Chemical Industry Co., Ltd., for the kind supply of (*R*)- and (*S*)-methyl 3-hydroxyisobutyrates.

Supplementary Material Available: Tables of hydrogen atom coordinates and B_{eq} values, anisotropic thermal parameters, bond angles, and torsion angles for two complexes, (*E*)-(MeO-$C_6H_4COCH{=}CHMe)Cr(CO)_3$ and (*E*)-(Me-$C_6H_4COCH{=}CHMe)Cr(CO)_3$, and ^1H NMR spectra (400 MHz) for compounds **13**, **17**, **20**, and **21** (18 pages). Ordering information is given on any current masthead page.

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Investigation of the Applicability of Molecular Mechanics (MMX) Calculations to a Conformational Investigation of Organometallic Compounds of the Types $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2R$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2C(=O)R$, and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R$ (R = H, Alkyl, Acyl)

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The potential utility and applicability of a new molcular modeling program, MMX, to organotransition-metal chemistry is assessed by comparing calculated ligand rotation conformational energy profiles with relevant experimental data. To this end, both the identity of the lowest energy conformation and the enthalpy differences between the various conformations arising from alkyl or acyl ligand rotation in the flexible organometallic complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2R$ (R = H, Me, Ph, C_6H_3(*m*-Me)$_2$, Me_3Si) $(\eta^5\text{-}C_5H_5)Fe(CO)_2C(O)R'$ (R′ = Me, Ph, C_6H_3(*m*-Me)$_2$), and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R''$ (R″ = H, Me, Et, CH_2Ph, CH_2SiMe_3, C(O)Me) are determined utilizing variable-temperature IR and NMR spectroscopy. For most of the compounds studied, the computed conformational energy profiles identify correctly the low-energy conformation, and provide surprisingly accurate estimates of the relative energies of the less stable conformations. The effects of electronic and entropic factors may complicate interpretations in a small number of cases, but the overall results seemingly validate the use of MMX to consider subtle steric effects on organometallic structural chemistry.

Molecular mechanics (MM) calculations have in recent years become a very valuable tool for rapid computation of the conformational energy profiles of a wide variety of types of molecules and complement the various quantum mechanical methodologies which are available.[1] Where comparisons with experimental data are possible, surprisingly accurate estimates of molecular properties are possible, and MM calculations are often the computational methodology of choice for the consideration of many medium-sized organic systems[2] and coordination[3] compounds.

With the development of many enantioselective organic reactions induced by chiral organotransition-metal compounds,[4] it would seem that MM calculations should be ideally suited for computational analyses of the factors involved in enantioselective steps, which are often believed to be strongly influenced by steric factors.[5] However, to date, very few such applications to organotransition-metal problems have been reported[5,6] and, of these, none has attempted to address closely the subtle energy differences which must of necessity be involved in many enantioselective processes (2–4 kcal mol^{-1}).[7] The parameterization

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necessary to consider complexes of many types of π-bonded ligands has not heretofore been available.

Recently, however, there has become available a molecular modeling program, MMX,[8a] which attempts to address the problems associated with π-bonded ligands in organotransition-metal chemistry. In view of the potential significance of MMX, testing of its utility is clearly desirable and we have embarked on a validation program in which the calculated conformational energy profiles for several series of representative organometallic compounds are compared with quantitative experimental information concerning ligand conformational preferences and/or barriers to ligand rotation. In this paper, we describe MMX calculations on the flexible organometallic complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2R$ (R = H (I), Me (II), Ph (III), $C_6H_3(m\text{-}Me)_2$ (IV), Me_3Si (V)), $(\eta^5\text{-}C_5H_5)Fe(CO)_2C(O)R'$ (R' = Me (VI), Ph (VII), $C_6H_3(m\text{-}Me)_2$ (VIII)), and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R''$ (R'' = H (IX), Me (X), Et (XI), CH_2Ph (XII), CH_2SiMe_3 (XIII), C(O)Me (XIV)), comparing the results with relevant experimental information concerning the ligand conformational preferences and, in one case (I), the barrier to methyl ligand rotation. Aspects of this work have appeared in a preliminary communication.[9a]

Experimental Section

Syntheses and Spectroscopy. All reactions and manipulations were carried out using Schlenk line techniques under a nitrogen atmosphere unless otherwise stated. Solvents were dried by refluxing over either sodium or potassium, unless otherwise indicated. THF was dried in two steps; it was first refluxed over CaH_2, and then over potassium. Regular solvents were degassed by bubbling with nitrogen for at least 20 min, while deuterated solvents were cycled at least four times through a freeze–thaw degassing procedure. Chemicals were purchased from Aldrich, BDH, Fisher Scientific, or MSD Isotopes and were normally used as received. The compounds $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2R$ (R = H, Me, Ph, $C_6H_3(m\text{-}Me)_2$, Me_3Si), $(\eta^5\text{-}C_5H_5)Fe(CO)_2COR'$ (R' = Me, Ph, $C_6H_3(m\text{-}Me)_2$), and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R''$ (R'' = H, Me, Et, CH_2SiMe_3, COMe) were prepared by utilizing standard procedures.[10] The compounds $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2C_6H_3(m\text{-}Me)_2)$ (IV) and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(COC_6H_3(m\text{-}Me)_2)$ (VIII) are new. Anal. Calcd for $C_{16}H_{16}FeO_2$ (IV): C, 64.89; H, 5.45. Found: C, 65.04; H, 5.27. ^1H NMR of IV in DMSO-d_6: δ 6.68 (s, 2 H, phenyl), 6.51 (s, 1 H, phenyl), 4.91 (s, 5 H, C_5H_5), 2.57 (s, 2 H, CH_2), 2.14 (s, 6 H, Me). $^{13}C\{^1H\}$ NMR in DMSO-d_6: δ 217.8 (CO), 152.7, 136.3, 125.0, 124.5 (ipso-, *m*-, *o*-, and *p*-phenyl carbons, respectively), 86.5 (C_5H_5), 21.1 (Me), 4.2 (CH_2). Calcd for $C_{16}H_{14}FeO_3$ (VIII): C, 61.97; H, 4.55. Found: C, 61.72; H, 4.72. ^1H NMR of VIII in CD_2Cl_2: δ 7.03 (s, 1 H, phenyl), 7.02 (s, 2 H, phenyl), 4.92 (s, 5 H, C_5H_5), 2.35 (s, 6 H, Me). $^{13}C\{^1H\}$ NMR in CD_2Cl_2: δ 254.5 (acyl carbon), 214.9 (C≡O), 152.1, 137.9, 131.8, 123.8 (ipso-, *m*-, *o*-, and *p*-phenyl carbons, respectively), 86.8 (C_5H_5), 21.4 (Me).

Table I. Carbonyl Stretching Frequencies (ν(CO), cm^{-1}) and Peak Widths ($\Delta\nu_{1/2}$, cm^{-1}) of the Compounds I–XIV at 290 K

compd	ν_{sym} ($\Delta\nu_{1/2}$)	ν_{asym} ($\Delta\nu_{1/2}$)	ν(C═O)
I	2014.7 (3.7)	1961.2 (4.1)	
II	2010.3 (3.4)	1955.3 (3.4)	
	2008.3 (sh, 3.4)	1953.3 (sh, 3.1)	
III	2013.0 (sh, 3.1)	1962.0 (sh, 3.9)	
	2009.7 (3.5)	1957.9 (4.2)	
IV	2012.9 (sh, 2.4)	1962.6 (sh, 3.2)	
	2009.7 (3.1)	1958.1 (3.6)	
V	2013.6 (2.9)	1961.9 (3.6)	
	2011.4 (sh, 2.9)	1958.1 (sh, 4.6)	
VI	2021.5 2015 (sh) (11.9)[a]	1964.6 (6.4)	1670.0 (10.2)
VII	2028.5 2022 (sh) (6.7)[a]	1971.6 1967 (sh) (5.2)[a]	1629.7 (10.2)
VIII	2026.5 2019 (sh) (7.2)[a]	1970.1 1965 (sh) (5.8)[a]	1629.0 (11.1)
IX	1940.3 1934.6 (sh) (12.7)[a]		
X	1921.5 (7.2)		
	1930.9 (sh, 6.6)		
XI	1917.5 (7.4)		
	1923.6 (sh, 7.5)		
XII[21a]	1917 (sh) 1925 (15)[a]		
XIII	1915.4 (6.9)		
XIV	1923.8 (5.8)		1627 (12.5) 1614 (10.8)

[a] Width of the two combined peaks.

IR spectra of saturated hydrocarbon solutions were obtained using a Bruker IFS-85 FT IR spectrometer equipped with an Aspect 2000 computer; data are listed in Table I. Spectra were collected in the absorbance mode; routine spectra of reaction solutions were collected at a resolution of 2.0 cm^{-1}, and spectra were collected in the temperature range 133–413 K at a resolution of 0.5 cm^{-1} using the Bruker IFS 85 equipped with a Specac solution IR cell fitted with AgCl windows. The sample cell was placed within a Specac variable-temperature cell, the temperature being monitored to within ±1 K using a Specac temperature controller equipped with a copper–constantan thermocouple. The solution cell was fitted with a continuous flow-through unit which allowed it to be filled and flushed while it was in the VT cell. Band-fitting calculations were carried out on the Aspect 2000, utilizing the Bruker program FIT. The calculations were also executed on the PC using both Spectra Calc and Program X (PC-116).[11]

A Bruker AM-400 FT NMR spectrometer, equipped with an Aspect 3000 computer, was used to obtain all the routine and variable-temperature ^1H and $^{13}C\{^1H\}$ NMR spectra. A pulse delay of >30 s was used for the ^1H spectra to accommodate the long relaxation time of the cyclopentadienyl hydrogens.

Molecular Mechanics Calculations. The MM calculations were performed on a Sun SPARCStation 1 using MMX, the minimization routine within PCMODEL 4.0, from Serena Software.[8a] Structures were built by utilizing PCMODEL structure input routines and X-ray crystallographic data when the structural coordinates were available for a compound,[12] data from struc-

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(8) (a) Available as PCMODEL from Serena Software, Bloomington, IN. See: Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. In *Advances in Molecular Modelling*; Liotta, D., Ed.; JAI Press: Greenwich, CT, 1990; Vol. 2, p 65. (b) Initial and final values for ω and the increment by which ω was changed were set using the dihedral driver command D-DRV in the MINIM mode of PCMODEL; the initial ω was usually the value of this angle in the optimized structure generated from crystallographic data, while the final ω was chosen such that the bond of interest was rotated through at least 360°. The dihedral driver function of PCMODEL is the standard MM2 driver;[1a-c] during its operation, initial and final dihedral angles, an angle increment, and a set of four atoms defining the angle are specified. For each angle of rotation, the first atom and the attachments to the first two atoms are rotated about the axis defined by the second and third atoms so that the dihedral angle has the desired value. The structure is then energy-minimized with all atoms free to move (unless other constraints unrelated to the dihedral driver are applied). During these minimization calculations, an extra torsion angle energy function is applied with both a high force constant and an energy minimum at the desired dihedral angle so that the angle tends to remain very close to the specified value. When the energy minimization is complete, the total energy of the system is recalculated, omitting the extra energy function. The ω increments were set to 5°, and each bond was rotated in both clockwise and counterclockwise directions. (c) In cases where pairs of atoms are not formally bonded, the FXDIS command creates for use in the minimization a pseudobond with a finite force constant. The final energy, calculated after minimization is complete, does not contain a contribution from the pseudobond.

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(11) *Program X* (*PC-116*), 2nd ed.; Jones, R. N., Pitha, J., Eds.; National Research Council of Canada Bulletin No. 12; NRC: Ottawa, Ontario, Canada, 1976. Spectra Calc is marketed by Galactic Industries Corp.; Lab Calc, an updated form, was also used.

turally similar compounds otherwise.[12] Structures generated from X-ray crystallographic data were first edited within the INPUT mode of PCMODEL to correct any errors, such as incorrect connectivities or bond orders, caused by the program when creating the structures from the data file. In all cases, the aromatic carbon atom type (atom type number 40; see supplementary material) was used to define the carbons of cyclopentadienyl and phenyl rings. The cyclopentadienyl ring was coordinated to the Fe using the COATM command (see supplementary material) in the INPUT mode of PCMODEL, and the Fe was defined as a saturated, 18-electron metal having zero charge. Since hydrogen atom coordinates are usually omitted from the reduced crystal coordinates of X-ray crystallographic structures, the hydrogens of the compounds studied had to be added to the structures with the H-A/D command. Structures were then optimized using MMX-M in the MINIM mode in order to refine the atom–hydrogen bonds, which were originally added without consideration of their optimal placement.

The dihedral driver of PCMODEL was employed to compute the ligand rotational conformational energy profile of each compound. Rotation about a bond within a molecule containing four bonded atoms, A–B–C–D, is expressed in terms of the change in dihedral (or torsional) angle ω, which is defined as the angle measured about the B–C axis between the two planes A–B–C and B–C–D. When looking down the B–C bond from B, ω is zero if A and D are mutually eclipsed, positive if D moves from the eclipsed position in a clockwise direction, and negative if D moves in a counterclockwise direction. The energy changes associated with bond rotations were computed using the dihedral driver within PCMODEL,[8b] and plots of energy versus torsional angle are used to illustrate the rotational energy profiles.

Prior to utilization of the dihedral driver, all metal–ligand bond distances were set to crystallographic distances and "fixed" with very high stretching force constants of 50 mdyne/Å, either by using the FXDIS command or by direct addition of information to the structure file. The Fe–cyclopentadienyl ring carbon distances were also "fixed" using FXDIS,[8c] either individually or to the average value of these distances in the appropriate X-ray structure; the two procedures gave similar results. A force constant for the Fe–Cp(C) interaction of 50 md/Å was used during operations of the dihedral driver. The output files from the dihedral driver calculation consisted of the atomic coordinates of the optimized structures and the energy (enthalpy) associated with each conformation. The values of the torsional angle of interest and corresponding energies were then extracted from the output file.[13]

For computational purposes, the torsional angle for alkyl rotation in the alkyl compounds I–V was defined as H–C(α)–Fe–CO (I), C(β)–C(α)–Fe–CO (II), C(ipso)–C(α)–Fe–CO (III, IV), and Si–C(α)–Fe–CO (V). A second dihedral angle, C(ortho)–C(ipso)–C(α)–Fe, (ω_2) was defined for the compounds III and IV; this served to rock the phenyl ring at each value of ω, thus producing a more symmetric curve. A second torsional angle, C–Si–C(α)–Fe, was also defined for V. The torsional angle for acyl rotation in the acyl compounds VI–VIII was defined as O(acyl)–C(acyl)–Fe–CO. A second dihedral angle, ω_2, (C(ortho)–C(ipso)–C(acyl)–Fe), was defined for VII and VIII.

The torsional angles for alkyl rotation in the compounds X–XIII were defined for computational purposes as H–C(α)–Fe–CO (X), C(β)–C(α)–Fe–CO (XI), C(ipso)–C(α)–Fe–CO (XII), and Si–C(α)–Fe–CO (XIII). A second dihedral angle, ω_2, was defined for XI and XIII such that the Me and $SiMe_3$ groups rotated 10° at 2° increments at each value of ω_1; ω_2 was defined as H–C(β)–C(α)–Fe for XI and C–Si–C(α)–Fe for XIII. The torsional angles for PPh_3 rotation in these compounds and in IX were defined as C(ipso)–P–Fe–CO. The torsional angles for acetyl and PPh_3 rotation in XIV were similarly defined as O(acyl)–C(acyl)–Fe–CO and C(ipso)–P–Fe–CO, respectively.

For ease of viewing and to facilitate comparisons, torsional angles in all energy profiles for alkyl and acyl rotation are defined such that $\omega = 0$ when the atom which is being driven eclipses the η^5-C_5H_5 group centroid.[13] Hereafter, all potential energy profiles are presented in this way.

Results and Discussion

MMX Methodology.[8] MMX is an extension of the well-known MM2 molecular modeling program[1a–c] and, since MMX utilizes the parameterization and energy minimization procedures previously published for MM2,[1a–c] detailed discussion of these is unnecessary here. MMX differs from MM2 by the inclusion of a number of enhancements such as, inter alia, the ability to accommodate π ligands, which are coordinated by invoking a $1/r^2$ attractive term between the metal and π ligands (see supplementary material). The term is a function of the basicity of the ligand atom, the covalent radius of the metal, and the angle between the metal and the axis of the p orbital on the ligand; while π-bonded ligands cannot be specifically rotated utilizing the dihedral driver, they are free to rotate and/or rock in response to the steric requirements of the other ligands.

The problem of ligand–metal–ligand (L–M–L) bond angles is addressed by removing the MM2 bending potential function and ignoring the torsional potentials involving the metal when a metal is the central atom. The 1,3 interactions that are normally ignored by MM2 are operative, however, and thus the calculated energies are dominated by interligand van der Waals interactions. The L–M–L bond angles are therefore determined primarily by the overall ligand steric requirements rather than by bending or torsional force constants involving the metal; essentially this approach has been successfully utilized elsewhere.[6a,p]

The default value for metal–ligand stretching force constants is 2.0 mdyne/Å, sufficiently low that it was found that metal–ligand bond lengths of structures of compounds in their global minima were in some cases longer by 0.02–0.05 Å than the sums of covalent radii or the crystallographically determined bond lengths. While this level of agreement might normally seem quite satisfactory, it was realized that the steep dependence of ligand–ligand van der Waals repulsions could result in underestimation of the interligand steric interactions during operation of the dihedral driver. Calculations of conformational energy profiles were therefore carried out with all metal–ligand distances set to appropriate (often crystallographic) distances and "fixed" with very high stretching force constants of 50 mdyne/Å.

Reproducibility of the calculated energies was generally within about 0.2 kcal mol^{-1}, and in most cases, conformational energy profiles were reproduced exactly after the torsional angle being driven had changed by about 60°. Moreover, the compounds investigated here have relatively few degrees of torsional freedom, and it was readily possible in each case to extend the calculations sufficiently that global minima were distinguishable from all possible local minima.

Computed Molecular Structures. Listed in Table II are bond distances and angles, computed with no bond length restrictions, for the minimum energy conformations of the compounds considered here; for purposes of comparison, relevant crystallographic literature for the same

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[13] Torsion.nawk is a program wwritten by Joel Polowin to calculate torsional angles of structures; a file containing the torsional angles and the corresponding energies is created. Similarly length.nawk and angle.nawk are programs written to calculate bond lengths and angles, respectively.

Table II. Selected Bond Lengths and Angles in the Optimized Structures of Compounds I–XIV[a]

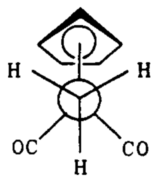
compd	bond lengths (Å) Fe–C_α	Fe–CO	Fe–P	Fe–(C_5H_5)[b]
I[12a]	2.08 (2.08)	1.78 (1.75)		2.11 (2.114)
II[12a]	2.08 (2.08)	1.760 (1.75)		2.11 (2.11)
III[12b]	2.08 (2.09)	1.77 (1.775)		2.12 (2.117)
IV[12b]	2.08 (2.09)	1.77 (1.775)		2.12 (2.117)
V[12c]	2.08 (2.079)	1.79 (1.733)		2.12 (2.110)
VI[12b]	1.96 (1.972)	1.780 (1.770)		2.12 (2.117)
VII[12b]	1.97 (1.972)	1.77 (1.770)		2.12 (2.117)
VIII[12b]	1.97 (1.972)	1.77 (1.770)		2.12 (2.117)
IX[12c,d]	1.61 (1.609)[c]	1.73 (1.719)	2.19 (2.186)	2.12 (2.115)
X[12c]	2.07 (2.065)	1.73 (1.719)	2.19 (2.186)	2.12 (2.115)
XI[12c]	2.07 (2.065)	1.72 (1.719)	2.19 (2.186)	2.12 (2.115)
XII[12c]	2.07 (2.079)	1.73 (1.733)	2.20 (2.195)	2.12 (2.115)
XIII[12c]	2.07 (2.079)	1.73 (1.733)	2.20 (2.195)	2.11 (2.110)
XIV[12e]	1.95 (1.939)	1.81 (1.801)	2.20 (2.188)	2.14 (2.135)

compd	bond angles (deg)[d] OC–Fe–CO	C_α–Fe–CO	C_α–Fe–P	P–Fe–CO	cent–Fe–CO	cent–Fe–P	cent–Fe–C_α
I	96.3 (93)	91.0 (87)			119.8		124.5
II	92.1 (93)	91.5 (87)			124.2		122.1
III	94.9 (93.1)	94.1 (90.4)			119.1		123.7
IV	94.9 (93.1)	94.1 (90.4)			119.1		123.7
V	92.1 (92.1)	93.6 (94.4)			124.1		119.7
VI	94.1 (93.1)	95.3 (90.4)			121.5		120.9
VII	93.5 (93.1)	90.2 (90.4)			122.3		126.6
VIII	93.5 (93.1)	90.2 (90.4)			122.6		126.7
IX		92.6 (92.7)	93.4 (92.9)	93.5 (93.4)	122.0	129.3	114.7[e]
X		92.6 (92.7)	93.4 (92.9)	93.5 (93.4)	122.3	128.2	118.4
XI		93.0 (92.7)	93.0 (92.9)	93.3 (93.4)	122.7	126.9	119.4
XII		93.0 (92.7)	92.5 (92.9)	93.3 (93.4)	121.5	115.3	120.7
XIII		94.9 (94.4)	90.8 (90.5)	92.1 (92.1)	123.4	126.5	120.3
XIV		92.5 (92.3)	91.6 (92.0)	91.3 (91.3)	122.9	129.3	119.7

[a] Available crystallographic data are in parentheses; for dicarbonyl compounds, references are to similar compounds. [b] Average. [c] Fe–H distance. [d] cent = η^5-C_5H_5 centroid. [e] Centroid–Fe–H.

(XI, XIII, XIV) or similar compounds are also presented. As can be seen, for those compounds (XI, XIII, XIV) for which crystallographic data are available, the agreement between computed and experimental bond lengths and angles is excellent. In addition, the optimized structures of those compounds for which no crystallographic data are available exhibit bond lengths and angles in generally very good agreement with those of similar compounds. The results thus lend credence to the MMX methodology, which is further applied below to considerations of the conformational energy profiles for alkyl (acyl) rotation in the compounds. In the following paper,[9b] we apply MMX to a consideration of torsional angles associated with rotation about the metal–phosphorus and phosphorus–carbon bonds in several coordination compounds of triphenylphosphine.

Conformational Energy Profiles. $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ (I). It is convenient to consider the iron atoms in this and related complexes to be topologically four-coordinate; thus various conformations in which the ligands on the iron and the substituents on the α-carbon atoms of coordinated alkyl groups are mutually staggered may be conceived, as in the Newman projection for $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ (A). As is clear from consideration of



A

A, the methyl group of the compound $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ (I) can assume only a single staggered rotamer, and thus

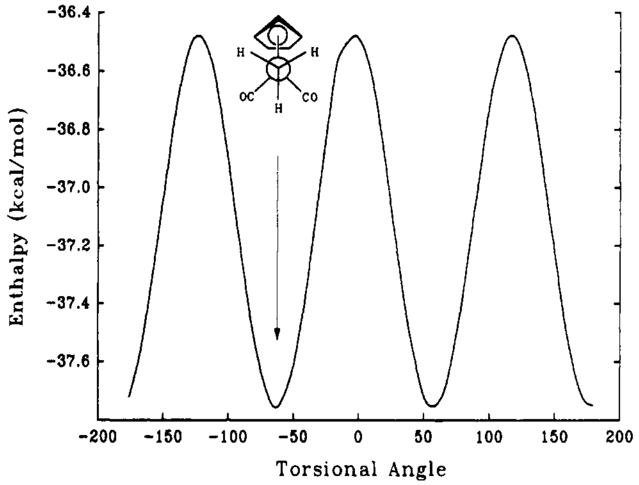


Figure 1. Conformational energy profile of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$.

rotational isomerism is unlikely. Consistent with this assumption, two very narrow carbonyl stretching bands of comparable intensity[14] are observed in IR spectra in a variety of solvents (Table I), and the peak widths, $\Delta\nu_{1/2}$ ($\sim$4 cm^{-1} in pentane), may be taken as an indication of the natural line widths of the carbonyl stretching modes of this class of compound. Interestingly, both modes shift to lower frequency and narrow considerably on cooling to 213 K (ν_{sym} 2013.7 cm^{-1}, $\Delta\nu_{1/2}$ 2.58 cm^{-1}; ν_{asym} 1959.4 cm^{-1}, $\Delta\nu_{1/2}$ 3.16 cm^{-1}); there are also small increases in the in-

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[14] As has been shown elsewhere,[15] the observation that the symmetric and the asymmetric carbonyl stretching absorptions have essentially the same intensities is consistent with the OC–Fe–CO bond angle being about 90°.

[15] Dalton, J.; Paul, I.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 2744.

tegrated intensities of the carbonyl stretching absorptions in this temperature range.[16]

MMX calculations of the methyl rotation conformational energy profile of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ are consistent with the assumption of a single staggered rotamer, indicating a degenerate, 3-fold barrier to rotation about the iron–methyl bond (Figure 1). The global minimum coincides essentially with the staggered rotamer, A, and the global maximum, in which one hydrogen atom eclipses the $\eta^5\text{-}C_5H_5$ group, results in an energy barrier to rotation calculated to be about 1.3 kcal mol^{-1}. This is somewhat less than the electronic barrier of 2.9 kcal mol^{-1} found utilizing extended Hückel calculations,[17] but considerably less than the minimum of 6 kcal mol^{-1} estimated on the basis of an assessment of the spin-rotation contribution to the ^{13}C spin–lattice relaxation time (T_1) of the methyl carbon atom of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(^{13}CH_3)$.[18] However, the latter estimate was based on a treatment of the data[20] which appears not to have been broadly tested.[19a] In addition, there is uncertainty in the method because the contribution of the spin-rotation mechanism is impossible to assess in cases where dipolar relaxation by directly bonded protons dominates.[19a]

A complementary approach[19a] is based on the fact that the rate of relaxation of the methyl carbon is dominated by dipolar coupling to the three hydrogen atoms and is strongly affected by molecular motion in solution, described by the overall correlation time τ_c. If the frequency of the motion is larger than the resonance frequency (the so-called extreme narrowing limit), the rate of relaxation is given by eq 1,[19] where n is 3, the number of hydrogen

$$\text{rate of relaxation} = 1/T_1 = n(\mu_0/4\pi)^2\gamma_C{}^2\gamma_H{}^2\hbar^2r^{-6}\tau_c \quad (1)$$

atoms attached to the carbon atom, μ_0 is the permeability of a vacuum, γ_C and γ_H are the ^{13}C and ^1H gyromagnetic ratios, respectively, $\hbar$ is Planck's constant divided by 2π, and r is the carbon–hydrogen distance. If a molecule undergoes essentially isotropic rotation, which may not be too reasonable for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$, the correlation time of a carbon atom not undergoing significant internal rotation is related to a diffusion coefficient D, i.e.

$$\tau_c = 1/6D \quad (2)$$

Since the methyl group of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ undergoes internal motion, however, its effective correlation time will be altered and an additional diffusion constant, D_i, must be taken into account. For a 3-fold methyl jump mechanism, as may well apply in the present situation, the rate of methyl carbon relaxation is given by

$$\frac{1}{T_1} = 3(\mu_0/4\pi)^2\gamma_C{}^2\gamma_H{}^2\hbar^2r^{-6}\left[\frac{A}{6D} + \frac{B + C}{6D + 1.5D_i}\right] \quad (3)$$

where A, B, and C are geometric parameters, the quantity in square brackets is the correlation time, and D_i is the methyl group jump rate.[19a] The last term is related to the methyl rotational barrier, V_o, by

$$D_i = D_{io}\exp(-V_o/RT) \quad (4)$$

where D_{io} is the jump rate of a freely rotating methyl group, i.e. when $V_o = 0$. If D_i is measured as a function of temperature, then an Arrhenius plot of eq 4 will yield V_o.

Since T_1 measurements were reported for only the methyl carbon of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(^{13}CH_3)$,[18] D cannot be determined and a full treatment of the data as outlined above is not possible. However, the T_1 data were reported for three temperatures and we have extended the range,[18] and thus an Arrhenius plot of these values should yield an activation energy for the overall motion of the methyl group, i.e. involving both the isotropic molecular motion and the internal rotation. Treatment in this way of the T_1 data given in ref 18 results in an activation energy for overall motion of about 2.8 kcal mol^{-1}, comparable with data for a variety of organometallic complexes.[21]

To pursue the matter further, an estimate of D can be made on the basis of τ_c values reported for other small organometallic molecules.[21] For instance, τ_c values reported for the molecules $Fe(CO)_5$[21a] and $(\eta^4\text{-isoprene})Fe(CO)_3$[21b] are respectively ~5 ps at 298 K and ~4 ps at 310 K. Making the reasonable assumption that τ_c of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ is about 5 ps at 300 K and interpolating[18] a T_1 value of 6.5 s for the methyl ^{13}C atom at this temperature, one calculates a value of D_i of 14.6×10^{10} s^{-1}. Assuming further that $D_{io} = 0.89 \times 10^{13}$ s^{-1},[19a] then one obtains $V_o = 2.8$ kcal mol^{-1}, somewhat higher than the barriers to methyl rotation, estimated in the same way, of a variety of organic molecules.[19a]

While the methyl rotational barrier calculated in this way is clearly very approximate, we note that the systematic errors inherent in the procedure generally result in significant *overestimations* of barriers in simple organic molecules for which experimental data are available.[19a] Thus the barrier calculated utilizing MMX (1.3 kcal mol^{-1}) may well be closer to the actual barrier than the published estimate based on experiment. The observation of only single, sharp methyl and $\eta^5\text{-}C_5H_5$ resonances in the ^1H NMR spectrum down to 193 K in CD_2Cl_2 is, of course, consistent with all of the possible barriers mentioned above.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2Et$ (II). As indicated in Table I, the IR spectrum of this compound in the carbonyl stretching region exhibits, in addition to the expected peaks of equal intensity, shoulders on the low-frequency side of each. Band fitting in fact suggests the presence of two pairs of absorptions, all peaks with $\Delta\nu_{1/2}$ of about 3 cm^{-1}. On cooling to 193 K, definite shoulders appear on the low-frequency sides of both peaks, but resonances in the ^1H NMR spectrum in CD_2Cl_2 remain unchanged.

As pointed out previously,[22] this type of behavior is to

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(16) Concentrations were corrected for changes in solvent density. See: Washburn, E. E., Ed. *International Critical Tables of Numerical Data Physics, Chemistry and Technology*; McGraw-Hill: New York, 1928; Vol. III.

(17) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(18) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4853. We have extended the T_1 measurements reported in this paper to 253 K in order to confirm the anticipated linear relationship between ln T_1 and T^{-1}.[19]

(19) (a) Lambert, J. B.; Nienhuis, R. J.; Keepers, J. W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 487. For convenience, we have utilized the SI forms of the equations, as shown.[20b] (b) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman Books: London, 1983.

(20) Zens, A. P.; Ellis, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 5685.

(21) (a) Aime, S.; Gobetto, R.; Osella, D.; Milone, L.; Hawkes, G. E.; Randall, E. W. *J. Chem. Soc., Chem. Commun.* **1983**, 794. (b) Aime, S.; Gobetto, R.; Osella, D.; Hawkes, G. E.; Randall, E. W. *J. Chem. Soc., Dalton Trans.* **1984**, 1863. (c) Brownlee, R. T. C.; O'Connor, M. J.; Shehan, B. P.; Wedd, A. G. *J. Magn. Reson.* **1985**, *61*, 22. (d) Brownlee, R. T. C.; O'Connor, M. J.; Shehan, B. P.; Wedd, A. G. *Aust. J. Chem.* **1986**, *39*, 931. (e) Aime, S.; Botta, M.; Gobetto, R.; Osella, D. *J. Chem. Soc., Dalton Trans.* **1988**, 791. (f) Adams, H.; Bailey, N. A.; Mann, B. E.; Taylor, B. F.; White, C.; Yavari, P. *J. Chem. Soc., Dalton Trans.* **1987**, 1947. (g) Mann, B. E.; Spencer, C. M.; Taylor, B. F.; Yavari, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2027. (h) Farrar, T. C.; Quinting, G. R. *J. Phys. Chem.* **1986**, *90*, 2834.

(22) (a) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 4292. (b) Jetz, W.; Graham, W. A. G. *J. Am. Chem. Soc.* **1967**, *89*, 2773. (c) Dalton, J. *Inorg. Chem.* 1971, *10*, 1822. (d) Dalton, J. *Inorg. Chem.* **1972**, *11*, 915.

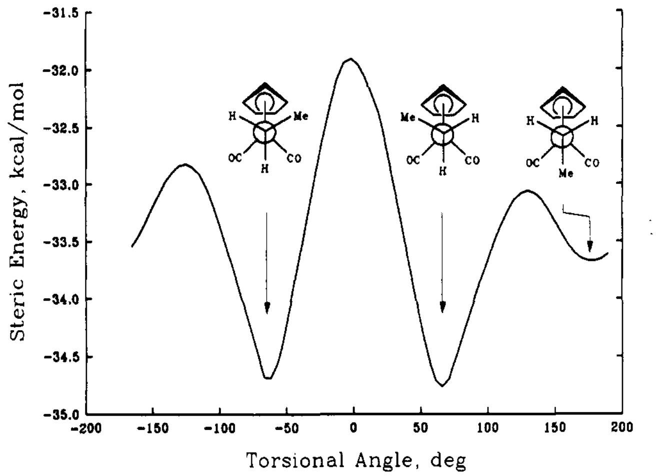
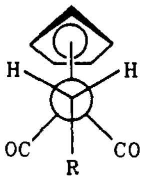
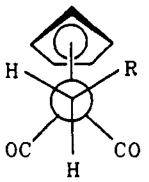


Figure 2. Conformational energy profile of (η^5-C_5H_5)Fe(CO)$_2$Et.

be interpreted in terms of population of two rotamers, B and C (R = Me), of C_s and C_1 symmetry respectively, i.e.



B



C

As the separations of the pairs of peaks are slight even at low temperatures, it was not possible to carry out satisfactory band-fitting calculations of the relative intensities. Thus determination of the relative energies of B and C was not possible although the energy difference would appear to be small. As shown in the conformational energy profile (Figure 2), however, MMX calculations suggest that C, the global minimum, is more stable than B, a local minimum, by 1.1 kcal mol^{-1}, consistent with the conformations of the compounds [(η^5-C_5H_5)Fe(CO)$_2$]$_2$(μ-CH_2)$_n$ (n = 3, 4) in the solid state.[12a] In addition, conformations in which the methyl group eclipses the η^5-C_5H_5 and CO groups represent energy maxima 2.8 and 1.8 kcal mol^{-1} above the global minimum. Thus, as anticipated, the steric barriers to rotation of the ethyl ligand in this compound are higher than the analogous barrier to methyl rotation in (η^5-C_5H_5)Fe(CO)$_2$Me.

(η^5-C_5H_5)Fe(CO)$_2$CH$_2$Ph (III). Rotational isomerism is anticipated for this compound also, and although the ^{1}H NMR spectrum in CD_2Cl_2 remains well resolved and essentially unchanged down to 193 K, shoulders on the main two carbonyl stretching bands in the IR spectrum are indeed apparent.[22a] In contrast to the ethyl analogue, the shoulders in this case are observed on the high-frequency sides of the major peaks (Table I). Moreover, the peak separations are sufficiently large that band-fitting results in the relative intensities being measurable over the temperature range 173–373 K in saturated hydrocarbon solvents. As expected, the ratios of the intensities of the shoulders relative to those of the main peaks increase as the temperature increases, in accord with equilibration between two rotamers of differing thermal stability. Better peak separations of the asymmetric carbonyl stretching absorptions result in data more precise than those from the symmetric carbonyl stretching absorptions, and the relative intensities, corrected for solvent expansion and for the changes in absolute intensities noted above for the methyl analogue, were used to determine the equilibrium constants and hence the thermodynamic parameters for the B $\rightleftarrows$ C interconversion. Representative spectra are shown in Figure 3, and the resulting plot of log K vs T^{-1} is shown in Figure 4. The measured enthalpy and entropy differences are 0.9 ± 0.2 kcal mol^{-1} and 0.4 ± 0.1 cal mol^{-1} K^{-1}. These values are somewhat different from those reported earlier[9a] because a larger data set, arising from further experimentation, is now available.

Identification of the more stable rotamer was possible by utilizing a procedure described elsewhere for similar compounds.[22c,d,23] Since the two carbonyl groups are identical in B but not in C, the ^{13}CO satellites in the IR spectrum of C should be split while those in the spectrum of B should not. The somewhat asymmetric satellites observed (288 K) in the IR spectrum of III at about 1998 and 1929 cm^{-1} were therefore also subjected to band fitting; the former is a shoulder and hence difficult to assess properly, but the latter was found to consist of a pair of absorptions at 1929.4 and ~1926 cm^{-1}. The former lies about 30 cm^{-1} below the asymmetric carbonyl stretching absorption of the major rotamer, and is thus clearly to be assigned as the ^{13}CO satellite of this species.[24]

Unfortunately, separations of the pairs of ^{12}CO carbonyl stretching bands of the two rotamers are much less pronounced than in other examples where this method has been previously applied,[22c,23] and the ^{13}CO satellites overlap sufficiently that assignments are somewhat ambiguous. However, significant differences in intensities of the pair of satellites at 1929.4 and ~1926 cm^{-1} rule out their attribution solely to the normal ^{13}CO modes of rotamer C, while the extreme narrowness of the more intense satellite peak rules out its assignment as the expected pair of satellites of rotamer C. Therefore the more stable rotamer would appear to be B.

MMX calculations have been carried out on (η^5-C_5H_5)Fe(CO)$_2$CH$_2$Ph, and the resulting conformational energy profile is shown in Figure 5. As can be seen, a conformation approximating B is found to represent the global minimum,[25] with a rotamer approximating C about 0.5 kcal mol^{-1} higher in energy, in excellent agreement with the experimental results. The steric barriers to rotation of the phenyl group past the η^5-C_5H_5 and CO groups are 2.3 and 0.9 kcal mol^{-1}, respectively, 0.5 and 0.9 kcal mol^{-1} less than the corresponding steric barriers estimated for the ethyl compound II. Although we hesitate to claim that these differences are significant, the relative values seem reasonable since the phenyl group can move past the other ligands in a face-on position.

(η^5-C_5H_5)Fe(CO)$_2$CH$_2$C$_6$H$_3$(*m*-Me)$_2$ (IV). The IR spectrum of IV in the carbonyl region is very similar to that of III, consisting of two main peaks, both with shoulders on the high-frequency sides. IR spectra over the temperature range 294–193 K also exhibited behavior similar to that observed for III, and thus the addition of two *m*-methyl groups to the phenyl ring has little effect on the conformational preferences. Thermodynamic parameters for the B $\rightleftarrows$ C equilibrium were calculated from the fitted data of the asymmetric carbonyl stretching absorptions, the measured enthalpy and entropy differences

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(23) Butler, I. S.; Sawai, T. *Inorg. Chem.* **1973**, *12*, 1994.

(24) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975.

(25) It was also found that the phenyl group is tilted at the global minimum such the rotamer does not have strict C_s symmetry in the symmetric rotamer. This tilting resulted in the phenyl group being locked in the initial orientation during operation of the dihedral drive into and beyond the global minimum, with the further result that the overall computed energy profile did not exhibit the anticipated plane of symmetry about the η^5-C_5H_5–Fe–C_α–C_{ipso} = 0° torsional angle. Rocking the phenyl group through a second torsional angle ω_2, as described in the Experimental Section, restored the symmetry of the energy profile.

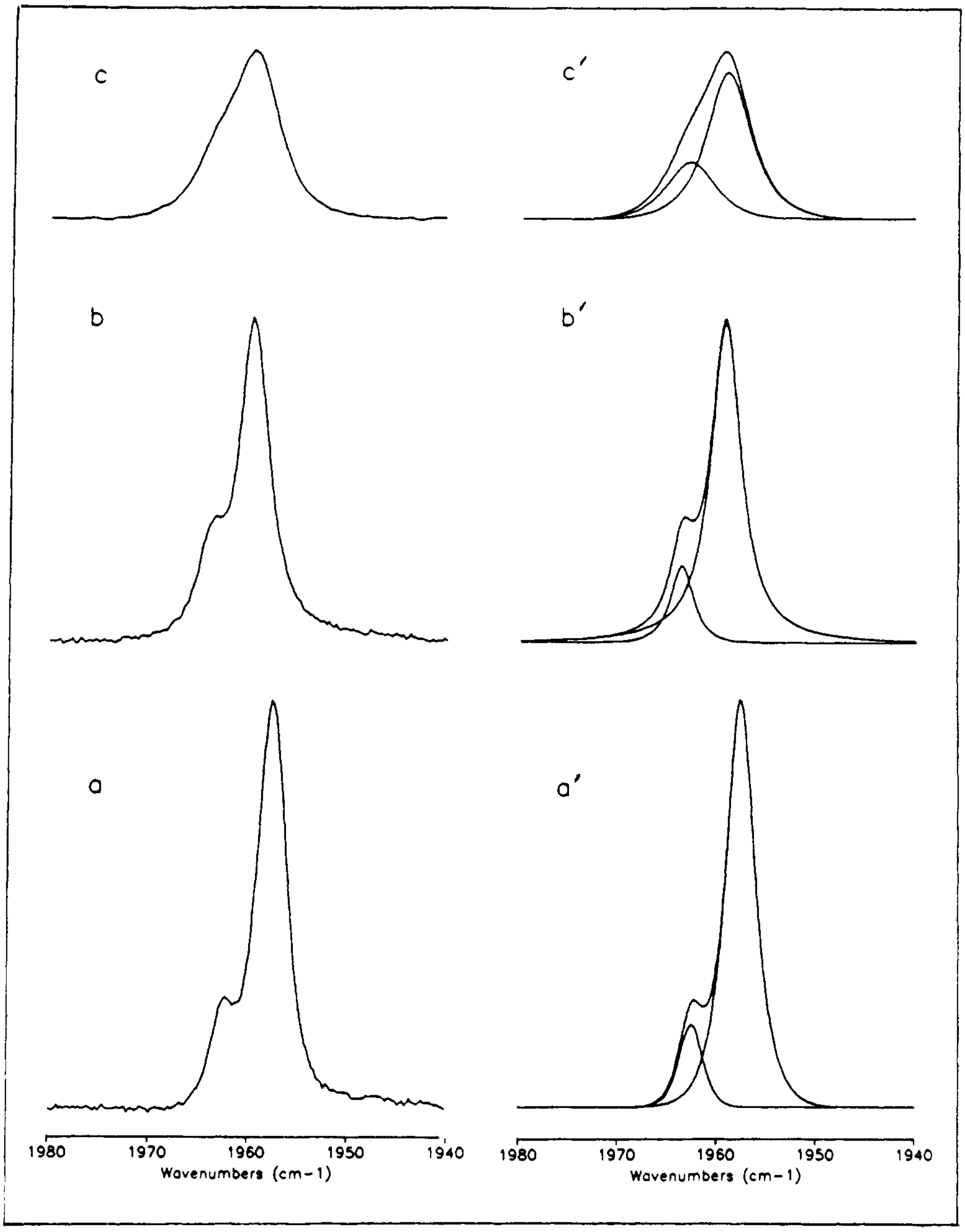


Figure 3. ν_{asym}(CO) of (η^5-C_5H_5)Fe(CO)$_2$CH$_2$Ph at 173 K (a), 288 K (b), and 413 K (c). a′, b′, and c′ illustrate the results of band fitting at the same temperatures, respectively.

being 0.4 ± 0.2 kcal mol^{-1} and −1.3 ± 0.3 cal mol^{-1} K^{-1}, respectively.

The IR spectrum of IV exhibited two rather asymmetric ^{13}CO satellites at 1996.6 and 1927.9 cm^{-1} (pentane, 288 K); band fitting of the satellite at 1927.9 cm^{-1} revealed bands at 1928.1 and 1924.9 cm^{-1}. The former is much the more intense and, in view of its position relative to the asymmetric carbonyl stretching absorption of the major rotamer, it is assigned as the ^{13}CO satellite of the more populated species.[24] A similar argument to that presented above for III can then be used to identify the more stable rotamer of IV as B.

In agreement with the experimental results, the calculated conformational energy profile of IV is also similar to that of III, conformation B lying 0.5 kcal mol^{-1} lower in energy than conformation C. The calculated steric barriers to rotation of the aryl ring past the η^5-C_5H_5 and CO ligands are 2.3 and 0.9 kcal mol^{-1}, respectively.

(η^5-C_5H_5)Fe(CO)$_2$CH$_2$SiMe$_3$ (V). As with the ethyl and benzyl analogues, the IR spectrum of V exhibits a pair of carbonyl stretching bands, each associated with a shoulder. The ^{1}H NMR spectrum exhibits only well-resolved, time-averaged resonances, and thus this compound also exists in solution as a pair of rapidly interconverting rotamers. On the basis of the ^{13}CO satellites, the major rotamer is C (R = SiMe$_3$; C_1), while consideration of the carbonyl stretching band intensity data showed that ΔH = 0.8 ± 0.1 kcal mol^{-1} and ΔS = 1.7 ± 0.4 cal mol^{-1} K^{-1} for rotamer conversion.

MMX calculations suggested that the C_1 rotamer is more stable than the C_s species by 1.3 kcal mol^{-1}, in excellent agreement with the experimental value, and that the steric barriers to rotation of the SiMe$_3$ group past the η^5-C_5H_5 and CO ligands are 5.7 and 3.4 kcal mol^{-1}, respectively. The differences in energy between the global and local minima, as well as the steric barriers to rotation are all greater than those of the ethyl and benzyl analogues, consistent with the greater steric demands of the SiMe$_3$ group.

(η^5-C_5H_5)Fe(CO)$_2$COMe (VI). The ^{1}H NMR spectrum

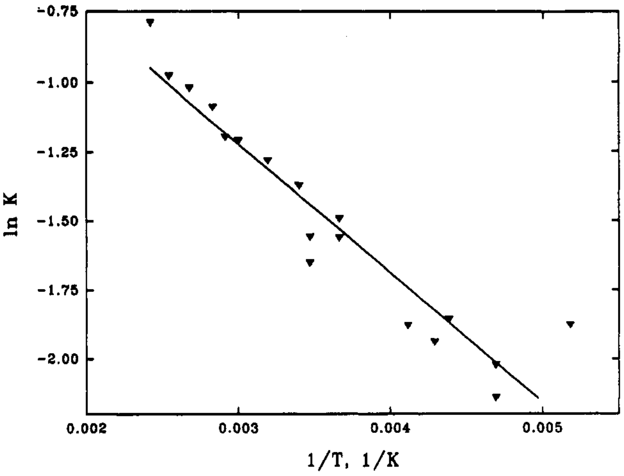


Figure 4. Plot of log K vs T^{-1} for interconversion of the rotamers of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Ph$.

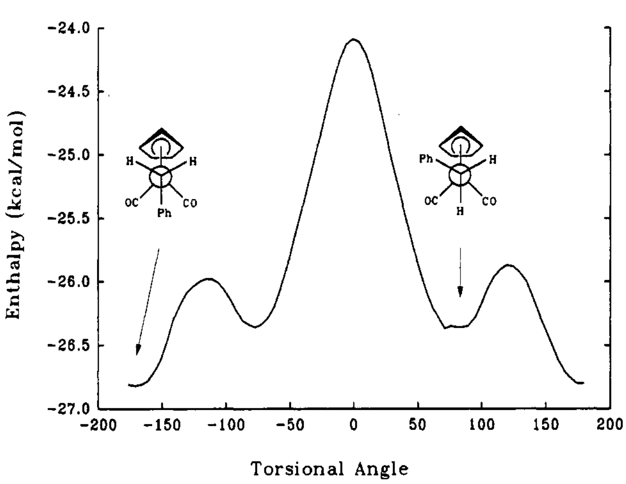
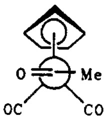
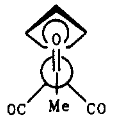


Figure 5. Conformational energy profile of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Ph$.

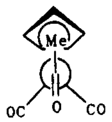
of VI in CD_2Cl_2 exhibits only a single set of well-resolved resonances, but the IR spectrum (Table I) presents firm evidence for rotational isomerism since both the symmetric carbonyl stretching and the acetyl stretching absorptions are very broad. Furthermore, on cooling to 193 K, the symmetric carbonyl stretching absorption separates into three peaks at 2024.0, 2017.7, and 2013.4 cm^{-1}, suggesting the presence of three rapidly interconverting isomers of approximately equal energy; approximate enthalpy and entropy differences were 0.4–1.1 kcal mol^{-1} and 2–9 cal mol^{-1} K^{-1}, respectively. In fact four rotamers, D–G, seem reasonable on the basis of steric or electronic grounds or literature precedents.



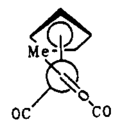
D



E



F



G

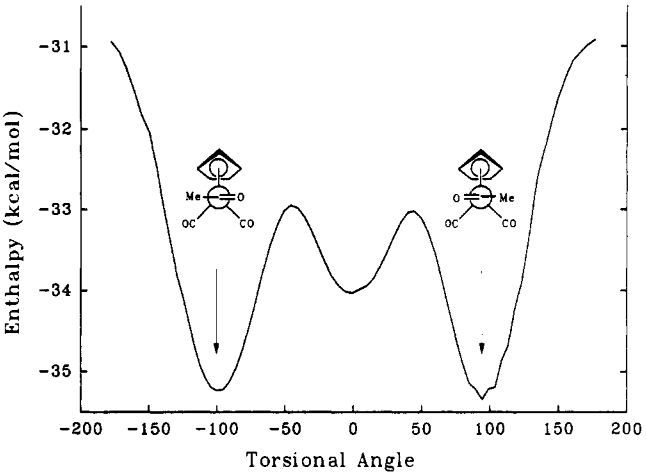


Figure 6. Conformational energy profile of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2COMe$.

Thus "parallel" rotamers such as D and G are assumed by similar compounds,[26] while "upright" rotamers E and F should be stabilized electronically since back-donation from the HOMO of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ fragment (a″) to the acetyl π^* orbital will be enhanced in the rotamers E and F.[17]

MMX calculations on VI resulted in the rotational energy profile shown in Figure 6. As can be seen, a rotamer corresponding essentially to D represents the global minimum, while E and F appear to be respectively a local minimum and a global maximum, some 1.3 and 4.4 kcal mol^{-1} higher in energy than D. A rotamer corresponding to G lies on the side of the major potential well some 1.7 kcal mol^{-1} higher in energy than D, while the energy barrier to D–E interconversion is also 2.3 kcal mol^{-1}. Since the already small differences in energy between the global minimum, D, and the higher energy rotamers, E and F, would be decreased further by Fe–acetyl π-bonding,[17] it seems likely that all conformations stabilized by steric and/or electronic factors on the potential energy surface are populated. This conclusion is, of course, consistent with the ^1H NMR spectrum discussed above, and provides a satisfactory qualitative rationalization for the observation of IR spectral evidence.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2COPh$ (VII). The IR spectrum of this compound also gives clear evidence of the presence of rotational isomers (Table I). However, while the symmetric carbonyl stretching absorption splits into three peaks at 193 K, the bands are unfortunately not sufficiently resolved so that satisfactory band fitting could be carried out. MMX calculations suggest that a rotamer corresponding to D is the global minimum, and that rotamers corresponding to E and F are 2.2 and 1.8 kcal mol^{-1}, respectively, higher in energy.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2CO\{C_6H_3(m\text{-}Me)_2\}$ (VIII). The room-temperature IR spectrum of this compound also gives clear evidence of the presence of rotational isomers, the two carbonyl stretching bands exhibiting shoulders and the acetyl stretching absorption being very broad. The presence of at least two rotamers in solution is moreover established by the observation of two symmetric carbonyl stretching absorptions at 2025.8 and 2020.8 cm^{-1} at 198 K, but again, satisfactory band fitting could not be carried out. The calculated conformational energy profile of VIII exhibits two energy minima corresponding to D, differing essentially in the orientation of the aryl group. Rotamers E and F constitute energy maxima some 2.2 and 1.8 kcal mol^{-1} higher, respectively.

$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$ (IX). The IR spectrum of this compound at room temperature exhibits a very broad carbonyl stretching absorption (Table I), and band fitting

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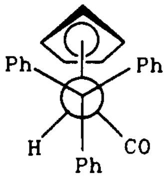
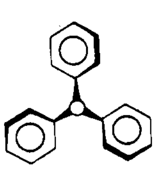
(26) (a) Blau, H.; Malisch, S.; Voran, S.; Blank, K.; Krüger, K. *J. Organomet. Chem.* **1980**, *202*, C33. (b) Eisenstadt, E.; Frolow, F.; Efraty, A. *J. Chem. Soc., Dalton Trans.* **1982**, 1013. (c) Hädicke, E.; Hoppe, W. *Acta Crystallogr.* **1971**, *B27*, 760.

(27) Willem, R.; Gielen, M.; Hoogzand, C.; Pepermans, H. *Adv. Dynamic Stereochem.* **1985**, *1*, 207.

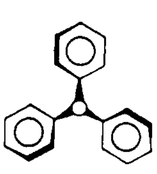
suggested the presence of two components at 1940.3 and 1934.6 cm^{-1} in a 1.4:1 ratio. Since the iron atom of this compound constitutes a chiral center, the three phenyl groups are formally nonequivalent, as shown in a Newman diagram (H) viewed along the P–Fe bond. However, since only a single staggered rotamer is anticipated for this compound, the presence of two carbonyl stretching bands seems best rationalized on the basis of significant population of the two diastereomers resulting from the two enantiomeric forms (right- and left-handed propeller conformations) of the coordinated PPh$_3$, I and J, respectively.[27] MMX calculations suggest that the energy difference between the two diastereomers is negligibly small, and that PPh$_3$ rotation involves a 3-fold energy barrier of 3.5 kcal mol^{-1}, reasonable in view of broadening observed for the phenyl ^{1}H and ^{13}C{^{1}H} resonances at low temperatures. These findings are discussed further in a subsequent paper.[9b]



H



I



J

(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)Me (X). The room-temperature IR spectrum of this compound exhibits a strong, relatively narrow carbonyl stretching band at 1921.5 cm^{-1} with a weak shoulder at 1930.9 cm^{-1} (Table I). As in the case of the corresponding hydride, IX, the observation of two carbonyl stretching bands suggests the presence of two diastereomers arising from the presence of the two enantiomeric forms of the PPh$_3$, I and J. Unlike the situation with IX, however, one diastereomer of X is greatly favored in solution since band-fitting calculations showed that the ratio of the two diastereomers is 8:1. Low-temperature ^{1}H and ^{13}C{^{1}H} NMR experiments (193 K, CD$_2$Cl$_2$) reveal extreme broadening of the phenyl resonances only, although the low-temperature, limiting spectrum was not reached. It seems likely that PPh$_3$ rotation was being slowed, ultimately to give a static structure with nonequivalent phenyl groups (see below).

MMX calculations suggest that the energy barrier to methyl rotation is 1.2 kcal mol^{-1}, comparable with the calculated methyl rotation barrier in (η^5-C$_5$H$_5$)Fe(CO)$_2$Me and similar to the value of 0.6 kcal mol^{-1} determined utilizing Chem-X,[6l] but considerably less than the 5.8 kcal mol^{-1} estimated utilizing the extended Hückel (EH) methodology.[6j] MMX calculations also suggest that PPh$_3$ rotation involves a 3-fold steric barrier of 6.6 kcal mol^{-1}, a reasonable conclusion in view of broadening observed for the phenyl ^{1}H and ^{13}C{^{1}H} resonances at low temperatures, and one which will be discussed further.[9b]

Apparently incompatible with the observed 8:1 ratio of diastereomers, however, the energy difference between the two is calculated to be negligibly small, suggesting either that the calculations are unreliable or that entropy differences may be a factor. In view of the general success of the MMX approach to this point, we favor the latter view and note that entropy contributions to rotational energy barriers can be very significant in sterically crowded molecules.[28] In the case under consideration here, greater loss of internal degrees of freedom (aryl and/or η^5-C$_5$H$_5$ rotation) in the more congested diastereomer could result in its being destabilized to an extent not reflected in the MMX (enthalpic) calculations.

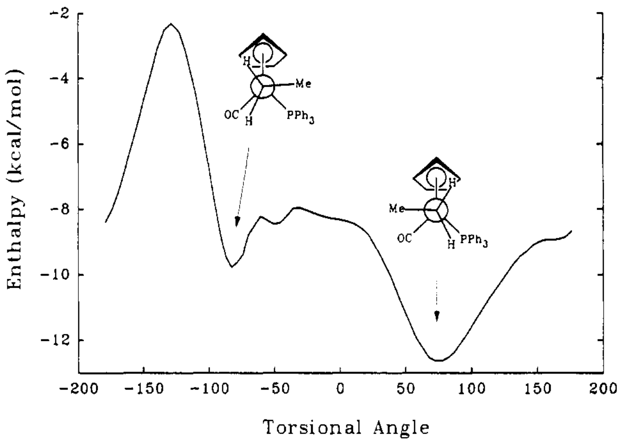
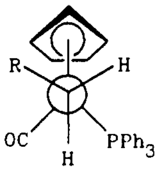
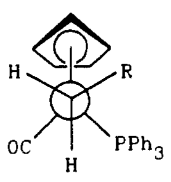


Figure 7. Conformational energy profile of (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)Et.

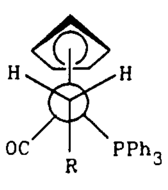
(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)Et (XI). By analogy with the dicarbonyl compound (η^5-C$_5$H$_5$)Fe(CO)$_2$Et, XI may presumably assume three essentially staggered conformations, K–M (R = Me). The ^{1}H NMR spectrum of this compound has been reported to exhibit separate resonances for the two diastereotopic methylene hydrogens, H′ and H″, with distinctly different values of ^3J(HP);[12c] the latter observation may be taken as evidence for very different H–C(α)–Fe–P torsional angles.[12c,22a] Since the values of ^3J(HP) were also found to be independent of temperature,[12c] it was suggested that only a single rotamer is significantly populated in solution and, on the basis of NOE difference experiments and by analogy with the solid-state structure, the stable rotamer was suggested to approximate K.[12c] As shown in Table I, however, the IR spectrum of XI exhibits two relatively narrow carbonyl stretching bands in the ratio 5:1, suggesting significant population of either two rotamers or of the two diastereomers arising from the presence of both propeller forms of the PPh$_3$. As with the methyl analogue, X, low-temperature ^{1}H and ^{13}C{^{1}H} NMR experiments (193 K, CD$_2$Cl$_2$) reveal extreme broadening of the phenyl resonances only, although the low-temperature, limiting spectra could not be reached. It seems likely again that aryl rotation and/or PPh$_3$ rotation are being slowed, an interpretation which will be discussed further.[9b]



K



L



M

The conformational energy profile calculated utilizing MMX is shown in Figure 7, where it is seen that the global minimum corresponds approximately to K, consistent with the X-ray structure.[12c] In the optimized conformation, the H″–C(α)–Fe–P torsional angle is ~91° while the H′–C-

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[28] Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566.

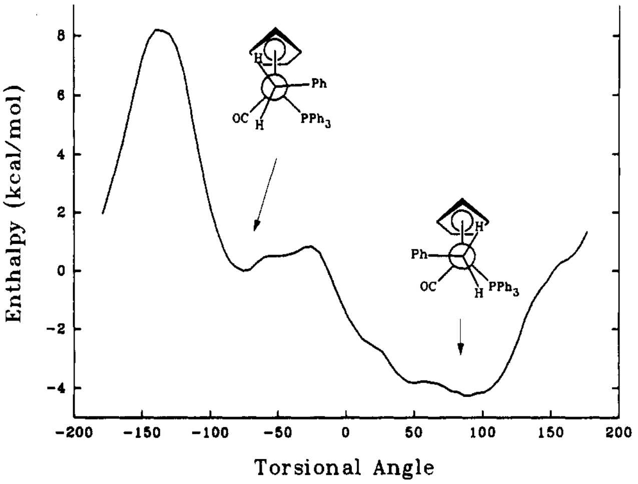


Figure 8. Conformational energy profile of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2Ph$.

(α)-Fe-P torsional angle is ~-25°, suggesting[29] that H″ is the hydrogen atom exhibiting the lesser value of ^3J(HP).[12c,22a] A local minimum corresponding approximately to conformation L lies only 2.9 kcal mol^{-1} higher in energy, suggesting that the weaker carbonyl stretching bands observed in the IR spectrum may indeed be assignable to this species. The global maximum corresponds approximately to eclipsing of the PPh_3 by the methyl group; the torsional angle at the global maximum is somewhat greater than -120°, presumably because of tilting of the phenyl groups.[30] Rotation of the PPh_3 and torsional angles involving the PPh_3 will be discussed in greater detail elsewhere.[9b]

Attempts to utilize the Chem-X[6l] and extended Hückel[6j] methodologies to calculate the conformational energy profile of this compound also identify K as the stablest rotamer but differ significantly with each other and with the MMX calculations in their conclusions with respect to the relative energies, both of the other rotamers and of the barriers to their interconversion. Neither methodology approaches the experimental data as closely as does MMX.

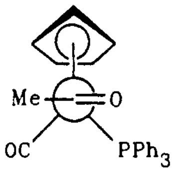
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2Ph$ (XII). Two groups[12c,22a] have previously shown that the values of ^3J(HP) of the two diastereotopic methylene hydrogen atoms of this compound vary significantly with temperature in a manner compatible with significant population of two conformations (in a 3:1 ratio; energy difference 2.5–3 kcal mol^{-1}).[6l] The IR spectrum gives clear evidence for the existence of at least two species in solution (Table I)[22a] and, since significant population of both propeller forms of the PPh_3 seems unlikely (see below), at least two rotamers must coexist in solution at room temperature.

The conformational energy profile for rotation about the Fe–benzyl bond, derived from MMX calculations, is shown in Figure 8. As can be seen, the global minimum lies in a broad potential well corresponding to a conformation approximating K (R = Ph), with a local minimum approximating L some 4.3 kcal mol^{-1} higher in energy. The global maximum corresponds approximately to a rotamer in which the benzylic phenyl group eclipses the PPh_3, and thus the overall energy profile is very similar to that of XI *albeit with a significantly greater energy difference between the global and local minima.* How then to rationalize the experimental data for these two compounds, which suggest that the ethyl compound exists essentially only as a single rotamer while the benzyl analogue, with an apparently much less thermally accessible rotamer L, is present in solution as at least two? A possible answer lies in the observation that the benzylic phenyl group in rotamer L of the benzyl compound approaches one of the PPh_3 phenyl groups in an orientation known to be result in π–π interactions attractive by at least 2 kcal mol^{-1}.[6m,31] Thus rotamer L in this case may well be stabilized sufficiently that it becomes thermally accessible, unlike the analogous conformation of XI.

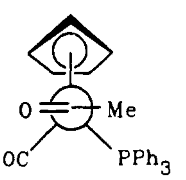
Our results contrast significantly with the results of Chem-X[6l] calculations, although the latter do predict correctly the structure of the global minimum.

$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2SiMe_3$ (XIII). The IR spectrum of this compound at room temperature exhibits a relatively narrow carbonyl stretching band, consistent with there being only a single conformation significantly populated. In addition, two studies of the temperature dependence of ^3J(HP) of the diastereotopic methylene hydrogen atoms are best interpreted in terms of the population of essentially only one conformation,[12c,22a] presumably a rotamer approximating K, as is found in the solid state.[12c] In agreement, MMX calculations suggest that K, the global minimum, lies in a very broad potential well. Interestingly, and in contrast to the compounds XI and XII, conformation L of XIII does not constitute a local minimum, but rather lies on a sloping plateau 7.8 kcal mol^{-1} higher in energy than the global minimum. This result is quite compatible with the experimental findings. We note also that the bond lengths and angles of the minimum energy conformation (Table II) are very similar to those reported on the basis of an X-ray crystallographic investigation of this compound.[12c] Rotation of the PPh_3 and torsional angles involving PPh_3 will be discussed in greater detail elsewhere.[9b]

$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ (XIV). By analogy with the dicarbonyl acetyl compound VI, XIV may be expected to assume two "parallel" structures, N and O, as well as, perhaps, electronically-stabilized "vertical" structures (see above).



N



O

The IR spectrum of this compound exhibits a relatively narrow carbonyl stretching band, suggesting that only one diastereomeric form arising from the two PPh_3 enantiomers is present in significant proportions, but two acetyl stretching bands, implying the presence of two rotamers of the acetyl group. The relative intensities of the two acetyl stretching bands are strongly temperature-dependent (Figure 9), and treatment of the variable-temperature IR data as above suggests that the enthalpy and entropy differences between the two putative rotamers involved are 1.6 ± 0.2 kcal mol^{-1} and 4.9 ± 0.3 cal mol^{-1} K^{-1}. Interestingly, and in contrast to the compounds X–XIII,

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[29] Our original attempts to relate conformations of this type of compound to values of ^3J(HP)[22a] eventually foundered[6j,12c] because of the reasonable but incorrect assumption that a relatively large vicinal coupling constant necessarily implied a conformation in which the hydrogen and phosphorus atoms were mutually trans rather than essential eclipsed. See: Thomson, J.; Keeney, W.; Baird, M. C.; Reynolds, W. F. *J. Organomet. Chem.* **1972**, *40*, 205.

[30] Brunner, H.; Hammer, B.; Krüger, C.; Angermund, K.; Bernal, I. *Organometallics* **1985**, *4*, 1063.

[31] Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

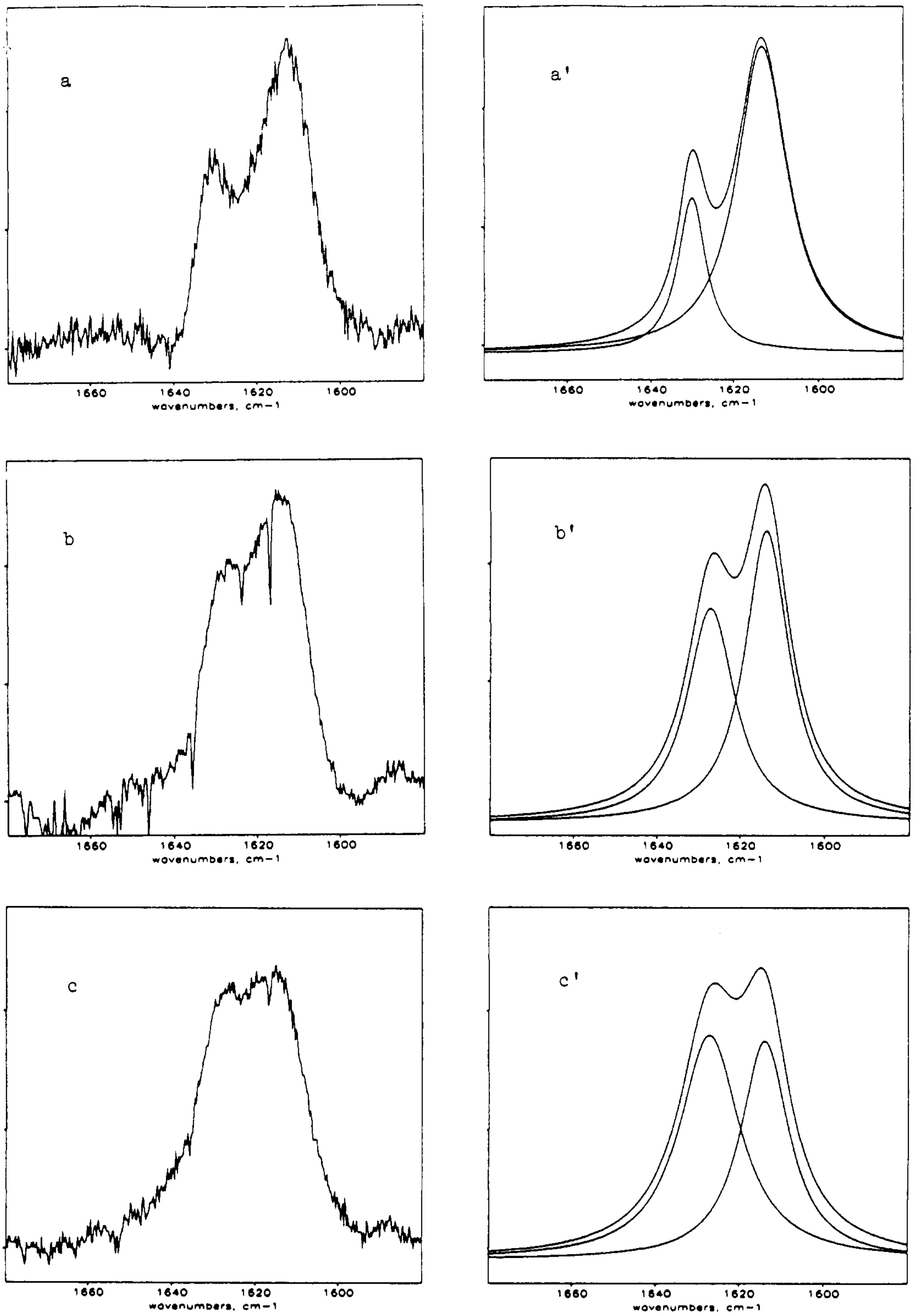

Figure 9. Acetyl stretching bands of (η^5-C_5H_5)Fe(CO)(PPh_3)COMe at 213 K (a), 294 K (b), and 343 K (c). a′, b′, and c′ illustrate the results of band fitting at the same temperatures, respectively.

while single, time-averaged sets of ^1H and $^{13}C\{^1H\}$ resonances are observed at room temperature, lower temperatures result in severe broadening and eventual narrowing and decoalescence of the $^{13}C\{^1H\}$ resonances below 233 K into three sets each of separate ipso (relative intensity 1), ortho (relative intensity 2), meta (relative intensity 2), and para (relative intensity 1) resonances at 193 K.[32] Thus rotation about the Fe–P bond is slowed sufficiently that resonances of the individual phenyl groups may be distinguished. Although the pairs of ortho and meta carbon atoms would be nonequivalent in the absence of phenyl rotation, such nonequivalence was not observed. Thus phenyl rotation must remain facile at the lowest temperature reached (193 K) even though small amounts of the second diastereomer could not be detected.

Our tentative conclusion that only a single diastereomer exists in significant proportions for the chiral iron com-

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[32] Similar results have been observed using a lower field instrument. See ref 6k.

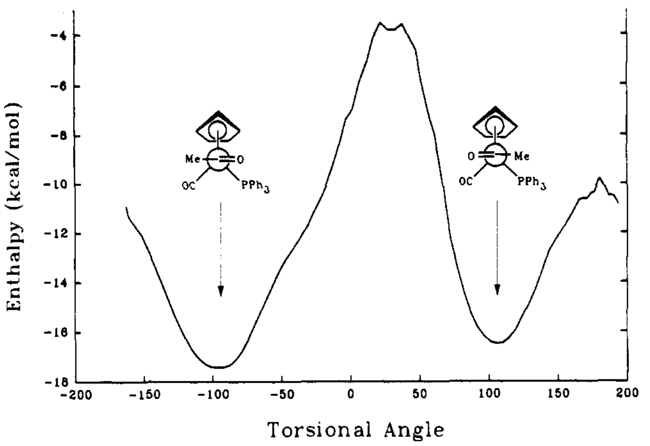

Figure 10. Conformational energy profile of (η^5-C_5H_5)Fe(CO)(PPh_3)COMe.

pounds X, XIII and XIV is in agreement with a claim that such is invariably the case with compounds containing the (η^5-C_5H_5)Fe(CO)(PPh_3) fragment.[6k,l] That significant amounts of both diastereomers apparently exist in the case of the hydride IX is probably not entirely anomalous, since the relatively small steric requirements of the hydride ligand presumably permit sufficient distortion that those steric factors which effectively destabilize one diastereomer of the other compounds can be alleviated. It follows that only single diastereomers should be present in solutions of the ethyl and benzyl compounds, XI and XII, and that observations of more than one carbonyl stretching band in these cases is best interpreted in terms of two alkyl rotamers being present.

MMX calculations involving acetyl group rotation result in the conformational energy profile shown in Figure 10. As can be seen, the global minimum corresponds to rotamer N, with O, a local minimum, lying only 0.9 kcal mol^{-1} higher in energy. The energy barriers for acetyl rotation past the η^5-C_5H_5 and PPh_3 ligands (methyl group eclipsed) are 7.6 and 13.6 kcal mol^{-1}, respectively, and thus both rotamers may well be populated at room temperature and the observation of two acetyl stretching bands is readily rationalized. As with X, rotation of the PPh_3 involves a 3-fold energy barrier of about 11 kcal mol^{-1}, similar to the result of Chem-X calculations[6k] and very consistent with the 12 kcal mol^{-1} barrier derived from full line shape analysis of the variable-temperature $^{13}C\{^1H\}$ NMR spectra in the phenyl region.[6k] Rotation of the PPh_3 and torsional angles involving the PPh_3 will be discussed in greater detail elsewhere.[9b]

Summary. The purpose of this investigation was to probe the utility of the MMX methodology to estimate subtle steric interactions in a series of flexible organometallic compounds. In the case of the compound (η^5-C_5H_5)Fe$(CO)_2$Me, MMX predicts an energy barrier to methyl rotation, 1.3 kcal mol^{-1}, which may well be within 1 kcal mol^{-1} of the actual value. In the case of the compounds (η^5-C_5H_5)Fe$(CO)_2CH_2R$ (R = Me, Ph, C_6H_3(m-Me)$_2$, Me_3Si), the calculated enthalpy differences between C_s and C_1 rotamers are within 0.5 kcal mol^{-1} of the experimental data. We also note that the calculated barriers to alkyl ligand rotation in the compounds correlate well with the relative steric requirements of the various alkyl substituents.

In contrast, the conformational energy profile for the acetyl compound (η^5-C_5H_5)Fe$(CO)_2$COMe (and two aroyl analogues) is expected to be complicated by electronic stabilization of those rotamers which are, according to the MMX calculations, disfavored for steric reasons. Experimentally, three rapidly interconverting rotamers appear to be populated, a conclusion not previously realized.[33]

The substituted compounds (η^5-C_5H_5)Fe(CO)(PPh_3)R″ (R″ = H, Me, Et, CH_2Ph, CH_2SiMe_3, and C(O)Me) are much more complicated because both the iron centers and the PPh_3 are chiral, and thus the compounds can exhibit diastereomerism as well as conformational isomerism of the alkyl/acyl ligands. We make some reference to the success of MMX in understanding the conformational preferences and barriers to rotation of the PPh_3 in these compounds but will defer a comprehensive discussion to the following paper.[9b]

The conformational energy profiles for alkyl rotation in the two compounds (η^5-C_5H_5)Fe(CO)(PPh_3)Et and (η^5-C_5H_5)Fe(CO)(PPh_3)CH_2SiMe_3 offer quite reasonable rationalizations of previously published variable-temperature ^1H NMR data; the predominant rotamer for both compounds approximates K, the alkyl groups being twisted, however, so that H′ almost eclipses the phosphorus atom. The MMX calculations and the experimental data are consistent in suggesting that a second rotamer, L, may be somewhat populated in the ethyl compound but not in the more crowded (trimethylsilyl)methyl compound. MMX calculations also suggest that K is the low-energy rotamer for (η^5-C_5H_5)Fe(CO)(PPh_3)CH_2Ph but that L should be populated much less than is observed for (η^5-C_5H_5)Fe(CO)(PPh_3)Et. This conclusion is inconsistent with experimental findings, but it is likely that rotamer L is stabilized electronically in the benzyl compound by an attractive π–π interaction between the benzyl phenyl group and a phenyl group of the PPh_3.

Our MMX calculations and experimental findings for (η^5-C_5H_5)Fe(CO)(PPh_3)COMe (XIV) are not in accord with a claim that this compound assumes only a single rotameric conformation in solution.[6k] The observation of two acetyl stretching bands, which have presumably not been hitherto reported because they are not resolved in the types of more polar solvents previously used for IR characterization of this compound, suggests that XIV exists in solution as at least two rapidly interconverting rotamers, rather similar to the situation with the dicarbonyl analogue, (η^5-C_5H_5)Fe$(CO)_2$COMe. Thus a number of stereoselective reactions which utilize the (η^5-C_5H_5)Fe(CO)(PPh_3) fragment as a chiral template for the enantioselective elaboration of the coordinated acetyl group[6l] may perhaps be interpretable mechanistically in terms of preferential reactivity of one rotamer over the other rather than in terms of there being only a single rotamer in solution.[34]

In conclusion, we find that the global minimum structures produced by the minimization routines of MMX are very good approximations of the actual structures, as deduced crystallographically. For all compounds investigated, we have carried out alkyl/acetyl rotations through 360°, during which concomitant rotation and rocking of the η^5-C_5H_5 group also occurred, as did, where applicable, rotation about Fe–P and P–C bonds. It would thus be most surprising if we had somehow missed the global minimum in any case. MMX also provides reasonable estimates of the conformational energy profiles for rotation of a variety of common types of ligands in the series of compounds studied here. Care must be taken both with compounds where electronic factors may be important and in highly crowded compounds where entropic factors may

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[33] Davies, S. G.; Smallridge, A. J. *J. Organomet. Chem.* **1990**, *397*, C13.

[34] For evidence of significantly decreased stereoselectivity in a related compound, (η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2Ph$, see: Guo, Z.-W.; Zamojski, A. *Tetrahedron Lett.* **1992**, *33*, 1105.

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contribute to the free energy differences.

Acknowledgment. We are indebted to Queen's University and the Natural Sciences and Engineering Research Council of Canada for financial support and to K. Gilbert, J. Polowin, Y.-S. Park and H. F. Shurvell for assitance with aspects of the computations.

Supplementary Material Available: Brief textual description of MMX, relating the methodology to MM2, with tables of atom type numbers, bond stretching parameters, nonbonded and coordination parameters, bond angle bending parameters, and torsion parameters (8 pages). Ordering information is given on any current masthead page.

OM910788H

Application of Molecular Mechanics (MMX) Calculations to an Investigation of the Conformations of Coordinated Triphenylphosphine in Organometallic Compounds of the Types $(\eta^6\text{-}C_6R_6)Cr(CO)_2PPh_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R'$ (R = H, Me; R' = H, Alkyl, Acyl)

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Received December 20, 1991

MMX calculations are utilized to determine the low-energy structures and hence the preferred conformations arising from metal–phosphorus and phosphorus–carbon bond rotation in the organometallic compounds $(\eta^6\text{-}C_6R_6)Cr(CO)_2PPh_3$ (R = H, Me) and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R'$ (R' = H, alkyl, acyl). In general, the computed bond lengths and angles and both the ligand–M–P–C(ipso) and the M–P–C(ipso)–C(ortho) torsional angles of the low-energy conformations are in very good agreement with X-ray crystallographic data. Conformational energy profiles are also computed, utilizing MMX, for PPh_3 rotation in the two series of compounds, and excellent agreement with the quantitative estimates of steric barriers to rotation reported in the literature is obtained.

A major development in the recent evolution of organotransition-metal chemistry has been the use of chiral compounds to effect enantioselective organic syntheses, both catalytic and stoichiometric.[1] However, although much is known mechanistically of many such processes, relatively little is known concerning details of the function(s) of chiral reagents in effecting enantioselectivity. For example, while the role of several rhodium(I) complexes of chiral phosphines in the enantioselective hydrogenation of prochiral olefins is by now well understood chemically, those subtle factors leading to enantioselective hydrogen transfer, amounting to differences in free energies of activation of less than a few kilocalories per mole, remain enigmatic.[2]

Presumably, steric factors are important,[2] but only the concept of the cone angle[3] has to this point proven to be generally applicable as a measure (semiquantitative) of the steric requirements of coordinated ligands. A related issue, the factors which determine the extent to which coordinated ligands exhibit conformational preferences and barriers to rotation, can be addressed very effectively by extended Hückel calculations when the system is under electronic control.[4] However, little concerning such matters can be suggested with confidence for systems in which steric factors dominate. Indeed, no computational methodology has to this point been sufficiently precise to warrant serious consideration or application to this type of problem.

However, molecular mechanics (MM) calculations have in recent years become a very valuable tool for rapid computation of the conformational energy profiles of a wide variety of organic and biological molecules.[5] Where comparisons with experimental data are possible, surprisingly accurate estimates of molecular properties are possible, and MM calculations are often the computational methodology of choice for the consideration of medium-sized organic systems[6] and coordination compounds.[7]

In contrast to the many applications to organic systems, however, there have, in fact, been very few attempts to apply MM methodologies to conformational problems of flexible organometallic compounds. Thus, where applications have been reported, they have either involved custom-made, not readily available software written to address particular problems or software which does not

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(1) For useful reviews, see: (a) Blystone, S. L. *Chem. Rev.* **1989**, *89*, 1663. (b) Morrison, J. D., Ed. *Asymmetric Synthesis*; Academic Press: New York, 1985; Vol. 5. (c) Scott, J. W. *Top. Stereochem.* **1989**, *19*, 209. (d) Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *45*, 6901. (e) Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press, Oxford, England, 1982; Vol. 8, p 463.

(2) Halpern, J. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 41.

(3) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Clark, H. C. *Isr. J. Chem.* **1976/77**, *15*, 210.

(4) Albright, T. A. *Tetrahedron* **1982**, *38*, 1339 and references therein.

(5) For general reviews, see: (a) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. (b) Ermer, O. *Struct. Bonding* **1976**, *27*, 161. (c) White, D. N. J. *Molecular Structure by Diffraction Methods*; Chemical Society: London, 1978; Vol. 6, p 38. (d) Ōsawa, E.; Musso, H. *Top. Stereochem.* **1982**, *13*, 117. (e) Frühbeis, H.; Klein, R.; Wallmeier, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 403. (f) van Gunsteren, W. F.; Berendsen, H. J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 992.

(6) See, for instance: (a) Beyer, A.; Wolschann, P.; Becker, A.; Buchbauer, G. *J. Mol. Struct.* **1989**, *196*, 371. (b) Tsuzuki, S.; Tanabe, K. *J. Chem. Soc., Perkin Trans. 2* **1991**, 181. (c) Gundertofte, K.; Palm, J.; Pettersson, I.; Stamvik, A. *J. Comput. Chem.* **1991**, *12*, 200. (d) Counts, R. W. *J. Comput.-Aided Mol. Des.* **1990**, *4*, 427.

(7) For reviews, see: (a) Brubaker, G. R.; Johnson, D. W. *Coord. Chem. Rev.* **1984**, *53*, 1. (b) Hancock, R. D. *Prog. Inorg. Chem.* **1989**, *37*, 187.