Reactions of [Chloro(1,2-phenylenedioxy)silyl]iron Complex $Cp(CO)_2FeSiCl(o\text{-}O_2C_6H_4)$ with Nucleophiles

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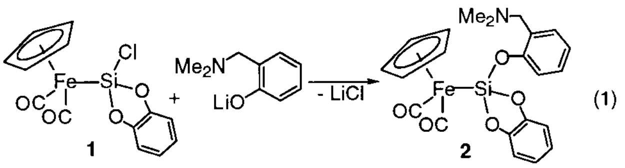
Reactions of FpSiCl(cat) (**1**: Fp = (η^5-C_5H_5)Fe(CO)$_2$, cat = o-$O_2C_6H_4$) with lithium 2-(dimethylaminomethyl)phenoxide (LiOAr^N) afforded FpSi(cat)(OAr^N) (**2**), while that with acetylacetone resulted in the formation of a mixture of a hexacoordinate silicon compound Si(cat)(acac)$_2$ (acac = η^2-$CH_3COCHCOCH_3$) and FpH. Structural determination of **2** by X-ray crystallography revealed that there is no interaction between the silicon atom and the dimethylamino group.

Hypervalent silicon compounds have attracted considerable interest in these decades.[1] Despite the extensive study on the hypervalent silicon compounds, transition metal complexes containing a hypervalent silicon-transition metal bond are quite rare. Fluorosilanes are known to form Lewis acid-base adducts with palladium[2a] and platinum[2b] complexes. Recently, Corriu *et al.* synthesized a [2,6-bis(dimethylaminomethyl)phenyl]silyl complex and reported that the silicon atom in the complex takes a hexacoordinate structure.[3] However, the structures of these complexes have not been determined by X-ray analysis and the nature of the hypervalent silicon species bound to transition metal still remains uncertain.

Recently, we synthesized a [chloro(1,2-phenylenedioxy)silyl]iron complex, FpSiCl(cat) (**1**: Fp = (η^5-C_5H_5)Fe(CO)$_2$, cat = o-$O_2C_6H_4$), and revealed the electron deficient character of the silicon atom.[4] Because 1,2-phenylenedioxyl group is known to stabilize hypervalent silicon species, we decided to investigate the reactions of **1** with lithium 2-(dimethylaminomethyl)phenoxide (LiOAr^N) and acetylacetone, aiming to obtain complexes containing hypervalent silicon species as ligands.

Reaction of **1** with LiOAr^N afforded FpSi(cat)(OAr^N) (**2**)[5] as yellow crystals in 47% yield (eq 1).



(1)

In order to know whether interaction between the silicon atom and the dimethylamino group exists or not in the solid state, X-ray structural study of **2** was performed.[6] The molecular structure of **2** is shown in Figure 1. The interatomic distance of Si····N is 4.392(4) Å, which indicates no interaction between the two atoms. It is notable that the Fe-Si distance (2.2227(13) Å) is significantly short compared to the typical Fe-Si distances (2.25~2.41 Å).[7] A similar short Fe-Si distance was observed in $FpSiCl_3$ (2.216(1) Å).[8] This has been rationalized by the strong electron-withdrawing effect of three chlorine atoms which causes the increase of π-back donation from the filled d-orbitals of the iron atom to the σ^*-orbitals of the Si-Cl bonds.[9] The same explanation is applicable to the short Fe-Si distance of **2**, because both 1,2-phenylenedioxyl and OAr^N groups have strong electron-withdrawing character. The enhanced π-back donation is disclosed in the elongated Si-O bonds composed of the silicon atom and the 1,2-phenylenedioxyl group (1.688(3) and 1.690(3) Å). Typical Si-O bond distances range from 1.61 to 1.67 Å.[7,10] The π-back donation and the steric crowding around the silicon atom make the coordination of the dimethylaminomethyl group to the silicon atom difficult.

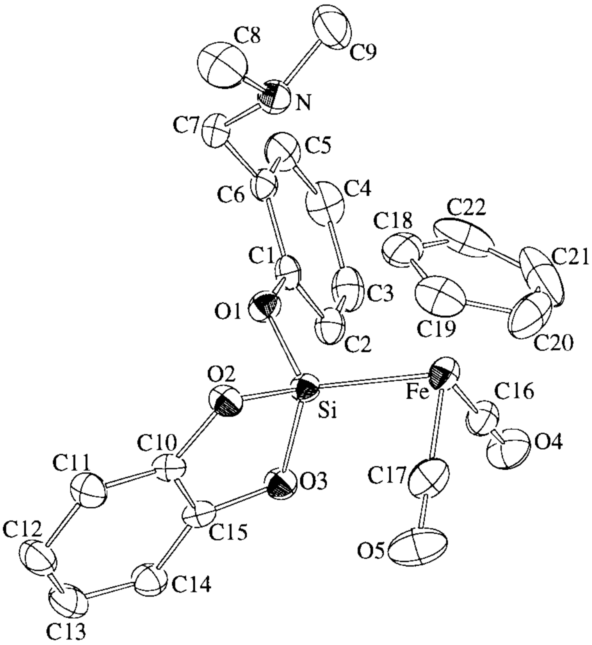
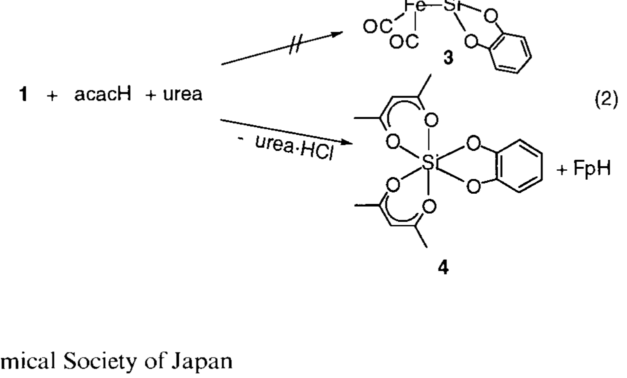


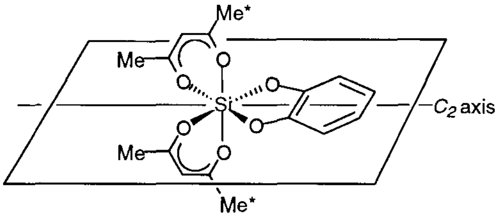
Figure 1. Molecular structure of FpSi(cat)(OAr^N) (**2**).
Selected interatomic distances (Å) and angles (deg): Fe-Si 2.2227(13), Si-O1 1.641(3), Si-O2 1.690(3), Si-O3 1.688(3), Si···N 4.392(4), Fe-Si-O1 117.24(11), Fe-Si-O2 116.20(11), O2-Si-O3 95.40(14).



(2)

Reaction of **1** with acetylacetone in the presence of urea did not afford [(acetylacetonato)(1,2-phenylenedioxy)silyl]iron complex FpSi(acac)(cat) (**3**), but a mixture of a hexacoordinate silicon compound, bis(acetylacetonato)(1,2-phenylenedioxy)silane (**4**)[11] (yield: 51%), and FpH (eq 2).

The ^{29}Si NMR signal of **4** appeared at considerable highfield (-170.4 ppm), which is characteristic of the hexacoordinate silicon species containing six silicon-oxygen bonds.[12] In the ^{1}H NMR spectrum of **4**, four methyl groups in the acetylacetonato ligands were observed as two singlets at 1.52 and 1.32 ppm. This result is consistent with the hexacoordinate structure of **4** having C_2 symmetry. Two methyl groups in the acetylacetonato ligands are located at axial positions and others are at equatorial positions described below.



4

Formation of **4** may be explained by the following mechanism: Substitution of the chlorine atom in **1** by an acetylacetonate gives complex **3** which contains a hypervalent silicon species. Then, **3** is readily converted to **4** and FpH by the substitution reaction of **3** and another acetylacetonate. In the case of the formation of **2**, the Fe-Si bond survived since there is no interaction between the silicon and the amino nitrogen atom. Therefore, to obtain complexes containing hypervalent silicon species as ligands, further reactions with various nucleophiles must be tried.

The two methyl signals in the ^{1}H NMR spectrum coalesced when temperature was raised to 339 K, accompanied by partial decomposition of **4**. The $\Delta G^{\neq}{}_{339}$ value of this dynamic behavior is estimated to be 70 kJ mol^{-1}. The mechanism of this dynamic process is most likely rationalized by the Si-O bond cleavage leading to the formation of a pentacoordinate intermediate followed by the site exchange between apical and equatorial positions on the silicon atom. A similar mechanism including the formation of a five coordinate intermediate has been proposed for the racemization of $[Si(acac)_3]ClO_4$[13a] and the dynamic behavior of $[Si(gallate)_3]^{5-}$. (gallateH$_4$= 3,4,5-trihydroxybenzoic acid)[13b] The rapid intramolecular site exchange reaction in pentacoordinate silicon species has widely been known.[1]

Two hexacoordinate silicon compounds, $[Si(acac)_3]^+$ and $[Si(cat)_3]^{2-}$, have been synthesized in 1903[14] and 1931,[15] respectively. But no mixed ligand silicon compound containing acetylacetonato and phenylenedioxyl ligands has been reported so far. In this work, the synthesis of **4** was achieved by an unusual but unique method via a (1,2-phenylenedioxysilyl)iron complex.

References and notes

1 C. Chuit, R. J. P. Corriu, C. Reyé, and J. C. Young, *Chem. Rev.*, **93**, 1371 (1993).

2 a) J. Grobe, R. Martin, and U. Möller, *Angew. Chem., Int. Ed. Engl.*, **16**, 248 (1977); b) T. R. Durkin and E. P. Schram, *Inorg. Chem.*, **11**, 1048 (1972).

3 R. J. P. Corriu, B. P. S. Chauhan, and G. F. Lanneau, *Organometallics*, **14**, 1646 (1995).

4 K. Yamaguchi, K. Ueno, and H. Ogino, *Chem. Lett.*, in press.

5 Data for **2**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 2.26 (s, 6H, NCH_3), 3.58 (s, 2H, NCH_2), 5.23 (s, 5H, C_5H_5), 6.76~6.92 (m, 8H, Ar). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 45.3 (NCH_3), 58.2 (NCH_2), 85.6 (C_5H_5), 112.7, 120.8, 149.4 (o-$C_6H_4O_2$), 120.2, 122.5, 128.3, 131.3, 152.7 ($OC_6H_4CH_2NMe_2$), 211.7 (CO). ^{29}Si NMR (59.6 MHz, CD_2Cl_2) δ 34.2. MS (EI, 70 eV) *m/z* 463 (M^+, 0.34), 435 (M^+-CO, 0.75), 407 (M^+-2CO, 1.29), 286 ($[Si(cat)(OAr^N)]^+$, 100). IR (toluene) 2023, 1973 cm^{-1} (ν_{CO}). Anal. Found: C, 56.27; H, 4.68; N, 2.99%. Calcd for $C_{22}H_{21}FeNO_5Si$: C, 57.03; H, 4.57; N, 3.02%. The elemental analysis of **2** did not give satisfactory results despite repeated attempts, because **2** was highly air sensitive. However, a variety of spectroscopic data and X-ray crystal data lead to the conclusion that **2** is FpSi(cat)(OAr^N).

6 Crystal data for **2**: $C_{22}H_{21}FeNO_5Si$, $M = 463.34$, monoclinic, space group $P2_1/a$, $a = 16.295(2)$, $b = 12.0067(13)$, $c = 11.1526(12)$ Å, $\beta = 96.54(2)°$, $V = 2167.8(4)$ Å^3, $Z = 4$, $D_c = 1.420$ g cm^{-3}. The structure was solved by heavy-atom methods (SHELXS-86) and refined by full-matrix least-squares techniques (SHELXL-93) on all F^2 data (6326 unique reflections). $R1 = 0.0637$ and $wR2 = 0.1133$ for 2823 reflections with $I > 2.0\ \sigma(I)$.

7 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, and R. Taylor, *J. Chem. Soc., Dalton Trans.*, **1989**, S1.

8 U. Schubert, G. Kraft, and E. Walther, *Z. Anorg. Allg. Chem.*, **519**, 96 (1984).

9 D. L. Lichtenberger and A. Rai-Chaudhuri, *J. Am. Chem. Soc.*, **113**, 2923 (1991).

10 P. Jutzi, E.-A. Bunte, U. Holtmann, B. Neumann, and H.-G. Stammler, *J. Organomet. Chem.*, **446**, 139 (1993).

11 Data for **4**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.37 (s, 6H, CH_3), 1.57 (s, 6H, CH_3), 5.02 (s, 2H, CH), 6.84 (dd, J_{HH} = 5.61, 3.48 Hz, 2H, o-$C_6H_4O_2$), 7.20 (dd, J_{HH} = 5.61, 3.48 Hz, 2H, o-$C_6H_4O_2$). ^{13}C NMR (75.5 MHz, C_6D_6) δ 25.1, 25.3 (CH_3), 102.2 (CH), 111.8, 118.9, 150.7 (o-$C_6H_4O_2$), 189.3, 193.1 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6) δ -170.4. MS (EI, 70 eV) *m/z* 334 (M^+, 66.8), 435 (M^+-acac, 100). Anal. Found: C, 57.59; H, 5.38%. Calcd for $C_{16}H_{18}O_6Si$: 57.47; H, 5.43%.

12 J. A. Cella, J. D. Cargioli, and E. A. Williams, *J. Organomet. Chem.*, **186**, 13 (1980).

13 a) T. Inoue and K. Saito, *Bull. Chem. Soc. Jpn.*, **46**, 2417 (1973); b) D. F. Evans, J. Parr, and E. R. Coker, *Polyhedron*, **6**, 813 (1990).

14 W. Dilthey, *Chem. Ber.*, **36**, 923 (1903).

15 A. Rosenheim, B. Raibmann, and G. Schendel, *Z. Anorg. Allg. Chem.*, **196**, 160 (1931).