Synthesis and Structure of Hexacoordinate Organosilicon Compounds Having Tropolonato Ligands[1]

Mitsuo Kira,* Luo Cheng Zhang, Chizuko Kabuto, and Hideki Sakurai*
Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980-77

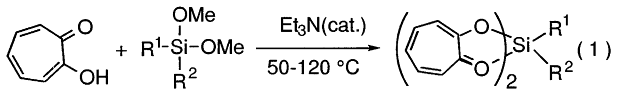
(Received May 2, 1995)

R_2SiT_2 type of compounds (R = alkyl, aryl, OMe; T = tropolonato) have been found to hold rather exceptionally hexacoordinate dialkyl- and diarylsilicon geometry with two bidentate tropolonato ligands both in the solid state and in solution. A facile intramolecular stereoisomerization of these neutral hexacoordinate silicon compounds was observed by temperature dependent NMR spectroscopy in solution .

Tropolonato (T) ligands are well known to stabilize hypercoordinate compounds of silicon and other elements. In 1960's, Muetterties et al.[2] reported that silicon cations like $T_3Si^+X^-$ (X = Cl, I, T, etc.) were produced via a reaction of tropolone and tetrachlorosilane. Neutral $(CH_3)_2SiT_2$ and $PhClSiT_2$ were also prepared[2e] by the reaction of tropolone with dimethyldichlorosilane and phenyltrichlorosilane, respectively. However, the coordination number at silicon and the other structural details have not been reported until now. On the other hand, an *O*-trialkylsilyltropolone has been known to have a tetracoordinate silicon and show facile degenerate silyl migration from oxygen to oxygen.[3]

We have revealed that R_2SiT_2 type of compounds (R = alkyl, aryl, and OMe) holds rather exceptionally hexacoordinate dialkyl- and diarylsilicon geometry with two bidentate tropolonato ligands both in the solid state and in solution. Although a number of hexacoordinate silicon compounds have been isolated and characterized, those having two Si–C bonds are very rare.[4]

Various bis(tropolonato)organosilicon compounds were synthesized by the reactions of tropolone (**1**) with the corresponding dimethoxysilanes (**2**) in the presence of a catalytic amount of triethylamine in moderate to good yields (eq 1). Interestingly, even when a large excess of dimethoxysilanes was used, two tropolonato ligands were introduced into a silicon atom; no mono-tropolonato silicon compounds were produced. Typically, Ph_2SiT_2 (**3b**) was prepared by the following procedure: a mixture of tropolone (200 mg, 1.64 mmol), diphenyldimethoxysilane (1 ml), and triethylamine (a drop) was heated at 110–120 °C for 4 h under argon atmosphere. Precipitates were collected and washed with dry ether giving **3b** in 45% yield.[5]



(1)

1 **2**

3a, $R^1 = R^2 = Me$, 41%;
3b, $R^1 = R^2 = Ph$, 45%;
3c, $R^1 = OMe$, $R^2 = Me$, 75%;
3d, $R^1 = OMe$, $R^2 = Ph$, 56%;
3e, $R^1 = R^2 = OMe$, 88%.

The molecular structure of **3b** was determined by X-ray single crystal diffraction analysis.[6] The silicon atom in **3b** is located at the center of distorted octahedron with the two phenyl groups at the *cis*-positions (Figure 1). The two tropolone-ring planes are arranged nearly in perpendicular to each other (the dihedral angle = 81.1°). The Si–O1 and Si–O3 bond distances (av. 1.80 Å) are comparable with the corresponding distances for the tris(*o*-phenyldioxy)silicates (1.78 Å),[7] while those for Si–O2 and Si–O4 bonds (av. 1.90 Å) are a little longer. The extent of the bond alternation in the tropolone ring is much smaller than that in 2-(*p*-chlorobenzoyloxy)-tropone.[8] These results suggest that there is significant contribution of the canonical structure where the tropolone rings serve as intramolecular countercations in the dianionic hexacoordinate silicon molecule. The details of the structure of **3b** will be discussed in a forthcoming paper.

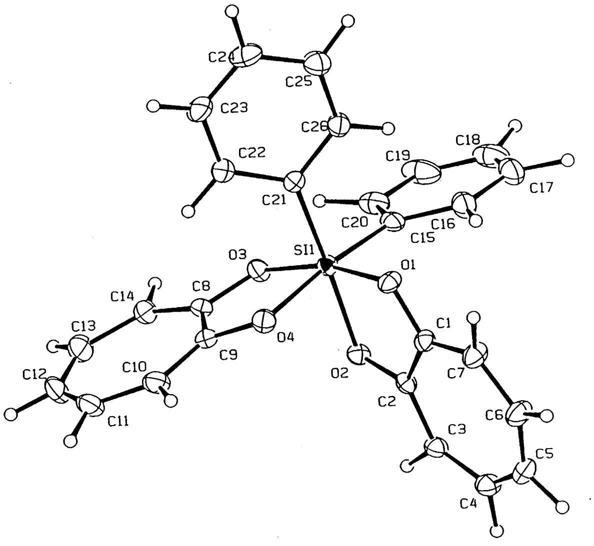
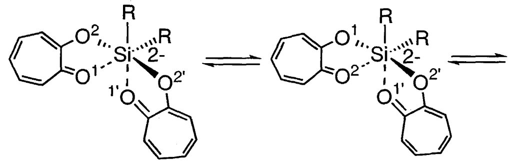


Figure 1. Perspective ORTEP drawing of **3b** showing 30% thermal ellipsoids for the non-hydrogen atoms. Selected bond distances (Å) and angles (deg): Si–O1, 1.793 (3); Si–O2, 1.923 (3); Si–O3, 1.805 (3); Si–O4, 1.879 (3); Si–C15, 1.926 (5); Si–C21, 1.928 (4); O1–C1, 1.311 (5); O2–C2, 1.289 (5); O3–C8, 1.313 (5); O4–C9, 1.295 (5); C1–C2, 1.442 (5); C1–C7, 1.388 (6); C2–C3, 1.401 (6); C3–C4, 1.379 (6); C4–C5, 1.383 (7); C5–C6, 1.369 (7); C6–C7, 1.393 (7); O1–Si–O2, 82.9 (1); O1–Si–O3, 166.0 (1); O1–Si–O4, 86.0 (1); O1–Si–C15, 96.8 (1); O2–Si–C21, 172.8 (1); C15–Si–C21, 97.8 (1).

The ^{29}Si NMR resonances for **3a**–**3e** appeared in the range between −105 and −146 ppm, being indicative of the hexacoordinate structure around silicon in solution. However, these hexacoordinate silicon compounds were stereochemically non-rigid in solution. Thus, while the ^{13}C NMR spectrum of **3a** in $CDCl_3$ revealed seven different signals for each tropolonato ligand at around 203 K, the ^{13}C signals broadened and then collapsed to four signals at higher temperatures than 230 K. Pairs of the signals due to C1-C2, C3-C7, and C4-C6 coalesced, while the C5 signal remained sharp throughout the temperature range examined. These results indicate that there exists an exchange process as shown in eq 2 at high temperatures. Following rate data were obtained for this process by analyzing the temperature dependent ^{13}C NMR spectra in $CDCl_3$: the first-order rate = 31.5 s^{-1} (298 K), $\Delta H^{\ddagger}$ = 19.0 kcal·mol^{-1}, $\Delta S^{\ddagger}$ = 12.2 cal·mol^{-1}·K^{-1}. Whereas similar dynamic behavior was observed in the other bis(tropolonato)silicates, the coalescence temperature (T_C) increased significantly with increasing electron-withdrawing ability of the substituents at silicon; the Tc's were 230 (**3a**), 300 (**3b**), 312 (**3d**), and >320 K (**3e**).



(2)

The following two mechanisms should be considered for the isomerization:[9] (1) A multi-step mechanism, where a rupture of one Si–O bond to give a five-coordinate intermediate followed by the recombination, and (2) a true intramolecular process without any Si–O bond rupture (twist mechanism). Remarkable substituent effects on the rates may suggest the bond-rupture-recombination process as the preferred mechanism. A study of the mechanistic details is now in progress.

We are grateful to the Ministry of Education, Science, and Culture of Japan for financial support (Grants-in-Aid for Specially Promoted Research No. 02102004 and for Scientific Research No. 05640587).

References and Notes

1 Chemistry of Organosilicon Compounds. 327.

2 a) E. L. Muetterties and C. M.Wright, *J. Am. Chem. Soc.*, **86**, 5132 (1964); **87**, 21 (1965); **87**, 4706 (1965); b) E. L. Muetterties, *ibid.*, **88**, 305 (1966); c) E. L. Muetterties, H. Roesky, and C. M. Wright, *ibid.*, **88**, 4856 (1966); d) E. L. Muetterties and C. W. Alegranti, *ibid.*, **91**, 4420 (1969).

3 H. Reich and D. A. Murcia, *J. Am. Chem. Soc.*, **95**, 3418 (1973); D. Menard and M. St-Jacques, *Can. J. Chem.*, **60**, 231 (1982).

4 For recent reviews, see: C. Chuit, R. J. P. Corriu, C. Reye, and J. C. Young, *Chem. Rev.*, **93**, 1371 (1993); R. J. P. Corriu and J. C. Young, in "The Chemistry of Organic Silicon Compounds", ed by S. Patai and Z. Rappoport, Part 2, Chapter 20, John-Wiley & Sons, Chichester (1989).

5 **3a**: yellow scales, mp 193–194 °C (lit.[2c] mp 205–216 °C); yield 41%; ^{1}H NMR (300 MHz, CD_2Cl_2, 295 K) δ 0.22 (s, 6H), 7.16 (tt, J = 10.9 and 1.1 Hz, 2H), 7.34 (dd, J = 10.5 and 1.1 Hz, 4H), 7.59 (ddd, J = 10.9, 10.5 and 1.1 Hz, 4H); ^{13}C NMR (75 MHz, CD_2Cl_2, 295 K) δ 10.0, 124.7, 128.5, 141.5, 173.9; ^{29}Si NMR (59 MHz, CD_2Cl_2, 295 K): δ –104.8 ; MS *m/z* (rel intensity) 285 (25), 122 (100), 94 (78); IR (KBr), 1595 cm^{-1} ($\nu_{C=O}$). **3b**: yellow scales; mp 244–245 °C (dec); ^{1}H NMR ($CDCl_3$, 245 K) δ 7.06 (tt, J = 7.2 and 1.5 Hz, 2H), 7.13 (dd, J = 7.9 and 7.2 Hz, 4H), 7.21 (t, J = 9.6 Hz, 2H), 7.29 (d, J = 10.9 Hz, 2H), 7.56 (dd, J = 10.9 and 9.6 Hz, 2H), 7.62 (dd, J = 7.9 and 1.5 Hz, 4H), 7.65 (dd, J = 9.8 and 9.6 Hz, 2H), 7.74 (d, J = 9.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 245 K) δ 124.6, 125.7, 126.4, 126.7, 130.2, 133.8, 141.8, 142.6, 153.5, 172.4, 174.4; ^{29}Si NMR ($CDCl_3$, 240K) δ –130.8; MS *m/z* (rel intensity) 347 (100), 303 (25), 122 (53), 94 (29); IR (KBr) 1595 cm^{-1} ($\nu_{C=O}$). Anal. Found: C, 73.19, H, 4.76%. Calcd for $C_{26}H_{20}O_4Si$: C, 73.56; H, 4.75%. **3c**: white powder; mp 195 °C (dec.); yield 75%; ^{1}H NMR (CD_2Cl_2, 295 K) δ –0.02(s, 3H), 3.44 (s, 3H) 6.98–7.64 (m, 10H). ^{13}C NMR (CD_2Cl_2, 245 K) δ 5.1, 50.9, 123.9, 124.0, 125.4, 125.7, 129.3, 129.8, 141.3, 141.4, 142.0, 142.1, 171.7, 172.2, 173.2, 173.9; ^{29}Si NMR (CD_2Cl_2, 295 K) δ –125.9; MS *m/z* (rel intensity) 271 (1), 122(100), 94 (23); Ir (KBr), 1594.9cm^{-1} ($\nu_{C=O}$). Anal. Found: C, 60.45, H, 4.90%. Calcd for $C_{16}H_{16}O_5Si$: C, 60.74, H, 5.09%. **3d**: white powder; mp 200–201 °C; yield 56%; ^{1}H NMR ($CDCl_3$, 295 K) δ 3.30 (s, 3H), 7.11 (tt, J = 8.0 and 1.4 Hz, 1H), 7.19 (t, J = 8.0 Hz, 2H), 7.13–7.23 (m, 3H), 7.44–7.51 (m, 2H), 7.63 – 7.67 (m, 5H), 7.73 (dd, J = 8.0 and 1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 245K) δ 52.2, 125.2, 125.3, 126.5, 126.6, 127.3, 130.4, 130.5, 134.3, 141.6 (2C), 142.1, 142.5, 142.6, 149.7, 172.1, 173.2, 173.9, 174.5; ^{29}Si NMR (DMSO-d_6, 295 K) δ –137.5; MS *m/z* (rel intensity) 347 (19), 301 (100), 271 (23), 257 (81), 122 (99), 94 (45), 77 (60); Ir (KBr), 1596 cm^{-1} ($\nu_{C=O}$). Anal. Found: C, 66.50; H, 4.41%. Calcd for $C_{21}H_{18}O_5Si$: C, 66.65; H, 4.79%. **3e**: pale yellow powder; mp 120 °C (dec); yield 88%; ^{1}H NMR (CD_2Cl_2 , 295 K) δ 3.38 (s, 6H), 7.32 (tt, J = 10.9 and 1.1 Hz, 2H), 7.37(dd, J = 10.5 and 1.1 Hz, 2H), 7.67 (dd, J = 10.9 and 1.1 Hz, 2H), 7.70 (td, J = 10.9 and 1.1Hz, 2H); 7.76 (td, J = 10.9 and 1.1 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 295 K) δ 51.3, 124.4, 125.8, 130.1, 141.7, 142.4, 172.4, 173.8; ^{29}Si NMR (CD_2Cl_2, 295 K) δ –145.7; MS *m/z* (rel intensity) 301 (29), 211 (100), 122 (93), 94 (52); Ir (KBr), 1596 cm^{-1}($\nu_{C=O}$). No reasonable analytical data for **3e** were obtained because of the instability in air and moisture.

6 Crystal data for **3b**: monoclinic, space group $P2_1/n$ (No. 14), a = 9.671 (4) Å, b = 16.139 (5) Å, c = 13.557 (4) Å, β = 102.27 (3)°, V = 2067.7 (2.6) Å^3, Z = 4, D_{calcd} = 1.364 g cm^{-3}. A total of 4790 reflections was measured, and of these 3174 reflections [$F_o > 3\sigma(F_o)$] were used in refinement. All non-hydrogen atoms were refined anisotropically. R = 0.067, R_w = 0.068. Data were collected at 200 K on a Rigaku AFC5R diffractometer. All calculations were performed by an ACOS-2200 computer at Tohoku University with the applied library program UNICS III system (T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku* , **55**, 69 (1979)).

7 J. J. Flynn and F. P. Boer, *J. Am. Chem. Soc.*, **91**, 5756 (1969).

8 J. P. Schaefer and L. L. Reed, *J. Am. Chem. Soc.*, **93**, 6429 (1971).

9 R. H. Holm, in "Dynamic Nuclear Magnetic Resonance Spectroscopy ", ed by L. M. Jackman and F. A. Cotton, Chapter 9, Academic Press, New York (1973).