In order to determine if the hydride migration from carbon to nitrogen is intramolecular or intermolecular, crossover experiments were performed (Scheme II). Amido complex Tp′W$(CO)_2$[NH(*p*-Tol)] (4) and nitrene complex [Tp′W$(CO)_2$(N-*p*-Tol)][PF_6] (5) were synthesized according to the procedure we reported for the corresponding phenyl complexes.[1] The difference between the amido proton ^{1}H NMR signals for Tp′W$(CO)_2$(NHPh) and Tp′W$(CO)_2$[NH(*p*-Tol)] (4) of 0.04 ppm in CD_2Cl_2 is readily detectable at 400 MHz. The reactivity of the two nitrene complexes [Tp′W$(CO)_2$(N-*p*-Tol)][PF_6] (5) and [Tp′W$(CO)_2$(NPh)][PF_6] toward hydride reduction is essentially the same. Separate solutions of Tp′W(CO)(NPh)(CHO) and Tp′W(CO)(N-*p*-Tol)(CDO) were prepared[9] at low temperature. Half of each solution was mixed and allowed to react together at −30 °C for 4 h before room-temperature isolation prior to monitoring the ^{1}H NMR spectrum of the products. The control was provided by the unmixed solutions, which were also held at −30 °C for 4 h before room-temperature isolation. The low level of proton incorporation into the Tp′W$(CO)_2$(ND-*p*-Tol) product was the same in both the crossover and the control as anticipated for an intramolecular transfer of the hydride. The complementary experiments using Tp′W(CO)(NPh)(CDO) and Tp′W(CO)(N-*p*-Tol)(CHO) gave similar results.

Acknowledgment. We are grateful to the National Institutes of Health (Grant GM28938) and the Department of Energy (Grant DE-FG05-85ER13430) for financial support.

Registry No. 1, 139495-12-8; 3, 139495-13-9; [Tp′W$(CO)_2$(NPh)][PF_6], 129812-91-5; $LiBH_4$, 16949-15-8.

Supplementary Material Available: Text giving experimental details, including preparations and characterization data, for complexes 1–5 (4 pages). Ordering information is given on any current masthead page.

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[9] Lithium borohydride is the best hydride reagent among those we tested, but we used sodium borohydride here because the borodeuteride is readily available.

Kinetic Study of Isomerization Reactions of (Trimethylsilyl)methylsilylene-Bridged Diiron Complexes

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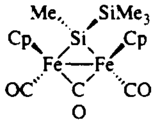
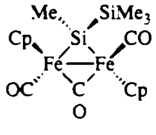
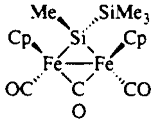
Summary: Kinetic study on the mutual isomerizations between three geometrical isomers of $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}SiMeSiMe_3)$ in C_6D_6 revealed that the reaction proceeds through the process cis($SiMe_3$) ⇄ trans ⇄ cis(Me). A mechanism containing a silylene-bridged diiron complex with no Fe–Fe bond is proposed as the key intermediate for the isomerization reactions.

Recently, both Pannell's group[1] and our own[2] reported the study of the photolysis of the disilanylene-bridged diiron complex $FpSiMe_2SiMe_2Fp$ (1; Fp = $CpFe(CO)_2$). During the early stages of the photolysis of 1 a mixture of a silylene-bridged diiron complex $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}SiMeSiMe_3)$ (2) and a bis(silylene)-bridged diiron complex $[CpFe(CO)]_2(\mu\text{-}SiMe_2)_2$ (3) was formed, while, upon prolonged irradiation, 2 was quantitatively converted to 3.[2] During the course of the study, we found that, in solution, the silylene-bridged complex 2 exists as a mixture of all three possible geometrical isomers, cis($SiMe_3$), cis(Me), and trans, which equilibrate in the ratio of 44.0:29.1:26.9, respectively, at 296 K in C_6D_6. We report here the kinetic study of the isomerization reactions of 2 in C_6D_6 and propose a possible mechanism for the reactions.


cis($SiMe_3$)


trans


cis(Me)

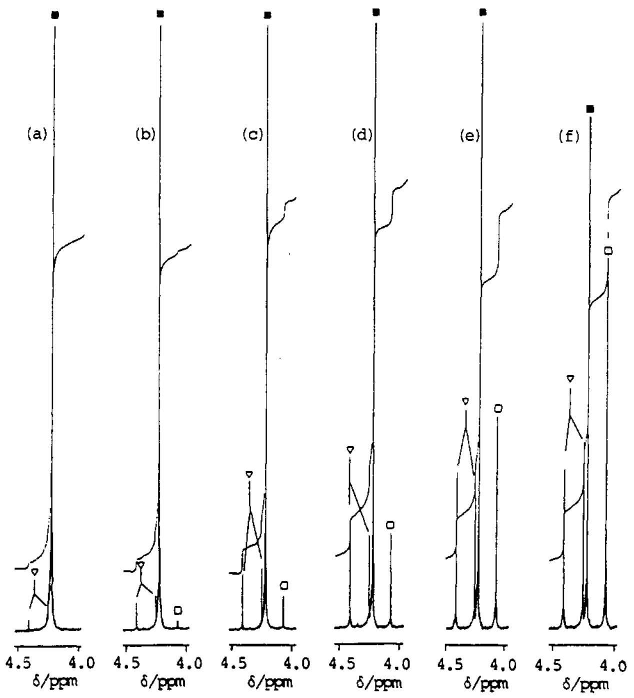


Figure 1. ^{1}H NMR spectral change of a C_6D_6 solution containing the cis($SiMe_3$) isomer at 296 K at (a) 5 min, (b) 15 min, (c) 35 min, (d) 66 min, (e) 135 min, and (f) 415 min after dissolution. Key: ■, cis($SiMe_3$); □, cis(Me); ▽, trans.

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[1] Pannell, K. H.; Sharma, H. *Organometallics* 1991, *10*, 954.

[2] Ueno, K.; Hamashima, N.; Shimoi, M.; Ogino, H. *Organometallics* 1991, *10*, 959.

[3] Hoshino et al. also reported a useful method for computing the rate constants of a reversible, first-order, triangular network: Hoshino, Y.; Takahashi, R.; Shimizu, K.; Sato, G. P.; Aoki, K. *Bull. Chem. Soc. Jpn.* 1989, *62*, 993.

0276-7333/92/2311-1435$03.00/0

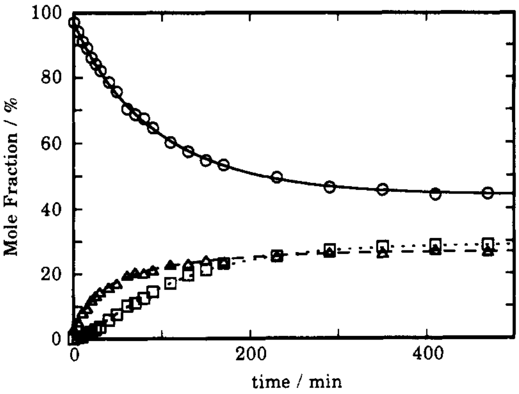
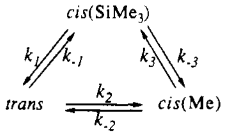


Figure 2. Variation of the mole fraction of each isomer with time at 296 K: ○, cis(SiMe$_3$); □, cis(Me); △, trans. The kinetic traces were calculated by use of the rate constants as determined by curve-fitting with the nonlinear least-squares method.

Fractional crystallization of 2 afforded crystals of the pure cis(SiMe$_3$) isomer.[2] This geometry was unequivocally confirmed by an X-ray structural analysis and further substantiated by ^{1}H NMR NOE measurements. The isomerization reactions were followed by monitoring the ^{1}H NMR spectra at 283, 296, 303, and 313 K. Figure 1 shows the ^{1}H NMR spectral change of the cis(SiMe$_3$) complex in C$_6$D$_6$ at 296 K. Spectrum a in Figure 1 shows one strong singlet assignable to the Cp protons of the cis(SiMe$_3$) isomer with a small doublet assignable to those of the trans isomer. The signal due to the cis(Me) isomer was not detectable 5 min after dissolution but could be seen 15 min after dissolution. Intensities of signals from both trans and cis(Me) isomers increased with time. Figure 2 shows a plot of the mole fraction of each isomer against time and appears to indicate that the cis(SiMe$_3$) isomer converts to the trans isomer but not directly to the cis(Me) isomer, the latter being formed from the trans isomer.

The rate constants for the conversions were determined as follows. At first, we assumed the reaction scheme as a triangular network:



(1)

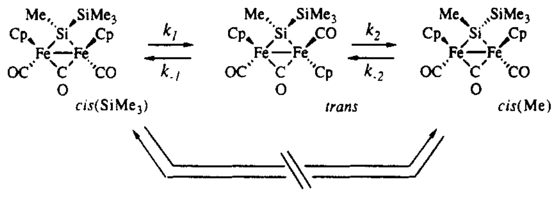
The kinetic equations for the reactions can be expressed as

$$\frac{d[cis(SiMe_3)]}{dt} = k_3\left\{[cis(Me)] - \frac{1}{K_3}[cis(SiMe_3)]\right\} - k_1\left\{[cis(SiMe_3)] - \frac{1}{K_1}[trans]\right\} \quad (2)$$

$$\frac{d[trans]}{dt} = k_1\left\{[cis(SiMe_3)] - \frac{1}{K_1}[trans]\right\} - k_2\left\{[trans] - \frac{1}{K_2}[cis(Me)]\right\} \quad (3)$$

$$\frac{d[cis(Me)]}{dt} = k_2\left\{[trans] - \frac{1}{K_2}[cis(Me)]\right\} - k_3\left\{[cis(Me)] - \frac{1}{K_3}[cis(SiMe_3)]\right\} \quad (4)$$

where k_i is the rate constant given in eq 1 and K_i is the equilibrium constant defined by k_i/k_{-i} (i = 1–3). These equations were evaluated using a technique of numerical integration via the fourth-order Runge–Kutta method. The first-order rate constants of the interconversions between the isomers were obtained by optimizing the fit between calculated and observed concentration–time data by the nonlinear least-squares method using a SALS package.[4] The result obtained clearly indicates that direct interconversion between the two cis isomers is forbidden or is very slow compared to those of the other isomerizations. Thus, we recalculated the rate constants with the assumption that the isomerization reactions proceed as follows:



(5)

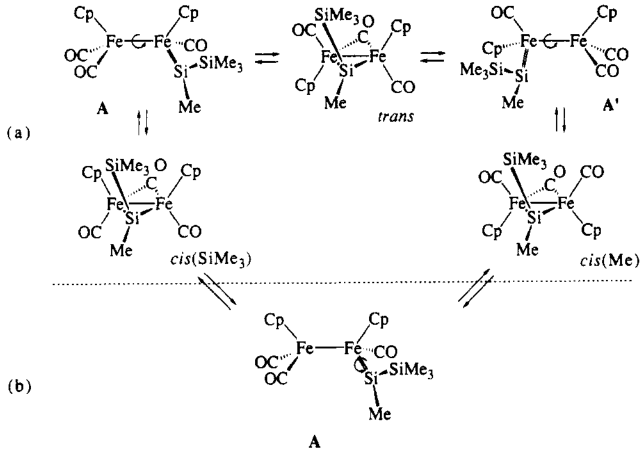
The rate constants thus obtained and the activation parameters are summarized in Table I.

Table I. Rate Constants and Activation Parameters for the Isomerization Reactions of 2

temp/K	$k_1/10^{-4}$ s^{-1}	$k_{-1}/10^{-4}$ s^{-1}	$k_2/10^{-4}$ s^{-1}	$k_{-2}/10^{-4}$ s^{-1}
283	0.22 ± 0.01	0.45 ± 0.03	0.53 ± 0.12	0.45 ± 0.10
296	1.16 ± 0.02	1.90 ± 0.04	2.9 ± 0.2	2.7 ± 0.1
303	2.97 ± 0.07	4.7 ± 0.1	6.4 ± 0.3	6.0 ± 0.3
313	9.5 ± 0.2	12.6 ± 0.3	21 ± 1	22 ± 1
$\Delta H^{\ddagger}$/kJ mol^{-1}	90 ± 1	80 ± 2	88 ± 1	92 ± 2
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	−16 ± 5	−46 ± 8	−16 ± 4	−3 ± 6
$\Delta G^{\ddagger}$/kJ mol^{-1} [a]	95 ± 3	93 ± 4	93 ± 3	93 ± 3

[a] At 296 K.

Scheme I



There have been several studies of the cis/trans isomerization reactions of μ-alkylidene, μ-silylene, and μ-germylene dinuclear complexes with formula Cp$_2$M$_2$(CO)$_3$(μ-ER$_2$) (M = Fe, Ru; E = group 14 elements).[5-16] In most cases, the isomerization is presumed to occur by the Adams–Cotton mechanism, i.e., the bridging ligands move to terminal positions, which allows rotation about the met-

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(4) Nakagawa, T.; Oyanagi, Y. In *Recent Developments in Statistical Inference and Data Analysis*; Matusita, K., Ed.; North Holland Publishing Co.: Amsterdam, 1980; pp 221–225.

(5) Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1985**, 1935.

(6) Davies, D. L.; Knox, S. A. R.; Mead, K. A.; Morris, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2293.

(7) Korswagen, R.; Alt, R.; Speth, D.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1049.

(8) Colborn, R. E.; Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Orpen, A. G.; Plaas, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2661.

(9) Malisch, W.; Ries, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 120.

(10) Schroeder, N. C.; Funchess, R.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1989**, *8*, 521.

(11) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417.

(12) Adams, R. D.; Brice, M. D.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1080.

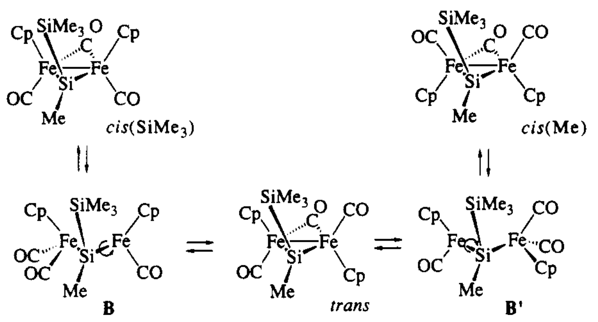
(13) Tobita, H.; Kawano, Y.; Ogino, H. *Chem. Lett.* **1989**, 2155.

(14) Colborn, R. E.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2099.

(15) Job, R. C.; Curtis, M. D. *Inorg. Chem.* **1973**, *12*, 2514.

(16) Altbach, M. I.; Muedas, C. A.; Korswagen, R. P.; Ziegler, M. L. *J. Organomet. Chem.* **1986**, *306*, 375.

Scheme II



al-metal bond, followed by a ring closure.[12] According to this mechanism, the conversion between the isomers of **2** can be depicted as shown in the Scheme Ia. The intermediate A or A′ has a terminal silylene ligand and an Fe–Fe single bond, such that both metal atoms retain an 18-electron configuration and rotation about the Fe–Fe bond becomes free. This mechanism, however, does not suitably account for the experimental results, since, in this mechanism, the silylene ligand in the intermediate may rotate freely about the Fe=Si bond suggesting that the cis(Me) isomer may be produced directly from the cis(SiMe$_3$) isomer (Scheme Ib).[17] Such a rotation would be expected to occur easily, since Gladysz et al. estimated that the rotation barrier around the Re=Si bond in [Cp(PPh$_3$)(NO)Re=SiMe$_2$]$^+$ is less than 34 kJ mol^{-1} at 183 K,[18] which is much smaller than the observed activation energy for the isomerization of **2**. In addition to this, the experimentally determined rotational energy barrier for [Cp(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Fe=CH$_2$]$^+$ was reported by Brookhart et al. to be 43.5 kJ mol^{-1} [19] and we also have estimated that the rotation energy around a Fe=Ge bond in Cp(OC)Fe{GeMe$_2$···O(Me)···SiMe$_2$} is much smaller than 62 kJ mol^{-1}.[20]

Thus, we propose a possible mechanism for the isomerization of **2** as shown in Scheme II: The Fe–(μ-CO) bond and the Fe–Fe bond of cis(SiMe$_3$) are cleaved to give the key intermediate B, which retains Fe–Si bonds. Subsequent rotation of the FeCpCO moiety about the Fe–Si bond and cyclization produces the trans isomer. Simultaneous rotation of two FeCp(CO)$_n$ moieties (n = 1, 2) about the respective Fe–Si bonds in the intermediate B may result in the direct formation of cis(Me) from cis(SiMe$_3$), but the probability of this is likely to be very small. Similarly, the trans isomer gives the cis(Me) isomer through the intermediate B′ and vice versa. The formation of the intermediate B or B′ from the reactants requires the cleavage of two bonds, i.e., Fe–(μ-CO) and Fe–Fe bonds. The $\Delta H^{\ddagger}$ values for the isomerizations of **2**, 80–92 kJ mol^{-1}, are comparable to the activation enthalpy for the cleavage of the Fe–Fe bond in Cp(CO)$_2$Fe–Fe(CO)$_2$Cp (95 kJ mol^{-1}) as estimated by Cutler et al.[21] This suggests that the rate-determining steps for the isomerization reactions reported herewithin are the breaking of the Fe–Fe bonds. A similar mechanism has been proposed for the cis/trans isomerization of [CpFe(CO)]$_2$(μ-CO)(μ-CH$_2$) (**4**) by Altbach et al.[16] The fact that the activation parameters for the isomerization of **4** in benzene ($\Delta H^{\ddagger}$ = 79 kJ mol^{-1} and $\Delta S^{\ddagger}$ = –52 J mol^{-1} K^{-1} for cis to trans isomerization; $\Delta H^{\ddagger}$ = 72 kJ mol^{-1} and $\Delta S^{\ddagger}$ = –70 J mol^{-1} K^{-1} for trans to cis isomerization) are comparable to those for the isomerization of **2** supports our mechanism, since, in both mechanisms, common processes operate: the Fe–(μ-CO) and the Fe–Fe bonds are cleaved.[22] Angelici also proposed a mechanism similar to that in Scheme II as one of the possible mechanisms for the cis/trans conversion of [CpM(CO)]$_2$(μ-CS)$_2$ (M = Fe, Ru).[23,24] In addition, it is noteworthy that Barrett and Sun proposed a monocarbonyl-bridged diiron complex, [CpFe(CO)$_2$][CpFe(CO)](μ-CO), as a key intermediate for the reaction of [CpFe(CO)$_2$]$_2$ with SnX$_2$ (X = Cl, Br) to produce [CpFe(CO)$_2$]$_2$(μ-SnX$_2$) in THF solution; however, they did note that the structure of this intermediate was by no means certain.[25]

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Registry No. **2** (cis-SiMe$_3$ isomer), 132724-37-9; **2** (trans isomer), 132830-34-3; **2** (cis-Me isomer), 132830-33-2.

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(17) A reviewer pointed out that the original Cotton–Adams mechanism will still explain the results, provided only that there is restricted rotation of the crowded =SiMe(SiMe$_3$) ligand. The consideration of the crystal structure of the cis(SiMe$_3$) isomer[2] and the inspection by a molecular model revealed that the steric hindrance between the SiMe(SiMe$_3$) and the CpFe(CO) moiety is insufficient to restrict the rotation of the =SiMe(SiMe$_3$) ligand. The notably small steric repulsion between the SiMe$_3$ substituent and Cp group in the cis(SiMe$_3$) isomer has been demonstrated in a previous paper.[2]

(18) Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 309.

(19) Brookhart, M.; Tucker, J. K.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203.

(20) Koe, J. R.; Tobita, H.; Ogino, H. Submitted for publication.

(21) Cutler, A. R.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *120*, 87.

(22) Negative $\Delta S^{\ddagger}$ values for the isomerizations of **2** and **4** may be attributed to the coordination of solvent molecules to the intermediates containing coordinatively unsaturated metal centers.

(23) Wnuk, T. A.; Angelici, R. J. *Inorg. Chem.* **1977**, *16*, 1173.

(24) Angelici, R. J.; Dunker, J. W. *Inorg. Chem.* **1985**, *24*, 2209.

(25) Barrett, P. F.; Sun, K. K. W. *Can. J. Chem.* **1970**, *48*, 3300.