chlorine atom at zirconium, the torsional angles Cl1–Zr···C27–C28, Cl1–Zr···C27–P1, and Cl1–Zr–O1–C27 being −165.8 (3), 8.5 (2), and −137.6 (9)° in **3** and 38.4 (3), −151.8 (2), and 67.2 (6)° in **5**, respectively. The enolato plane is accessible from both axial directions in **3** and **5**.

Compounds **2**, **3**, and **5** will allow us to introduce the Ph_2P substituent by use of the enolato methodologies and, in addition, to show how we can control the chemistry of the enolato moiety by the use of different metals.

Acknowledgment. We thank the Swiss National Foundation for Scientific Research (Grant No. 20-28470.90) and Ciba-Geigy Co. (Basel, Switzerland) for financial support.

Supplementary Material Available: A description of the crystal structure determination and tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, and thermal parameters for complexes 3 and 5 (11 pages); tables of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

Combined Spectroscopic and Molecular Mechanics Investigation of the Flexible Organometallic Compounds (η^5-C_5H_5)Fe(CO)$_2$R (R = $PhCH_2$, Et, MeCO) and (η^5-C_5H_5)Fe(CO)(PPh_3)COMe

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Received February 4, 1991

Summary: Variable-temperature IR spectroscopy is utilized to investigate the conformational preferences of the title compounds; complementary information concerning the conformational energy profiles is successfully obtained by utilizing the molecular modeling program MMX.

Molecular mechanics (MM) calculations have long been utilized to estimate conformational properties of flexible organic molecules[1] and, when used appropriately, are capable of reproducing experimental values of conformational differences as small as a fraction of a kilocalorie per mole.[2] In large part for this reason, the MM approach is often the method of choice for the calculation of conformational energy differences of a variety of organic molecules, more accurately reproducing experimental energy differences than do ab initio and some semiempirical methodologies.[3] In contrast, there have been reported very few attempts to apply MM or any other methodologies to organometallic conformational problems, and only rarely have there been attempts to estimate conformational energy differences as delicate as those mentioned above;[4] as has been pointed out,[3] appropriate computational software has not been available.

In order to explore a possible remedy to this situation, we have been investigating the potential applications of a new molecular modeling package, MMX,[5] to our knowledge the only commercially available MM software which attempts to address the problem of ligand π coordination in organometallic compounds. In an attempt to assess the utility of this software, we have carried out calculations to estimate the relative conformational energies and barriers to alkyl and acyl ligand rotation of a series of flexible organometallic compounds, (η^5-C_5H_5)Fe(CO)L(CH_2R) and (η^5-C_5H_5)Fe(CO)L(COR) (R = methyl, phenyl; L = CO, PPh_3).[6] We have also obtained relevant experimental spectroscopic information on the conformational energy profiles of these compounds, thus making possible comparison of experimental data with the results of the MMX calculations.

To begin, we have utilized IR spectroscopy to experimentally determine the conformational preferences of compounds of the type (η^5-C_5H_5)Fe(CO)$_2$$CH_2R$; as shown previously,[7] this and related classes of compounds can exist in solution as two staggered rotamers, A and B, of C_s and C_1 symmetry, respectively (Chart I). The IR spectra of both rotamers are expected to exhibit pairs of peaks at-

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[1] Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1.

[2] See, for instance: Gundertofte, K.; Palm, J.; Pettersson, I.; Stamvik, A. *J. Comput. Chem.* **1991**, *12*, 200.

[3] A brief summary of the present situation has been recently presented. See: Counts, R. W. *J. Comput.-Aided Mol. Design* **1990**, *4*, 427.

[4] For examples of interesting applications, see: (a) Lauher, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 1521. (b) Slovokhotov, Y. L.; Timofeeva, T. V.; Struchkov, Y. T. *J. Struct. Chem. (Engl. Transl.)* **1987**, *28*, 463. (c) Johnston, P.; Denner, L.; Marais, C. F.; Boeyens, J. C. A.; Coville, N. J. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 403. (d) Newsam, J. M.; Bradley, J. S. *J. Chem. Soc., Chem. Commun.* **1985**, 759. (e) Bradley, J. S.; Harris, S.; Newsam, J. M.; Hill, E. W.; Leta, S.; Modrick, M. A. *Organometallics* **1987**, *6*, 2060. (f) Bogdan, P. L.; Horowitz, C. P.; Shriver, D. F. *J. Chem. Soc., Chem. Commun.* **1986**, 553. (g) Brown, J. M.; Evans, P. L. *Tetrahedron* **1988**, *44*, 4905. (h) Bogdan, P. L.; Irwin, J. J.; Bosnich, B. *Organometallics* **1989**, *8*, 1450. (i) Casey, C. P.; Whitecker, G. T. *Isr. J. Chem.* **1990**, *30*, 299.

[5] Available as PCMODEL from Serena Software, Bloomington, IN. MMX is based on the MM2 (77) force field, with data for several heteroatoms and transition-metal complexes with π-bonded ligands added; 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. The calculations were carried out on a Sun SPARCStation 1 utilizing PCMODEL 4.0. Default parameters were found to be appropriate, in general, but it was found best to utilize fixed metal–ligand distances comparable with published crystallographic data. During geometry optimizations, all ligand atoms were free to move, ligand rotation and tilting being only under the influence of van der Waals forces. Barriers to rotation were estimated by varying the η^5-C_5H_5 centroid–Fe–C_α–C_β torsional angle by 5° increments and optimizing each structure while holding only the torsional angle fixed. A similar approach has been utilized to calculate barriers to rotation in medium sized organic molecules; see: Beyer, A.; Wolschann, P.; Becker, A.; Buchbauer, G. *J. Mol. Struct.* **1989**, *196*, 371.

[6] (a) Krüerke, U., Ed. *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer-Verlag: Berlin, 1983; Part B11. (b) Krüerke, U., Ed. *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer-Verlag: Berlin, 1984; Part B12.

[7] (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.

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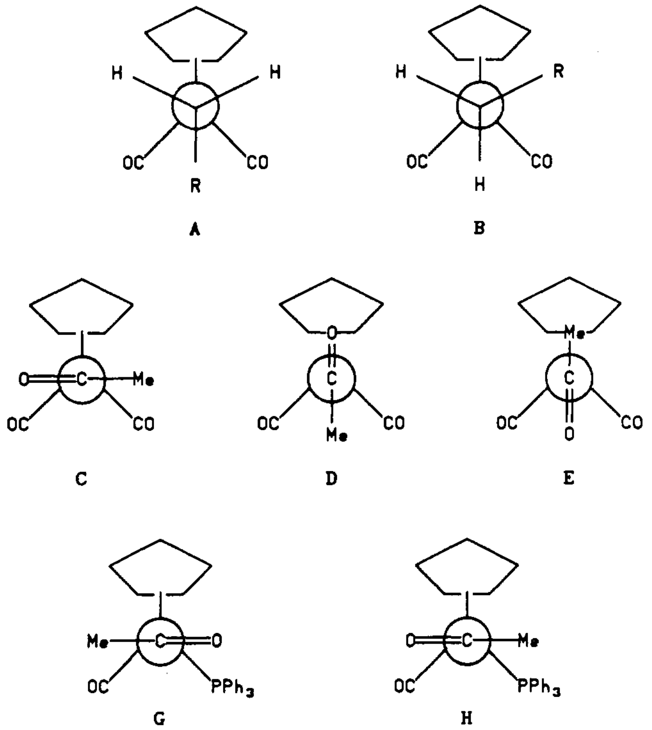
Chart I



tributable to symmetric and antisymmetric ν(CO), of comparable intensities and line widths ($\Delta\nu_{1/2}$). As a result, observation of more than two ν(CO) bands in the solution IR spectra of these and similar compounds has been taken as evidence for the presence of this type of rotational isomerism.[7] In the case of the benzyl derivative $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Ph$, we have confirmed an earlier report[7a] of doubling in the ν(CO) region, finding two strong bands at 2009.7 and 1957.9 cm^{-1}, each associated with a shoulder to higher frequency (pentane solution, 293 K).[8] In addition, we find that the ratio of intensities of the shoulders relative to the stronger pair of bands increases on raising the temperature incrementally over the range 173–373 K in pentane or *n*-decane and 11–173 K in Nujol, as anticipated if an equilibrium were established between two rotamers of different stability.

Band fitting[9] of spectra obtained over the temperature range 173–373 K permitted determination of the frequencies and intensities of all four absorptions, but the pair of ν_{asym} peaks were somewhat better separated and provided more accurate data. Intensity data, corrected for solvent expansion,[10] made possible calculation of the thermodynamic parameters for the A $\rightleftarrows$ B interconversion, and the measured enthalpy and entropy differences are 1.1 ± 0.3 kcal mol^{-1} and 1.1 ± 0.3 cal mol^{-1} K^{-1}, respectively.

The identity of the more stable rotamer was determined by utilizing a procedure adopted by Dalton for the compound $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_2Me$[7c,d] and subsequently applied successfully by Butler and Sawai to compounds of the type $(\eta^5\text{-}C_5H_5)Mn(CO)_2(R_2S)$.[11] Since the two carbonyls are identical in A but not in B, the ^{13}CO satellites in the IR spectrum of rotamer B should be split, while those of A should not. Since the ^{13}CO satellite of the major rotamer is not split, the order of rotamer energies would appear to be A < B.

In an effort to better understand the conformational dynamics of the compound $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Ph$, we have carried out molecular mechanics calculations which suggest that rotamer A is indeed more stable than a rotamer approximating B by 0.6 kcal mol^{-1}, reasonably close to the value found experimentally (see above).[12] The energy profile for this compound suggests that the barriers to rotation of the phenyl group past the $\eta^5\text{-}C_5H_5$ and CO groups are 2.3 and 0.8 kcal mol^{-1}, respectively.

To complement our investigation of the benzyl compound, we have also obtained variable-temperature IR spectra and carried out MM calculations on the ethyl and acetyl compounds $(\eta^5\text{-}C_5H_5)Fe(CO)_2Et$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2COMe$, and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$. In an interesting contrast to our results with the benzyl compound, the calculations for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Et$ suggest that rotamer B should be the more stable, in excellent agreement with crystal structures of the analogous compounds $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(\mu\text{-}CH_2)_n$ (n = 3, 4),[13] although in fact our experimental findings suggest little preference in solution. In this case, the barriers to rotation of the methyl group past the $\eta^5\text{-}C_5H_5$ and CO groups are 2.8 and 1.9 kcal mol^{-1}, respectively.

The IR spectrum of $(\eta^5\text{-}C_5H_5)Fe(CO)_2COMe$ at 298 K suggests the presence of at least two rotamers, since ν_{sym}(CO) at 2021 cm^{-1} exhibits considerable broadening ($\Delta\nu_{1/2}$ = 13.2 cm^{-1}); in contrast, $\Delta\nu_{1/2}$ for ν_{asym}(CO) at 1965 cm^{-1} is 6.4 cm^{-1}, much closer to the $\Delta\nu_{1/2}$ value of ~4 cm^{-1} observed for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$. When the compound was cooled to 193 K, ν_{sym}(CO) became better resolved and exhibited at least three separate components, strongly suggesting the presence of comparable amounts of at least three rotamers. Indeed, at least three rotamers (C–E; Chart I) seem plausible; rotamer C is assumed by similar compounds,[14] while rotamers such as D and E should be favored electronically.[15] In addition, a fourth rotamer, in which the acyl oxygen essentially eclipses a terminal carbonyl group (F; not shown), also finds precedent in structures of similar compounds,[16] although an unfavored conformation may result from crystal-packing forces.

MMX calculations on $(\eta^5\text{-}C_5H_5)Fe(CO)_2COMe$ suggest a rather pronounced steric preference for C, which is the global minimum; D and the global maximum, E, lie 1.3 and

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(8) Spectra in the temperature range 133–373 K were obtained with resolution of 0.5 cm^{-1} on pentane, 2-methylpentane, heptane, or decane solutions by utilizing a Bruker IFS-85 FT-IR spectrometer equipped with a Specac AgCl variable-temperature cell. Spectra in the temperature range 11–284 K were obtained with resolution of 1 cm^{-1} on a Perkin-Elmer Model 983G IR spectrometer with an Air Products and Chemicals Inc. Displex closed-cycle helium cryostat.

(9) Band-fitting calculations were carried out on the Aspect 2000 computer of the IFS-85 instrument, utilizing the Bruker program FIT, and on a Zenith 158 microcomputer utilizing both Spectra Calc and: Jones, R. N., Pitha, J., Eds. *Program X (PC-116)*, 2nd ed.; *National Research Council of Canada Bulletin No. 12*; NSERC: Ottawa, 1976. Essentially identical results were obtained in all three cases, suggesting that the results are not an artifact of the software used.

(10) Washburn, E. E., Ed. *International Critical Tables of Numerical Data Physics, Chemistry and Technology*; McGraw-Hill: New York, 1928; Vol. III.

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

(12) The calculated energy differences are small but no more so than has been reported for other systems.[2] However, while fixing the positions of the CO and $\eta^5\text{-}C_5H_5$ ligands resulted in increasing the rotamer energy differences and the barriers to rotation to values which are calculationally much more significant, the relative orderings remained unchanged.

(13) Pope, L.; Sommerville, P.; Laing, M.; Hindson, K. J.; Moss, J. R. *J. Organomet. Chem.* **1976**, *112*, 309.

(14) (a) Blau, H.; Malisch, S.; Voran, S.; Blank, K.; Kruger, K. *J. Organomet. Chem.* **1980**, *202*, C33. (b) Eisenstadt, E.; Frolow, F.; Efraty, A. *J. Chem. Soc., Dalton Trans.* **1982**, 1013.

(15) 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 "upright" rotamers D and E. See: Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(16) (a) Hädicke, E.; Hoppe, W. *Acta Crystallogr.* **1971**, *B27*, 760. (b) Chen, J.; Yin, J.; Lei, H.; Wang, W.; Lin, G. *J. Chem. Soc., Dalton Trans.* **1989**, 635.

4.4 kcal mol^{-1} higher, respectively. Rotamer F is not a local minimum but lies on the side of a potential well some 2.3 kcal mol^{-1} higher in energy than C. The barrier to interconversion between C and D is about 2.3 kcal mol^{-1}. Since the energy differences between conformations are rather small and would be decreased further by metal–acetyl π bonding,[15] it seems likely that all conformations stabilized by electronic and/or steric factors on the potential energy surface are populated. Furthermore, since the ^1H NMR spectrum of $(\eta^5\text{-}C_5H_5)Fe(CO)_2COMe$ exhibits only a single set of resonances, it is clear that interconversion between conformations is rapid on the NMR time scale, also consistent with the nature of the proposed potential energy surface.

The IR spectrum of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ at 298 K exhibits two broadened $\nu(C{=}O)$ bands, at about 1627 and 1614 cm^{-1}, although the terminal $\nu(CO)$ signal at 1924 cm^{-1} is rather narrow ($\Delta\nu_{1/2}$ = 5.8 cm^{-1}). The relative intensities of the two $\nu(C{=}O)$ bands are strongly temperature-dependent (making possible determination of the relevant thermodynamic parameters), but only a single, averaged set of ^1H resonances is observed in the ^1H NMR spectrum at 294 K. Thus, at least two rapidly interconverting conformations must exist for this compound.

MMX calculations on $\eta^5\text{-}C_5H_5Fe(CO)(PPh_3)COMe$ suggest that rotamer G (Chart I), the global minimum, is more stable than rotamer H, a local minimum, by 0.9 kcal mol^{-1}, a value in excellent agreement with the enthalpy difference (1.3 kcal mol^{-1}) between the species giving rise to the two observed $\nu(C{=}O)$ bands. In addition, the calculated barrier to interconversion between G and H (methyl eclipsing $\eta^5\text{-}C_5H_5$) is 7.6 kcal mol^{-1}, consistent with the observed facile interchange.

The calculated and experimental results for $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = $PhCH_2$, Et) are mutually consistent and suggest that the MMX methodology is indeed appropriate for assessing subtle features of the conformational energy profiles of this type of compound. However, the energy profiles calculated for the types of compounds discussed here differ somewhat from those obtained elsewhere[17] with the extended Hückel (EH)[17a,b] and ab initio methodologies[17b] and another MM program, Chem-X.[17c–e] Thus, for instance, EH calculations[17a] suggest that the barrier to rotation of a benzyl group past the $\eta^5\text{-}C_5H_5$ group is significantly lower than the barrier to rotation of an ethyl group, which was estimated to be almost 40 kcal mol^{-1}. These results are clearly incompatible with the results of the MMX calculations and also with observations utilizing space-filling molecular models.[18]

It is with the two acetyl compounds, however, that our experimental and calculated results differ significantly with conclusions reported elsewhere. Thus, it has been asserted on the basis of ab initio[17b] and MM (Chem-X)[17c–e] calculations that $(\eta^5\text{-}C_5H_5)Fe(CO)_2COMe$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ exist in solution and in the solid state only as rotamers C and G, respectively.[19] In the case of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$, near-degenerate global minima corresponding to G and H have been estimated, but with a barrier to interconversion of about 45 kcal mol^{-1}. The subtle difference in energy between the two conformations, suggested by the MMX calculations and verified by our NMR and low-temperature IR experiments, was not inferred, while the barrier to rotation was clearly overestimated.[20]

Our work demonstrates experimentally that the conformational energy profiles of the compounds $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = $PhCH_2$, Et, MeCO) and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ are much more complicated than originally thought and that MMX provides an apparently more appropriate calculational approach than has been used previously to providing estimates of the conformational preferences and barriers to rotation of coordinated alkyl ligands.[21]

Acknowledgment. We acknowledge financial assistance from the Natural Sciences and Engineering Research Council to M.C.B. and H.F.S. We also thank Dr. Kevin Gilbert, of Serena Software, for use of a prerelease version of PCMODEL for the Sun SPARCStation.

Supplementary Material Available: Figures showing profiles for $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = $PhCH_2$, MeCO) and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ (3 pages). Ordering information is given on any current masthead page.

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(17) (a) Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* 1985, *107*, 6522. (b) Davies, S. G.; Seeman, J. I.; Williams, I. H. *Tetrahedron Lett.* 1986, *27*, 619. (c) Blackburn, B. K.; Davies, S. G.; Sutton, K. H.; Whittaker, M. *Chem. Soc. Rev.* 1988, *17*, 147. (d) Blackburn, B. K.; Davies, S. G.; Whittaker, M. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: New York, 1989; Vol. 3, p 141. (e) Davies, S. G.; Derome, A. E.; McNally, J. P. *J. Am. Chem. Soc.* 1991, *113*, 2854. In order to simplify the calculational complexities, energy profiles were apparently in all cases performed with models much more severely simplified than those utilized here.

(18) While not very elegant, accurately scaled, space-filling molecular models (Fisher–Hirschfelder–Taylor adapted for multihapto ligands) do permit useful qualitative comparisons of the energy profiles of the compounds under consideration here. On the basis of such models, there would appear to be little difference in the steric requirements of the rotating ethyl and benzyl groups.

(19) In fact, the claim for $(\eta^5\text{-}C_5H_5)Fe(CO)_2COMe$ is inconsistent with the energy profile given in ref 17c. If, as seems likely, Figure 16 of ref 17c is misdrawn and the global maximum actually occurs at a torsional angle of 180° (as defined in this paper), then the global minima would occur for conformation F.

(20) The narrow $\nu(CO)$ band observed for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ is consistent with an observation[17d] that only a single rotor of the PPh_3 coordinates to each enantiomeric form of the chiral iron center in the solid state. Utilizing $^{13}C\{^1H\}$ NMR spectroscopy at 100 MHz, we have found that PPh_3 rotation is slowed at low temperatures and that only a single rotor of the PPh_3 is observed but that the presumed acetyl rotation is still rapid on the NMR time scale; similar results have been found at 62.9 MHz.[17e]

(21) Note[5] that MMX has been developed from MM2,[1] which has been shown to reproduce experimental small conformational energy differences of many types of organic molecules much better than does Chem-X;[2] furthermore, the latter has not been parameterized for the types of compounds under consideration here. In addition, inasmuch as the extended Hückel approximation is intrinsically incapable of optimizing geometries,[3] energy profiles determined with this approach cannot be expected to be accurate in spite of the success of this methodology for systems in which conformational preferences arise from electronic factors.[22]

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