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Preparation, Stereoisomerism, and Dynamic Properties of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiXBu^t)]$ (X = Cl, Br, I, and Me)

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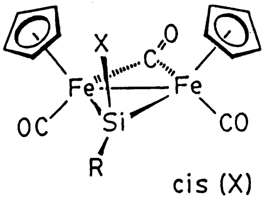
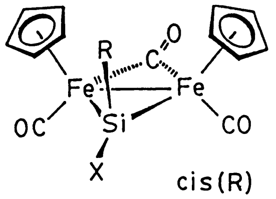
Replacement of a hydrogen on the silylene bridge of $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiHBu^t)]$ (Cp = $\eta^5\text{-}C_5H_5$) by a bulkier group (Cl, Br, I, or Me) caused the proportion of the *trans* isomer to increase from 0 to 7 - 38%. Dynamic ^{1}H NMR study for the methyl derivative revealed that the $\Delta G^{\ddagger}_{362\ K}$ values of the process *cis* isomer → *trans* isomer and of the reversed process were 83.1 ± 1.0 and 81.7 ± 1.0 kJ mol^{-1}, respectively.

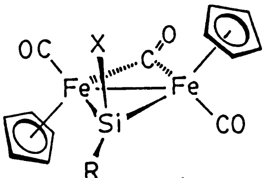
We have recently reported the photochemical one-step synthesis of silylene-bridged diiron complexes $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiHR)]$ (**1a**: R = *t*-Bu; **1b**: R = $(CMe_2)_2H$), and the *X*-ray crystal structure of **1a**.$^{1)}$ For these complexes, only *cis*(H) isomer exists either in solution or in the solid state. This has been tentatively explained by an enormous difference of steric hindrance between a *t*-butyl or thexyl group and a hydrogen on the silylene bridge.



cis (X)



cis(R)

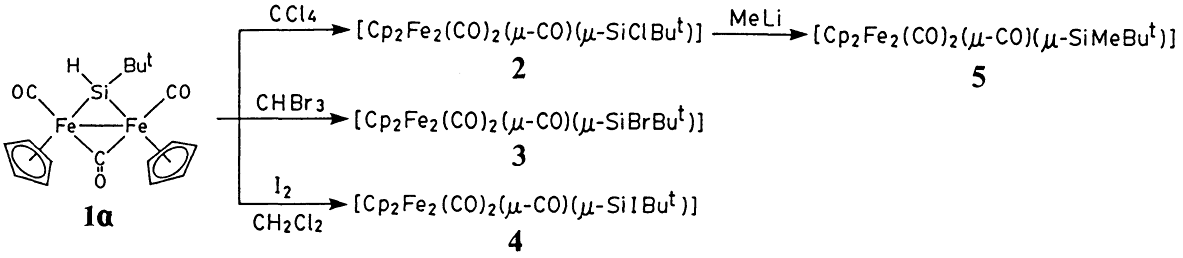


trans

We now report that when the hydrogen on the silylene bridge is replaced by a bulkier halogen or alkyl group, the *trans* isomer turns out to be observed and *trans*-to-*cis*(X) ratio in $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiXBu^t)]$ increases correlating to both the size and Fe-X distance of the group X. We also report the free energies of activation for the interconversion between *cis*(X) and *trans* isomers.

The substitution reaction of the hydrogen at the silylene bridge of **1a** by halogen proceeds smoothly at or below room temperature (Scheme 1). Thus, reaction of **1a** with $CCl_4$$^{2)}$ at room temperature completed after 17.5 h to give red, microcrystalline **2**$^{3)}$ in 95% yield. Similarly, bromination and iodination of **1a** are achieved by reactions with $CHBr_3$ at room temperature and by treatment with iodine in dichloromethane at 0 °C,$^{4)}$ respectively, to afford **3**$^{5)}$ (65%) and **4**$^{6)}$ (23%).

Nucleophilic substitution of chlorine on the silicon atom of **2** was attempted with several nucleophiles. Methyllithium reacted with **2** in ether at room temperature to give **5**$^{7)}$ in 70% yield. In contrast, the reaction of **2** with ethyllithium or *t*-butyllithium afforded only an unidentified, intractable black



Scheme 1.

oil. Treatment of 2 with p-$CH_3C_6H_4MgCl$ or $Na[FeCp(CO)_2]$ caused no reaction.

^1H NMR data and the relative abundance of *cis* and *trans* isomers of five complexes **1a** - 5 are shown in Table 1. The values of relative abundance in Table 1 denote that steric interaction between the X group and Cp rings is an important factor to determine the relative stability of *trans* isomer to *cis* one. For complex **1a**, the distances between X(= H) and hydrogens of Cp rings are longer than 2.6 Å.$^{1)}$ Since the effective van der Waals radius of hydrogen is 1.20 Å,$^{8)}$ the steric interaction between them are negligible and therefore **1a** adopts only *cis*(H) form. On the other hand, when X is Cl, Br, I, or Me with effective van der Waals radii of 1.80, 1.95, 2.15, and 2.0 Å, respectively,$^{8)}$ the steric interaction between X and Cp rings is considered no longer negligible and, as a result, lets an appreciable amount of *trans* isomer exist. Interestingly, the proportion of *trans* isomer does not increase markedly when X is changed from Cl to bulkier Br or I. This is rationalized by longer Si-X bond lengths for X in the later rows (typical bond lengths: Si-Cl 2.02, Si-Br 2.16, and Si-I 2.46 Å).$^{9)}$ In fact, though the van der Waals radius of Me is smaller than that of iodine (vide supra), 5 has the highest proportion of *trans* isomer among the prepared complexes perhaps by virtue of very short Si-Me bond length (typical Si-C_{alkyl} 1.87 Å).$^{9)}$

The IR spectrum of 5 in the solid state (KBr disk) exhibits four terminal and

Table 1. ^1H NMR Chemical Shifts and the Relative Abundance of *cis* and *trans* Isomers of $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiXBu^t)]$ (X = H, Cl, Br, I, and Me) in C_6D_6 Solution at Room Temperature

Complex	X	^1H NMR Chemical Shifts$^{a)}$						Rel. Abundance	
		cis(X)			*trans*			%	
		t-Bu	Cp	X	*t*-Bu	Cp	X	*cis*(X)	*trans*
1a$^{b)}$	H	1.32	4.50	7.23				100	0
2	Cl	1.55	4.24		1.46	4.36, 4.38		93	7
3	Br	1.55	4.24		1.47	4.34, 4.40		93	7
4	I	1.56	4.24		1.46	4.33, 4.40		92	8
5	Me	1.42	4.08	1.00	1.31	4.25, 4.44	1.15	62	38

a) δ/ppm. b) Data in CS_2 solution.$^{10)}$

two bridging ν_{CO} bands.7) This offers an indirect evidence that 5 also exists as a mixture of *cis* and *trans* isomers in the solid state.

Dynamic ^1H NMR investigation of 5 was carried out in toluene-d_8 to evaluate the barrier of *cis-trans* isomerization. On heating, the two *t*-Bu singlets ($\nu_{cis} - \nu_{trans} = 5.61 \pm 0.10$ Hz on the 90 MHz NMR apparatus) coalesced at 362 ± 4 K (Fig. 1). The signals of Si-Me and cyclopentadienyls did not coalesce at this temperature. The application of the usual coalescence approximation11) leads to the value of $\Delta G^{\ddagger}_{362\ K} = 83.1 \pm 1.0$ kJ mol^{-1} for $k_{cis \rightarrow trans}$ and $\Delta G^{\ddagger}_{362\ K} = 81.7 \pm 1.0$ kJ mol^{-1} for $k_{trans \rightarrow cis}$. These values are close to the activation energy of the *cis*-to-*trans* isomerization of $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}GeMe_2)]$ (E_a = 85.8 kJ mol^{-1}),12) and are consistent with the slow *cis-trans* isomerization of $[Cp_2Fe_2(CO)_2\text{-}(\mu\text{-}CO)(\mu\text{-}SiHMe)]$ at room temperature.13)

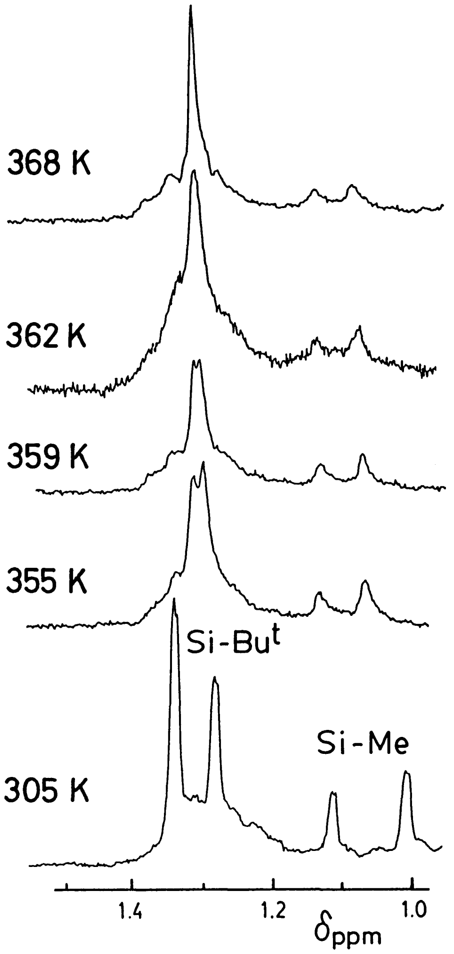
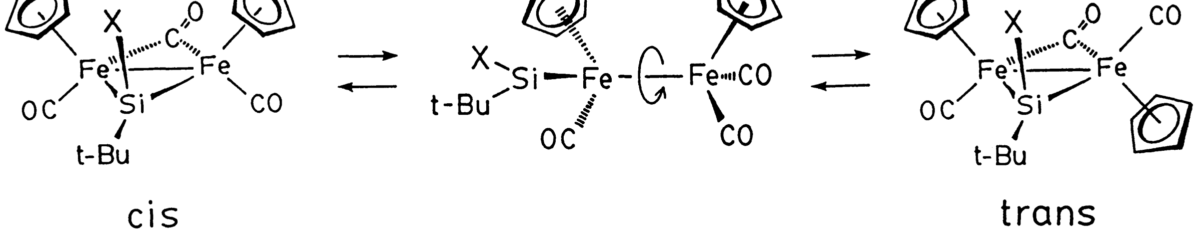


Fig. 1. The ^1H NMR spectra of the methyl region of 5 in toluene-d_8 at various temperatures.

We propose a possible mechanism for this dynamic process in 5 and presumably in other complexes **1a** - **4** which involves concerted bridge openings and internal rotation (Scheme 2). Similar mechanisms have been proposed for the carbon and germanium analogues, namely $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$14) and $[Cp_2Fe_2(CO)_2\text{-}(\mu\text{-}CO)(\mu\text{-}GeMe_2)]$.12) It is reasonable to postulate terminal silylene complexes as intermediates in this mechanism, since their mononuclear analogues have been recently isolated as donor-stabilized forms.15) However, the barrier for *cis-trans* isomerization of 5 is significantly higher than that of $Cp_2Fe_2(CO)_4$ (< 30 kJ mol^{-1}).16) This can be interpreted to be a result of the instability of terminal silylene ligands in comparison with carbonyl ligands.



Scheme 2.

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References

1) H. Tobita, Y. Kawano, M. Shimoi, and H. Ogino, Chem. Lett., 1987, 2247.
2) B. J. Aylett, Adv. Inorg. Chem. Radiochem., 25, 1 (1982).
3) IR (KBr disk) $\nu(CO_{term.})$ 1952, 1918 cm^{-1}; $\nu(CO_{brid.})$ 1763 cm^{-1}; MS(EI) m/e 446 (10, M^+), 418 (26, M^+-CO), 390 (8, M^+-2CO), 362 (34, M^+-3CO), 215 (100, $Cp_2Fe_2H^+$); Exact Mass Found: 445.9496. Calcd for $C_{17}H_{19}ClFe_2O_3Si$: 445.9491.
4) W. H. Nebergall and O. H. Johnson, J. Am. Chem. Soc., 71, 4022 (1949).
5) IR (KBr disk) $\nu(CO_{term.})$ 1952, 1924 cm^{-1}; $\nu(CO_{brid.})$ 1773 cm^{-1}; MS(EI) m/e 490 (39, M^+), 462 (75, M^+-CO), 406 (50, M^+-3CO), 215 (100, $Cp_2Fe_2H^+$); Exact Mass Found: 489.8981. Calcd for $C_{17}H_{19}BrFe_2O_3Si$: 489.8986.
6) IR (KBr disk) $\nu(CO_{term.})$ 1952, 1925 cm^{-1}; $\nu(CO_{brid.})$ 1772 cm^{-1}; MS(EI) m/e 538 (27, M^+), 510 (100, M^+-CO), 454 (57, M^+-3CO); Exact Mass Found: 537.8865. Calcd for $C_{17}H_{19}BrFe_2O_3Si$: 537.8847.
7) IR (KBr disk) $\nu(CO_{term.})$ 1990, 1947, 1937sh, 1914 cm^{-1}; $\nu(CO_{brid.})$ 1751, 1712sh cm^{-1}; MS(EI) m/e 426 (29, M^+), 398 (63, M^+-CO), 286 (100); Exact Mass Found: 426.0036. Calcd for $C_{18}H_{21}Fe_2O_3Si$: 426.0037.
8) L. Pauling, "The Nature of the Chemical Bond," 3rd ed , Cornell University Press, Ithaca, New York (1960), pp. 257 - 264.
9) A. J. Gordon and R. A. Ford, "The Chemist's Companion," John Wiley & Sons, New York (1972), pp. 107 - 108.
10) The chemical shift of the Si-H of **1a** (δ 4.23 ppm) reported in the previous paper[1)] was found to be incorrect. Since in C_6D_6 the Si-H signal is completely covered up with that of C_6D_5H, this time we used CS_2 as a solvent. Similarly, the correct ^1H NMR data for **1b** measured in CS_2 is as follows: δ 1.13 (s, 6H, α-Me), 1.14 (d, J = 6.6 Hz, 6H, β-Me), 2.16 (septet, J = 6.6 Hz, 1H, methyne), 4.47 (s, 10H, Cp), 7.32 (s, 1H, Si-H).
11) D. Kost, E. J. Carlson, and M. Raban, J. Chem. Soc., Chem. Commun., 1971, 656.
12) R. D. Adams, M. D. Brice, and F. A. Cotton, Inorg. Chem., 13, 1080 (1974).
13) W. Malisch and W. Ries, Angew. Chem., Int. Ed. Engl., 17, 120 (1978).
14) A. F. Dyke, S. A. R. Knox, M. J. Morris, and P. J. Naish, J. Chem. Soc., Dalton Trans., 1983, 1417.
15) D. A. Straus, T. D. Tilley, A. L. Rheingold, and S. J. Geib, J. Am. Chem. Soc., 109, 5872 (1987); C. Zybill and G. Müller, Angew. Chem., Int. Ed. Engl., 26, 669 (1987); Organometallics, 7, 1368 (1988); C. Zybill, D. L. Wilkinson, and G. Müller, Angew. Chem., Int. Ed. Engl., 27, 583 (1988); C. Zybill, D. L. Wilkinson, C. Leis, and G. Müller, *ibid.*, 28, 203 (1989); K. Ueno, H. Tobita, M. Shimoi, and H. Ogino, J. Am. Chem. Soc., 110, 4092 (1988).
16) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 5th ed , John Wiley & Sons, New York (1988), pp. 1325 - 1327.

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