Synthesis of the Cationic Silyleneiron Complex [(η-C₅H₅)Fe(CO)₂=SiMe{2-(Me₂NCH₂)C₆H₄}]PF₆ by Hydride Abstraction from a (Hydrosilyl)iron Complex with Ph₃CPF₆

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Summary: A cationic intramolecular base-stabilized silyleneiron complex, $[(\eta-C_5H_5)Fe(CO)_2=SiMe\{2-(Me_2-NCH_2)C_6H_4\}]PF_6$, was synthesized by hydride abstraction from the (hydrosilyl)iron complex $(\eta-C_5H_5)Fe(CO)_2SiHMe\{2-(Me_2NCH_2)C_6H_4\}$ with Ph_3CPF_6 . Reaction of the silylene complex with MeOH afforded the methoxysilyl complex $[(\eta-C_5H_5)Fe(CO)_2SiMeOMe\{2-(Me_2N(H)CH_2)C_6H_4\}]PF_6$ in good yield. The molecular structures of the silylene and methoxysilyl complexes were determined by X-ray crystal structure analysis.

One of the useful synthetic routes for carbene complexes is abstraction of a leaving group from the carbon atom of an alkylmetal complex with an electrophile.¹ A similar strategy, i.e., abstraction of a leaving group from the silicon atom of a silylmetal complex, seems applicable for the synthesis of silylene complexes. However, such attempts to prepare silylene complexes have failed, principally due to the occurrence of secondary reactions.² For example, reaction of FpSiCl₃ (Fp = CpFe(CO)₂; Cp = η -C₅H₅) with 3 equiv of AgBF₄ caused fluorination of the silyl group and FpSiF₃ was isolated (eq 1).^{2a} In 1987, Tilley and his colleagues succeeded



in obtaining the cationic silylene complex $[Cp^*(Me_3P)_2-Ru=SiPh_2\cdot NCMe]BPh_4$ ($Cp^* = \eta \cdot C_5Me_5$) by the abstraction method.³ They selected $Cp^*Ru(PMe_3)_2SiPh_2OTf$ as a precursor complex, which contains the good leaving group OTf and the electron-rich ruthenium fragment $Cp^*Ru(PMe_3)_2$ to stabilize the generated silylene ligand.

In addition, they used a mild electrophile which does not contain a fluorine source, NaBPh₄, to prevent undesirable secondary reactions. Their result clearly shows that selection of the leaving group and the electrophile, especially the counteranion in the electrophile, is important for the preparation of the silylene complex by the abstraction method.

Many hydrosilyl complexes have been prepared so far.⁴ Thus, it would be worthwhile to find a new synthetic route to silylene complexes using hydrosilyl complexes as precursors. This prompted us to investigate hydride abstraction from the hydrosilyl complex by electrophiles. Our efforts, at first, were focused on finding substituents for the silicon atom which sufficiently stabilize the cationic silylene complex generated by hydride abstraction. We employed an Ar^N group $(Ar^{N} = 2 - (Me_2NCH_2)C_6H_4)$ for the substituent on the silyl ligand, since the generated silylene ligand may be effectively stabilized by the intramolecular base.^{5,6} We then attempted to abstract the hydride from FpSiMe- HAr^{N} (1)⁷ with several electrophiles and finally found that the reaction of the (hydrosilyl)iron complex 1 with Ph₃CPF₆ resulted in the formation of the cationic silylene complex $[Fp=SiMeAr^{N}]PF_{6}(2)$. This is a surprising result, since the cationic silylene complex is stable enough even in the presence of PF_6^- ions. Here we report the details of the synthesis of the cationic silyleneiron complex by hydride abstraction and the reactivity of the silylene complex.

An initial attempt to carry out the hydride abstraction from the silyl group of FpSiHMeAr^N (1) with Ph₃CBF₄ was unsuccessful. For example, reaction of FpSiH-MeAr^N (1) with 1 equiv of Ph₃CBF₄ in dichloromethane at room temperature afforded a complex reaction mix-

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 $[\]begin{array}{l} 7.21-7.34 \ (m, 5H, AF), \ 7.61-7.64 \ (m, 1H, AF). \ -Si \ NMR (95.6 \ MR2, CD_2Cl_2): \ \delta \ 13.4. \ ^{13}\text{C} \ NMR (75.5 \ MHz, \ CD_2Cl_2): \ \delta \ 2.9 \ (SiMe), \ 45.0 \ (NMe_2), \ 64.1 \ (CH_2), \ 84.5 \ (Cp), \ 126.3, \ 128.0, \ 129.3, \ 135.1, \ 143.7, \ 144.5 \ (Ar), \ 215.4, \ 215.8 \ (CO). \ IR \ (KBr): \ \bar{\nu} \ (cm^{-1}) \ 2107 \ (\nu_{SiH}), \ 1994, \ 1911 \ (\nu_{CO}). \ MS \ (EI, \ 70 \ eV): \ m/z \ 354 \ (2.9, \ M^+ - H), \ 179 \ (100), \ 135 \ (100), \ 121 \ (100). \ Anal. \ Calcd \ for \ C_{17}H_{21}FeNO_{2}Si: \ C, \ 57.47; \ H, \ 5.96; \ N, \ 3.94. \ Found: \ C, \ 57.42; \ H, \ 5.89; \ N, \ 3.92. \end{array}$

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ture. NMR investigation revealed that the mixture contained Ph₃CH, BF₃, and compounds with Si-F bonding. This result suggests that hydride abstraction occurred during the reaction but was followed by secondary reactions. Our attention then turned to Ph3- CPF_6 , since fluoride ion affinity toward PF_5 is considerably greater than that toward BF₃.⁸

The reaction of $FpSiHMeAr^{N}$ (1) with $Ph_{3}CPF_{6}$ in dichloromethane afforded complex 2 and Ph₃CH.⁹ Complex 2 crystallized out as an air-sensitive yellow solid when the reaction mixture was cooled to -30 °C. The ²⁹Si NMR spectrum of **2** in acetonitrile- d_3 showed a singlet peak at δ 118.3 ppm, which appears at much lower field than that of the precursor complex 1 (δ 13.4 ppm) and at comparable field to those of the known silvlene complexes stabilized by the Ar^N group (δ 110-145 ppm).^{5,6} The fact that the ²⁹Si NMR gave a singlet peak and the SiMe signal in the ¹H NMR spectrum was observed as a singlet peak at δ 0.92 ppm shows that fluorination of the silicon did not take place during the reaction. From the spectroscopic and mass spectral data as well as the elemental analysis, complex 2 was identified as a cationic silvlene complex with PF_6^- , $[Fp=SiMeAr^{N}]PF_{6}(2; eq 2)$. The existence of PF_{6}^{-} ions was also confirmed by ¹⁹F NMR and IR spectroscopy. The structure of the complex 2 was unequivocally confirmed by X-ray crystal structure analysis.



Figure 1 shows an ORTEP drawing of the cationic silvleneiron moiety $[Fp=SiMeAr^{N}]^{+}$ in complex 2.¹⁰ The short Fe-Si bond distance (2.2659(11) Å) of 2 suggests the unsaturated character of the Fe-Si bond, which is shorter than those of the usual silvliron complexes $(2.32-2.37 \text{ Å})^4$ and comparable to those of the known base-stabilized silvleneiron complexes (2.21-2.29 Å).^{6a,13,14}



Figure 1. ORTEP drawing for the cationic silyleneiron moiety $[Fp=SiMeAr^{N}]^{+}$ in 2. Atoms are represented by thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Fe-Si, 2.2659(11); Fe-C(1), 1.748(5); Fe-C(2), 1.748(5); Fe-C(Cp), 2.097 (av); Si-C(3), 1.867(4); Si-C(4), 1.871(4); Si-N, 1.949(3); O(1)-C(1), 1.148(5); O(2)-C(2), 1.149(5); C(1)-Fe-Si, 89.85(14); C(2)-Fe-Si, 87.92(14); C(1)-Fe-C(2), 93.4(2); N-Si-Fe, 118.53-(10); C(3)-Si-Fe, 116.6(2); C(4)-Si-Fe, 120.02(12); C(3)-Si-C(4), 107.0(2).

The Si-N bond distance (1.949(3) Å) is longer than the normal values of Si-N σ -bonds (1.70-1.76 Å) and much shorter than the sum of the van der Waals radii (3.2 Å). 6,15 Interestingly, the Si–N distance is shorter than that of the dative bonding in $H_2Si \leftarrow NH_3$ (2.06 Å) obtained by ab initio calculations¹⁶ and those of other silylene complexes stabilized by the Ar^N group (1.962-2.046 Å).^{5,6a} The sum of bond angles of the three covalently bonded substituents at silicon (343.6°) is also slightly smaller than those of other silvlene complexes stabilized by the Ar^N group (346.7-351.3°).^{5,6a} These results suggest that the Si-N dative interaction in 2 is relatively strong, which is expected due to the high electrophilicity of the silylene ligand imparted by the presence of a monopositive charge on complex 2. The strong coordination of NMe₂ to the silvlene ligand is also revealed by a VT¹H NMR experiment. The silyleneiron complex 2 shows a rigid coordination of the dimethylamino group to silicon even at 80 °C in CD₃CN solution (300 MHz); i.e., no broadening of the diastereotopic Me₂N signals and the AB pattern signals of the CH₂ group was observed. This is in contrast to Zybill's silylene complex (OC)5Cr=SiPhAr^N, which shows si-

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N, 2.80. (10) Crystal data for **2**: $C_{17}H_{20}F_6FeNO_2PSi$, $M_r = 499.25$, triclinic, space group $P\bar{1}$, a = 9.4771(14) Å, b = 13.267(2) Å, c = 8.8592(14) Å, $\alpha = 104.94(2)^\circ$, $\beta = 102.778(14)^\circ$, $\gamma = 79.516(13)^\circ$, V = 1040.3(2) Å³, Z = 2, $D_{calcd} = 1.594$ g/cm³, $\mu = 0.925$ mm⁻¹, F(000) = 508. Data in the range $1.60 \le \theta \le 32.49^\circ$ were collected with graphite-monochromated Mo K α radiation at 293 K (7524 reflections). The structure was solved hyperpresent weak solve (SUEI VS 260). by heavy-atom methods (SHELXS-86)¹¹ and refined by full-matrix least-squares techniques on all measured F^2 data (SHELXL-93);¹² GOF = 1.008. R1 = 0.0637 and wR2 = 0.1399 for 3647 reflections with I > 1.008 $2\sigma(I)$

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multaneous coalescence of both Me₂N and CH₂ signals at 95 °C.⁵ It is noteworthy that the cationic silyleneiron complex coexists with the fluorine-containing anion, PF_6^- . The surprising inertness of the cationic complex 2 toward the PF_6^- ion even at elevated temperature could be attained by the strong intramolecular coordination of the dimethylamino group in Ar^N to the highly electrophilic silylene ligand.

Some reactivity studies of complex 2 were carried out. Heating a CD₃CN solution of complex 2 in a sealed tube at 95 °C for 3 days afforded Ar^NSiMeF₂, Fp⁻, and Fp₂, which would be generated by a reaction including fluorination of the silylene ligand by PF₆⁻ and successive cleavage of the silicon-iron linkage by PF₅.^{2a} Thus, the stabilization of the silylene ligand by the Ar^N group is critical for the reactivity toward PF₆⁻.

The silylene complex shows particular susceptibility to nucleophiles. Reaction of 2 with 1 equiv of MeOH led to the formation of the cationic methoxysilyl complex [FpSiMeOMeAr^{NH}]PF₆ (3, Ar^{NH} = 2-{Me₂N(H)CH₂}-C₆H₄; eq 3).¹⁷ The ²⁹Si NMR signal of 3 appeared at



much higher field (δ 7.40 ppm) than that of the silylene complex 2, indicating the loss of unsaturated character of the Fe-Si bond. The complex 3 showed a broad ¹H NMR signal at 8.8 ppm, which is assignable to the proton in the dimethylammonium group. The signals of the diastereotopic Me₂N and the CH₂ groups appeared as two doublets and an ABX pattern, respectively, due to the spin-spin coupling with the proton on the nitrogen atom.

Figure 2 shows an ORTEP drawing of the cationic (methoxysily)iron moiety $[FpSi(OMe)MeAr^{NH}]^+$ of complex 3.¹⁸ The Fe-Si bond distance of 3 (2.305(2) Å) is longer by 0.04 Å than that of the silylene complex 2 but is still shorter than those of the known (alkylsilyl)iron complexes (2.32-2.37 Å).⁴ The relatively short Fe-Si distance of 3 may be attributed to the presence of the electron-withdrawing methoxy substituent on the silicon



Figure 2. ORTEP drawing for the cationic (methoxysily)iron moiety [FpSi(OMe)MeAr^N]⁺ in 3. Atoms are represented by thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Fe-Si, 2.305-(2); N···O3, 2.721(8); Fe-C(1), 1.723(10); Fe-C(2), 1.761-(11); O(1)-C(1), 1.156(10); O(2)-C(2), 1.121(10); Si-O(3), 1.670(5); Si-C(4), 1.878(8); Si-C(5), 1.889(8); Fe-C(Cp), 2.071 (av); C(4)-Si-C(5), 108.3(4); O(3)-Si-Fe, 114.3(2); C(4)-Si-Fe, 112.3(3); C(5)-Si-Fe, 114.8(2); C(1)-Fe-C(2), 94.5(5); C(1)-Fe-Si, 87.5(3); C(2)-Fe-Si, 88.3(3); O(3)-Si-C(4), 104.7(3); C(3)-O(3)-Si, 123.3(5); O(1)-C(1)-Fe, 177.6(10); O(2)-C(2)-Fe, 179.2(10).

atom.⁴ The Si–O(3) bond distance lies within the range for a covalent bond (1.670(5) Å).¹⁵ The sum of the C–Si–C and two C–Si–Fe bond angles in **3** (335.4°) is smaller than that of **2** (343.6°), indicating the sp³ character of the silicon atom in **3**. The N–H(N) bond in the dimethylammonium unit is directed toward oxygen O(3) (N···O(3) = 2.74(1) Å) by hydrogen bonding (N–H(N)···O(3)).

The cationic silyleneiron complex 2 reacts with some nucleophiles, such as HMPA, HCl, H_2O , and PMe₃. Further studies on the reactivity of the silylene complex 2 and related complexes are in progress.

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Supporting Information Available: Text giving experimental details for the syntheses of 1-3 and the crystal structure analyses of 2 and 3 and tables of crystal data and structural refinement, positional and thermal parameters, and bond lengths and angles for 2 and 3 (18 pages). Ordering information is given on any current masthead page.

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⁽¹⁸⁾ Crystal data for 3: $C_{19}H_{26}Cl_2F_6FeNO_3PSi$, $M_r = 616.22$, monoclinic, space group $P2_1/n$, a = 14.157(2) Å, b = 16.027(3) Å, c = 11.843-(2) Å, $\beta = 92.83(2)^\circ$, V = 2683.8(3) Å³, Z = 4, $D_{calcd} = 1.525$ g/cm³, $\mu = 0.928$ mm⁻¹, F(000) = 1256. Data in the range $1.92 \le 6 \le 27.51^\circ$ were collected with graphite-monochromated Mo K α radiation at 293 K (6474 reflections). The structure was solved by heavy-atom methods (SHELXS-86)¹¹ and refined by full-matrix least-squares techniques on all collected F^2 data (SHELXL-93);¹² GOF = 0.990. R1 = 0.0729 and wR2 = 0.1622 for 1864 reflections with $I > 2\sigma(I)$.