drocarbon ligands and potential differences between solution- and gas-phase chemistry.

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Supplementary Material Available: Text describing experimental details on the pyrolysis, isolation, and characterization of the new compounds prepared in this work and a figure showing a hot wall reactor (3 pages). Ordering information is given on any current masthead page.

Reversible Thermal and Photochemical Interconversion between Cis and Trans Isomers of the Silylene-Bridged Diiron Complex $Cp'_2Fe_2(CO)_3(\mu\text{-}SiHTol)$ ($Cp' = \eta\text{-}C_5Me_5$, $Tol = p\text{-}CH_3C_6H_4$)

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Summary: Isomerization between *cis*-$Cp'_2Fe_2(CO)_3(\mu\text{-}SiHTol)$ (*cis*-**1**; $Cp' = \eta\text{-}C_5Me_5$, $Tol = p\text{-}CH_3C_6H_4$) and *trans*-**1** was found to occur both thermally and photochemically. The composition in the thermal equilibrium state (*cis*-**1**:*trans*-**1** = 2:98 in cyclohexane-d_{12}) is considerably different from that in the photostationary state (*cis*-**1**:*trans*-**1** = 70:30).

It is well-known that an ER_2 group (E = group 14 (4B) elements; R = alkyl, aryl, hydrogen, halogen) can function as a bridging unit across a metal–metal bond.[1] The group of complexes with formula $Cp_2M_2(CO)_3(\mu\text{-}ER_2)$ is particularly interesting because geometrical isomers are possible for these complexes and, moreover, they are interconvertible. In fact, isomerism and interconversion between these isomers have been reported for $Cp_2M_2(CO)_3(\mu\text{-}CR_2)$ (M = Fe, Ru; R = H, alkyl, alkenyl, Ph, SR, etc.),[2a–i] $Cp_2M_2(CO)_3(\mu\text{-}C{=}CHR)$ (M = Fe, Ru; R = H, alkyl, Ph),[2g,i] $Cp_2Fe_2(CO)_3(\mu\text{-}SiHMe)$,[3] $Cp_2Fe_2(CO)_3(\mu\text{-}SiXBu^t)$ (X = Cl, Br, I, Me),[4] and $Cp_2Fe_2(CO)_3(\mu\text{-}GeMe_2)$.[5]

We previously reported photoinduced direct synthesis of the silylene-bridged dinuclear iron complexes $Cp_2Fe_2(CO)_3(\mu\text{-}SiHR)$ (R = *t*-Bu, $(CMe_2)_2H$) from $CpFe(CO)_2SiMe_3$ and $RSiH_3$.[6] These complexes exist only in the cis form, probably due to the steric interaction between the tertiary alkyl group and the Cp rings. This observation prompted us to synthesize the analogous but bulkier pentamethylcyclopentadienyl derivatives, in an attempt to encourage formation of the less hindered trans isomer.

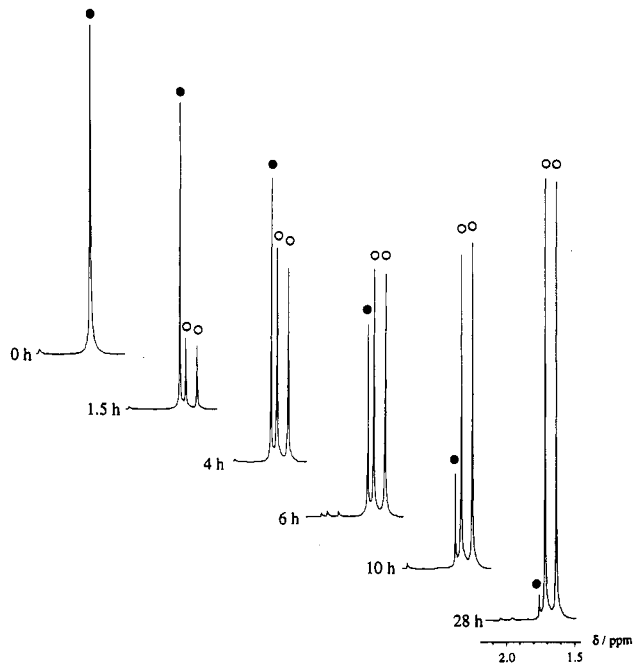

Figure 1. ^1H NMR spectral change of *cis*-**1** in cyclohexane-d_{12} at 40 °C: (●) *cis*-**1**; (○) *trans*-**1**.

Here we report the synthesis of the diiron complex $Cp'_2Fe_2(CO)_3(\mu\text{-}SiHTol)$ (**1**) and the thermal and photochemical interconversion of the cis and trans isomers. In this interconversion, remarkably different cis–trans ratios have been observed between the thermal equilibrium and the photostationary state.

When a mixture of $Cp'Fe(CO)_2SiMe_3$ and *p*-tolylsilane in a 2:1 molar ratio was irradiated in dry pentane using a 450-W medium-pressure mercury lamp, red crystals of the silylene-bridged diiron complex **1** were obtained as the major product. This consists of both cis and trans isomers (eq 1), which can be separated by silica gel flash chromatography. Isolated yields of *cis*- and *trans*-**1** immediately after the photolysis were 41% and 3%, respectively.

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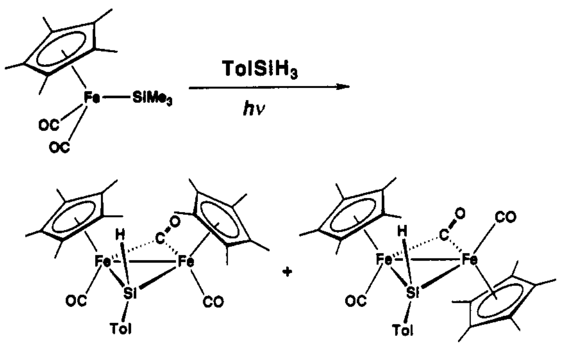


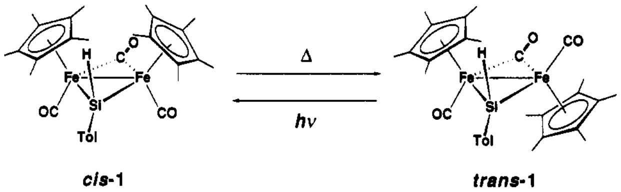
(1)

Each isomer of 1 was characterized by NMR, IR, and mass spectroscopy and elemental analysis.[7] Both isomers of 1 give remarkably low field resonances in their ^{29}Si NMR spectra: In C_6D_6, *cis*- and *trans*-1 exhibit μ-Si signals at δ 250.4 and 235.5 ppm, respectively. In the ^{1}H and ^{13}C NMR spectra, as is expected, *cis*-1 exhibits only one Cp′ signal, while *trans*-1 shows two Cp′ signals. In the IR spectrum of *cis*-1, the $\nu(CO_{sym})$ band is stronger than the $\nu(CO_{asym})$ band, while in that of *trans*-1, this relationship is reasonably reversed.

It was found that the isomerization between *cis*- and *trans*-1 occurs both thermally and photochemically in solution. Figure 1 shows the ^{1}H NMR spectral change in the area of the Cp′ signals accompanying the thermal isomerization of 1 at 40 °C. After preparation of a solution of *cis*-1, signals for the trans isomer slowly increased with concomitant decrease of the signal for *cis*-1. This spectral change was complete after 28 h, indicating establishment of equilibrium. The ^{1}H NMR spectrum at ambient temperature showed that in cyclohexane-d_{12} the equilibrium ratio of *cis*-1 to *trans*-1 was 2:98. Thus, the trans isomer is thermodynamically more stable than the cis isomer, apparently due to the large steric repulsion between the two Cp′ rings in the latter. In fact, the closely related complex $Cp'_2Fe_2(CO)_4$ is known to exist only as the trans isomer.[8]

The thermal isomerization was followed by monitoring the electronic spectral change. When *cis*-1 was dissolved in decalin, the absorption peak at 535 nm shifted to slightly longer wavelength with time and an isosbestic point was observed at 449 nm. The final spectrum was almost identical with that of *trans*-1. The following parameters of activation were obtained from measurements of the electronic spectral change at 25.0, 35.0, 40.0, 45.0, and 55.0 °C: $\Delta H^{\ddagger} = 71.1 \pm 6.4$ kJ mol^{-1}, $\Delta S^{\ddagger} = -90.3 \pm 20.5$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{298} = 98.0 \pm 12.5$ kJ mol^{-1} for cis → trans, and $\Delta H^{\ddagger} = 80.6 \pm 9.1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -90.0 \pm 30.7$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{298} = 107.4 \pm 18.2$ kJ mol^{-1} for trans → cis. The equilibrium constant (K = [*trans*-1]/[*cis*-1]) at 25.0 °C was found to be 44.5. The large negative entropies of activation imply either the existence of a sterically congested intermediate or the participation of solvent.

In sharp contrast to the thermal process, the photochemical isomerization proceeds mostly in the opposite way (eq 2)!



(2)

When a cyclohexane-d_{12} solution of *trans*-1 was irradiated, the trans isomer decreased while the cis isomer increased. After 20 min this reaction reached a photostationary state in which the ratio of *cis*-1 to *trans*-1 was 70:30. In the photochemical synthesis of 1, the yield of *cis*-1 was higher than that of *trans*-1, although the trans isomer is thermodynamically more stable. The predominance of the cis isomer at the photostationary state can explain this result, at least partly.

$Cp'_2Fe_2(CO)_3(\mu\text{-SiHTol})$ (1) is a rare example of transition-metal complexes for which the photostationary and thermal equilibrium compositions differ considerably.[9] The introduction of bulky Cp′ ligands is undoubtedly responsible for this behavior. The mechanism of this geometrical isomerization of 1 and other related complexes is currently under active investigation.

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Supplementary Material Available: Experimental details, including figures and tables, of the kinetics and photoisomerization studies (10 pages). Ordering information is given on any current masthead page.

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[7] Data for *cis*–1: ^{1}H NMR (200 MHz, cyclohexane-d_{12}) δ 1.74 (s, 30 H, η-C_5Me_5), 2.35 (s, 3 H, C_6H_4Me), 7.44 (s, 1 H, Si*H*), 7.02 and 7.87 (AB q, J = 8.1 Hz, 2 H × 2, C_6H_4Me); ^{13}C NMR (50 MHz, C_6D_6) δ 10.1 (η-C_5Me_5), 21.5 (C_6H_4Me), 94.8 (η-C_5Me$_5$), 136.4, 137.5, 139.0, and 144.2 (C_6H$_4$Me), 214.9 (CO), 281.4 (μ-CO); IR (KBr) 2052 (m, ν(SiH)), 1938 (vs, $\nu(CO_{sym})$), 1899 (m, $\nu(CO_{asym})$), 1738 cm^{-1} (s, $\nu(CO_{brid})$); mass (FAB, *m*-nitrobenzyl alcohol matrix, Xe) *m/z* 586 (68, M$^+$), 530 (100, M$^+$ – 2CO), 498 (71); UV–vis (decalin) λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 535 (1100), 353 (8800). Anal. Found: C, 61.44; H, 6.57. Calcd for $C_{30}H_{38}Fe_2O_3Si$: C, 61.45; H, 6.53. Data for *trans*-1: ^{1}H NMR (200 MHz, cyclohexane-d_{12}) δ 1.62 and 1.70 (s, 15 H × 2, η-C_5Me_5), 2.40 (s, 3 H, C_6H_4Me), 7.01 (s, 1 H. Si*H*), 7.21 and 7.97 (AB q, J = 8.0 Hz, 2 H × 2, C_6H_4Me); ^{13}C NMR (50 MHz, C_6D_6) δ 9.7 and 9.9 (η-C_5Me_5), 21.6 (C_6H_4Me), 95.4 and 95.8 (η-C_5Me$_5$), 128.7, 137.6, 139.0, and 142.9 (C_6H$_4$Me), 215.1 and 216.0 (CO), 283.1 (μ-CO); IR (KBr) 2040 (m, ν(SiH)), 1927 (m, $\nu(CO_{sym})$), 1905 (vs, $\nu(CO_{asym})$), 1748 cm^{-1} (s, $\nu(CO_{brid})$); mass (FAB, *m*-nitrobenzylalcohol matrix, Xe) *m/z* 586 (100, M$^+$), 558 (24, M$^+$ – CO), 530 (75, M$^+$ – 2CO); UV–vis (decalin) λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 539 (1900), 344 (8300); exact mass found *m/z* 586.1287, calcd for $C_{30}H_{38}Fe_2O_3Si$ 586.1289.

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