL) of TMEDA was added dropwise by syringe. The solution was stirred for 2 h and transferred to a clean flask. Experimental details for compounds **3**, **5**, and **6** can be found in the literature.[15]

Ca(THF)₃(Si(SiMe₃)₃)₂ (1): yield 0.54 g, 72%; mp 152−156 °C. ^1H NMR (300 MHz, 25 °C, C_6D_6) δ (ppm): 3.66 (m, br, 12H, THF), 1.32 (m, br, 12H, THF), 0.50 (s, 54H, $SiMe_3$). ^{13}C NMR (75 MHz, 25 °C, C_6D_6) δ (ppm): 6.48 ($SiMe_3$), 25.20, 68.76. ^{29}Si NMR (99 MHz, 25 °C, C_6D_6) δ (ppm): −6.75 Si(*Si*Me₃), −172.32 *Si*(SiMe₃). IR (cm⁻¹) (KBr plates, Nujol mull): 2923 (s), 2853 (s), 1462 (m), 1377 (m), 1296 (w), 1233 (w), 1031 (w), 830 (m), 728 (w), 669 (w), 619 (m).

Sr(THF)₃(Si(SiMe₃)₃)₂ (2): yield 0.60 g, 75%; mp 168−170 °C. ^1H NMR (300 MHz, 25 °C, C_6D_6) δ (ppm): 3.66 (m, br, 12H, THF), 1.33 (m, br, 12H, THF), 0.52 (s, 54H, $SiMe_3$). ^{13}C NMR (75 MHz, 25 °C, C_6D_6) δ (ppm): 6.85 ($SiMe_3$), 25.11, 68.67. ^{29}Si NMR (99 MHz, 25 °C, C_6D_6) δ (ppm): −6.07 Si(*Si*Me₃), −170.51 *Si*(SiMe₃). IR (cm⁻¹) (KBr plates, Nujol mull): 2923 (s), 2853 (s), 1462 (m), 1377 (m), 1296 (w), 1232 (w), 1033 (w), 828 (m), 729 (w), 671 (w), 619 (w).

Sr(TMEDA)(THF)(Si(SiMe₃)₃)₂ (4): yield 0.53 g, 69.3%; mp 167−170 °C. ^1H NMR (300 MHz, 25 °C, C_6D_6) δ (ppm): 3.67 (m, br, 4H, THF), 1.90 (s, 12H, Me), 1.65 (s, 4H, CH_2), 1.40 (m, br, 4H, THF), 0.49 (s, 54H, $SiMe_3$). ^{13}C NMR (75 MHz, 25 °C, C_6D_6) δ (ppm): 7.09 ($SiMe_3$), 25.04, 45.42, 56.01, 69.17. ^{29}Si NMR (99 MHz, 25 °C, C_6D_6) δ (ppm): −6.01 Si(*Si*Me₃), −172.43 *Si*(SiMe₃). IR (cm⁻¹) (KBr plates, Nujol mull): 2924 (s), 2853 (s), 1460 (m), 1377 (w), 1290 (w), 1233 (w), 1160 (w), 1129 (w), 1075 (w), 1031 (w), 945 (w), 829 (m), 728 (w), 671 (w), 619 (w).

X-ray Crystallographic Studies. X-ray-quality crystals for all compounds were grown as described in the Experimental Section. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected under the microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.[37] Due to the extreme moisture and oxygen sensitivity of the compounds, the microscope was placed inside the diffractometer enclosure, and the crystals were removed under inert gas from the mother liquor in immediate proximity to the microscope. All data sets were collected using a Siemens SMART system, complete with three-circle goniometer and CCD detector operating at low temperature. The data sets were collected using a custom-built low-temperature device from Professor H. Hope (UC Davis). Compound **1** was collected at 94 K, **2** at 88 K, **3** at 98 K, **4** at 86 K, **5** at 91 K, and **6** at 85 K. Monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was employed in all cases. The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different ϕ angle and each exposure covering 0.3° in ω. Repeating the initial frames at the end of the data collection and analyzing the duplicate reflections monitored crystal decay. In all cases, no decay was observed. An absorption correction was applied utilizing the program SADABS.[38] The crystal structures of all compounds were solved by either direct or Patterson methods, as included in the SHELX program package.[39] Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures were refined by full-matrix least-squares refinement on F^2.[39] Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C−C bonds for methyl groups. Thermal parameters for hydrogen atoms were refined with U_{iso} constrained at 1.2 (for non-methyl groups) and 1.5 (for methyl groups) times U_{eq} of the carrier C atom. The crystallographic programs used for structure refinement and solutions were installed on a PC clone or a Silicon Graphics Indigo² R10000 Solid Impact. Scattering factors were those provided with the SHELX program system.[39] All non-hydrogen atoms, with the exception of some disordered or restrained positions, were refined anisotropically. Disorder was handled by including split positions for the affected groups and included the refinement of the respective occupancies. A set of restraints was applied to aid in modeling the disorder. Further details about the refinements and how disorder was handled are outlined in the Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. 222535−222537 (compounds **1**, **2**, and **4**) and 206684−206686 (compounds **3**, **5**, and **6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information Available: Details about the refinements and how disorder was handled. This material is available free of charge via the Internet at http://pubs.acs.org.

(37) Hope, H. *Prog. Inorg. Chem.* **1994**, *41*, 1.

(38) Sheldrick, G. M. *SADABS, Program for Absorption Correction Using Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.

(39) Sheldrick, G. M. *SHELXTL, Program package for structure solution and refinement*; BrukerAXS: Madison, WI, 2003.