Steric Limit of *cis*-[(C_5R_5)Fe(CO)$_2$]$_2$ Complexes in Solution

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*Summary: The symmetrical dimers [(C_5H_5)Fe(CO)$_2$]$_2$ **(1)**, [(C_5Me_5)Fe(CO)$_2$]$_2$ **(2)**, and [(C_5Me_4H)Fe(CO)$_2$]$_2$ **(3)** have been used to synthesize the unsymmetrical dimers (C_5Me_4H)(C_5H_5)Fe_2(CO)$_4$ **(4)**, (C_5Me_5)(C_5H_5)Fe_2(CO)$_4$ **(5)**, and (C_5Me_5)(C_5Me_4H)Fe_2(CO)$_4$ **(6)**. All of the new compounds show cis/trans isomerization to varying extents, depending on the degree of substitution. The crystal structures of **3** and **4** have been determined. The limit of the observable cis-bridged isomer is found in **6** which is 14% cis in CH_3CN solution.*

Introduction

It has been more than 25 years since the correct interpretation of the ν(MC−O) IR spectrum of [(C_5H_5)Fe(CO)$_2$]$_2$ (**1**) showed that in solution it exists as a solvent dependent mixture of *cis* and *trans* CO-bridged isomers, together with a small amount of the nonbridged form, Scheme 1.[1]

The nonpolar *trans* form dominates in nonpolar solvents, and the polar *cis* form is stabilized in polar solvents. The rapid interconversion of the principal isomers has also been demonstrated by ^{1}H and ^{13}C NMR methods.[2−6]

Even before the ν(MC−O) solution IR spectra of **1** was correctly understood, it was known that its pentamethyl counterpart [(C_5Me_5)Fe(CO)$_2$]$_2$ (**2**) was exclusively *trans* in solution.[7] This total exclusion of the *cis* form in **2** was assumed to be due to steric repulsions between the methyl groups. The influence of mono- and disubstitution on the *cis/trans* ratio has been examined, and both have been shown to exert almost no steric influence.[8,9] In this paper the effect of a greater degree of substitution is examined in an attempt to determine the steric limit of the *cis*-bridged isomer.

Results and Discussion

Synthesis. The unsymmetrical dimers were synthesized from **1**, **2**, and [(C_5Me_4H)$_2$Fe(CO)$_2$]$_2$ **(3)**. Complex **4**, for example, was synthesized by reaction of the anion obtained by reductive cleavage of **1**, using a 1% Na/Hg amalgam, with the iodide obtained by reaction of **3** with iodine. All three possible dimers are formed in these reactions, but the use of an excess of the iodide favors the desired mixed dimer. Chromatography and recrystallization gave analytically pure products. A difficult chromatographic separation was the principal reason for the low yield of **6**. The compounds are stable in the solid state but decompose slowly in solution.

Crystal Structures of 3 and 4. Several attempts were made to obtain crystals of the dimers in the *cis* form. In all cases, only the *trans* form was found in the crystals. These *cis* structures would have been useful in establishing the effect of substitution on the angle formed by the ring centroid and the metal−metal bond. This angle will have an important influence on the magnitude of the steric interactions between the substituted rings in the *cis* isomer.

In the absence of any suitable *cis* crystals, the crystal structures of the *trans* forms of the **3** and **4** systems were examined. Crystal data for **3** and **4** are given in Table 1, and the structures are shown in Figures 1 and 2, together with selected bond lengths and angles. Compound **4** is the first unsymmetrical dimer of this type to be structurally characterized and by inference supports the ν(MC−O) IR identification of **5** and **6**. The observed distances and angles in **3** and **4** are close to those reported for *trans*-**1** and **2**, with the exception of slight asymmetry in the CO bridges induced by the unsymmetrical position adopted by the lone hydrogen on the C_5Me_4H ligand. The structure of **3** (in common with other symmetrical *trans* dimers)[10,11] contains an inversion center at the midpoint of the Fe−Fe bond and the cyclopentadienyl rings are parallel. The cyclopentadienyl rings of **4** are almost parallel, with an angle of 2.2° between the least-squares planes defined by the ring atoms. The ring centroid−Fe−Fe angles are also close to those of **1** and **2** being 140.0° for **3** and 140.3 and 139.4° for the substituted and unsubstituted rings of **4**, respectively.

The orientation of the rings relative to the rest of the molecule may be such that a ring carbon is eclipsed or staggered with respect to the adjacent terminal CO. Thus, for **3** ring orientation is defined by the dihedral angle C(3)−ring centroid−Fe−C(11), Figure 1. This angle is 0° and 36° for the eclipsed and staggered geometries, respectively. Compounds **2** and *trans*-**1** are eclipsed and staggered with dihedral angels of 4.6° and 34.0°, and this pattern of substitution favoring on eclipsed geometry is observed in **3** and **4**. Thus, in **3** the adjacent terminal CO is almost eclipsed, 8.4°, and the substituted and unsubstituted rings of **4** have dihedral angels C(3)−ring centroid−Fe(1)−C(15) and C(11)−ring centroid−Fe(2)−C(18) at 7.6° and 30.6°, respectively. The unsymmetrical CO bridge systems in

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Scheme 1

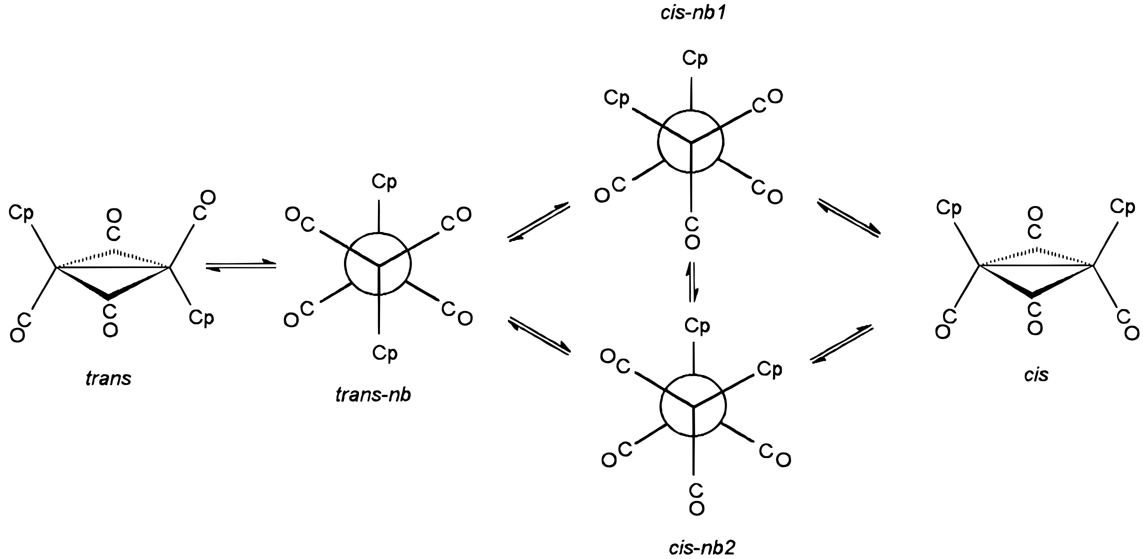

Table 1. Crystal Data and Structure Refinement

	3	4
empirical formula	$C_{22}H_{26}Fe_2O_4$	$C_{18}H_{18}Fe_2O_4$
formula wt	466.12	410.02
temp	293(2) K	293(2) K
wavelength	0.710 69 Å	0.710 69 Å
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
unit cell dimensions	$a = 7.5750(10)$ Å	$a = 9.165(9)$ Å
	$b = 8.2990(10)$ Å	$b = 16.151(9)$ Å
	$c = 9.1390(10)$ Å	$c = 11.595(2)$ Å
	$\alpha = 112.14(2)°$	
	$\beta = 103.49(2)°$	$\beta = 101.07(3)°$
	$\gamma = 96.69(2)°$	
vol	503.98(11) $Å^3$	1684(2) $Å^3$
Z	1	4
density (calcd)	1.536 Mg/m^3	1.617 Mg/m^3
abs coeff	1.464 mm^{-1}	1.740 mm^{-1}
F(000)	242	840
crystal size	0.35 × 0.40 × 0.21 mm	0.47 × 0.28 × 0.19 mm
θ range for data collection	2.52−37.92°	2.19−27.97°
index ranges	$-13 \le h \le 12, -14 \le k \le 13, -4 \le l \le 15$	$-1 \le h \le 7, -6 \le k \le 21, -15 \le l \le 15$
reflns collected	5644	3416
independent reflns	5198 ($R_{int} = 0.0292$)	3107 ($R_{int} = 0.0921$)
reflns obsd (>2σ)	4289	1523
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	5198/0/133	3107/0/221
goodness-of-fit on F^2	1.069	0.882
final *R* indices ($I > 2\sigma(I)$)[a]	$R_1 = 0.0368$ $wR_2 = 0.1007$	$R_1 = 0.0871$ $wR_2 = 0.2048$
R indices (all data)	$R_1 = 0.0478$ $wR_2 = 0.1057$	$R_1 = 0.1574$ $wR_2 = 0.2393$
largest diff. peak and hole	1.011 and −0.616 e·$Å^{-3}$	1.889 and −1.148 e·$Å^{-3}$

[a] $R_1 = [\sum||F_o| - |F_c||]/\sum|F_o|$ (based on *F*), $wR_2 = [[\sum_w (|F_o^2 - F_c^2|)^2]/[\sum_w (F_o^2)^2]]^{1/2}$ (based on F^2), $w = 1/[(\sigma F_o)^2 + (a^*P)^2 + b^*P]$, Goodness-of-fit $= [\sum_w (F_o^2 - F_c^2)^2/(N_{obs} - N_{params})]^{1/2}$.

3 and **4** are a consequence of the unsymmetrical orientation of the hydrogen on C(1) of the C_5Me_4H ligand, which is staggered with respect to the metal−metal bond; the corresponding dihedral angels, C(1)−ring centroid−Fe−Fe, for **3** and **4** are 30.6° and 30.3°.

IR Determination of Solution Structure. The ν(MC−O) IR spectra were recorded in hexane and acetonitrile solutions, Table 2. The electron donation from the methyl groups is clearly seen, especially in the case of the asymmetric terminal band (e.g., the 1961 cm^{-1} band for **1**), and the effect is precisely additive with a value close to 3 cm^{-1} per methyl. This is, of course, in accord with the accepted bonding scheme for metal carbonyls and indicates very effective delocalization. This effect has been previously found in $(C_5H_4Me)(C_5H_5)Fe_2(CO)_4$, which is the only other unsymmetrical dimer reported.[8] The relative intensities of the ν(MC−O) terminal bands can be used, as described by Manning,[1] to calculate the relative *cis*/*trans* ratio. The results are given in Table 3. All of the ν(MC−O) band widths were identical, and the concentration of non-bridged species was assumed to be negligible.

The results confirm the literature finding that solutions of **2** exhibit no detectable bands due to the *cis* form either in hexane or in the more polar mixture 55/45 CH_3CN/CH_2Cl_2. The insolubility of **2** in CH_3CN is also interesting as this contrasts with that of **6** which does dissolve in CH_3CN, where it is found to be 14% *cis*. Clearly, a sterically available *cis* isomer increases the solubility in polar CH_3CN. It is interesting that when

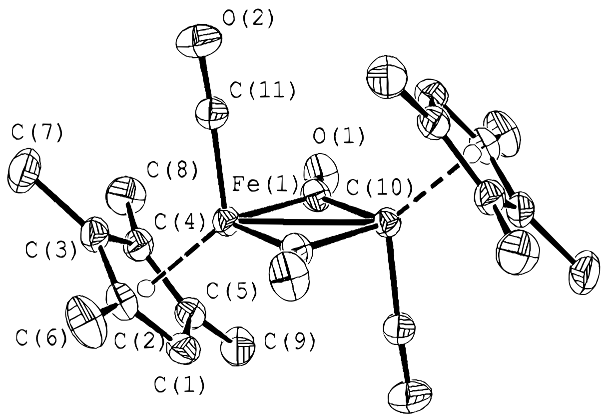

Figure 1. ORTEX drawing of **3** 40% ellipsoids. Selected bond lengths and angles: Fe−Fe, 2.5480(9); Fe−C(11), 1.752(1); Fe−C(10), 1.930(1); Fe−C(10), 1.920(1); and C(11)−Fe−Fe, 95.60(5).

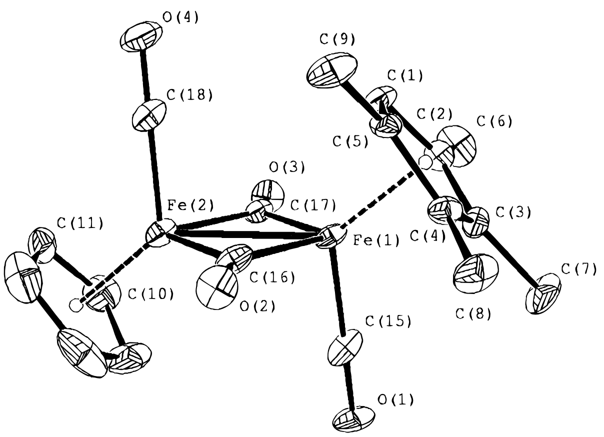

Figure 2. ORTEX drawing of **4**, 20% ellipsoids. Selected bond lengths and angles: Fe(1)−Fe(2), 2.534(3) Å; Fe(1)−C(15), 1.74(1) Å; Fe(2)−C(18), 1.74(1) Å; Fe(1)−C(16), 1.888(9) Å; Fe(1)−C(17), 1.931(9) Å; Fe(2)−C(17), 1.930(9) Å; Fe(2)−C(16), 1.938(9) Å; C(18)−Fe(2)−Fe(1), 94.9(4)° and C(15)−Fe(1)−Fe(2), 96.7(4)°.

Table 2. ν(MC−O) IR Spectral Data (Relative Absorbances in Parentheses)

complex	hexane	CH_3CN solution
$[(C_5H_5)_2Fe(CO)_2]_2$ **(1)**	2006.0 (0.45)	1991.6 (1.00)
	1961.5 (1.00)	1848.9 (0.20)
	1794.0 (0.93)	1775.4 (0.87)
$(C_5Me_4H)(C_5H_5)Fe_2(CO)_4$ **(4)**	1995.1 (0.19)	1974.2 (1.00)
	1948.4 (1.00)	1934.2 (0.50
	1780.2 (0.72)	1760.9 (0.86)
$(C_5Me_5)(C_5H_5)Fe_2(CO)_4$ **(5)**	1993.1 (0.72)	1979.4 (0.68)
	1945.4 (1.00)	1937.7 (0.88)
	1777.8 (0.71)	1761.3 (1.00)
$[(C_5Me_4H)_2Fe(CO)_2]_2$ **(3)**	1985.0 (0.53)	1970.0 (0.57)
	1936.6 (1.00)	1928.4 (1.00)
	1769.0 (0.55)	1755.3 (1.00)
$(C_5Me_5)(C_5Me_4H)Fe_2(CO)_4$ **(6)**	1933.6 (0.57)	1968.5 (0.17)
	1769.0 (1.00)	1924.5 (1.00)
		1751.1 (0.83)
$[(C_5Me_5)_2Fe(CO)_2]_2$ **(2)**	1930.1 (1.00)	1922.1 (1.00)[a]
	1762.0 (0.54)	1748.9 (0.71)

[a] 55:45 CH_3CN/CH_2Cl_2 solution.

the photogenerated $(C_5Me_5)Fe(CO)_2^{\bullet}$ radical is allowed to decay in cyclohexane solution, a 1:1 mixture of *cis*- and *trans*-**2** is observed, using fast time-resolved IR spectroscopy, and this mixture isomerizes to *trans*-**2** at 25 °C.[12] It has also been suggested that steric factors may not be important in the dimerization of this radical.

Table 3. Relative Amounts (%) of *cis* and *trans* in Solution

complex	hexane		CH_3CN		no. of interacting Me groups
	trans	cis	*trans*	cis	
1	69	31	17	83	0
4	84	16	32	68	1
3	93	7	57	43	2
5	95	5	62	38	2
6	100	0	86	4	3
2	100	0	100[a]	0	4

[a] 55:45 CH_3CN/CH_2Cl_2.

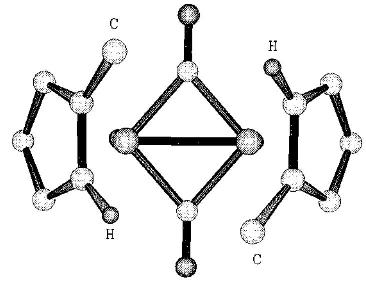

Figure 3. Conformation of *cis*-**3**.

However, these results are likely due to the initial formation of the three nonbridged form of **2**, which rapidly convert to bridged forms, Scheme 1. It is likely that, by analogy with **1**, relatively slow interconversion between these nonbridged forms allows the initial observation of *cis*-**2**.[13]

It is interesting that almost identical *cis*/*trans* ratios are observed for the **3** and the **5** systems in both solvents. The following simple explanation is offered. The important region for steric interactions in the *cis* isomer is over the metal−metal bond, and it is assumed that in all cases the *cis* isomer would have the ring substituents arranged as shown in Figure 3, where four groups are directed over the metal−metal bond.[14−16] If these interactions are approximately additive, then the **3** and **5** systems have similar steric interactions and, hence, similar *cis*/*trans* ratios, even though they have differing degrees of ring substitution. The total number of methyl groups in this region for each complex is given in Table 3. It is also clear that the *cis* content rises rapidly when methyl groups are removed from this region. Thus, **4** which has only one methyl group in this region, is 68% *cis* in CH_3CN. In the case of mono- and disubstituted dimers, there is no decrease in the *cis*/*trans* ratio, relative to the unsubstituted dimer, even when the substituents are very bulky.[8,9] In these cases, the rings may adopt a conformation with only hydrogens pointing over the bridge and the steric bulk in the critical region is, therefore, similar to the unsubstituted dimer. In the case of **6** there are three methyl groups over the metal−metal bond region and no *cis* form is detected in hexane solution, while in acetonitrile, only 14% is present in this form. The steric limit of the observable *cis* isomer is therefore achieved in **6**.

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Experimental Section

General Procedures. All experimental procedures were carried out under an atmosphere of nitrogen, using solvents dried and distilled by standard methods. Chromatography was carried out on Merck silica gel 60 (particle size, 0.063−0.200 mm). $Fe(CO)_5$ was used as supplied from Aldrich chemicals. Compound **2**, $(C_5Me_5)Fe(CO)_2I$,[7] $(C_5Me_4H)Fe(CO)_2I$,[17] **1**[18] and $C_5Me_4H_2$[19] were all prepared according to literature methods.

^1H NMR spectra were recorded on a JEOL GX 270 spectrometer, as $CDCl_3$ solutions. Microanalyses were carried out on a Perkin-Elmer 2400 CHN analyzer in the University College, Galloway microanalytical laboratory. Infrared spectra were recorded on a Perkin-Elmer1600 FT-IR spectrometer, using 0.1 mm NaCl solution cells.

$[(C_5Me_4H)Fe(CO)_2]_2$ (3). Tetramethylcyclopentadiene (4 g, 32.7 mmol) and 19.28 g of iron pentacarbonyl (98 mmol) in 20 mL of ethylbenzene were refluxed under nitrogen, with constant stirring, for 24 h. After the mixture was cooled to room temperature, the solution was filtered and the solid residue washed with toluene. The resulting red powder was recrystallized from dichloromethane/hexane to yield 4.19 g of pure **3** (57%). Crystals suitable for crystallographic analysis were grown from a concentrated dichloromethane solution, under nitrogen, at 0 °C. ^1H NMR ($CDCl_3$): δ 1.75 (s, 6H), 1.79 (s, 6H), 3.87 (s, 1H). Anal. Calcd for $C_{22}H_{26}Fe_2O_4$: C, 56.15; H, 5.58. Found: C, 56.65; H, 5.47.

$(C_5Me_4H)(C_5H_5)Fe_2(CO)_4$ (4). $[(C_5H_5)_2Fe(CO)_2]_2$ (1 g, 2.8 mmol) in 20 mL of THF was shaken with a 1% Na/Hg amalgam for 1 h. The amalgam was removed, and 2.52 g (7 mmol) of $(C_5Me_4H)Fe(CO)_2I$ in 15 mL of dry THF was added slowly to the sodium salt using a syringe. After 15 min at 25 °C, the THF was removed *in vacuo.* The IR spectrum of the crude product showed that **4** was dominant. The mixture was chromatographed on a silica gel column, using petroleum ether/diethyl ether as eluant (90:10), to yield 1.40 g of crude **4** (61%). The elution order was **3**, **4**, and **1**. Analytically pure samples were obtained by recrystallization from dichloromethane/hexane. ^1H NMR ($CDCl_3$): δ 1.78 (s, 6H), 1.81 (s, 6H), 3.84 (s, 1H), 4.77 (s, 5H). Anal. Calcd for $C_{18}H_{18}Fe_2O_4$: C, 52.68; H, 4.30. Found: C, 52.39; H, 4.21.

$(C_5Me_5)(C_5H_5)Fe_2(CO)_4$ (5). The above procedure was used with 1 g (2.8 mmol) of **1** and 2.55 g (7 mmol) of $(C_5Me_5)Fe(CO)_2I$. After chromatography on a silica gel column, 1.56 g (66%) of crude **5** was obtained. The elution order was **2**, **5**, and **1**. Analytically pure samples were obtained by crystallization from dichloromethane/hexane. ^1H NMR ($CDCl_3$): δ 1.85 (s, 15H), 4.89 (s, 5H). Anal. Calcd for $C_{19}H_{20}Fe_2O_4$: C, 53.77; H, 4.70. Found: C, 54.11; H, 4.74.

$(C_5Me_5)(C_5Me_4H)Fe_2(CO)_4$ (6). The above procedure was used with 1 g (2.15 mmol) of **3** and 1.87 g (5 mmol) of $(C_5Me_5)Fe(CO)_2I$. After chromatography with activated silica gel and using petroleum ether/toluene (95:5) as the eluant, 0.15 g (15%) of crude **6** was obtained. The elution order was **2**, **6**, and **3**. Analytically pure **6** was obtained by crystallization from hexane. ^1H NMR ($CDCl_3$): δ 1.73 (s, 6H), 1.76 (s, 6H), 1.86 (s, 15H), 3.85 (s, 1H). Anal. Calcd for $C_{23}H_{28}Fe_2O_4$: C, 57.50; H, 5.80. Found: C, 57.05; H, 6.03.

X-ray Crystallography. The structure was solved by direct methods, SHELXS-86,[20] and refined by full-matrix least-squares, using SHELXL-93.[21] SHELX operations were rendered paperless using ORTEX which was also used to obtain the drawings.[22] Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions, with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. All calculations were performed on a Silicon Graphics R4000 computer.

Supporting Information Available: For **3** and **4**, figures giving additional ORTEP views and tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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