Conversion of Trifluoromethyl-Substituted π-Vinylcarbeneiron to Difluorotrimethylenemethane Complexes

Ken-ichi Fujita, Yoshihisa Watanabe, and Take-aki Mitsudo*

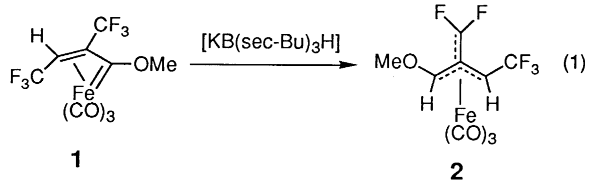
Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01

(Received March 8, 1996)

A trifluoromethyl-substituted π-vinylcarbeneiron complex reacts with [KB(sec-Bu)$_3$H] or phenyllithium to afford difluorinated trimethylenemethane iron complexes. This is the first example of the conversion of a π-vinylcarbeneiron complex to a trimethylenemethane complex.

Recently, chemistry of π-vinylcarbene complexes have received much attention,[1,2] especially concerning the mechanism of Dötz reaction. We now report a novel reactivity of a trifluoromethyl substituted π-vinylcarbeneiron complex **1**[1b] (eqs 1 and 2). The complex **1** reacts with strong nucleophiles such as a hydride or phenyllithium to give trimethylenemethaneiron complexes.

The reaction of **1** with a hydride, [KB(sec-Bu)$_3$H], gave a trimethylenemethaneiron complex **2**,[3] which has a difluoromethylene group.



The structure of **2** was confirmed by X-ray crystallographic analysis[4] (Figure 1). The trimethylenemethane ligand has a usual structure[5] with C1-C2, C2-C3, C2-C4 distances 1.43(1), 1.43(1), 1.44(1) Å, respectively. The C2 atom is closest to the Fe1 atom (1.959(8) Å). The Fe1-C3 bond is somewhat longer (2.249(10) Å), while the Fe1-C1 and Fe1-C4 bonds are 2.09(1), 2.019(9) Å, respectively. It is notable that in **2** the difluoromethylene group and the trifluoromethyl group are in *cis* configuration, though the starting complex **1** had two trifluoromethyl groups in *trans* configuration.[1b]

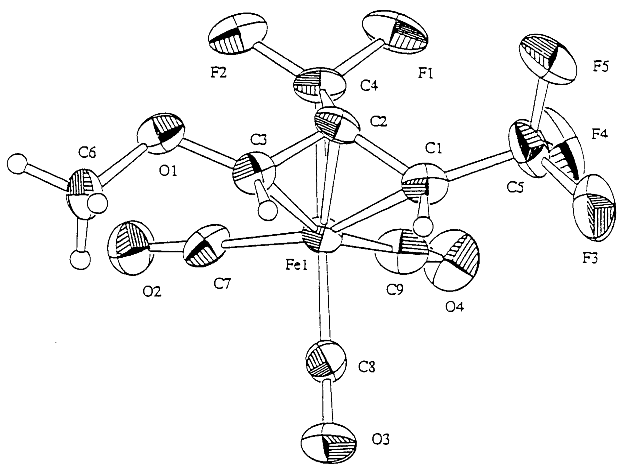
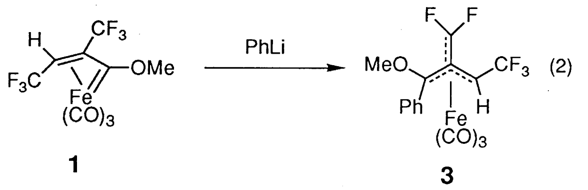
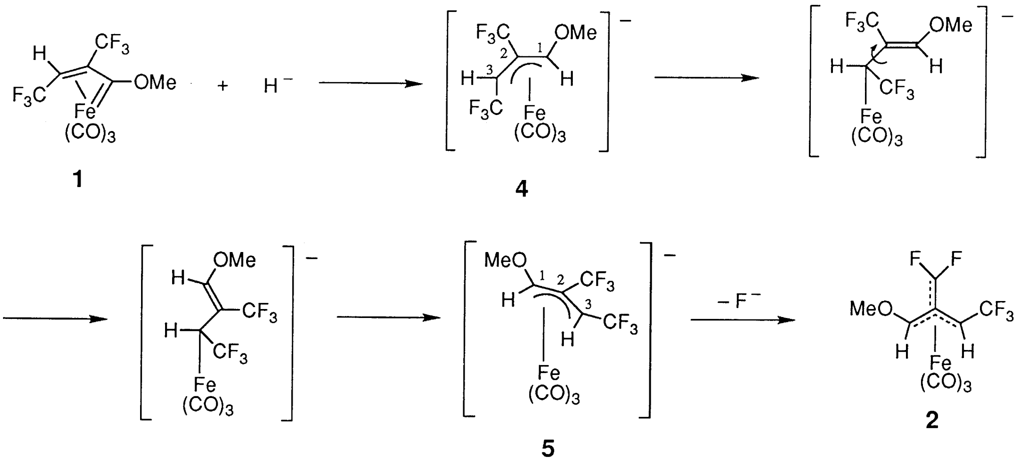


Figure 1. Molecular structure of **2** (ORTEP, 30% probability thermal ellipsoids). Selected bond lengths [Å]: Fe1-C1 2.09(1), Fe1-C2 1.959(8), Fe1-C3 2.249(10), Fe1-C4 2.019(9), Fe1-C7 1.79(1), Fe1-C8 1.791(9), Fe1-C9 1.80(1), C1-C2 1.43(1), C2-C3 1.43(1), C2-C4 1.44(1).



The reaction of **1** with phenyllithium also gave a trimethylenemethane complex **3**.[6]



Scheme 1. A possible mechanism for the formation of **2**.

In the ^{13}C NMR spectrum of **3**, similar to that of **2**, a triplet signal at $\delta = 143.3$ ppm (^1J(C,F) = 327.2 Hz) assigned to a difluorinated sp^2-carbon was observed, which indicates elimination of one fluoride ion from **1** occurred. All spectral data for **3** were consistent with the structure of the trimethylenemethaneiron complex. But the stereochemistry of **3** was not fully determined.

A possible mechanism for the formation of **2** is shown in the Scheme 1. The first step of this reaction is nucleophilic attack of the hydride to the carbene carbon affording a π-allyliron anion complex **4** as an intermediate. The formation of π-allyl complexes by the reaction of hydrides with π-vinylcarbene complexes was already reported.[1c,2c] Isomerization of **4** to **5** would occur via a σ-allyliron complex,[7] because of steric hindrance of the trifluoromethyl group at C$_3$ position (see Scheme 1) of **4**. Then one fluoride ion of the trifluoromethyl group at C$_2$ position of **5** leaves to give the neutral trimethylenemethaneiron complex **2**.

These reactions are the first example of the formation of trimethylenemethane metal complexes from π-vinylcarbene metal complexes. The result provides a novel route for the difluoro-substituted trimethylenemethane complexes, which would be a useful starting material for synthesis of fluoro-organic compounds.

References and Notes

1 a) T. Mitsudo, H. Nakanishi, T. Inubushi, I. Morishima, Y. Watanabe, and Y. Takegami, *J. Chem. Soc., Chem. Commun.*, **1976**, 416. b) T. Mitsudo, K. Fujita, S. Nagano, T. Suzuki, Y. Watanabe, and H. Masuda, *Organometallics,* **14**, 4228 (1995). c) T. Mitsudo, H. Watanabe, T. Sasaki, Y. Takegami, Y. Watanabe, K. Kafuku, and K. Nakatsu, *Organometallics,* **8**, 368 (1989).

2 a) T. Valeri, F. Meier, and E. Weiss, *Chem. Ber.*, **121**, 1093 (1988). b) A. Mayr, M. F. Asaro, and T. J. Glines, *J. Am. Chem. Soc.*, **109**, 2215 (1987). c) K. E. Garrett, J. B. Sheridan, D. B. Pourreau, W. C. Feng, G. L. Geoffroy, D. L. Staley, and A. L. Rheingold, *J. Am. Chem. Soc.*, **111**, 8383 (1989). d) S. G. Feng, A. S. Gamble, and J. L. Templeton, *Organometallics*, **8**, 2024 (1989). e) J. Park, S. Kang, D. Whang, and K. Kim, *Organometallics*, **11**, 1738 (1992). f) J. Barluenga, F. Aznar, A. Martin, S. G. Granda, and E. P. Carreno, *J. Am. Chem. Soc.*, **116**, 11191 (1994).

3 **2**: To a solution of **1** (0.73 g, 2.1 mmol) in dichloromethane (4 mL) was added a THF solution of [KB(sec-Bu)$_3$H] (1.0 M, 2.1 mL, 2.1 mmol) at -78 °C, and then the reaction solution was stirred at room temperature for 2 h. After evaporation of the solvent, the residue was extracted with n-pentane. The solvent of extract was evaporated and the residue was recrystallized from n-pentane to give orange-yellow crystals of **2** (0.23 g, 0.71 mmol, 34%). mp: 38-39 °C; IR (KBr): $\nu = 2081, 2024, 1997$ cm^{-1} (C≡O); ^{1}H NMR (270 MHz, CD$_2$Cl$_2$, 25 °C, TMS): $\delta = 5.01$ (br, d, 1H; CH), 3.57 (s, 3H; OMe), 1.65 (m, 1H; CH); ^{13}C NMR (68 MHz, CD$_2$Cl$_2$, 25 °C, TMS): $\delta = 208.1$ (s, Fe-CO), 206.9 (d, Fe-CO), 205.0 (d, Fe-CO), 154.5 (t, ^1J(C,F) = 332.0 Hz, CF$_2$), 126.4 (q, ^1J(C,F) = 271.0 Hz, CF$_3$), 110.1 (d, ^1J(C,H) = 190.5 Hz, CH), 61.8 (q, ^1J(C,H) = 146.5 Hz, OMe), 57.7 (m, center-C), 44.4 (dq, ^2J(C,F) = 39.1 Hz, ^1J(C,H) = 195.3 Hz, CH). Anal. Found: C, 32.67; H, 1.73; F, 28.91%. Calcd. for $C_9H_5F_5O_4Fe$: C, 32.96; H, 1.54; F, 28.96%.

4 X-ray structure analysis of **2**: $C_9H_5F_5O_4Fe$, *F.W.* = 327.98, space group $P\bar{1}$, $Z = 2$, $a = 9.279(1)$, $b = 11.935(1)$, $c = 5.9948(8)$ Å, $\alpha = 101.845(9)$, $\beta = 106.92(1)$, $\gamma = 102.184(10)°$, $V = 595.1(1)$ Å^3, $\rho_{calcd} = 1.830$ gcm^{-3}. 2859 measured, 2351 independent reflections, of which 893 were considered as observed [$I > 2.50\sigma(I)$]. $R = 0.058$, $R_w = 0.035$.

5 M. D. Jones, R. D. W. Kemmitt in *Advances in Organometallic Chemistry, Vol. 27* (Eds.: F. G. A. Stone, R. West), Academic Press, inc., London (1987), p. 279, and references therein.

6 **3**: To a solution of **1** (0.62 g, 1.8 mmol) in diethyl ether (5 mL) was added a diethyl ether solution of phenyllithium (1.7 M, 1.1 mL, 1.9 mmol) at -78 °C, and then the reaction mixture was stirred at -78 °C for 3.5 h. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with n-hexane gave yellow oil of **3** (0.081 g, 0.20 mmol, 11%). IR (KBr): $\nu = 2045, 2018$ cm^{-1} (C≡O); ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 7.34$ (m, 5H; Ph), 3.54 (q, ^3J(H,F) = 10.2 Hz, 1H; CH), 3.21 (s, 3H; OMe); ^{13}C NMR (68 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 207.8$ (d, Fe-CO), 207.3 (d, Fe-CO), 203.4 (s, Fe-CO), 143.3 (t, ^1J(C,F) = 327.2 Hz, CF$_2$), 141.5 (s, Ph), 132.7 (s, Ph), 130.0 (s, Ph), 128.4 (s, C(OMe)Ph), 128.0 (s, Ph), 126.7 (q, ^1J(C,F) = 272.1 Hz, CF$_3$), 66.0 (m, center-C), 58.7 (q, ^1J(C,H) = 146.5 Hz, OMe), 49.7 (dq, ^2J(C,F) = 36.6 Hz, ^1J(C,H) = 161.1 Hz, CH).

7 For the *anti* to *syn* isomerization of π-allyl complexes, for example: R. W. Fish, W. P. Giering, D. Marten, and M. Rosenblum, *J. Organomet. Chem.*, **105**, 101 (1976).