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Synthesis and Structure of the First Donor-Stabilized Bis(silylene)manganese Complex

Tamiko Takeuchi, Hiromi Tobita, and Hiroshi Ogino*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan

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Summary: The first manganese derivative of the donor-stabilized bis(silylene) complex $(OC)_4Mn\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ has been synthesized by the photolysis of $(OC)_5MnSiMe_2SiMe_2OMe$. The X-ray structure analysis of this complex revealed its distorted-octahedral structure with two short Mn–Si bonds and a planar $MnSi_2O$ chelate ring.

Silylene transition-metal complexes, the species containing a metal–silicon double bond, are attracting great attention from organometallic chemists as a synthetic target. Tilley et al.,[1] Zybill and Müller,[2] and we[3] have recently achieved some important developments in this field by the syntheses and structural studies of several donor-stabilized silylene complexes. Quite recently, Tilley et al. have claimed the synthesis of the first donor-free, cationic silylene complexes.[4]

Our method utilizes intramolecular addition of an Si–Si bond to a coordinatively unsaturated metal center,[5] giving donor-stabilized bis(silylene)iron complexes,[3] and is potentially applicable to a variety of transition-metal complex systems. We now report an application of this method to the synthesis of the first manganese derivative of donor-stabilized bis(silylene) complexes.

The photochemical precursor $(OC)_5MnSiMe_2SiMe_2OMe$ (**1**) has been prepared by applying the preparative method for $(OC)_5MnSiMe_2SiMe_3$ reported by Nicholson and Simpson:[6] The reaction of equimolecular amounts of $Na[Mn(CO)_5]$ (prepared from $Mn_2(CO)_{10}$ and Na/Hg) and $ClMe_2SiSiMe_2Cl$ (eq 1) followed by treatment of the product with MeOH in the presence of pyridine in hexane (eq 2) afforded **1** as a relatively air-stable, colorless oil in 28% yield based on $Mn_2(CO)_{10}$.[7]

$$\mathrm{Na[Mn(CO)_5] + ClMe_2SiSiMe_2Cl \rightarrow (OC)_5MnSiMe_2SiMe_2Cl + NaCl} \quad (1)$$

$$\mathrm{(OC)_5MnSiMe_2SiMe_2Cl + MeOH + C_5H_5N \rightarrow \underset{\mathbf{1}}{(OC)_5MnSiMe_2SiMe_2OMe} + C_5H_5N{\cdot}HCl} \quad (2)$$

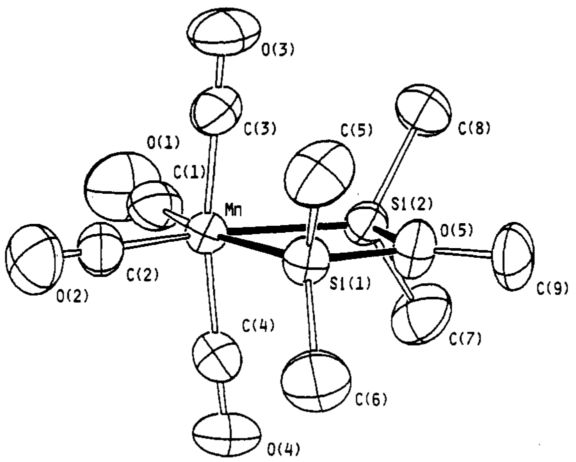

Figure 1. ORTEP drawing of $(OC)_4Mn\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ (**2**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Mn–Si(1) = 2.336 (2), Mn–Si(2) = 2.344 (2), Si(1)–O(5) = 1.784 (5), Si(2)–O(5) = 1.795 (4), O(5)–C(9) = 1.459 (8), Si(1)⋯Si(2) = 2.723 (2), Mn⋯O(5) = 3.064 (4); Si(1)–Mn–Si(2) = 71.18 (5), Si(1)–O(5)–Si(2) = 99.1 (2), Mn–Si(1)–O(5) = 95.1 (2), Mn–Si(2)–O(5) = 94.6 (1), C(1)–Mn–C(2) = 101.6 (3), C(3)–Mn–C(4) = 170.9 (3).

Photolysis of a degassed C_6D_6 or hexane solution of **1** in a Pyrex tube with a 450-W medium-pressure Hg lamp resulted in quantitative conversion to the air-sensitive product **2**[8] (eq 3). In hexane, **2** precipitated out as a off-white powder.

The ^1H NMR spectrum of **2** in C_6D_6 shows a singlet of Si–Me at δ 0.43 ppm. The equivalence of all four Si–Me's

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[7] A solution of $Mn_2(CO)_{10}$ (2.00 g, 5.13 mmol) in THF (10 mL) was added to a sodium amalgam prepared from Na (0.44 g, 19 mmol) and Hg (3.6 mL, 49 g), and the mixture was stirred vigorously for 3 h. The organic layer including $Na[Mn(CO)_5]$ was transferred into a flask connected to a vacuum line, and THF was removed under high vacuum. To this residue was trap-to-trap-transferred a mixture of $ClMe_2SiSiMe_2Cl$ (2.36 g, 12.6 mmol) and hexane (20 mL), and the mixture was stirred at room temperature for at least 12 h. After the reaction mixture was filtered under nitrogen, the deep red filtrate was concentrated in vacuo. Molecular distillation of the residue with a Kugelrohr (30–95 °C/0.2 Torr) afforded crude $(OC)_5MnSiMe_2SiMe_2Cl$ (2.28 g, 6.58 mmol, 64% yield) as a yellow oil: ^1H NMR (C_6D_6, 90 MHz) δ 0.58 (6 H, s, Me), 0.53 (6 H, s, Me). This crude product was used in the next step without further purification. To $(OC)_5MnSiMe_2SiMe_2Cl$ (1.01 g, 2.91 mmol) in hexane (10 mL) was slowly added methanol (95 mg, 3.0 mmol) and then pyridine (230 mg, 3.0 mmol) with use of microsyringes. After the mixture was stirred for 10 min, the white salt formed was filtered off and the solvent removed from the filtrate in vacuo. Purification of the residue by silica gel flash chromatography (solvent 50/1 hexane/ether) afforded crude **1** as a colorless oil. Molecular distillation of the product gave pure **1** (432 mg, 1.26 mmol, 43%). The overall yield of **1** is 28%. $CF_3SO_3Me_2SiSiMe_2SO_3CF_3$ can also be used for this preparation instead of $ClMe_2SiSiMe_2Cl$, but the overall yield of **1** is somewhat lower (25%). Spectral data for **1**: ^1H NMR (C_6D_6, 90 MHz) δ 3.30 (3 H, s, OMe), 0.56 (6 H, s, Me), 0.30 (6 H, s, Me); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 214.6 (CO), 212.0 (CO), 50.0 (OMe), 1.7 (Me), –1.2 (Me); ^{29}Si NMR (C_6D_6, 17.8 MHz) δ 19.3, –12.6; IR (C_6D_6) ν(CO) 2090 (s), 1993 (vs), 1985 (vs) cm^{-1}; UV λ_{max} 222 (sh) nm (ϵ 27 000); MS (14 eV) *m/z* 342 (1.5, M^+), 314 (31.4), 286 (8.0), 258 (12.3), 230 (11.7), 202 (45.2), 147 (100, $SiMe_2SiMe_2OMe^+$); exact mass calcd for $C_{10}H_{15}MnO_6Si_2$ 341.9788, found 341.9786.

[8] Spectral data for **2**: ^1H NMR (C_6D_6, 90 MHz) δ 2.48 (3 H, s, OMe), 0.43 (12 H, s, Me); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 220.7 (CO), 53.6 (OMe), 5.4 (Me); ^{29}Si NMR (C_6D_6, 17.8 MHz) δ 115.4; MS (14 eV) *m/z* 314 (100, M^+), 286 (18.3), 258 (71.9), 230 (15.9), 202 (10.3); exact mass calcd for $C_9H_{15}MnO_5Si_2$ 313.9839, found 313.9847.

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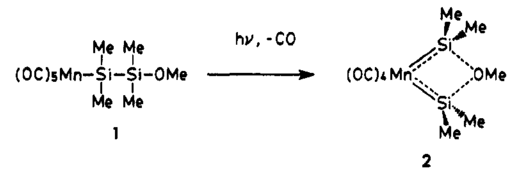


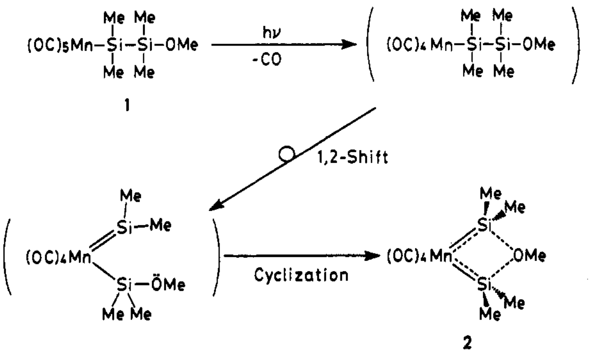
(3)

in the product 2 confirms its highly symmetric structure. In addition, the signal for the methoxy protons of 2 appears at very high field (δ 2.48 ppm), which is typical of methoxy-bridged bis(silylene) complexes.[3]

The structure of 2 has been unambiguously determined by an X-ray crystal structure analysis.[9] An ORTEP view is shown in Figure 1. The coordination geometry of manganese can be described as a distorted octahedron. The Mn–Si(1) and Mn–Si(2) bond lengths (2.336 (2) and 2.344 (2) Å, respectively) are nearly equal to each other and are very short for Mn–Si bonds with no halogens on Si atoms (2.40–2.56 Å for known complexes).[10,11] They almost rival the Mn–$SiCl_3$ bond length (2.254 (1) Å), in which strong back-donation from Mn to Si is assumed.[12] On the other hand, the distances of Si(1)–O(5) and Si(2)–O(5) (1.784 (5) and 1.795 (4) Å, respectively) are significantly longer than usual Si–O single bonds (typically 1.63 Å)[13] and are comparable with the corresponding distances of the methoxy-stabilized bis(silylene)iron complex $(\eta^5\text{-}C_5Me_5)(CO)Fe\{SiMe_2\cdots O(Me)\cdots SiMe(OMe)\}$ (1.793 (9) and 1.799 (8) Å).[3]

Two methyl groups on each silicon atom are greatly bent away from the manganese center: The sum of the bond angles C–Si–C and Mn–Si–C at each silicon is 350.3 and 350.9°, respectively. This structural feature implies the existence of partial sp^2 character of the Si atom and thus of the p_π–d_π interaction between the Si and Mn atoms. Interestingly, the planarity of the chelate ring consisting of Mn, Si(1), O(5), and Si(2) is quite good (dihedral angle between the Si(1)–Mn–Si(2) and Si(1)–O(5)–Si(2) planes: 1.17°). This is in contrast to the nonplanar geometry of the corresponding chelate ring in $(\eta^5\text{-}C_5Me_5)(CO)Fe\{SiMe_2\cdots O(Me)\cdots SiMe(OMe)\}$, in which the corresponding dihedral angle is 21.2°.[3b] In the latter complex, however, there is a large steric interaction between the substituents on the $\eta^5\text{-}C_5Me_5$ ring and the chelate ring that may cause the puckering of the latter ring.[3b] Therefore, the M–Si–O–Si ring in bis(silylene) complexes is presumed to be intrinsically planar. These structural characters are consistent with the description of 2 as an alkoxy-stabilized bis(silylene)metal complex.

Scheme I



The sp^2 character of silicon atoms in 2 is supported by the remarkable downfield shift of its ^{29}Si NMR signal from 19.3 and −12.6 ppm for 1 to 115.4 ppm for 2. Furthermore, each of the ^1H, ^{13}C, and ^{29}Si NMR spectra of 2 gives only a singlet peak for $SiMe_2$ groups,[8] showing that two $SiMe_2$ groups are equivalent on the NMR time scale in solution as well as in the solid state as described above. The ^{13}C NMR spectrum of 2 exhibits only one carbonyl signal in the temperature range 203–353 K, and the signal becomes sharper with lowering temperature (half-width 22 Hz at 203 K). This result implies the presence of fast exchange between cis and trans carbonyl ligands even at 203 K, although coincidence of the chemical shifts of these carbonyl ligands cannot be ruled out.

Solid 2 rapidly reacts with excess methanol-d_4 at room temperature to give a mixture of $(OC)_4Mn\{SiMe_2\cdots O(CD_3)\cdots SiMe_2\}$ (2-d_3)and 2 (2-d_3:2 > 8 according to the mass spectrum). Prolonged reaction of 2 with methanol or methanol-d_4 for several hours causes the cleavage of Mn–Si bonds to give dimethyldimethoxysilane, decacarbonyldimanganese, etc.

The formation of 2 can be explained by the mechanism shown in Scheme I, which is essentially the same as that for the formation of the bis(silylene)iron complexes.[3]

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Supplementary Material Available: Tables of crystal data, atomic positional and thermal parameters, bond distances, and bond angles for 2 and figures giving ^1H (1), ^{13}C (1 and 2), and ^{29}Si (1 and 2) NMR spectra (8 pages); a listing of observed and calculated structure factors for 2 (11 pages). Ordering information is given on any current masthead page.

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(9) Crystals of 2 suitable for X-ray structure analysis were obtained by cooling its concentrated C_6D_6 solution. Crystal data for 2: orthorhombic, space group $P2_12_12_1$, $a = 11.515$ (1) Å, $b = 16.551$ (2) Å, $c = 7.861$ (1) Å, $V = 1498.3$ (3) Å^3, $Z = 4$, $d_{calcd} = 1.39$ g cm^{-3}, $F(000) = 648$. X-ray diffraction data were collected at 21 °C on a Rigaku AFC-6A diffractometer with graphite-monochromated Mo Kα radiation. Reflections (4535) with $3° < 2\theta < 75°$ were collected by the ω–2θ scan technique. The crystal structure was solved by the heavy-atom method and refined with block-diagonal least squares by using individual anisotropic thermal parameters for non-hydrogen atoms. Refinement of 2346 unique reflections with $|F_o| > 3\sigma(F_o)$ converged with final residuals $R = 0.056$ and $R_w = 0.083$.

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