thanks the Nuclear Energy Research Institute for a research fellowship.

Registry No. **1**, 36091-97-1; **3a**, 109064-32-6; **3c**, 109283-40-1; **3d**, 109283-39-8; **4a**, 109283-36-5; **4b**, 109283-37-6; **4c**, 109283-38-7; **6**, 109283-42-3; (η^5-C_5H_5)$Mo(CO)_3$, 12079-65-1; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; (SiF_2(Bu-*t*)C=$CHSiF_2$)Mo(CO)5, 75311-40-9; (SiF_2(Bu-*t*)C=$CHSiF_2$)$W(CO)_5$, 109283-41-2; 1,3-butadiene, 106-99-0; 2,3-dimethyl-1,3-butadiene, 513-81-5; 2-methyl-1,3-butadiene, 78-79-5.

Metal Carbonyl Mediated Isomerization of 1,4-Disilacyclohexa-2,5-dienes Involving Cleavage of C–Si Bonds

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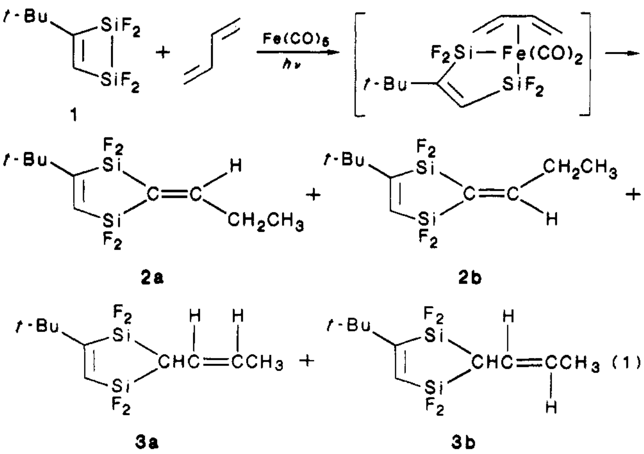
Received April 3, 1987

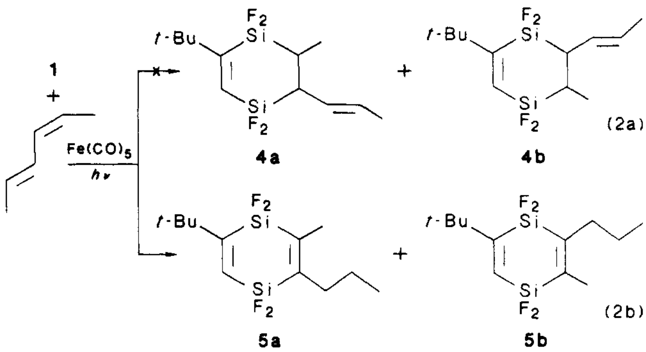
The isomerization between 2,5- and 2,6-disubstituted 1,4-disilacyclohexa-2,5-diene derivatives is studied under photochemical conditions in the presence of $Fe(CO)_5$. Strong evidence is given for the process involving two metal-assisted Si–C bond cleavages to form an alkyne complex as the intermediate. Other possible mechanisms are discussed for comparison.

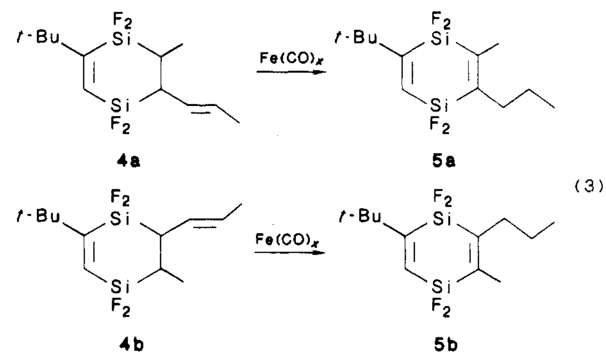
Recently we reported the novel cycloaddition reactions between 1,1,2,2-tetrafluoro-1,2-disilacyclobutene (**1**) and conjugated dienes mediated by metal carbonyls.[1-4] All these reactions involved the disilametallacycle intermediates which facilitated the migration of silyl groups to the dienes via various routes, for example, in the case of butadiene,[2,4] eq 1.



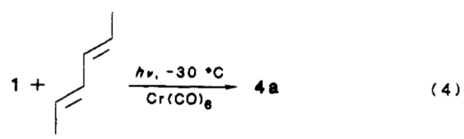
During the course of our study of the iron-mediated cycloaddition reaction of **1** with *cis,trans*-2,4-hexadiene,[3] products from direct 1,2-addition reaction, namely, 1,4-disilacyclohexa-2-enes **4a,b**, were not obtained. Instead, 1,4-disilacyclohexa-2,5-dienes **5a,b** were found to be the major products (eq 2).

It is believed that 1,4-disilacyclohexa-2-enes **4a,b** were formed first but converted to **5a** and **5b**, respectively, by the iron carbonyl species that existed in the reacting system (eq 3).





Fortunately, it was possible to obtaine **4a** from the reaction of *trans,trans*-2,4-hexadiene,[3] which provided an opportunity to verify the idea described above (eq 4).

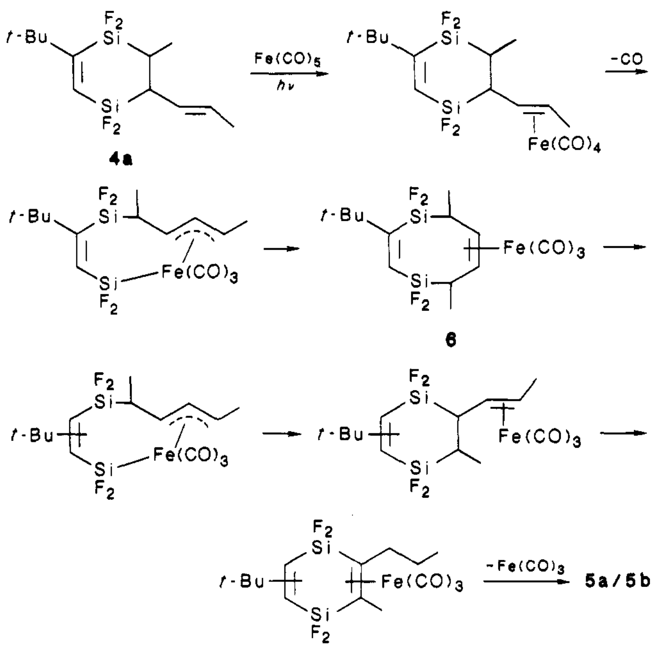


However, when **4a** was treated with $Fe(CO)_5$ photochemically, not only **5a** but also a mixture of **5a** and **5b** (in a ratio of 2:3) were obtained (eq 5).[3]

$$\mathbf{4a} \xrightarrow[h\nu]{Fe(CO)_5} \mathbf{5a/5b} \tag{5}$$

(1) Lin, C. H.; Lee, C. Y.; Liu, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 1323.
(2) Lin, C. H.; Lee, C. Y.; Liu, C. S. *Organometallics*, first four papers in this issue.
(3) Lee, C. Y.; Lin, C. H.; Liu, C. S. *Organometallics*, second of four papers in this issue.
(4) Lee, C. Y.; Lin, C. H.; Liu, C. S. *Organometallics*, third of four papers in this issue.

Scheme I

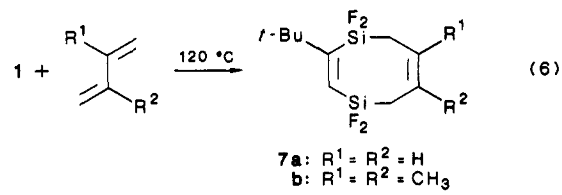


It is obvious that the standard mechanisms of metal-catalyzed olefin isomerization cannot account for the observed isomerization between these isomers. This transformation may involve cleavage and formation of Si–C bonds, although the exact manner is unknown. It was hoped that a more thorough understanding of these isomerizations should provide more insight into the mechanism of the metal-mediated silyl migration to coordinated dienes.

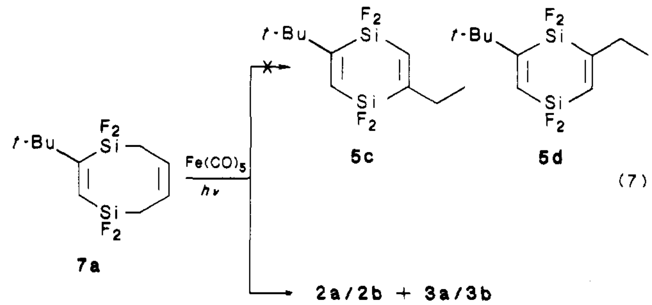
Results and Discussion

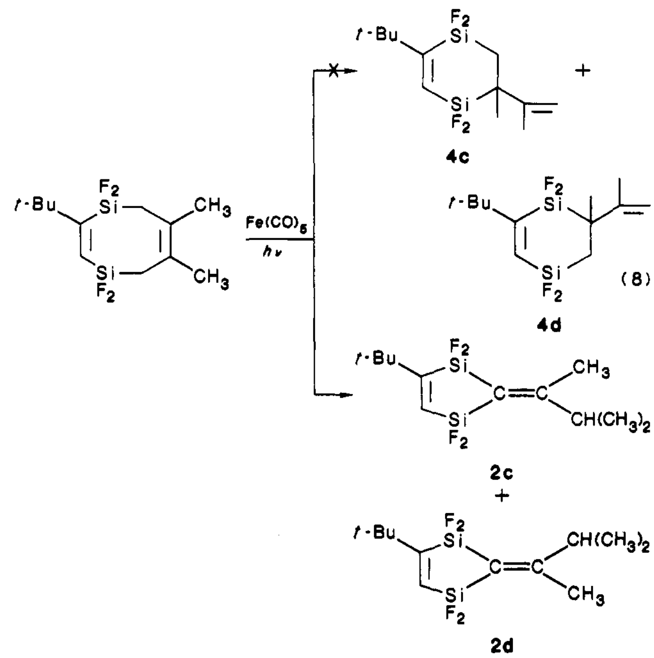
There are two possible mechanisms that can in principle be responsible for the isomerization between these isomers. The first involves the insertion of the metal into a Si–C bond of **4a** or **4b** (oxidative addition of the Si–C bond)[5,6] which was followed by the formation of a Fe-bonded 1,4-disilacycloocta-2,6-diene intermediate (**6**). This intermediate allows the reversed formation of 1,4-disilacyclohex-2-enes via metal insertion in either one of the two Si–C bonds; thus formation of the products of both isomers of **5a** or **5b** becomes possible (Scheme I).

To test the mechanism proposed above, 1,4-disilacycloocta-2,6-diene derivatives **7a** and **7b** were prepared by thermally reacting 1 with 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, respectively (eq 6).


(6)

According to the mechanism in Scheme I, isomer pairs **5c**/**5d** and **4c**/**4d** were expected when **7a** and **7b** were irradiated with $Fe(CO)_5$, respectively. However, none of these products were observed. Instead, compounds **2a**/**2b** and **3a**/**3b** were obtained in the reaction of **7a**, and the compounds **2c** and **2d** were obtained in the reaction of **7b** (eq 7 and 8). These are exactly the same products obtained in the Fe-mediated 1,1-cycloaddition reactions of 1 with 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, respectively.[2]


(7)


(8)

It is obvious that the mechanism described in Scheme I cannot be responsible for the isomerization of **4a** (or **4b**). What really happened can perhaps be best illustrated in Scheme II.

It seems that the cycloaddition reaction of 1 with 1,3-butadiene and the reaction of **7a** with $Fe(CO)_5$ proceeded via a common intermediate X, which preferred hydrogen migration to formation of the six-membered ring.[2]

The second possible mechanism involves the insertion of Fe into two Si–C bond, leading to the formation of an alkyne complex of the disilametallacycle (Y) as an intermediate. The reversed reaction, namely, migration of silyl groups back to the coordinated alkyne, would result in the formation of both forms of isomers of the 1,4-disilacyclohexa-2,5-dienes (Scheme III).

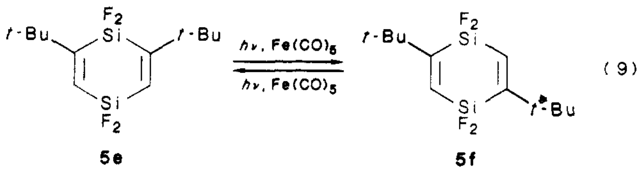
The intermediacy of an alkyne complex of a silametallacycle, a close analogue of Y, was proposed by Seyferth et al. to explain the observation of unusual products in the Pd-catalyzed cycloaddition reactions between silacyclopropene and alkynes.[5]

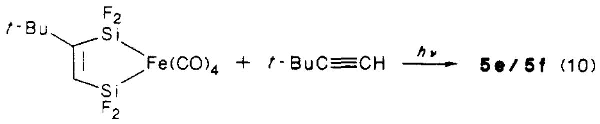
For a test of the mechanism described in Scheme III, a comparison was made between the isomerization of 1,4-disilacyclohexa-2,5-dienes and the reactions of the disilametallacycle with the corresponding alkynes, for example, the isomerization between **5e** and **5f** and the reaction of $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2\text{–})Fe(CO)_4$ with *tert*-butylacetylene (eq 9 and 10).

Indeed, the two reactions gave exactly the same results. In the range of −55 to 65 °C both reactions resulted in the

(5) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 47.

(6) (a) Pitt, C.; Skillern, K. R. *J. Organomet. Chem.* **1967**, *7*, 525. (b) Cundy, C. S.; Eaborn, C.; Lappert, M. F. *Ibid.* **1972**, *44*, 291. (c) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

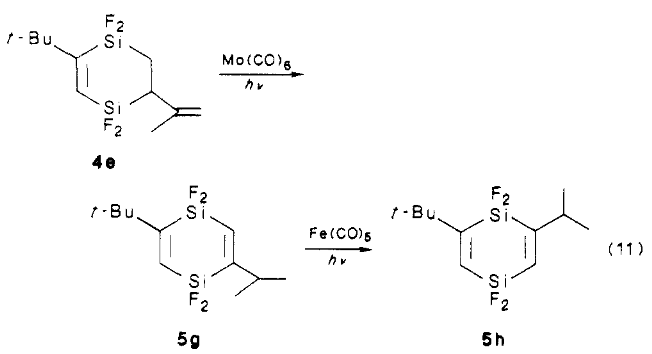




same ratio of **5e**/**5f** for each particular temperature (Scheme IV). Obviously in the presence of catalytic iron carbonyl species, interconversion of **5e** and **5f** is reversible. This observation strongly suggests that those two reactions proceed via a common intermediate, namely, compound Y.

In fact, a catalytic amount of either $Fe(CO)_5$ or $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2\text{-})Fe(CO)_4$ would catalyze the formation of **5e** and **5f** from a large amount of starting materials (**1** and *tert*-butylacetylene). All these observations are summarized in Scheme V.

It is interesting to note that the isomerization of 1,4-disilacyclohexa-2-ene derivatives can be completed in two separate steps. For example, **4e** could be converted to the corresponding 1,4-disilacyclohexa-2,5-diene **5g** by $Mo(CO)_6$. Compound **5g** was isolated and then isomerized to **5h** by treating with $Fe(CO)_5$ (eq 11).



Experimental Section

Vacuum distillation and chemical manipulations were carried out on vacuum lines at 10^{-3} torr. Photochemical preparations employed a 450-W medium-pressure Hg lamp. Isoprene (Aldrich), iron pentacarbonyl (Strem), and molybdenum hexacarbonyl (Strem) were used as received. Solvents were dired and distilled over calcium hydride. The following compounds were prepared according to the published procedures respectively: **1**,[7] **4a**,[3] **4b**,[3] $(F_2Si(t\text{-}Bu)C{=}C(HSiF_2\text{-})Mo(CO)_5$,[8] $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2\text{-})Fe(CO)_4$,[9] t-Bu≡CH.[10]

Spectra. All mass spectra were recorded on a JEOL JMS-100 mass spectrometer operating at 12 eV. The NMR spectra were obtained from a JEOL JMS FX-100 spectrometer operating at 99.55, 93.65, and 25.0 MHz for ^1H, ^{19}F, and ^{13}C spectra, respectively, and a Bruker AM 400 spectrometer operating at 400.0, 376.5, and 100.0 MHz for ^1H, ^{19}F, and ^{13}C spectra, respectively. Chemical shifts of ^1H and ^{13}C NMR spectra were measured in δ values. ^{19}F NMR chemical shifts were measured in parts per million upfield from the internal standard CCl_3F. In the ^{13}C NMR data, the spectral multiplicity is due to couplings with heteronuclei, whereas the couping patterns in $^{13}C\{^1H\}_{CW}$ are included in the parentheses.

Preparation and characterization of compounds **2a**–**2d**, **3a**, **3b**, **5a**, and **5b** have been described previously.[2-4]

Preparation of 7a and 7b. Compound **1** (0.43 g, 2 mmol) was allowed to react with the respective butadiene ($CH_2{=}CHRCHR{=}CH_2$, R = H, CH_3) in slightly excess amount in isooctane solution at 120 °C for 3 h. The reaction mixture was kept under a dry nitrogen atmosphere. The products were purified by distillation at 90 °C under vacuum. The yields of **7a** and **7b** were 60% and 70%, respectively.

Anal. Calcd for **7a**: C, 44.78; H, 6.00; F, 28.36. Found: C, 44.34; H, 6.12; F, 28.07. Mass spectrum of **7a**: m/e 268 (M^+, $C_{10}H_{16}Si_2F_4^+$); 253 ($C_9H_{13}Si_2F_4^+$); 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$); 54 ($C_4H_6^+$). ^1H NMR of **7a**: δ 11.16 (s), 9 H, t-Bu; 1.92 (br), 4 H, CH_2; 5.52 (c), 2 H, $-CH{=}CH-$; 6.36 (t), 1 H, $=CHSiF_2-$. $^{19}F\{^1H\}$ NMR of **7a**: 127.26 (t), $=CHSiF_2$; 134.63 ppm (t), $=C(t\text{-}Bu)SiF_2$; $^3J_{=CH\text{-}SiF} = 4.0$, $^4J_{CH\text{-}SiF} = 1.0$ Hz. ^{13}C NMR of **7a**: δ 167.66 m (m), $=C(t\text{-}Bu)SiF_2$; 130.44 m (dm), $=CHSiF_2$; 122.89 and 122.64 s (d), $-CH{=}CH-$; 39.55 s (s), $(CH_3)_3C$; 28.95 s (q), $C(CH_3)_3$; 15.07 and 14.63 t (tt), CH_2.

Anal. Calcd for **7b**: C, 48.64; H, 6.76; F, 25.68. Found: C, 48.24; H, 6.67; F, 25.70. Mass spectrum of **7b**: m/e 296 (M^+, $C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 252 ($C_9H_{12}Si_2F_4^+$), 240 ($C_8H_{12}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 197 ($C_6H_{12}Si_2F_3^+$), 149 ($C_6H_{11}SiF_2^+$), 82 ($C_6H_{10}^+$), 57 ($C_4H_9^+$). ^1H NMR of **7b**: δ 1.12 (s), 9 H, t-Bu; 1.68 (s), 6 H, CH_3; 1.86 (c), 4 H, CH_2; 6.32 (t), 1 H, $=CHSiF_2$. ^{19}F NMR of **7b**: 125.13 (t), $=CHSiF_2$; 132.24 ppm (t), $=C(t\text{-}Bu)SiF_2$. ^{13}C NMR of **7b**: δ 167.98 c (c), $=C(t\text{-}Bu)SiF_2$; 130.72 tt (dtt), $=CHSiF_2$; 121.87 s (s) and 121.64 s (s), $CH_3C{=}$; 39.32 s (s), $(CH_3)_3C$; 29.0 s (q), $CH_3)_3C$; 23.14 t (tt), CH_2; 21.50 and 20.86 s (q), $=CCH_3$.

Isomerization of 7a and 7b. A 10-mL, n-pentane solution containing 1.0 mmol of **7a** and 3.0 mmol of $Fe(CO)_5$ was degassed and irradiated at 70 °C for 7 days. After filtration and removal of solvent, the residue was distilled under vacuum. The colorless distillate collected at 80–90 °C was found containing 0.6 mmol of **3a**/**3b** (**3a**:**3b** = 1:1). When **7b** was irradiated under similar conditions, about 15% of **7b** isomerized to a mixture containing equimoles of **2c** and **2d**.

Preparation of 5e. **1** (5.0 mmol), 10.0 mmol of 3,3-dimethylbut-1-yne, and 1.0 mmol of $Fe(CO)_5$ or $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2\text{-})Fe(CO)_4$ were transferred into a quartz reaction tube filled with dry nitrogen. Dried and degassed n-pentane (10 mL) was used as solvent. The reaction was carried out under irradiation at −55 °C. The reaction tube was subjected to degassing every 4–5 h. Compound **1** was completely consumed after 24 h. After removal of the solvent and $Fe_3(CO)_{12}$, compound **5e**, a pale yellow liquid, was obtained by distillation under vacuum at 90 °C (3.5 mmol, yield 70%). If the irradiation temperature was changed from −55 to 65 °C, both **5e** and **5f** were obtained.

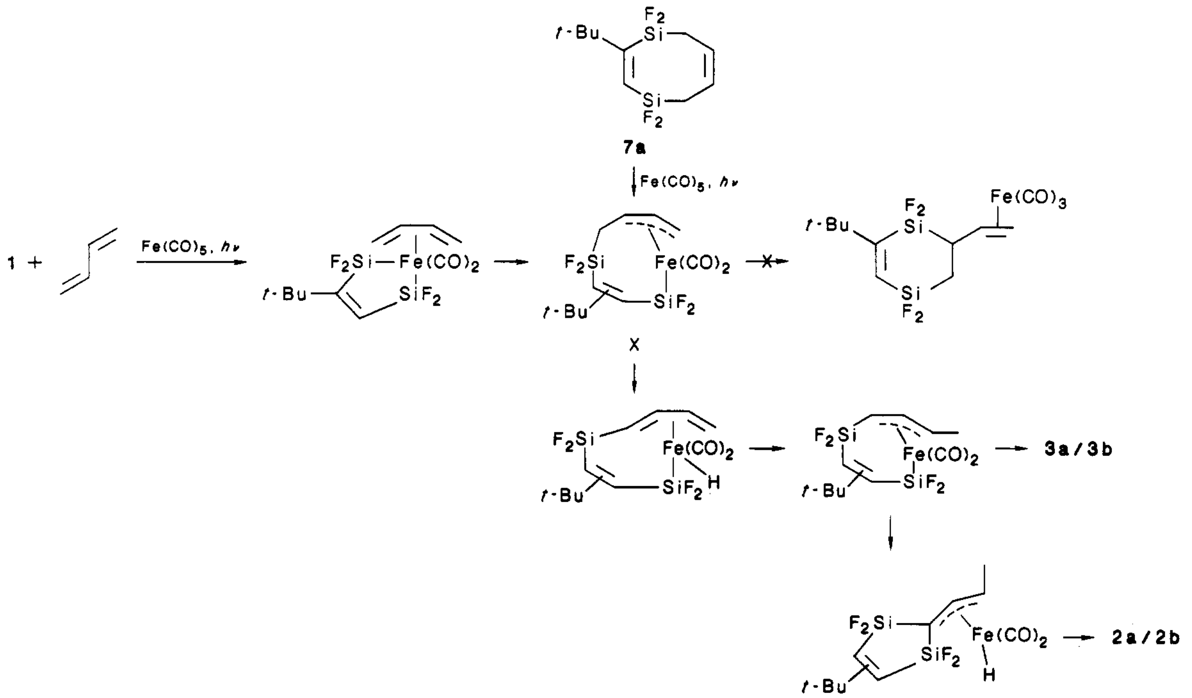
Mass spectrum of **5e**: m/e 296 (M^+, $C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 239 ($C_8H_{11}Si_2F_4^+$), 225 ($C_7H_9Si_2F_4^+$), 129 ($C_6H_{10}SiF^+$), 57 ($C_4H_9^+$). ^1H NMR of **5e**: δ 1.03 (s), 18 H, t-Bu; 6.5 (m), 2 H, $F_2SiCH{=}$. $^{19}F\{^1H\}$ NMR of **5e**[11]: 127.8 (t), $F_2SiCH{=}$; 142.0 (t), $=C(t\text{-}Bu)SiF_2$; $^5J_{F,F} \le 1.0$ Hz. ^{13}C NMR of **5e**: δ 29.3 s (q), $(CH_3)_3C-$; 40.0 s (s), $(CH_3)_3C-$; 135.3 t (dt), $F_2SiCH{=}$; 173.74 m (m), $=C(t\text{-}Bu)SiF_2$.

Reaction of 5e with $Fe(CO)_5$ or $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2\text{-})Fe(CO)_4$. A n-pentane solution (10 mL) containing 5.0 mL of **5e** and 1.0 mmol of $Fe(CO)_5$ was irradiated under nitrogen atmosphere at 65 °C for 72 h. The reaction mixture was degased every 4–5 h. during the irradiation. After removal of solvent and $Fe_3(CO)_{12}$ a colorless liquid was obtained by distillation under vacuum at 90 °C. It contained compound **5e** and **5f** (0.42 mmol, **5e**:**5f** = 1:5). When $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2\text{-})Fe(CO)_4$ instead of $Fe(CO)_5$ was used, the reaction gave the same result.

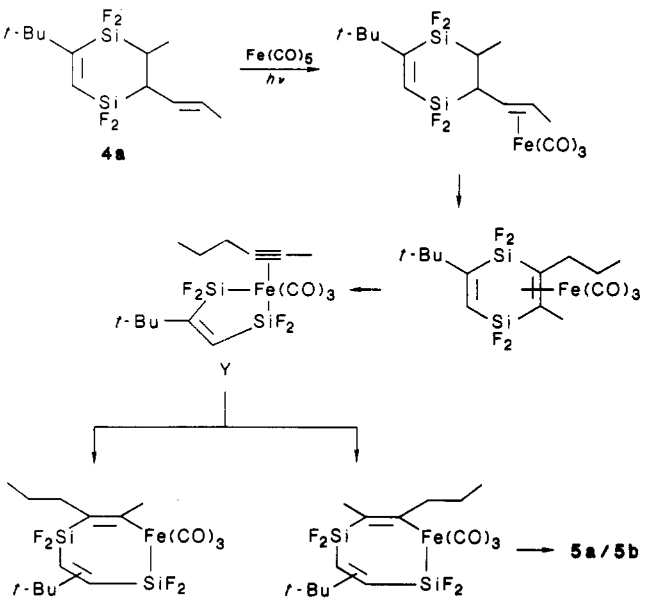
Mass spectrum of **5f**: m/e 296 (M^+, $C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 225 ($C_7H_9Si_2F_4^+$), 129 ($C_6H_{10}SiF^+$), 57 ($C_4H_9^+$). ^1H NMR of **5f**: δ 1.0 (s), 18 H, t-Bu; 6.5 (m), 2 H, $SiF_2CH{=}$.

(7) Liu, C. S.; Margrave, J. L.; Thompson, J. C. *Can. J. Chem.* **1972**, *50*, 465.
(8) Hseu, T. H.; Chi, Y.; Liu, C. S. *Inorg. Chem.* **1981**, *20*, 199.
(9) Chi, Y.; Liu, C. S. *Inorg. Chem.* **1981**, *20*, 3456.
(10) Bartlet, P. D.; Rosen, L. J. *J. Am. Chem. Soc.* **1942**, *64*, 543.
(11) The ^{19}F NMR spectra of **5e** and **5f** were misinterpreted previously. The spectra reported previously were actually due to the two isomers of $(\eta^4\text{-}C_{12}H_{20}Si_2F_4)Ni(CO)_2$ (so the four fluorines were different). See; Liu, C. S.; Cheng, C. W. *J. Am. Chem. Soc.* **1975**, *97*, 6746.

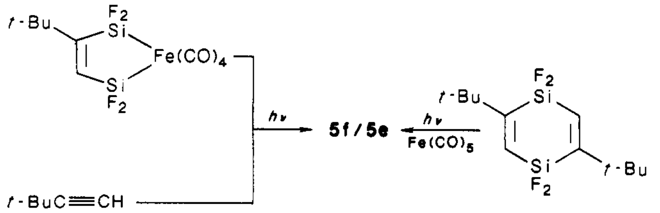
Scheme II



Scheme III



Scheme IV

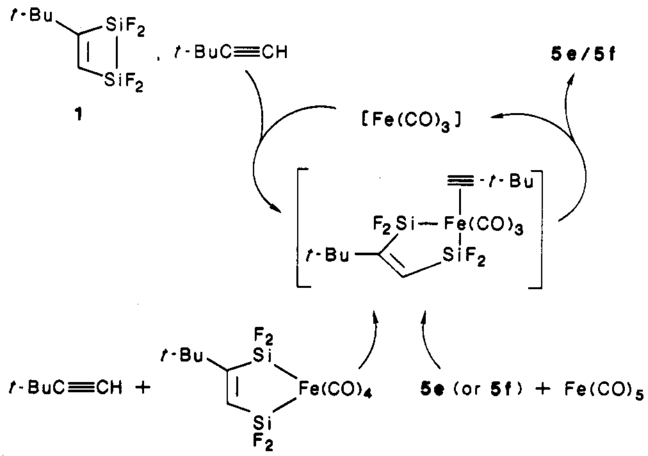


65 °C	5:1	65 °C
25 °C	3:2	25 °C
0 °C	1:2	0 °C
-27 °C	2:5	-27 °C
-55 °C	1:10	-55 °C

$^{19}F\{^1H\}$ NMR of **5f**: 135.2 ppm (s), =C(*t*-Bu)SiF_2CH=. ^{13}C NMR of **5f**[11]: δ 135.1 tt(dtt), F_2SiCH=; 174.2 m (m), =*C*(*t*-Bu)SiF_2; 39.1 s (s), $(CH_3)_3C$; 29.1 s (q), $(CH_3)_3C$.

Preparation of 4e. A *n*-pentane solution (10 mL) containing 5.0 mmol of (F_2Si(*t*-Bu)C=C(H)SiF_2–)Mo$(CO)_5$ and 10.0 mmol of isoprene was irradiated under nitrogen atmosphere at -50 °C for 72 h. The reaction mixture was degassed every 4–5 h during the irradiation. After removal of solvent and Mo$(CO)_6$, compound **4e**, a colorless liquid (3.0 mmol, yield 60%), was obtained by distillation under vacuum.

Scheme V



Anal. Calcd for **4e**: C, 46.81; H, 6.38; F, 26.95. Found: C, 46.78; H, 6.59; F, 26.56. Mass spectrum of **4e**: *m/e* 282 (M^+, $C_{11}H_{18}Si_2F_4^+$), 267 ($C_{10}H_{15}Si_2F_4^+$), 215 ($C_{10}H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). ^1H NMR of **4e**: δ 1.1 (s), 9 H, *t*-Bu; 1.2 (c), 2 H, F_2SiCH_2; 11.7 (s), 3 H, =CCH_3; 2.0 (C), 1 H, F_2SiC*H*; 4.75 (c), 2 H, =CH_2; 6.5 (m), 1 H, F_2SiC*H*=. $^{19}F\{H\}$ NMR of **4e**: 136.24, 140.4 (d), =C-(*t*-Bu)SiF_2; 139.24, 139.74 (d), F_2SiCH=. ^{13}C NMR of **4e**: δ 10.43 t (tt), F_2SiCH_2–; 24.9 t (dt), F_2SiCH–; 29.43 s (q), $(CH_3)_3C$; 30.4 s (q), =CCH_3; 39.25 s (s), $(CH_3)_3C$; 115.4 s (t), =CH_2; 128.0 s (s), =*C*CH_3; 134.85 tt (dtt), F_2SiCH=, 180.4 m (m), F_2SiC(*t*-Bu)=.

Isomerization of 4e. 4e (5.0 mmol), 2.0 mmol of Mo$(CO)_6$, and 10 mL of *n*-pentane were transferred into a reaction tube under vacuum. The reaction was carried out under irradiation at 40–50 °C for 72 h. The solution was concentrated to a brown liquid and then subjected to disillation under vacuum. Compound **5g**, a colorless liquid, was obtained (yield 68%). Under the same conditions, **5g** reacted with Fe$(CO)_5$ to give equimoles of **5g** and **5h** (yield 95%).

Mass spectrum of **5g**: *m/e* 282 (M^+, $C_{11}H_{18}Si_2F_4^+$), 267 ($C_{10}H_{15}Si_2F_4^+$), 252 ($C_9H_{12}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$).

^{1}H NMR of **5g**: δ 1.1 (s), 9 H, *t*-Bu; 1.5 (d), 6 H, $-CH(CH_3)_2$; 2.3 (m) 1 H, $-CH(CH_3)_2$; 6.5 (m), 2 H, F_2SiCH=. $^{19}F\{^1H\}$ NMR of **5g**: 130.6 (t), =C(*t*-Bu)SiF_2; 141.65 ppm (t), =C(*i*-Pr)SiF_2. Mass spectrum of **5g**/**5h**: very similar to that of **5g**. $^{19}\{^1H\}$ NMR of **5h** (obtained by comparing spectra): 139.5 (t), =C(*i*-Pr)SiF_2; 126.1 ppm (t), =CHSiF_2.

Acknowledgment. We thank the Chinese National Science Council for financial support of this work. C.-h.L. thanks the Nuclear Energy Research Institute for a research fellowship.

Registry No. **1**, 36091-97-1; **2a**, 109034-53-9; **2b**, 109034-54-0; **2c**, 109034-56-2; **2d**, 109034-57-3; **3a**, 109064-32-6; **3b**, 109034-55-1; **4e**, 109034-58-4; **5e**, 55499-35-9; **5f**, 55499-34-8; **5g**, 109034-59-5; **5h**, 109034-60-8; **7a**, 109034-51-7; **7b**, 109034-52-8; $Fe(CO)_5$, 13463-40-6; $F_2Si(t\text{-}Bu)C{=}C(H)SiF_2Fe(CO)_4$, 78514-11-1; $Fe_3(CO)_{12}$, 17685-52-8; $F_2Si(t\text{-}Bu)C{=}C(H)SiF_2Mo(CO)_5$, 75311-40-9; $Mo(CO)_6$, 13939-06-5; t-BuC≡CH, 917-92-0; 1,3-butadiene, 106-99-0; 2,3-dimethyl-1,3-butadiene, 513-81-5; isoprene, 78-79-5.

Formation of Metal–Metal Bonds by Ion-Pair Annihilation. Dimanganese Carbonyls from Manganate(–I) Anions and Manganese(I) Cations

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Received February 17, 1987

The coupling of the anionic $Mn(CO)_5^-$ and the cationic $Mn(CO)_6^+$ occurs upon mixing to afford the dimeric $Mn_2(CO)_{10}$ in essentially quantitative yields. Dimanganese decacarbonyl is formed with equal facility from the coupling of $Mn(CO)_5^-$ with $Mn(CO)_5(py)^+$ and $Mn(CO)_5(NCMe)^+$. By way of contrast, the annihilation of $Mn(CO)_4PPh_3^-$ with $Mn(CO)_6^+$ yields a pair of homo dimers $Mn_2(CO)_{10}$ and $Mn_2(CO)_8(PPh_3)_2$ together with the cross dimer $Mn_2(CO)_9PPh_3$. Extensive scrambling of the carbonylmanganese moieties also obtains with $Mn(CO)_4P(OPh)_3^-$ and $Mn(CO)_5PPh_3^+$, as indicated by the production of $Mn_2(CO)_8[P(OPh)_3]_2$, $Mn_2(CO)_8[P(OPh)_3](PPh_3)$, and $Mn_2(CO)_8(PPh_3)_2$ in more or less statistical amounts. These diverse Mn–Mn couplings can be accounted for by a generalized formulation (Scheme VI), in which the carbonylmanganese anions $Mn(CO)_4P^-$ and the cations $Mn(CO)_5L^+$ undergo an initial electron transfer to produce $Mn(CO)_4P^\bullet$ and $Mn(CO)_5L^\bullet$, respectively. The behaviors of these 17- and 19-electron radicals coincide with those independently generated in a previous study of the anodic oxidation of $Mn(CO)_4P^-$ and the cathodic reduction of $Mn(CO)_5L^+$, respectively. The facile associative ligand substitution of 17-electron carbonylmanganese radicals by added phosphines provides compelling evidence for the interception of $Mn(CO)_4P^\bullet$ and its interconversion with 19-electron species in the course of ion-pair annihilation. The reactivity trend for the various ion pairs qualitatively parallels the driving force for electron transfer based on the oxidation and reduction potentials of $Mn(CO)_4P^-$ and $Mn(CO)_5L^+$, respectively, in accord with the radical-pair mechanism in Scheme VI.

Introduction

A wide variety of organometallic dimers are now known.[1,2] The formation of the metal–metal bonds in dimeric metal carbonyls commonly derives from various reductive procedures including the use of carbon monoxide, metals, alkylmetals, etc. as reagents.[3] The oxidation of carbonylmetalate anions is also known to lead to carbonylmetal dimers.[4] Heterobimetallic carbonyls result from the interaction of carbonylmetalates with different types of metal halides and homo dimers.[5,6] The latter can be generally classified as nucleophilic substitution processes, although mechanistic studies of such metal–metal bond formations are generally lacking.

The heterolytic coupling of carbonylmetal cations and anions is indicated in an earlier report of the treatment of tetracarbonylcobaltate(–I) with hexacarbonylrhenium(I) to afford the mixed carbonyl,[7,8] i.e., eq 1. Similarly the

$$Co(CO)_4^- + Re(CO)_6^+ \rightarrow ReCo(CO)_9 + CO \qquad (1)$$

(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980. (b) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley CA, 1980. (c) Lukehart, C. M. *Fundametal Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985.

(2) Compare also: (a) Werner, H. *Adv. Organomet. Chem.* **1981**, *19*, 155. (b) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207.

(3) (a) Podall, H. E.; Dunn, J. H.; Shapiro, H. *J. Am. Chem. Soc.* **1960**, *82*, 1325. (b) Hieber, W.; Fuchs, H. *Z. Anorg. Allg. Chem.* **1941**, *248*, 256. (c) Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133. (d) Hieber, W.; Schulten, H.; Marin, R. *Z. Anorg. Allg. Chem.* **1939**, *240*, 261. (e) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211. (f) Ungurenasu, C.; Palie, M. *J. Chem. Soc., Chem. Commun.* **1975**, 388.

(4) (a) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 193. (b) Birdwhistell, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239. (c) Armstead, J. A.; Cox, D. J.; Davis, R. *J. Organomet. Chem.* **1982**, *236*, 213. (d) Dessy, R. E.; Weissman, P. M.; Pohl, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5117.

(5) (a) Dessy, R. E.; Weissman, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 5129. (b) Pandey, V. N. *Inorg. Chim. Acta* **1977**, *23*, L26. (c) Fontana, S.; Orama, O.; Fischer, E. O.; Schubert, U.; Kreissl, F. R. *J. Organomet. Chem.* **1978**, *149*, C57. (d) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1972**, *36*, 113. (e) Roberts, D. A.; Mercer, W. C.; Zahurak, S. M.; Geoffroy, G. L.; DeBrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* **1982**, *104*, 910. (f) Bennett, M. A.; Patmore, D. J. *Inorg. Chem.* **1971**, *10*, 2387. (g) Anders, U.; Graham, W. A. G. *J. Am. Chem. Soc.* **1967**, *89*, 539. (h) Ruff, J. K. *Inorg. Chem.* **1968**, *7*, 1818. (i) Fischer, E. O.; Lindner, T. L.; Kreissl, F. R.; Braunstein, P. *Chem. Ber.* **1977**, *110*, 3139. (j) Michels, G. D.; Svec, H. J. *Inorg. Chem.* **1981**, *20*, 3445. (k) Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *J. Chem. Soc., Chem. Commun.* **1982**, 1001. (l) Compare also: Hriljac, J. A.; Swepston, P. N.; Shriver, D. *Organometallics* **1985**, *4*, 158.

(6) (a) Dessy, R. E.; Weissman, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 5124. (b) See also: Morse, D. L.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *125*, 71.

0276-7333/87/2306-1886$01.50/0