Manganese and Cesium Derivatives of the Bulky Bidentate Ligand $C(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2C$. Crystal Structures of $Li(THF)_{2.75}(Et_2O)_{0.25}(\mu$-$Cl)$-$MnC(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2C$ and $(C_6H_6)_3CsC(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2CCs(C_6H_6)_3$

Colin Eaborn,* Peter B. Hitchcock, J. David Smith,* and Suobo Zhang

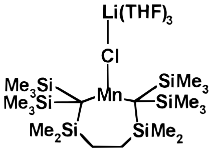
School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, BN1 9QJ, U.K.

William Clegg, Keith Izod, and Paul O'Shaughnessy

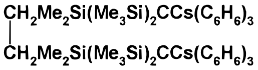
Department of Chemistry, University of Newcastle, Newcastle upon Tyne, NE1 7RU, U.K.

Received December 21, 1999

Summary: The reaction between the lithate $[Li(THF)_4]$-$[CH_2SiMe_2C(SiMe_3)_2LiC(SiMe_3)_2SiMe_2CH_2]$ *and* $MnCl_2$ *has given a chloride-bridged high-spin lithium manganate, isolated as* $Li(THF)_{2.75}(Et_2O)_{0.25}(\mu$-$Cl)MnC(SiMe_3)_2$-$SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2C$, *shown by an X-ray study to contain three-coordinate planar manganese. The ligand precursor* $HC(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2CH$ *reacts with methylcesium to give a compound isolated after recrystallization from benzene as* $(C_6H_6)_3$-$CsC(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2CCs(C_6H_6)_3$, *in which benzene solvate molecules show a variety of hapticities.*

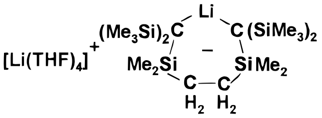


1

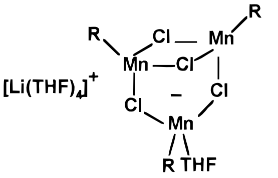


$$\begin{array}{l}CH_2Me_2Si(Me_3Si)_2CCs(C_6H_6)_3\\ |\\ CH_2Me_2Si(Me_3Si)_2CCs(C_6H_6)_3\end{array}$$

2



3



4 R = $C(SiMe_3)_3$

$(C_6H_6)_2KC(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2CK(C_6H_6)_2$

5

Introduction

We recently reported the attachment of the bidentate "trisiamyl" ligand $C(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2C$ (R−R) to Li, Hg,[1] Pb,[2] Zn, Yb, K, and Sn.[3,4]

The structures of the organometallic compounds were of two types. In the first the mole ratio of ligand R−R to metal was 1, and a neutral (Hg, Zn, Yb, Sn, or Pb) or anionic (Li) seven-membered metallacycle was formed. In the second, the mole ratio of ligand R−R to metal was 0.5, and open chain compounds L_nMR−RML_n, ML_n = $K(C_6H_6)_2$, $K(THF)_2$, or $SnCl_3$, were obtained (THF = tetrahydrofuran). We have now determined the crystal structures of two more derivatives, **1** and **2**, of the ligand R−R and both show unusual and noteworthy features.

Results and Discussion

The syntheses of the new derivatives were straightforward. Compound **1** was obtained by treatment of a slurry of anhydrous $MnCl_2$ in THF with the lithium compound $[Li(THF)_4][CH_2SiMe_2C(SiMe_3)_2LiC(SiMe_3)_2$-$SiMe_2CH_2]$, **3**,[1] but an X-ray diffraction study showed that in crystals obtained from diethyl ether some THF had been displaced by Et_2O. Compound **2** was obtained by metalation of $HC(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2CH$ with CsMe followed by recrystallization from benzene.

Compound **1** was found to have a magnetic moment of 5.4 μ_B, suggesting that it contained high-spin Mn^{II}. It crystallized in a monoclinic unit cell with a very long *c* axis, but by use of an area detector it was possible to resolve and collect sufficient data in reasonable time to solve the structure. There were four independent molecules in the asymmetric unit: three contained three molecules of coordinated THF, and the fourth two molecules of THF and one of diethyl ether. The bond lengths and angles of the skeleton were reasonably well defined and remarkably consistent over the four sites. None of the bond lengths differed significantly from the mean values, but minor conformational differences between the molecules were reflected in the range of

---

(1) Eaborn, C.; Lu, Z.-R.; Hitchcock, P. B.; Smith, J. D. *Organometallics* **1996**, *15*, 1651.

(2) Eaborn, C.; Ganicz, T.; Hitchcock, P. B.; Smith, J. D.; Sözerli, S. E. *Organometallics* **1997**, *16*, 5621.

(3) Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Smith, J. D.; Zhang, S.; Ganicz, T. *Organometallics* **1999**, *18*, 2342.

(4) Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Patel, D.; Smith, J. D.; Zhang, S. *Organometallics* **2000**, *19*, 49.

10.1021/om991020g CCC: \$19.00
Publication on Web 02/25/2000

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2[a]

			1		
Mn−C	2.178(5)	Si−C(1)	1.862(5)	Si−CH_2	1.884(6)
Mn−Cl	2.4105(15)	Si−Me	1.883(7)	C−C	1.549(8)
Li−Cl	2.330(9)	Li−O	1.927(12)		
Mn−C−Si	103.8(2)−110.1(2)	Cl−Li−O	105.0(4)−115.6(4)	Me-Si−CH_2	103.7(3)
C−Mn−C	140.30(18)	O−Li−O	104.5(5)−115.5(5)	Si−C−Si	111.4(3)
C−Mn−Cl	108.62(13)−110.79(13)	C−Si−Me	111.3(2)−115.9(3)	C−Si−CH_2	116.3(3)
Mn−Cl−Li	157.7(2)−176.0(3)	Me-Si−Me	104.6(3)	Si−C−C	119.4(4)
			2		
Cs1−C(1)	3.245(13)	Cs2−C(1)	3.350(18)	Cs3−C(1)	3.320(15)
Cs1−C η^4 [b]	3.517(17)−3.698(19)[c]	Cs2−C η^4 [b]	3.587(14)−3.661(16)[c]	Cs3−C η^6 [b]	3.639(16)−3.686(16)
η^2 [b]	3.565(17)−3.639(19)[c]	η^2 [b]	3.65(3)−3.70(3)[c]	η^6 [b]	3.588(15)−3.623(13)
η^1 [b]	3.633(17)[d]	η^1 [b]	3.846(17)[e]	η^1 [b]	3.921(17)[e]
Si−CH_2	1.868(11)	Si−C(1)	1.810(16)	Si−Me	1.884(13)
C−C	1.594(17)				
Cs−C−Si	89.0(6)−103.2(6)	Me-Si−Me	93.8(10)−110.7(10)	C−Si−Me	108.2(11)−128.6(11)
Si−C−Si	115.6(8)−122.0(9)	Me-Si−CH_2	103.8(7)−108.5(6)	C−Si−CH_2	112.2(6)−115.9(7)
Si−C−C	110.2−116.5				

[a] A single value indicates the average for chemically equivalent bonds and angles; the esd's in parentheses show the precision in individual measurements, none of which differs significantly from the mean. A range of values indicates significant deviation from the mean. [b] Distances to the carbon atoms in the three benzene rings bound to each Cs. See text for assignment of hapticities. [c] All other Cs−C > 3.70 Å. [d] Also 3.872(17) and 3.891(15) Å; others > 4.3 Å. [e] All others >4.0 Å.

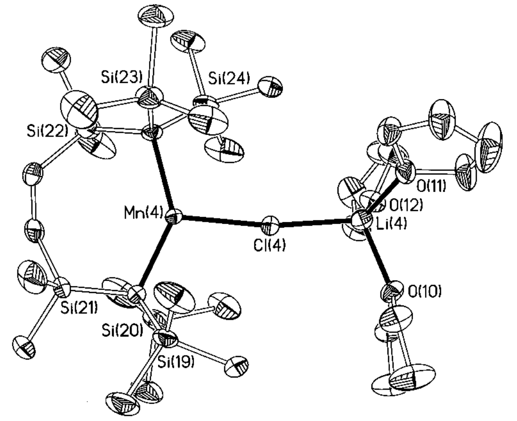


Figure 1. Structure of one of the independent molecules of **1** with 50% probability ellipsoids.

angles within the $O_3LiClMn$ system. Selected data are given in Table 1, and the structure of one of the molecules, containing only coordinated THF, is shown in Figure 1.

As far as we are aware,[5] compound **1** is the first fully characterized example of a monomeric lithium dialkylhalogenomaganate(II), though similar species have been suggested as intermediates in reactions such as the conjugate addition of organometallic compounds to alkylidenemalonic esters.[6] The reaction between $LiC(SiMe_3)_3$ and $MnCl_2$ in 1:1 mole ratio gave a lithium alkylchloromanganate which had the more complicated ionic structure **4**.[7a] A number of lithium alkylmanganates(II) and manganates(III) have also been described.[5,8] Compounds containing manganese−alkyl bonds show a variety of coordination numbers, oxidation states, and spin states, so that care is required in making comparisons of bond lengths. Among the Mn^{II} (high-spin) compounds that have been characterized structurally the Mn−C bond of **1** [2.178(5) Å] is, as expected, longer than those [2.01(3)−2.104(6) Å] in MnR_2 (R = $C(SiMe_3)_3$,[7b] $CH(SiMe_3)_2$,[9a] or CH_2CMe_3[9b]), in which the manganese is two-coordinate. It is shorter than the Mn−C bonds (2.22(6)−2.28(1) Å) in the manganates $[Li(TMEDA)]_2[MnR_4]$ (R = Me, Et, Bu, or CH_2SiMe_3, TMEDA = tetramethylethylenediamine)[8] but, surprisingly, longer than the terminal bonds in a number of other compounds in which the manganese is four-coordinate, for example, $[(Me_3P)RMn(\mu\text{-}R)_2MnR(PMe_3)]$ (2.111(3)−2.146(6) Å, R = CH_2SiMe_3, CH_2CMe_3, or CH_2Ph),[10a] $[Mn(CH_2CMe_2Ph)_2(PMe_3)_2]$,[10b] or a number of Mn_3 or Mn_4 cage molecules.[11] It has been suggested[12] that the spread in Mn−C bond lengths may be attributed to the fact that the bonds are more ionic than metal−carbon bonds in compounds of other transition metals and are free from crystal field effects. Few chelated dialkylmanganese compounds have been described. One with a less sterically demanding bidentate ligand than that in **1** is $[Mn\{o\text{-}(CH_2)_2C_6H_4\}(DMPE)_2]$ (DMPE = 1,2-bis(dimethylphosphino)ethane);[10b] the Mn is six-coordinate and the four phosphorus atoms give a sufficiently large crystal field to make the complex low spin with short Mn−C bonds (2.104−2.110 Å). The Mn−Cl distance in **1** (2.4105(15) Å) is similar to that (2.412(4) Å) in the single chloride bridges of compound **4**.[7a] Compound **1** is the first example of a three-coordinate metal compound involving the chelating ligand R−R. The bonds at manganese are coplanar (sum of angles

---

[5] For a review see: Girolami, G. S.; Morris, R. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., Vol. 6, 1995; p 127.

[6] Cahiez, G.; Laboue, B. *Tetrahedron Lett.* **1992**, *33*, 4439. Cahiez, G.; Chavant, P.-Y.; Metais, E. *Tetrahedron Lett.* **1992**, *33*, 5245. Cahiez, G.; Alami. M. *Tetrahedron* **1989**, *45*, 4163.

[7] (a) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1985**, 534. (b) Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1380.

[8] (a) Andersen, R. A.; Carmona-Guzman, E.; Gibson, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 2204. (b) Morris, R. J.; Girolami, G. S. *Organometallics* **1989**, *8*, 1478; **1991**, *10*, 799.

[9] (a) Andersen, R. A.; Berg, D. J.; Fernholt, L.; Faegri, K.; Green, J. C.; Haaland, A.; Lappert, M. F.; Leung, W.-P.; Rypdal, K. *Acta Chem. Scand. Ser. A* **1988**, *42*, 554. (b) Andersen, R. A.; Haaland, A.; Rypdal, K.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1807.

[10] (a) Howard C. G.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2025. (b) Howard, C. G.; Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2631.

[11] Koschmieder, S. U.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1992**, 19.

[12] Chiswell, B.; McKenzie, E. D.; Lindoy, L. F. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., Vol. 4, 1987; p 1.

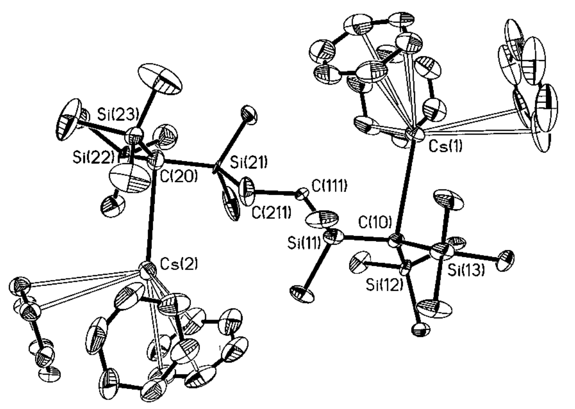


Figure 2. Structure of the non-centrosymmetric molecule of **2** with 50% probability ellipsoids.

360°); three-coordinate Mn is rare.[13] The C−Mn−C angle, 140°, is intermediate between the angles in $\overline{\mathrm{RSnR}}$ or $\overline{\mathrm{RPbR}}$ (117°) and $\overline{\mathrm{RZnR}}$ or $\overline{\mathrm{RHgR}}$ (166−170°). The intraligand bond lengths and angles are however not very different from those in the compounds $\overline{\mathrm{RMR}}$, indicating that the ligand can make subtle adjustments in conformation to meet the electronic requirements at the metal center.

The mass spectrum of **1** showed ions assigned to $\overline{\mathrm{RMnR}}$, presumably obtained by elimination of LiCl. When **1** was heated to 90 °C at 0.01 mmHg, a pale yellow sublimate was formed. This contained no lithium (flame test), but attempts to crystallize it from toluene, benzene, methylcyclohexane, hexane, or $(Me_3Si)_2O$ were unsuccessful, so that a full characterization could not be obtained.

The cesium compound **2** also crystallized in a monoclinic lattice with a very long *c* axis. There were six molecules in the unit cell, four symmetry equivalent molecules in general positions and a pair of equivalent molecules lying on inversion centers. The asymmetric molecule, containing atoms Cs1 and Cs2, is shown in Figure 2. The structure stands in contrast to that of the dialkyllithate **3**; it resembles that of the potassium analogue **5**, but there are three instead of two molecules of benzene per cluster of two cations and one dianion. (As far as we are aware, no dialkylcesates are known.) The data in Table 1 indicate that there is no significant variation in chemically equivalent intramolecular bond lengths and that the different molecular symmetries result from small differences in bond angles. The mean Cs−C1 bond length, 3.305 Å, is similar to those in $CsCPh_3$, 3.348(4) Å,[14] or $CsC(SiMe_3)_3{\cdot}3.5C_6H_6$, 3.325(12) Å,[16] confirming that the radius of Cs in σ-bonds is about 2.53 Å.[15] The distance in $CsC(SiMe_2Ph)_3$[16] is much longer (3.655(7) Å). The coordination sphere of the cesium is made up of interactions with a carbanionic center from a neighboring dianion and those with π-electrons from benzene. There are no close contacts with methyl groups on the periphery of the anion such as were found in the potassium compound **5**. A similar relation between potassium and cesium compounds is shown in the derivatives $MC(SiMe_3)_3$; the potassium compound crystallizes solvent-free from benzene with chains of alternate potassium cations and planar carbanions and short K⋯Me contacts,[17] whereas in the cesium compound the chains are broken and the crystal contains isolated $[(C_6H_6)_3CsC(SiMe_3)_3]$ units. Selected Cs−C distances in **2** are tabulated in Table 1. The assignment of hapticities to solvate molecules, especially when they are disordered, necessarily involves somewhat arbitrary judgments, but the assignments shown in Table 1 reflect breaks between Cs−C distances in the range 3.5−3.7 Å and those that are greater. On this basis η^4-, η^2-, and η^1-coordination is indicated in the molecules shown in Figure 2, and η^6-, η^6-, and (weaker) η^1-coordination in the centrosymmetrical molecules. Coordination of arene solvent molecules or phenyl groups to cesium is common, and Cs−C distances of 3.3−3.8 Å have been reported.[18] Most examples so far have been for η^6-coordination, but there are some for η^4 or η^3.[19] The wide range of hapticities found for the arene solvent molecules in **2** is unusual.

Table 2. Summary of Crystallographic Data for 1 and 2

	1	**2**
empirical formula	$C_{32}H_{76.5}ClLiMnO_3Si_6$	$C_{56}H_{88}Cs_2Si_6$
fw	775.30	1195.62
cryst size (mm)	0.4 × 0.4 × 0.2	0.38 × 0.28 × 0.14
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	17.3569(9)	18.3982(11)
b (Å)	19.6492(10)	9.6528(6)
c (Å)	53.194(3)	53.866(3)
β (deg)	90.228(2)	96.851(2)
Z	16	6
V (Å^3)	18142(2)	9498.0(10)
d_c (Mg m^{-3})	1.135	1.254
F(000)	6744	3708
μ (mm^{-1})	0.536	1.296
θ range (deg)	1.10−25.00	1.99−23.00
index range	$-20 \le h \le 11$ $-22 \le k \le 23$ $-63 \le l \le 62$	$-19 \le h \le 20$ $-10 \le k \le 10$ $-59 \le l \le 58$
temperature (K)	160	160
no. of reflns collected	94 141	47 568
no. of unique reflns	31 868, R_{int} = 0.0766	13 211, R_{int} = 0.0636
no. of reflns with $I > 2\sigma(I)$	20 248	9583
transmission	max 0.695, min 0.445	max 0.773, min 0.540
R1 ($I > 2\sigma(I)$)	0.072	0.119
wR2 (all data)	0.171	0.258
no. of data/restrts/params	31 868/1536/1585	13 211/6356/1024
GOF on F^2	1.015	1.026

---

(13) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1, and references therein. Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Organometallics* **1988,** *7*, 1801.

(14) Hoffmann, D.; Bauer, W.; Schleyer, P. v. R.; Pieper, U.; Stalke, D. *Organometallics* **1993**, *12*, 1193.

(15) This value is given in a compilation published by VCH, Weinheim, in 1991, but in view of the very few Cs−C bond lengths that have been measured, it is not clear how it was derived.

(16) (a) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 687. (b) Eaborn, C.; Clegg, W.; Hitchcock, P. B.; Hopman, M.; Izod, K.; O'Shaughnessy, P. N.; Smith, J. D. *Organometallics* **1997**, *16*, 4728.

(17) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Jaggar, A. J.; Smith, J. D. *Organometallics* **1994**, *13*, 753.

(18) Smith, J. D. *Adv. Organomet. Chem.* **1998**, *43*, 267, and references therein.

(19) Klinkhammer, K. W.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1777. Clark, D. L.; Deacon, G. B.; Feng, T.; Hollis, R. V.; Scott, B. L.; Skelton, B. W.; Watkin, J. G.; White, A. H. *Chem. Commun.* **1996**, 1729. Rabe, G. W.; Kheradmandan, S.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1404.

Experimental Section

Air and moisture were excluded as far as possible by the use of Schlenk tube techniques, flame-dried glassware, and Ar blanket gas. NMR spectra were recorded from samples in sealed tubes at 300.13 (^{1}H), 75.43 (^{13}C), 99.36 (^{29}Si), and 65.59 MHz (^{133}Cs): chemical shifts are relative to $SiMe_4$ or CsF in H_2O/D_2O.

Preparation of 1. A solution of **3** (1.2 g, 2.2 mmol) in THF (10 mL) was added to a stirred slurry of anhydrous $MnCl_2$ (0.28 g, 2.2 mmol) in THF (15 mL) at −78 °C. The mixture was allowed to warm slowly to room temperature and stirred overnight. The solvent was pumped off, the residue extracted with Et_2O (20 mL), and the extract cooled to −20 °C to give colorless blocks of **1**. Yield: 1.0 g, 60%. Anal. Calcd for $C_{32}H_{76.5}ClLiMnO_3Si_6$: C, 49.6; H, 9.9; Cl, 4.6. Found: C, 47.1; H, 9.9; Cl, 5.2. (The low *C* value is attributed to loss of coordinated THF during manipulation.) MS: *m*/*z* 515 (4%, $\overline{\mathrm{RMnR}}$), 500 (2, $\overline{\mathrm{RMnR}}$ − Me), 462 (1, HR−RH), 217 (100, $[(Me_3Si)_2(Me_2Si)CH]$). The magnetic moment at 25 °C was determined by the Evans' method, without a diamagnetic solvent correction.[20]

Preparation of 2. A solution of MeLi (6.4 mmol) in Et_2O (4.0 mL) was added to a cold (−78 °C) solution of 2-ethylhexoxycesium (1.57 g, 6.0 mmol) and HR−RH (1.30 g, 2.80 mmol) in Et_2O (30 mL), and the mixture was allowed to attain room temperature, then stirred for a further 1.5 h. The solvent was removed in a vacuum, the residue extracted with warm benzene, and the extract filtered. The filtrate was reduced to 10 mL and warmed to redissolve the solid that had separated. Crystals of **2** were obtained as the solution cooled. Yield: 1.95 g, 58%. The compound was too reactive to obtain a satisfactory C, H analysis, but the structure was determined by an X-ray study. ^{1}H NMR (C_6D_6−THF): δ −0.07 (s, 12H, $SiMe_2$), −0.05-(s, 36H, $SiMe_3$), 0.37 (s, 4H, CH_2). ^{13}C NMR: δ 5.17 ($SiMe_2$), 6.30 (CSi_3, J_{SiC} 57.4 Hz), 8.31 ($SiMe_3$), 18.44 (CH_2). ^{29}Si NMR: δ −13.9 ($SiMe_3$), −9.0 ($SiMe_2$). ^{133}Cs NMR: δ 25.8.

Crystallography. Data were collected on a SMART CCD area detector diffractometer by use of Mo Kα radiation (λ = 0.71073 Å), and the structures were solved by heavy atom methods and full-matrix least squares refinement on F^2. Non-H atoms were anisotropic, and H atoms were refined in riding mode with $U_{iso} = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for Me groups. Further details are given in Table 2.

Acknowledgment. We thank the EPSRC for financial support and the Royal Society for the award of a China Royal Fellowship to S.Z.

Supporting Information Available: Crystal data for **1** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM991020G

---

[20] Evans, D. F. *J. Chem. Soc.* **1959**, 2003. Grant, D. H. *J. Chem. Educ.* **1995**, *72*, 39.