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Restricted Rotation about the Arene−Iron Bond in (arene)Fe(CO)$(SiCl_3)_2$ Complexes

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Complexes of formula (η^6-$C_6H_{6-x}R_x$)Fe(CO)$(SiCl_3)_2$ have been prepared from the reaction of $Fe(CO)_4(SiCl_3)_2$ and the appropriate arene at 210 °C. The characterization of the complexes included the crystal structures of the 1,4-$C_6H_4Pr^i{}_2$ and C_6Me_6 derivatives. As ascertained by variable-temperature ^{1}H NMR spectroscopy, the (η^6-1,4-$C_6H_4R_2$)Fe(CO)$(SiCl_3)_2$ (R = Me, Et, Pr^i) compounds exhibit restricted rotation of the arene ring about the iron atom. Line-shape analyses of the NMR spectra reveal the barriers to the rotation in the three compounds are approximately the same ($\Delta G^{\ddagger}{}_{298} = 9.6-10.8$ kcal mol^{-1}). This finding is rationalized in terms of gearing of the R and $SiCl_3$ groups with the rotation. The 1,3,5-$C_6H_3Me_3$ and C_6Me_6 derivatives do not show restricted rotation of the arene ring by ^{1}H NMR spectroscopy to −120 °C. It is concluded from these observations that both ground-state and transition-state effects are important in determining the barrier to rotation of the arene ring in organometallic molecules.

Introduction

The barriers to rotation of aromatic rings π-bonded to transition metals are normally so low as to be undetectable by NMR line-broadening techniques.[1] In special cases, however, such restricted rotation has been observed by NMR spectroscopy. Higher barriers to arene−metal rotation can be brought about by the introduction of electronic constraints, such as the incorporation of a heteroatom into the ring as in (η^5-2,5-$C_5H_2Me_2S$)$Cr(CO)_3$,[2] or by the introduction of localized double-bond character into the ring, as in *endo*-(η^6-starphenylene)$Cr(CO)_3$ derivatives.[3] Restricted rotation of this type may also be brought about by steric constraints within the molecule. Recent examples where this has been observed include {η^6-C_6(1,3,5-Et_3)-[2,4,6-$(SiMe_3)_3$]}$Mo(CO)_2(PPh_3)$,[4] (η^6-1,4-$C_6H_4Bu^t{}_2$)Cr-$(CO)_2(PPh_3)$,[5] and the elegant studies by McGlinchey and co-workers on such species as [(η^6-C_6Et_6)Cr-(CO)(CS)(NO)]$^+$ and (η^6-C_6Et_5COMe)$Cr(CO)_3$,[6,7] and by Kilway and Siegel on {η^6-C_6[1,4-$(C_2H_4COBu^t)_2$(2,3,5,6-Et_4)}$Cr(CO)_3$.[8] The subject of slowed tripodal rotation in arene-chromium complexes, that at times has been controversial,[9] has been reviewed by McGlinchey.[10]

In 1980, work from this laboratory reported the restricted rotation of the arene ring in (η^6-1,4-$C_6H_4Bu^t{}_2$)-Ru(CO)$(SiCl_3)_2$.[11] It was found by ^{1}H NMR spectroscopy that there was free rotation of the arene ring in the corresponding 1,4-$C_6H_4Pr^i{}_2$ derivative in solution to −120 °C.[12] At that time we were unable to prepare the iron analogues of these compounds. We now find that under more stringent conditions complexes of formula (η^6-arene)Fe(CO)$(SiCl_3)_2$ can indeed be isolated, although we have still been unable to synthesize the 1,4-$C_6H_4Bu^t{}_2$ compound. As expected, the (η^6-arene)Fe-(CO)$(SiCl_3)_2$ complexes have significantly higher barriers to rotation of the arene ring about the metal atom than those in the corresponding Ru and Os analogues. The study of the iron complexes allows, for the first time, the determination of the change in the barrier with a change in size of the substituents on the arene ring. This in turn has allowed some important conclusions regarding the barriers to rotation of organic rings about metal atoms in organometallic complexes. Herein we report the details of this study along with the crystal structure

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Table 1. Analytical Data for the (arene)Fe(CO)($SiCl_3$)$_2$ Complexes

arene	MS[a]	C found (calcd), %	H found (calcd), %
C_6H_6	430	19.73 (19.51)	1.55 (1.40)
C_6H_5Me	444	21.84 (21.60)	1.88 (1.81)
1,4-$C_6H_4Me_2$	458	24.21 (23.56)	2.21 (2.20)
1,4-$C_6H_4Et_2$	485	27.32 (27.13)	2.89 (2.90)
1,4-$C_6H_4Pr^i{}_2$	514	30.39 (30.32)	3.46 (3.52)
1,3,5-$C_6H_3Me_3$	472	25.63 (25.40)	2.61 (2.56)
C_6Me_6	514	30.49 (30.32)	3.46 (3.52)

[a] Parent ion in each case.

determination of (η^6-1,4-$C_6H_4Pr^i{}_2$)Fe(CO)($SiCl_3$)$_2$ and (η^6-C_6Me_6)Fe(CO)($SiCl_3$)$_2$.

Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Heptane and the liquid arenes were refluxed over potassium, distilled, and stored over molecular sieves before use: olefins had been previously removed from the heptane by the accepted procedure.[13] Dichloromethane was dried in a similar manner to the hydrocarbons, except that P_2O_5 was employed as the drying agent. Solid arene reagents were recrystallized from hexane and sublimed before use. The precursor complex Fe(CO)$_4$($SiCl_3$)$_2$ was prepared by a literature procedure; it was also freshly sublimed before use.[14] The reactions were carried out in thick-walled Carius tubes of approximate volume 100 mL, fitted with a Teflon valve; the tubes were only immersed in the temperature baths to a point just above that of the reaction solution. Although no problems were experienced with this procedure, precautions against explosion were taken since the reaction temperatures were far above those of the boiling points of the solvent or the arene reagent.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Electron-impact (70 eV) mass spectra were obtained with a Hewlett-Packard 5985 GC-MS instrument. NMR spectra were recorded on a Bruker WM400 spectrometer. Microanalyses were determined by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University. Analytical and spectroscopic data for the new compounds are given in Tables 1 and 2, respectively.

Preparation of (η^6-arene)Fe(CO)($SiCl_3$)$_2$ Compounds. A Carius tube was charged with Fe(CO)$_4$($SiCl_3$)$_2$ (100 mg, 0.229 mmol) and either the liquid arene (10 mL) or olefin-free heptane (2 mL) and the solid arene (1.0 g). The vessel and contents were cooled to −196 °C, and the vessel was evacuated; the solution was rigorously degassed with three freeze−pump−thaw cycles. The vessel was warmed to room temperature and placed in an oil bath at 210 °C (located behind a protective shield) for 17 h. For the reactions that involved liquid arenes, the vessel was cooled and volatiles were removed on the vacuum line (with heating for reactions that involved arenes with high boiling points). The remaining solid was extracted with CH_2Cl_2 (3 × 10 mL); the extracts were filtered through Celite, and the solvent was removed on the vacuum line. The crude product remaining after this procedure was recrystallized from toluene/hexane to give the desired product as pale yellow, air-sensitive crystals. For the reactions that involved solid arenes, the reaction mixtures (after cooling) were extracted with CH_2Cl_2 (3 × 10 mL); the extracts were filtered through Celite and all volatiles removed on the vacuum line. The arene was removed by sublimation at elevated temperatures (<0.02 mmHg). The remaining crude product was recrystallized from toluene/hexane as described above. The yields in both procedures were 15−30%.

NMR Studies. The solvent used in the variable-temperature ^1H NMR studies was $CDFCl_2$ (prepared by a literature method[15]) containing ~20% CD_2Cl_2. The thermometer of the NMR spectrometer had been previously calibrated with a thermocouple. For the complexes that exhibited decoalescence of the singlet in the ^1H NMR spectrum for the protons of the arene ring (Table 2), at least seven spectra in the region of decoalescence were acquired and simulated with the use of the program DNMR3.[16] Because of the low temperatures needed to obtain spectra due to the rigid forms, the temperature dependencies of the resonances at still lower temperatures were not determined. We have, however, observed that changes in the chemical shifts of ^1H NMR resonances of related molecules with temperature are small.[12] The errors quoted for the activation parameters (Table 3) are the standard deviations obtained from fitting the rates obtained from the simulations to the Eyring equation. The solvent used for the low-temperature $^{13}C\{^1H\}$ spectra was CH_2Cl_2/CD_2Cl_2 (~4/1).

X-ray Analyses. (η^6-1,4-$C_6H_4Pr^i{}_2$)Fe(CO)($SiCl_3$)$_2$ (1). A yellow crystal of **1** was mounted in a glass capillary. Data were recorded with the crystal at 195 K with an Enraf-Nonius CAD4F diffractometer (at Simon Fraser University) with an extensively in-house-modified low-temperature attachment with graphite-monochromated Mo Kα radiation. Unit cell dimensions were determined from 25 well-centered reflections ($40° \leq 2\theta \leq 45°$). Two standard reflections were measured every 1 h of exposure time and showed only small fluctuations in intensity during the course of the measurements. The data were corrected for absorption by the Gaussian integration method, and corrections were carefully checked against measured ψ-scans. Data reduction also included corrections for Lorentz and polarization effects. Crystallographic details are summarized in Table 4. The structure was solved by direct methods. After the non-hydrogen atoms were located and refined with isotropic thermal parameters, an electron density difference map showed peaks consistent with anisotropic thermal motion of most atoms as well as the locations of many of the hydrogen atoms. Anisotropic thermal parameters were included in the refinement for those atoms for which there was evidence that they were appropriate. The methyl carbon atoms of one of the isopropyl groups exhibited disorder. Two sites with equated isotropic thermal parameters for each of these two carbon atoms were refined along with a relative occupancy parameter. The result was interpreted in terms of an unequal disorder between two different rotational orientations of the isopropyl group about the bond connecting it to the arene ring. A single relative occupancy parameter for the disorder was therefore refined as well as an isotropic thermal parameter for each pair of the fractionally occupied methyl groups. Each pair of C−C bond distances for the disordered methyl groups was softly restrained towards the respective mean value. Hydrogen atoms, with appropriate occupancies, were included in calculated positions (C−H = 0.95 Å) and recalculated periodically in the early stages. In the final cycles of refinement the coordinate shifts for the hydrogen atoms on the arene ring were linked with those of the carbon atoms to which they were bound. The methyl groups were refined as rigid groups subject to angle restraints which maintained approximate axial symmetry with respect to the appropriate C−C bonds. A single isotropic thermal parameter was refined for each of the following groups of hydrogen atoms: those on the arene ring; those bonded to the tertiary carbon atoms; those of each methyl group or disordered pair of methyl groups. The final full-matrix least-squares refinement involved 219 parameters, using 2972 data ($I_o \geq 2.5\sigma(I_o)$) and 22 restraints. An empirical weighting scheme based on counting statistics was applied such that $\langle w(|F_o| - |F_c|)^2\rangle$ was near constant as a function of both $|F_o|$ and $(\sin\theta)/\lambda$. The refinement converged at $R_F = 0.024$ and $R_{wF} = 0.032$. The programs used for

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Table 2. Spectroscopic Properties of the (arene)Fe(CO)($SiCl_3$)$_2$ Complexes

			^{13}C NMR, δ (CH_2Cl_2/CD_2Cl_2)	
arene	ν(CO) cm^{-1} (CH_2Cl_2)	^{1}H NMR, δ ($CDCl_3$ or CD_2Cl_2)	CO	arene
C_6H_6	2001	6.24 (s)	206.6	100.9
C_6H_5Me	1996.5	5.84 (t), 6.07 (d, $J = \sim6.5$ Hz), 6.33 (t), 2.49 (s)	207.5	116.1, 103.0, 99.7, 98.1, 20.6
1,4-$C_6H_4Me_2$	1995	6.04 (s) (6.31, 5.83, $J = 5.5$ Hz),[a] 2.42 (s)[b]	208.9	113.7 (117.5, 109.1)[c], 101.7 (105.4, 94.9)[c], 19.8 (19.9, 18.2)[c]
1,4-$C_6H_4Et_2$	1993.5	6.06 (s) (6.32, 5.86, $J = \sim4$ Hz[d]),[a] 2.74 (q),[b] 1.30 (t, $J = 7.5$ Hz)[e]	208.8	119.2, (126.7, 122.3)[c], 100.8 (105.0, 94.3)[c], 27.3 (27.0, 25.7)[c],15.2 (16.2, 14.4)[c]
1,4-$C_6H_4Pr^i_2$	1992.5	6.10 (s) (6.32, 5.87, $J = 5.3$ Hz),[f] 3.12 (sept),[f] 1.35 (d, $J = 5.7$ Hz)[f]	209.3	124.3 (126.2, 119.6)[c], 98.8 (102.6, 92.5)[c], 31.4 (31.6, 28.9)[c]
1,3,5-$C_6H_3Me_3$	1989.5	6.02 (s), 2.45 (s)	208.5	112.2, 104.1, 20.1
C_6Me_6	1977	2.38 (s)	210.3	112.8, 17.9

[a] At ≤ −100°C in $CDFCl_2/CD_2Cl_2$. [b] Broadened at −95 °C. [c] At −95 °C. [d] Poorly resolved. [e] Doublet at −95 °C ($\Delta\delta = \sim0.13$ ppm). [f] Doublet at −95 °C ($\Delta\delta = \sim0.27$ ppm). [g] Doublet at −95 °C ($\Delta\delta = \sim0.08$ ppm).

Table 3. Activation Parameters for Arene−Metal Rotation for (arene)M(CO)($SiCl_3$)$_2$ (M = Fe, Ru) Complexes

arene	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal mol^{-1} deg^{-1}	$\Delta G^\ddagger_{298}$, kcal mol^{-1}
	M = Fe[a]		
1,4-$C_6H_4Me_2$ (**3**)	6.8 ± 0.1	−9.2 ± 0.4	9.6 ± 0.1
1,4-$C_6H_4Et_2$ (**4**)	6.3 ± 0.2	−11.3 ± 0.8	9.7 ± 0.3
1,4-$C_6H_4Pr^i_2$ (**1**)	7.2 ± 0.1	−12.2 ± 0.6	10.8 ± 0.2
1,3,5-$C_6H_3Me_3$ (**7**)			<∼5.3[b]
C_6Me_6 (**2**)			<∼5.3[b]
	M = Ru[c]		
1,4-$C_6H_4Pr^i_2$ (**6**)			<∼5.3[b]
1,4-$C_6H_4Bu^t_2$ (**5**)	10.5 ± 0.3	−7.5 ± 1.0	12.8

[a] This work. [b] At −120 °C; see text. [c] From ref 12.

Table 4. Crystal Structure Data for (η^6-1,4-$C_6H_4Pr^i_2$)Fe(CO)($SiCl_3$)$_2$ (1) and (η^6-C_6Me_6)Fe(CO)($SiCl_3$)$_2$ (2)

	1	2
empirical formula	$C_{13}H_{18}Cl_6FeOSi_2$	$C_{13}H_{18}Cl_6FeOSi_2$
color	yellow	yellow
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	*Pbca*
a (Å)	8.437(5)	14.649(2)
b (Å)	9.067(3)	16.480(2)
c (Å)	14.986(6)	34.074(3)
α (deg)	101.00(3)	
β (deg)	100.20(4)	
γ (deg)	111.01(4)	
V, Å^3; *Z*	1012.1; 2	8225.8(2); 16
D(calcd) Mg m^{-3})	1.690	1.663
abs coeff (cm^{-1})	16.6	16.3
no. of indpdt rflns	2972 ($I_o \geq 2.5\sigma(I_o)$)	4349 ($I_o \geq 3.5\sigma(I_o)$)
R_F[a]	0.024	0.039
R_{wF}[b]	0.032	0.042

[a] $R_F = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$. [b] $R_{wF} = [\Sigma(w(|F_o| - |F_c|)^2)/\Sigma(wF_o^2)]^{1/2}$; $w = [\sigma^2(F_o)^2 + kF_o^2]^{-1}$.

absorption corrections, data reduction, structure solution, preliminary refinement, and plot generation were from the NRCVAX Crystal Structure System.[17] Refinement was made using CRYSTALS.[18] Complex scattering factors for neutral atoms were used in the calculation of structure factors.[19] Computations were carried out on 80486 and Pentium computers.

(η^6-C_6Me_6)Fe(CO)($SiCl_3$)$_2$ (2). The analysis was carried out as for **1,** except as follows: the structure was determined at St. Mary's University; the data were collected at room temperature on an Enraf CAD-4 diffractometer; all crystallographic calculations were effected with the NRCVAX program package;[17] disorder was not observed; an empirical weighting scheme based on statistical variation of standards was employed; final $R_F = 0.039$ and $R_{wF} = 0.042$ were obtained.

Results and Discussion

The complexes (η^6-arene)Fe(CO)($SiCl_3$)$_2$ were obtained in moderate yield by heating the arene and Fe(CO)$_4$($SiCl_3$)$_2$ (an inseparable mixture of the cis and trans isomers[20]) in an evacuated sealed tube at 210 °C (eq 1).

$$\text{arene} + \text{Fe(CO)}_4(\text{SiCl}_3)_2 \xrightarrow{210\ °\text{C}} (\eta^6\text{-arene})\text{Fe(CO)}(\text{SiCl}_3)_2 \quad (1)$$

$$\text{arene} = \text{C}_6\text{H}_{6-x}\text{Me}_x\ (x = 0, 1, 2, 3, 6);\quad 1{,}4\text{-C}_6\text{H}_4\text{R}_2\ (\text{R} = \text{Me, Et, Pr}^\text{i})$$

Rigorously purified reagents, thoroughly degassed solutions, and strict temperature control were found to be required in order to obtain satisfactory yields of the compounds, which are pale yellow, air-sensitive crystalline solids. The temperature required for the syntheses is comparable to that needed for the preparation of the osmium analogues but is some 80 °C above that used for the corresponding ruthenium compounds.[12] This can be attributed to the greater CO lability of the compound with the second-row transition metal, that is, Ru(CO)$_4$($SiCl_3$)$_2$.[21] Although we have been able to prepare (η^6-1,4-$C_6H_4Bu^t_2$)Ru(CO)($SiCl_3$)$_2$ and (η^6 -1,3,5-$C_6H_3Bu^t_3$)-Ru(CO)($SiCl_3$)$_2$,[12] attempts to prepare the iron analogues of these compounds were unsuccessful, which can undoubtedly be attributed to excessive steric interactions between the *tert*-butyl groups and the trichlorosilyl ligands which prevents formation of the iron complexes.

The spectroscopic data for the new compounds in solution at room temperature (Table 2) are as expected. The single carbonyl stretch that the compounds exhibit in the IR spectrum shifts to lower stretching frequency with increasing methyl substitution of the aromatic ring, consistent with the methyl groups increasing the electron density on the iron atom and thereby increasing the back-donation to the carbonyl ligand. The ^{1}H and ^{13}C NMR resonances of the atoms involved in the aromatic ring show the upfield shift from the values of the free arene as is typically observed for arene−transition-metal complexes.[22]

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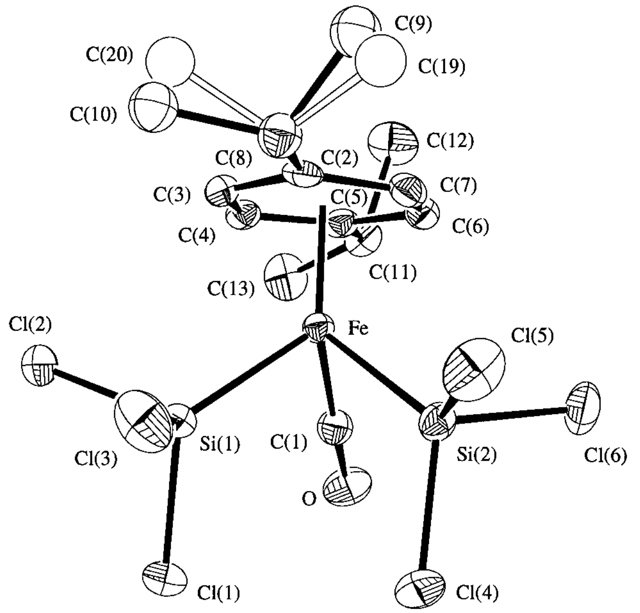

Figure 1. Molecular structure of $(\eta^6\text{-}1,4\text{-}C_6H_4Pr^i{}_2)Fe(CO)(SiCl_3)_2$ (**1**).

The crystal structures of $(\eta^6\text{-}1,4\text{-}C_6H_4Pr^i{}_2)Fe(CO)(SiCl_3)_2$ (**1**) and $(\eta^6\text{-}C_6Me_6)Fe(CO)(SiCl_3)_2$ (**2**) were determined by X-ray crystallography. There are two independent molecules in the unit cell of **2**. Both structures reveal a typical piano-stool arrangement of ligands about the iron atom, and this is shown for **1** in Figure 1. Views of **1** and one molecule of **2** down the vector that passes through the Fe atom and the center of the arene ring are given in Figure 2. As can be seen from this figure, **1** has an eclipsed conformation, whereas in **2** the conformation is slightly staggered. The distances of the iron atom to the centroid of the arene ring (Fe−Cent) in **1** (1.652 Å) and in **2** (1.699 and 1.704 Å) are significantly different, whereas all other comparable bond lengths in **1** and the two independent molecules of **2** are remarkably consistent (Table 5). The Fe−Cent distances in **1** and **2** are, as expected, far shorter than the corresponding Ru−Cent distance in $(\eta\text{-}C_6H_6)Ru(CO)(GeCl_3)_2$ (1.806 Å)[23] and $(\eta^6\text{-}1,4\text{-}C_6H_4Bu^t{}_2)Ru(CO)(SiCl_3)_2$ (1.888 Å).[24] This parameter will be important in the discussion of the barriers to the rotation of the arene ring about the metal atom in these complexes that is presented below. The average Fe−Si distance in **1** is 2.262 Å, whereas in **2** it is 2.260 Å. Both Fe−Si distances are in good agreement with 2.252(3) Å, the Fe−Si bond length in $(\eta\text{-}C_5H_5)Fe(CO)(H)(SiCl_3)_2$.[25]

Klabunde and co-workers have recently reported the crystal structures of $(\eta^6\text{-arene})Fe(H)_2(SiCl_3)_2$ derivatives (arene = benzene, toluene, *p*-xylene) prepared by metal vapor deposition techniques.[26] The Fe−Si bond lengths in these compounds range from 2.207(3) to 2.226(2) Å; the Fe−Cent distances are 1.608 or 1.609 Å. That these distances are somewhat shorter than the corresponding distances in **1** and **2** can be attributed to more steric interactions in **1** and **2** than in the $(\eta^6\text{-arene})Fe(H)_2(SiCl_3)_2$ compounds.

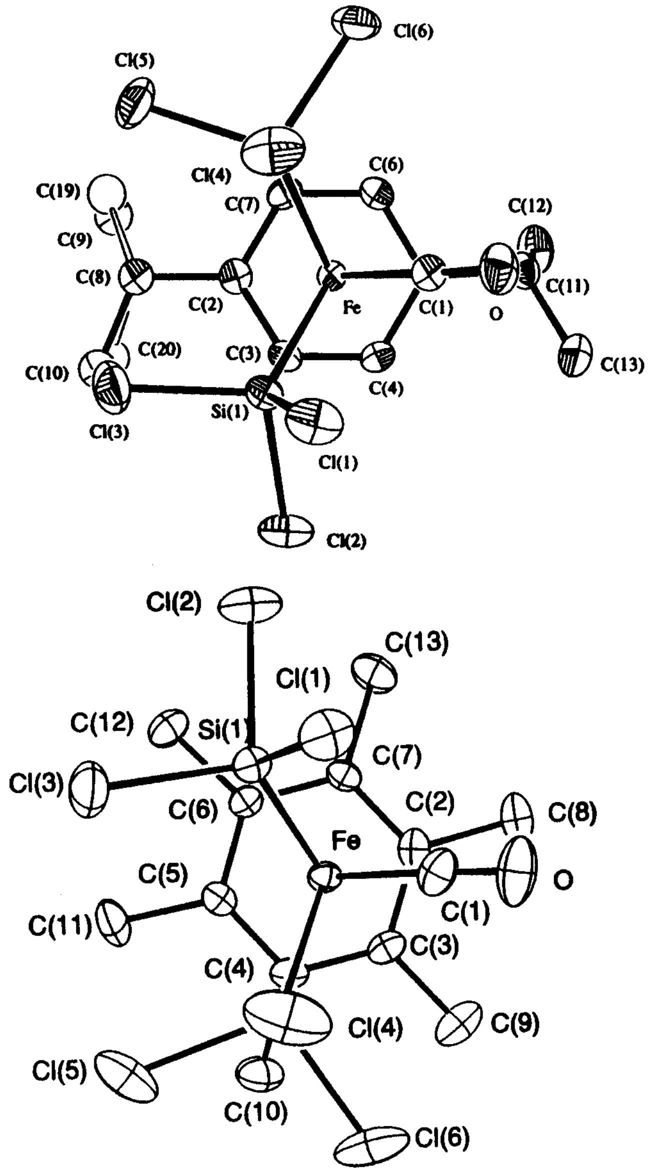

Figure 2. A second view of **1** (top) and a similar view of $(\eta^6\text{-}C_6Me_6)Fe(CO)(SiCl_3)_2$ (**2**) (bottom).

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $(\eta^6\text{-}1,4\text{-}C_6H_4Pr^i{}_2)Fe(CO)(SiCl_3)_2$ (1) and $(\eta^6\text{-}C_6Me_6)Fe(CO)(SiCl_3)_2$ (2a and 2b)

	1	2a	2b
	Bond Lengths		
Fe−Si(1)	2.258(1)	2.262(2)	2.258(2)
Fe−Si(2)	2.266(2)	2.252(2)	2.269(2)
Fe−C(1)	1.746(3)	1.744(6)	1.731(5)
Fe−Cent[a]	1.652	1.704	1.699
Fe−C(arene)	2.150(3)−2.221(3)	2.166(5)−2.250(5)	2.166(5)−2.234(5)
Si−Cl	2.057(2)−2.092(2)	2.061(2)−2.085(2)	2.061(2)−2.083(2)
C−C(arene)	1.398(3)−1.418(3)	1.409(7)−1.428(7)	1.406(8)−1.432(7)
	Bond Angles		
Si(1)−Fe−Si(2)	91.83(7)	88.46(6)	88.66(6)
C(1)−Fe−Si(1)	86.8(1)	86.3(2)	83.6(2)
C(1)−Fe−Si(2)	83.6(1)	84.1(2)	86.4(2)
Fe−Si−Cl	108.9(1)−120.2(1)	116.7(1)−122.2(1)	112.5(1)−120.6(1)
Cl−Si−Cl	99.6(1)−103.0(1)	96.4(1)−103.7(1)	96.9(1)−103.2(1)

[a] Cent = center of mass of the arene ring.

NMR Studies. The ^1H NMR spectra of $(\eta^6\text{-}1,4\text{-}C_6H_4R_2)Fe(CO)(SiCl_3)_2$ (R = Me (**3**), Et (**4**), Pr^i (**1**)) in $CDFCl_2/CD_2Cl_2$ exhibit a sharp singlet for the aromatic protons to −40 °C. Below this temperature there is decoalescence of the signal to two singlets (with H-H

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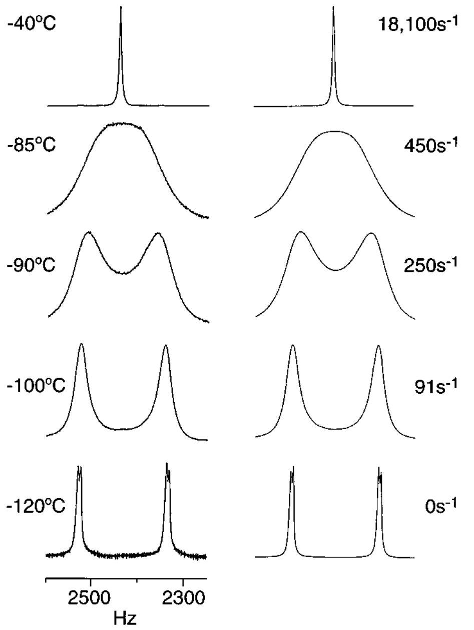

Figure 3. Observed (left) and simulated (right) variable-temperature ^{1}H NMR spectra of (η^6-1,4-C$_6$H$_4$Pr$^i{}_2$)Fe(CO)(SiCl$_3$)$_2$ (**1**) in CDFCl$_2$/CD$_2$Cl$_2$.

coupling) at −120 °C. This is shown for **1** in Figure 3. There is also a similar decoalescence of some of the signals due to the alkyl substituents (Table 2). As has been previously found for (η^6-1,4-C$_6$H$_4$Bu$^t{}_2$)Ru(CO)(SiCl$_3$)$_2$ (**5**),[11] this behavior indicates restricted rotation on the NMR time scale, of the arene ring about the metal atom. If rotation of the arene ring in **1** is slowed on the NMR time scale then the protons bonded to C(3) and C(7) (Figure 2) are no longer equivalent to those attached to C(4) and C(6).

This study represents the first where molecules show restricted rotation about an arene−metal bond and in which the arene ligand contains substituents of different sizes. Complete line-shape analyses of the spectra for the three cases were carried out and the activation parameters for arene−Fe rotation determined (Table 3). The free energies of activation for **3** and **4** were found to be the same within experimental error (9.6 ± 0.1 kcal mol^{-1} and 9.7 ± 0.3 kcal mol^{-1}, respectively) and the free energy of activation for the isopropyl derivative **1**, only marginally higher at 10.8 ± 0.2 kcal mol^{-1}. The entropies of activation range from −9.2 ± 0.4 to −12.2 ± 0.8 cal mol^{-1} deg^{-1} and are comparable to values we have found for **5** (Table 3) and related complexes.[12] The negative entropies of activation are consistent with an intramolecular transition state. The similar barriers to arene rotation in molecules **1**, **3**, and **4** are interpreted in terms of a similar transition state in each case, in which a hydrogen rather than a methyl substituent of the alkyl group is closest to the trichlorosilyl ligand at the moment the alkyl group passes over the SiCl$_3$ ligand in question. This is the conformation of the isopropyl substituent closest to the silyl ligands found in the solid-state structure of **1** (Figure 1).

The similarities of the barriers to arene−Fe rotation in **1**, **3**, and **4** are reminiscent of the conformational free energies in the corresponding cyclohexyl derivatives: C$_6$H$_{11}$Me (1.8 kcal mol^{-1}), C$_6$H$_{11}$Et (1.8 kcal mol^{-1}), and C$_6$H$_{11}$Pr^i (2.1 kcal mol^{-1}). It is only in C$_6$H$_{11}$Bu^t that the repulsive interactions between the alkyl group and the *syn*-axial hydrogen atoms of the ring become excessive (>4.5 kcal mol^{-1}).[27] Several attempts were made to prepare (η^6-1,4-C$_6$H$_4$Bu$^t{}_2$)Fe(CO)(SiCl$_3$)$_2$, including by an arene exchange reaction on **3**, but without success.

Of the (η^6-1,4-C$_6$H$_4$R$_2$)Ru(CO)(SiCl$_3$)$_2$ complexes, only the C$_6$H$_4$Bu$^t{}_2$ derivative (**5**) exhibits restricted rotation of the arene ring on the NMR time scale (Table 3)[11,12] and, therefore, a direct comparison of the barriers to arene-metal rotation between the Fe and Ru compounds is not possible. An upper limit for the size of the barrier to arene−metal rotation in (η^6-1,4-C$_6$H$_4$Pr$^i{}_2$)Ru(CO)(SiCl$_3$)$_2$ (**6**) may, however, be estimated, given that it exhibits a sharp singlet for the aromatic protons in the solution ^{1}H NMR spectrum to −120 °C.[12] For a mutual two-site exchange as in these molecules, in order to observe a broadening of the averaged signal of 0.5 Hz due to exchange, the limiting rate constant is $\pi(\delta\nu)^2$, where $\delta\nu$ is the chemical shift difference between the two sites in Hz.[28] A $\delta\nu$ value of 100 Hz therefore yields a limiting rate constant of $\sim 3 \times 10^4$ s^{-1}. The chemical shift difference between adjacent aromatic protons in the rigid form of **5** is 92 Hz, whereas in **1** it is 180 Hz. Furthermore, from Figure 3 it is seen that a rate constant of at least 1×10^4 s^{-1} is required to cause complete coalescence of the resonances of the aromatic protons in these complexes. If one assumes this latter rate constant, it allows an upper limit to the barrier to rotation in complexes that exhibit free rotation by ^{1}H NMR spectroscopy (such as **6**) of approximately ∼5.3 kcal mol^{-1}. The barriers to arene−metal rotation in (η^6-1,4-C$_6$H$_4$R$_2$)Fe(CO)(SiCl$_3$)$_2$ are therefore at least 5.5 kcal mol^{-1} greater than those in the corresponding Ru derivatives. This increase in barriers may be attributed to the increased energy of the transition state during arene rotation in the Fe complexes. This in turn arises from the increase in the steric interactions between the arene substituents and the SiCl$_3$ ligands due to the shorter metal−arene distance in the iron compounds (see above). A decrease of 2.8 kcal mol^{-1} in the barrier to arene−metal rotation on going to the metal lower in a chemical group has been observed in {η^6-C$_6$[1,4-(C$_2$H$_4$COBu^t)$_2$](2,3,5,6-Et$_4$)}M(CO)$_3$ (M = Cr, Mo).[29]

A decoalescence similar to that described above is observed in the ^{13}C{^{1}H} NMR spectra of **1**, **3**, and **4**: the singlets due to the various chemically different carbon atoms of the arene ligand split into doublets at low temperature (e.g., Figure 4). An exception is the resonance at δ 22.6 due to the methyl substituents of **1**, which remains a singlet in the spectrum at low temperature (Figure 4). It is probable that the conformer of **1** that is predominant in solution is similar to that found in the solid state, namely, with the methyl groups located on the side of the arene ring that is distal to the Fe atom and its ligands. In such a location, the chemical environment of the methyl groups would be insensitive to the substituents on the metal atom. On the other hand, the protons of the two isopropyl substituents in the rigid form would be expected to exhibit a large chemical shift difference, since they are close to either the carbonyl or SiCl$_3$ ligands. Consistent with this view is that the ^{1}H NMR resonances for these

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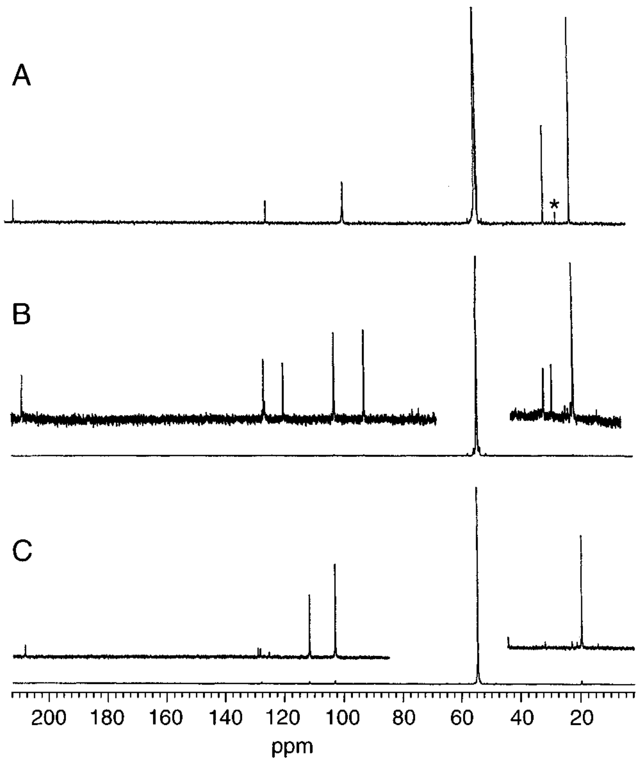
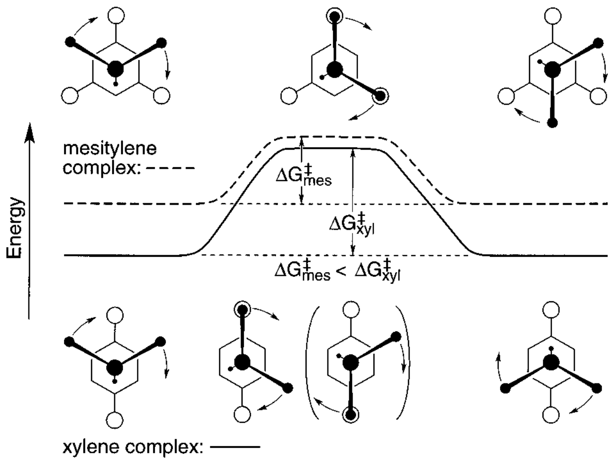


Figure 4. $^{13}C\{^1H\}$ NMR spectrum of **1** at 21 °C (A) and at −95 °C (B) and of (η^6-1,3,5-$C_6H_3Me_3$)Fe(CO)($SiCl_3$)$_2$ (**7**) at −95 °C (C). The solvent in each case is CH_2Cl_2/CD_2Cl_2 (4/1); the peak marked with an asterisk in spectrum A is due to an impurity which was not present in the sample used to obtain spectrum B.

protons have a relatively large chemical shift difference (~0.27 ppm) in the low-temperature spectrum, whereas the corresponding difference in the 1,4-$C_6H_4Me_2$ compound is negligible (Table 2).

It was pointed out many years ago by Cotton that in an investigation of a series of molecules for nonrigidity valuable information can be gained from those examples that do not exhibit nonrigidity.[30] A similar situation occurred in the present study, but with respect to the molecules that in solution showed free rotation of the arene ring by ^1H NMR spectroscopy. It was expected that (η-C_6H_6)Fe(CO)($SiCl_3$)$_2$ would show free rotation of the benzene ring at all temperatures, and this was observed. Surprisingly, the ^1H NMR spectra of both (η^6-1,3,5-$C_6H_3Me_3$)Fe(CO)($SiCl_3$)$_2$ (**7**) and (η^6-C_6Me_6)Fe(CO)($SiCl_3$)$_2$ (**2**) indicate free rotation of the arene ring about the iron atom in solution to −120 °C (sharp singlet for the resonances of the aromatic-H and methyl-H atoms). Likewise, the $^{13}C\{^1H\}$ NMR spectra of **2** and **7** in CD_2Cl_2/CH_2Cl_2 exhibit sharp singlets for the methyl groups and the various types of arene carbon atoms to −95 °C (this is shown for **7** in Figure 4). We have previously reported that (η^6-1,3,5-$C_6H_3Me_3$)Ru(CO)($SiCl_3$)$_2$ (**8**) has a significantly lower barrier to arene−Ru rotation than the η^6-1,4-$C_6H_4Bu^t{}_2$ analogue, an observation that we rationalized in terms of more favorable ring tilting of the tri-*tert*-butylbenzene ring in **8** so as to allow the bulky alkyl substituents to pass over the bulky silyl ligands.[12] Such an explanation could be invoked to explain the difference in the barriers in **7** and the *p*-xylene derivative **3**, but it cannot be used to explain why **3** has a lower barrier than that in the hexamethylbenzene compound **2**. The difference in barriers can, however, be explained in terms of the relative stabilities of the ground state compared to that of the transition state. It is probable that the transition state for both the $C_6H_3Me_3$ and the C_6Me_6 compounds, **7** and **2,** lies at a higher energy to that in the $C_6H_4Me_2$ derivative (**3**), but the ground state of **3** is more stabilized relative to the ground states of **7** and **2**, so that overall the barrier to rotation is greatest in **3**. This is illustrated for the xylene and mesitylene compounds (i.e., **3** and **7**) in Chart 1. As mentioned above, the Fe−Cent distance in **2** (1.699 and 1.704 Å) is significantly longer than the corresponding distance in **1** (1.652 Å), consistent with ground-state destabilization in **2**.

Chart 1



In other words, it is not necessary to propose ring tilting to explain differences in the arene−metal rotation barriers in these and related compounds, although it cannot be ruled out. We did not fully appreciate the importance of ground-state destabilization effects in these systems until this study. They obviously must be taken into account when the barriers to rotation of ligands in organometallic complexes are discussed. For example, the concept may be used to rationalize why the barrier to arene−Cr rotation is greater in (η^6-C_6Et_6)Cr(CO)$_2$(CS)[9] than that in (η^6-1,4-$C_6H_4Bu^t{}_2$)Cr(CO)$_2$(PPh_3),[5] which in turn is greater than that in (η^6-1,3,5-$C_6H_3Bu^t{}_3$)Cr(CO)$_2$(PPh_3).[31,32]

It has now been established that in solution three of the ethyl groups in (η^6-C_6Et_6)Cr(CO)$_2$(CS) are distal to the metal and three proximal, as found in the solid state.[9c] In solution this complex has a measurable barrier to arene−Cr rotation which may be attributed to the inability of the methyl substituent of the proximal ethyl groups to rotate away from the carbonyl and thiocarbonyl ligands during arene rotation. This lack of free rotation of the proximal ethyl groups is, of course, due to the presence of the adjacent distal ethyl groups in the C_6Et_6 ring (the barrier to ethyl rotation is slightly higher than the barrier to arene-Cr rotation).[9] On the other hand, the methyl substituents on the isopropyl

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[31] Campi, E. V.; Gatehouse, B. M. K.; Jackson, W. R.; Rae, I. D.; Wong, M. G. *J. Chem. Soc., Chem. Commun.* **1984**, 175.

[32] A detailed study by Howell and co-workers on the last two molecules, which appeared after the original submission of this paper, reached similar conclusions: Howell, J. A. S.; Beddows, C. J.; O'Leary, P. J.; Yates, P. C.; McArdle, P.; Cunningham, D.; Gottlieb, H. E. *J. Organomet. Chem.* **1997**, *537*, 21.

groups of (η^6-1,4-C$_6$H$_4$Pr$^i{}_2$)Ru(CO)(SiCl$_3$)$_2$[12] are free to rotate away from the carbonyl and SiCl$_3$ ligands during arene rotation. This is not to say that the maximum energy state during arene rotation in the Ru complex is at lower energy than that in the Cr complex; it probably is not. What can be said, however, is that the ground state of the Cr compound with the carbon atoms of the distal ethyl groups eclipsing the thiocarbonyl and carbonyl ligands is at much lower energy than that in the Ru compound. Kilway and Siegel have investigated this steric complementarity between the substituents on the arene ring and metal tripod in some complexes of the type [η^6-C$_6$(1,4-R$_2$)(2,3,5,6-Et$_4$)]Cr(CO)$_3$ (R = (CH$_2$)$_2$Bu^t, etc.).[33]

Conclusions

The energy barriers to rotation of the arene ligand π-bound to the iron atom in (η^6-1,4-C$_6$H$_4$R$_2$)Fe(CO)(SiCl$_3$)$_2$ (R = Me, Et, Pr^i) complexes are similar and follow the pattern observed for the conformational energies of the cyclohexyl compounds C$_6$H$_{11}$R. The explanation of why the arene-rotation barriers in the iron complexes are similar parallels that used to rationalize the conformational energies of the cyclohexyl compounds: there is rotation of the alkyl groups so as to minimize the steric interactions, which in the case of the iron complexes involves a hydrogen atom of the alkyl group in closest approach to the bulky silyl ligand as the alkyl and silyl groups pass by each other during arene−Fe rotation.

Furthermore, whereas the 1,4-C$_6$H$_4$R$_2$ derivatives have measurable barriers to arene−Fe rotation by ^{1}H NMR line-broadening techniques, the corresponding C$_6$H$_3$Me$_3$ and C$_6$Me$_6$ complexes exhibit no detectable barriers to such rotation by this method. We believe that although the transition state for the rotation is at a higher energy in the complexes with the more highly methyl-substituted arenes there is, however, even greater destabilization of the ground state for the (η^6-C$_6$H$_{6-x}$Me$_x$)Fe(CO)(SiCl$_3$)$_2$ ($x = 3, 6$) derivatives, since in these compounds the silyl ligands are always in close contact with two methyl substituents (Chart 1). The net result is that the activation barriers to arene−Fe rotation in the (η^6-C$_6$H$_{6-x}$Me$_x$)Fe(CO)(SiCl$_3$)$_2$ compounds are smaller than the corresponding barrier in (η^6-1,4-C$_6$H$_4$Me$_2$)Fe(CO)(SiCl$_3$)$_2$. That the barrier to rotation about metal−ligand bonds is determined not just by the energy of the transition state but also by that of the ground state should be taken into account in the study of barriers to rotation of metal−ligand bonds. Mislow and co-workers have made similar arguments in the discussion of dynamic gearing in organic molecules.[34]

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Supporting Information Available: Tables of crystal structure and refinement data, atomic coordinates, thermal parameters, and bond lengths and angles for compounds **1** and **2** (13 pages). Ordering information and Internet access instructions are given on any current masthead page.

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