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Structural Features of $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_3(C=NR)$ and $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_2(C=NR)_2$

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Synopsis. The structure of isonitrile substituted diiron carbonyl complexes, $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_3(C=NR)$ (**1**) and $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_2(C=NR)_2$ (**2**) (R=*t*-butyl, cyclohexyl, and bornyl), in solution was studied by IR and NMR spectroscopy using variable-temperature and 2D NMR techenique.

It is known that in the diiron complexes, $Cp_2Fe_2(CO)_{4-n}(C=NR)_n$, CO and isonitrile ligands can be interchanged between the bridging and terminal coordination, and cis–trans isomerization of cyclopentadienyl ligands can also take place.[1] This fluxional nature causes difficulty in the structure analysis of these complexes. It is, therefore, preferable to fix the cis and trans isomers into one isomer in order to investigate the structural behavior of CO and isonitrile ligands. In the course of study on the ligand substitution reaction of $Cp_2Fe_2(CO)_4$ with isonitriles,[2] we found that a diiron carbonyl complex, $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_4$, which has only cis configuration, carried out the substitution reaction with isonitriles to give the mono- and di-substituted complexes similarly to $Cp_2Fe_2(CO)_4$, and the rearrangement of these ligands in the isonitrile disubstituted complexes, $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_2(C=NR)_2$, was significantly suppressed compared to the monosubstituted one, $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_3(C=NR)$. We report here the study on the structural feature of the isonitrile mono- and di-substituted complexes of $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_4$ by FT-IR and NMR spectroscopy using variable-temperature and 2D NMR technique.

Experimental

Nuclear magnetic resonance spectra were taken on a JEOR JNM-GX 270 FT-NMR spectrometer in $CDCl_3$. IR spectra were measured with a JASCO FT-IR 5000 spectrometer in $CHCl_3$.

General Procedure. A mixture of tetracarbonylbis(η^5-cyclopentadienyl)(dimethylsilane)diiron (410 mg, 1.0 mmol), isonitrile (3.0 mmol) and benzene (15 ml) was heated at 80 °C for 8—20 h. After evapolation of the solvent, the residue was chromatographed on silica gel to give isonitrile monosubstituted complexes $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_3(C=NR)$ (**1**) as dark red solids (from dichloromethane) and isonitrile disubstituted complexes $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_2(C=NR)_2$ (**2**) as from dark green to dark red solids (from dichloromethane–ethyl acetate=1 : 1).

$(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_3(C=NR)$

1

1a : R=Bu^t, **1b** : cyclohexyl (Cy)

1c : R=  (Bor)

$(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_2(C=NR)_2$

2

2a : R=Bu^t, **2b** : cyclohexyl (Cy)

2c : R=  (Bor)

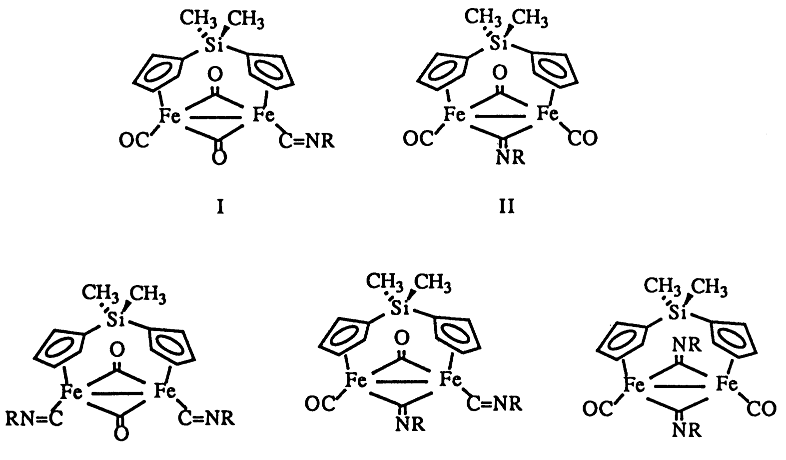

Chart 1.

Results and Discussion

Isonitrile monosubstituted complexes **1** and disubstituted complexes **2** were obtained from the reaction of $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_4$ with 3 equiv of isonitriles in benzene at 80 °C. These complexes were separated by column chromatography on silica gel. Yields of these complexes and their IR and NMR data are given in Tables **1**—**3**.

As two cyclopentadienyl ligands in these complexes are fixed into cis configuration, kinds of isomeric forms are limited to I and II for the monosubstituted complexes, and III, IV, and V for disubstituted complexes, in which CO and isonitrile ligands coordinate as terminal and bridging ligands. IR spectra of monosubstituted complexes **1** show peaks in the region of 2138-2118 cm^{-1} which are assigned to ν_{CN} vibration of a terminal isonitrile ligand, indicating **1** to be isomer I (Table 1). Signals due to CO and isonitrile ligands did not appear in their ^{13}C NMR spectra recorded at 25 °C, while their spectra recorded below −20 °C exhibit two kinds of signals assigned to terminal and bridging CO ligands and also one signal assigned to a terminal isonitrile ligand (Table 3). However, ^1H NMR spectra of **1** remained almost unchanged in the range of 25 °C to −50 °C. These results suggest that complexes **1** exist as isomer I below −20 °C but interchange between I and II at ambient temperature.

Table 1. Yields and IR Data of $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_{4-n}(C{=}NR)_n$ $(CHCl_3)$

Complex	Ligand	Yields of **1** and **2**/%[a)]	ν_{CN}[b)]	ν_{CO}[b)]	ν_{CO}[c)]	ν_{CN}[c)]
1a	$(CO)_3(C{=}NBu^t)$	40	2118	1941	1783[d)] 1744	
1b	$(CO)_3(C{=}NCy)$	48	2118	1943	1787 1752	
1c	$(CO)_3(C{=}NBor)$	33	2138	1941	1788[d)] 1752	
2a	$(CO)_2(C{=}NBu^t)_2$	24	2104 2062		1734	
2b	$(CO)_2(C{=}NCy)_2$	37	2120	1939	1771	1698
2c	$(CO)_2(C{=}NBor)_2$	26	2112	1939	1772	1696

a) Isolated yields. b) Terminal coordination. c) Bridging coordination. d) Weak peak.

Table 2. ^1H NMR Data of $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_{4-n}(C{=}NR)_n$ (δ, $CDCl_3$)

Complex	C_5H_4	R	CH_3Si
1a	5.37 (t, *J*=2 Hz), 5.24 (t, *J*=2 Hz) 4.99 (t, *J*=2 Hz), 4.95 (t, *J*=2 Hz)	1.16 (s, CH_3)	0.34 (s)
1b	5.43—5.38 (m), 5.29—5.25 (m) 5.00—4.97 (m)	3.60—3.48 (m), 2.10—0.90 (m)	0.33 (s)
1c	5.39—5.37 (m), 5.28—5.26 (m), 5.01—4.98 (m)	0.81 (s), 0.69 (s), 0.76 (s)	0.34 (s)
2a	4.46 (s), 4.37 (s), 4.19 (s)	1.13 (s, CH_3)	0.37 (s) 0.36 (s)
2b	5.11—3.75 (m)	3.75—3.50 (m), 3.33—3.05 (m), 2.07—0.90 (m)	0.28 (s)
2c	5.10—3.90 (m)	3.58—3.45 (m), 3.28—3.36 (m), 2.60—0.70 (m)	0.37 (s) 0.35 (s)

Table 3. ^{13}C NMR Data of $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_{4-n}(C{=}NR)_n$ (δ, $CDCl_3$)

Complex	CO[a)]	CO[b)]	C=N[a)]	C=N[b)]	C_5H_4	CH_3Si
1a[c)]	282.1	212.8		160.0	97.9, 97.8, 86.7, 86.2, 85.4, 80.2	−3.75
1b[c)]	282.1 281.8	212.8		159.8	97.8, 97.6, 86.7, 86.2, 86.1, 80.2	−3.70
1c[c)]	282.2 281.9	212.8		159.6	97.8, 97.4, 86.8, 86.2, 86.1, 80.3	−3.64
2a	285.1			173.1 167.4	94.2, 91.8, 90.4, 89.1, 88.5	−0.09
2b	286.0[d)] 279.8	214.4	251.8	171.5[d)] 163.8	95.4, 93.2, 91.2, 90.6, 89.5, 89.4, 88.6, 88.5, 88.1, 86.8	−0.15 −0.33
2c	286.1[d)] 281.0	214.7	248.6	171.1 165.1	Many signals	0.00 −0.19

a) Bridging ligand. b) Terminal ligand. c) Recorded at −20 °C. d) Weak peak.

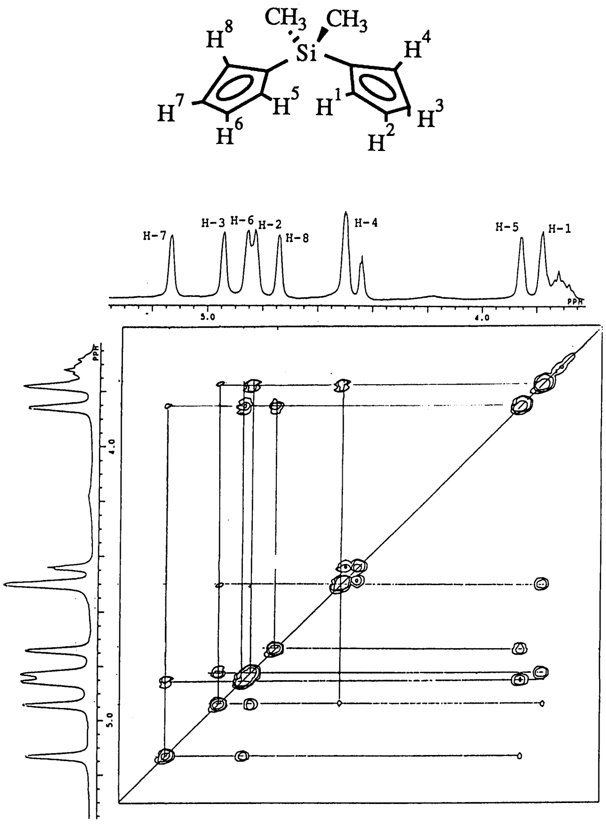

Fig. 1. 2D COSY spectrum of **2b**.

IR spectrum of the disubstituted complex **2a** shows absorptions at 2104, 2062, and 1734 cm^{-1}. The two bands at 2104 and 2062 cm^{-1} are assigned to ν_{CN} vibration of terminal C=NBu^t, and the band at 1734 cm^{-1} is assigned to ν_{CO} vibration of bridging CO. ^{13}C NMR spectrum of **2a** exhibits a signal of bridging CO at 285.1 ppm, two signals at 173.1 and 167.4 ppm assigned to the terminal C=NBu^t, but lack of the signal due to bridging C=NBu^t. These results suggest that both of two C=NBu^t ligands coordinate as terminal ligands, indicating only III to be present. On the other hand, the IR spectrum of **2b** shows four bands assigned to terminal CO and isonitrile ligands and also bridging CO and isonitrile ligands (Table 1). ^{13}C NMR spectrum of **2b** exhibits four strong signals assigned to terminal CO and isonitrile ligands and also bridging CO and isonitrile ligands, accompanying with two weak signals due to bridging CO and terminal isonitrile ligands. From these results **2b** is a mixture of two isomers (III and IV), indicating IV to be a major compound. The ratio of two isomers (III : IV) was calculated to be 1 : 6 from the ^{1}H and ^{13}C NMR for quantitative analysis. To investigate the structural feature of the complexes in detail, 2D COSY spectrum of **2b**$^{3)}$ was recorded in CDCl$_3$. The spectrum is shown in Fig. 1, illustrating the assignment of cyclopentadienyl protons. This COSY spectrum is completely consistent with the isomer IV. The structural characteristic of **2c** is almost same as that of **2b**. However, many signals due to cyclopentadienyl and isonitrile ligands appeared in their ^{1}H and ^{13}C NMR spectra because **2c** is a mixture of diastereomers, and these signals could not be fully assigned.

^{1}H and ^{13}C NMR spectra of disubstituted complexes (**2a** and **2b**) remained entirely unchanged in the range of 25 °C to −50 °C. In particular, signals of CO and isonitrile ligands can be observed even at ambient temperature in their ^{13}C NMR spectra. These results indicate that the disubstituted complexes **2a**—**c** did not show fluxional behavior in solution even at ambient temperature. It is noteworthy that the rearrangement of CO and isonitrile ligands in **1** and **2** is strongly suppressed in comparison with the corresponding dicyclopentadienyl monoisonitrile complexes, $Cp_2Fe_2(CO)_3(C{=}NBu^t)$ and $Cp_2Fe_2(CO)_3(C{=}NCy)$,$^{1)}$ and also diisonitrile complexes, $Cp_2Fe_2(CO)_2(C{=}NCH_3)_2$$^{4-6)}$ and $Cp_2Fe_2(CO)_2(C{=}NCBu^t)_2$,$^{7)}$ in which CO and isonitrile ligands can easily rearrange. Isomerization of **2b** among III, IV, and V did not occur in other solvents such as benzene, methanol and acetone even at 25 °C. The structural stability of these complexes provably arises from the rigid structure of bis(cyclopentadienyl)dimethylsilane ligand.

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