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Application of molecular mechanics (MMX) calculations to an investigation of the conformations of coordinated triphenylphosphine in organometallic compounds of the types (.eta.6-C6R6)Cr(CO)2PPh3 and (.eta.5-C5H5)Fe(CO)(PPh3)R' (R = H, Me; R' = H, alkyl, acyl)

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contribute to the free energy differences.

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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.

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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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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.

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(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.

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incorporate force fields appropriate for many of the common types of organometallic compounds.[8]

As we have pointed out recently,[9] however, the appearance of new molecular modeling software, MMX,[10] which explicitly addresses the problems involved with organotransition-metal compounds, makes possible the carrying out of routine MM calculations on a variety of flexible organometallic compounds. In view of the potential significance of MMX, assessment of its utility is clearly desirable and we have carried out an investigation in which quantitative experimental information concerning ligand conformational preferences and/or barriers to ligand rotation is compared with the conformational energy profiles calculated for several series of representative organometallic compounds.

We have previously shown that MMX calculations on several alkyl- and acyliron compounds of the types $(\eta^5\text{-}C_5H_5)Fe(CO)LR$ (R = alkyl, acyl; L = CO, PPh_3) result in computed conformational energy profiles for alkyl and acyl ligand rotation which agree very well with the results of experimental studies.[9] We now address the problem of rotation and preferred conformations of coordinated tertiary phosphines, in particular of triphenylphosphine (PPh_3). Variable-temperature NMR studies of several triphenylphosphine complexes of chromium[11] and iron[8k,9b] have resulted in reliable estimates of barriers to rotation about metal–phosphorus bonds in a variety of types of complexes, thus providing further scope for validation of the MMX methodology. Interestingly, the calculations are also found to provide possible insight on the dynamics involved in exchange between the two chiral conformations of idealized C_3 symmetry of coordinated PPh_3.[12]

Experimental Section

All MM calculations were carried out utilizing MMX on a Sun SPARCStation 1. Input and optimization procedures were carried out much as described previously,[9b] and PPh_3 ligand rotation was forced by use of the dihedral driver function of the commercial modeling program PCMODEL;[10] metal–ligand bond distances were set at crystallographic distances. The dihedral (torsional) angle for PPh_3 rotation is defined as L–metal–P–C(ipso); thus clockwise rotation involves holding the positions of the L–metal–P fragment constant, with L toward the viewer, while rotating the metal–P–C(ipso) fragment in a clockwise direction. The dihedral angle for phenyl rotation in complexes was defined as metal–P–C(ipso)–C(ortho), and that for free PPh_3 as (lone pair)–P–C(ipso)–C(ortho).

For ease of viewing and to facilitate comparisons, torsional angles in all energy profiles for PPh_3 rotation are defined such that the L–metal–P–C(ipso) torsional angle is 0° when the atom which is being driven eclipses the $\eta^5\text{-}C_5H_5$ or η^6-arene group.

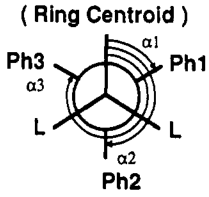
Results and Discussion

MMX Methodology.[10] We have previously discussed the similarities and differences of MMX to the well-known MM2 molecular modeling program[5a] and pointed out that MMX utilizes the parameterization and energy minimization procedures previously published for MM2. Thus further detailed discussion would seem unnecessary here. MMX differs from MM2 by the inclusion of a number of enhancements such as the ability to accommodate π ligands, which cannot be specifically rotated utilizing the dihedral driver but which are free to rotate and/or tilt in response to the steric requirements of the other ligands.

Furthermore, since bending and torsional force constants involving metal atoms are generally not available as input data, calculations of ligand–metal–ligand bond angles largely involve consideration only of 1,3 interactions, which are ignored by MM2. Thus the calculated steric energies are in essence dominated by interligand van der Waals repulsive forces, and ligand–metal–ligand bond angles are determined primarily by the overall ligand steric requirements, with internal ligand bending and torsional force constants being of lesser importance.

Reproducibility of the calculated energies was generally within about 0.2 kcal mol^{-1}, conformational energy profiles in most cases being reproduced exactly after the torsional angle being driven had changed by about 60°.

Conformations of Coordinated Triphenylphosphine. Coordination of a PPh_3 to pseudopyramidal metal–ligand fragments of the type $(\eta^5\text{-}C_5R_5)MLL'$ or $(\eta^6\text{-arene})MLL'$ results in complexes which are predicted to adopt the staggered conformation shown as A in the Newman diagram



A

Brunner et al. have published a survey of the published X-ray crystallographic data for such compounds,[13] finding that the three phenyl rings, identified in A as Ph1, Ph2, and Ph3, do generally assume essentially staggered conformations in which two of the rings, Ph1 and Ph3, are situated more or less gauche to the multihapto ligand. However, these two "gauche" phenyl rings are also found to assume widely differing (ring centroid)–M–P–C(ipso) torsional angles, defined as $\alpha 1$ and $\alpha 3$ in A. Thus $\alpha 1$ varies between ≈24 and ≈58°, and $\alpha 3$ between ≈262 and ≈302°; the torsional angle ($\alpha 2$) of the "anti" phenyl group Ph2 thus ranges from ≈145 to ≈179°. The distortions from apparent ideality are in large part a result of the relative stereochemical requirements of the other ligands,[13] which

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(8) For applications of MM and similar calculations to conformational problems of organotransition-metal chemistry, 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. Trans.*) **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.; Horwitz, C. P.; Shriver, D. F. *J. Chem. Soc., Chem. Commun.* **1986**, 553. (g) Casey, C. P.; Whiteker, G. T. *Isr. J. Chem.* **1990**, *30*, 299. (h) Blackburn, B. K.; Davies, S. G.; Sutton, K. H.; Whittacker, M. *Chem. Soc. Rev.* **1988**, *17*, 147. (i) Krajewski, J. W.; Gluziński, P.; Zamojski, A.; Mishnyov, A.; Kemme, A.; Zhong-Wu, G. *J. Crystallogr. Spectrosc. Res.* **1991**, *21*, 271. (j) Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 6522. (k) Davies, S. G.; Derome, A. E.; McNally, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2854. (l) 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. (m) Brown, J. M.; Evans, P. L. *Tetrahedron* **1988**, *44*, 4905. (n) Bogdan, P. L.; Irwin, J. J.; Bosnich, B. *Organometallics* **1989**, *8*, 1450.

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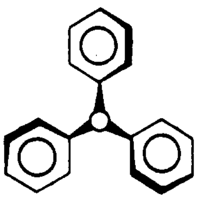
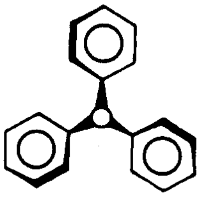
(13) Brunner, H.; Hammer, B.; Krüger, C.; Angermund, K.; Bernal, I. *Organometallics* **1985**, *4*, 1063.

also result in twisting of the phenyl rings about the P–C(ipso)–C(para) axes (see below). For each compound discussed in this paper, the energy minima in the conformational energy profiles for PPh_3 rotation may be correlated with the (ring centroid)–M–P–C(ipso) torsional angles of the compound in its optimized conformation.

Phenyl ring twisting adds a further complication, chirality, to the general stereochemical picture. The three rings, Ph1, Ph2, and Ph3, of a coordinated PPh_3 generate a helical (propeller-like) configuration,[12] the chirality arising from twisting of the rings away from an idealized C_{3v} structure. Thus the two enantiomeric conformations of C_3 symmetry (right- and left-handed propellers) may be described, as are helices, by M and P descriptors.[12c]



M



P

This nomenclature is related to the torsional angles of the rings with respect to the M–P bond.[13,14] Each phenyl ring, Ph1, Ph2, and Ph3, assumes a M–P–C(ipso)–C(ortho) torsional angle (defined as $\tau1$, $\tau2$, and $\tau3$, respectively, in ref 13) which is between 0 and +90° for a ring in an "M-like" configuration and between 0 and −90° for a ring in a "P-like" configuration. The pairs of ortho carbons on each ring give torsional angles 180° apart, of course, but only the smaller ($|\tau| < 90°$) is used. For torsional angles of 0° (180°), the ring eclipses the M–P bond, while for angles of ±90°, the ring is "flat" with respect to this bond (i.e. a line perpendicular to the ring plane eclipses the M–P bond). For rings at these angles, the question of M/P chirality is meaningless.

In the case of the ideal propeller, of C_3 symmetry, the rings have the same torsional angle with respect to the M–P bond and hence the same M or P chiral sense. In real systems, however, this is often not the case. While the crystal structures of the compounds $Mn(NO)_3PPh_3$, $Co(CO)_2(NO)PPh_3$, and $Fe(CO)(NO)_2PPh_3$ show that the individual phenyl torsional angles are relatively constant (45 ± 5°), the PPh_3 is bonded in each to a sterically undemanding metal–ligand moiety of essentially 3-fold symmetry.[13] In contrast, in complexes of the types $(\eta^5\text{-}C_5H_5)ML_2PPh_3$ and $(\eta^6\text{-arene})ML_2PPh_3$, the three phenyl rings may assume widely differing M–P–C(ipso)–C(ortho) torsional angles, apparently because of significantly different stereochemical requirements of the various ligands.[13] In complexes with a sterically demanding ligand, the tendency for the two phenyl rings gauche to such a ligand to twist in order to minimize strain competes with the tendency for all three rings to assume the same M/P chiral sense. Severe steric interactions can thus result in an increased torsional angle for one of the gauche phenyl groups and a decreased angle for the other; in some cases, one ring twists well into the chiral sense different from that assumed by the other two phenyl rings.[13]

Triphenylphosphine Conformations and Rotation in $(\eta^6\text{-Arene})Cr(CO)_2(PPh_3)$ (Arene = Benzene, Hexamethylbenzene). Hunter et al.[11] have reported variable-temperature $^{13}C\{^1H\}$ NMR spectra of a species of compounds of this type. It was anticipated that extensive alkyl substitution on the arene rings might result in sufficient slowing of the arene and/or PPh_3 rotation that decoalescence of the various time-averaged resonances would be observable at low temperatures. For $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$, however, decoalescence of none of the time-averaged resonances was observed at low temperatures, and a barrier to ligand rotation could therefore not be estimated.

Table I. Important Bond Lengths (Å), Bond Angles (deg), and Torsional Angles (deg) in $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$ (I, Calcd), $(\eta^6\text{-}C_6Me_6)Cr(CO)_2PPh_3$ (II, Calcd), and $(\eta^6\text{-}C_6Et_6)Cr(CO)_2PPh_3$ (III[11])

	bond lengths		
bond	I	II	III
Cr–arene (av)	2.22	2.26	2.24
Cr–P	2.36	2.36	2.321
Cr–CO(1)	1.86	1.86	1.802
Cr–CO(2)	1.86	1.86	1.819

	bond angle		
angle	I	II	III
OC–Cr–CO	92.5	89.1	89.60
P–Cr–CO(1)	89.3	86.0	85.40
P–Cr–CO(2)	88.8	89.3	89.15
Cr–P–C(ipso)(1)	112.5	109.6	120.59
Cr–P–C(ipso)(2)	113.3	116.9	115.41
Cr–P–C(ipso)(3)	106.7	109.2	114.78
C(ipso)(1)–P–C(ipso)(2)	105.3	109.3	97.48
C(ipso)(1)–P–C(ipso)(3)	109.2	110.7	104.12
C(ipso)(2)–P–C(ipso)(3)	109.8	100.9	109.84
(arene centroid)–Cr–CO(1)	118.8	120.7	122.05
(arene centroid)–Cr–CO(2)	121.7	120.1	124.98
(arene centroid)–Cr–P	134.6	138.4	132.77

	torsional angle		
angle	I	II	III
$\alpha1$	37.3	45.8	48.45
$\alpha2$	156.6	167.2	166.00
$\alpha3$	277.6	280.8	282.64
$\tau1$	44.3	58.5	60.08
$\tau2$	46.7	78.9	52.19
$\tau3$	75.1	−1.9	22.66

Optimization of the geometry of $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$, utilizing MMX as described in the Experimental Section, resulted in a structure similar to that established crystallographically for the compounds $(\eta^6\text{-}C_6R_6)Cr(CO)_2PPh_3$ (R = Et, n-Pr).[11] Important bond lengths, bond angles, and torsional angles for $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$, as derived using MMX, are shown in Table I; in order to facilitate comparisons, the three phenyl groups are numbered as in A.[13] Also shown for purposes of comparison are the analogous structural data for the hexamethyl- (see below for MMX calculations) and hexaethylbenzene[11] analogues. While comparisons between computational results and data from the solid state must always be treated with caution, it has been suggested that intra- rather than intermolecular interactions have the greater influence on the conformations exhibited by the types of compounds under consideration here.[13]

Given this caveat, we note that the calculated metal–ligand bond lengths of $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$ correspond very well with the corresponding distances of $(\eta^6\text{-}C_6Et_6)Cr(CO)_2PPh_3$, the average Cr–arene distance being about 0.02 Å shorter and the Cr–P and Cr–CO distances being 0.04–0.05 Å longer. In addition, all ligand–Cr–ligand bond angles are within 4° of the crystallographic data. As is the case with the substituted arene complexes,[11] the PPh_3 is essentially staggered with respect to the other ligands such that one of the phenyl rings (Ph2) is remote from and the

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[14] For a detailed, relatively unambiguous description of the procedure for assigning a stereochemical descriptor to a propeller-like molecule such as C_3 PPh_3, see pp 60–61 of ref 12c. Note that the M enantiomer is referred to as the "anticlockwise rotor"[8l] and the "right handed propeller"[12b] elsewhere.

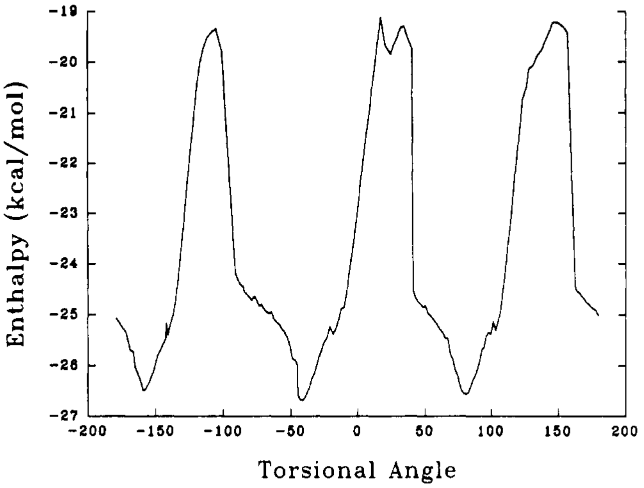

Figure 1. Conformational energy profile for rotation of PPh_3 in the compound $(\eta^6\text{-}C_6H_6)Cr(CO)_2(PPh_3)$.

others (Ph1, Ph3) are closer to the arene ring.

The conformational energy profile for PPh_3 rotation in $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$ was calculated utilizing metal–ligand bond lengths fixed to the experimental distances, as described previously,[9b] and is shown in Figure 1. In the calculation, PPh_3 rotation in $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$, in its global minimum structure with the PPh_3 assuming essentially the P conformation, was induced by driving one of the OC–Cr–P–C(ipso) torsional angles in the clockwise direction. As anticipated, PPh_3 rotation is periodic, with maxima and minima occurring every 120° near eclipsed and staggered conformations, respectively. The calculated steric barrier to rotation was found to be 6.7 kcal mol^{-1}.

Interestingly, the 3-fold steric barriers shown in Figure 1 are neither symmetric nor are they centered such that the minima correspond exactly to the staggered conformation of the solid state. The latter distortion is a result of the propeller-like structure of the coordinated PPh_3 (see above),[12] whereby twisting of each phenyl group results in the ortho CH groups, which dominate the intramolecular van der Waals interactions, trailing the ipso carbon atoms during PPh_3 rotation. Thus eclipsing of the chromium–ligand bonds by the P–C bonds does not coincide with the energy maxima. Considering the optimized structure of $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$, the calculated magnitudes (and trends) of the OC–M–P–C(ipso) and M–P–C(ipso)–C(ortho) torsional angles (Table I) are similar to those observed previously in crystal structures of the similarly unencumbered complexes $(\eta^5\text{-}C_5H_5)Mn(CO)_2PPh_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3{}^+$.[13] If, as suggested previously,[13] the conformations assumed in the solid state reflect intramolecular steric repulsions, then the results with $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$ speak well for the utility of the MMX methodology.

Under the conditions of the calculations, the three rings of the rotating PPh_3 maintain the P configuration, and each tilted phenyl ring approaches the other ligands in a glancing, face-on, rather than a more direct, edge-on, interaction; all three rings twist back and forth during a full rotation of the PPh_3, but do not themselves rotate. Recall now the asymmetry in the barriers to PPh_3 rotation, as illustrated in the conformational energy profile of Figure 1. Detailed consideration of the interactions of the phenyl groups with the other ligands shows that the energy of the system rises drastically as an eclipsed conformation is approached. When the rings finally move past the other ligands, they rotate sharply, the system relaxes relatively suddenly, and as shown, the total steric energy declines precipitously. During rotation, the closest approaches of the ortho phenyl hydrogen atoms to the carbonyl carbon atoms and the benzene hydrogen atoms are respectively 2.52 and 2.19 Å, i.e. ≈0.8 and ≈0.9 Å less than the respective sums of van der Waals radii. Thus the overall barrier to triphenylphosphine rotation presumably involves concerted steric interactions between the ortho phenyl hydrogen atoms of all three phenyl groups and the other ligands on the chromium.

Interestingly, forcing the same initial structure to rotate in the opposite direction resulted in the PPh_3 changing from the P to the M conformation. The former may be disfavored for PPh_3 rotation in this direction because the phenyl rings approach the other ligands in the edge-on rather than the more glancing face-on fashion discussed above. In any case, within one-sixth of a rotation of the PPh_3, all three phenyl rings were found to have rotated to the now more favored M conformation. The mode of enantiomer interconversion was found to be essentially the "two-ring flip" described elsewhere,[12a,b] although the three rings did not actually change chirality simultaneously. Two of the rings rotated so as to eclipse the P–Cr bond while the third rocked in the opposite direction, so that it was perpendicular to the bond. As anticipated, the conformational energy profile for PPh_3 rotation in the counterclockwise direction mirrored that described above for the clockwise direction.

Hunter et al. have also reported variable-temperature $^{13}C\{^1H\}$ NMR spectra of several extensively substituted arene complexes, finding that substitutions on the arene ring can result in sufficient slowing of PPh_3 rotation that decoalescence of the phosphine aryl carbon resonances may be observed below about 205 K.[11] With the exception of complexes in which two or more adjacent arene ring positions were unsubstituted, the low-temperature spectra exhibited clearly differentiated pairs of ipso and ortho carbon resonances in 2:1 ratios; the corresponding pairs of meta and para resonances were generally less well resolved. In all cases, the low-temperature, limiting spectra were interpreted in terms of the solid-state structures of $(\eta^6\text{-}C_6R_6)Cr(CO)_2(PPh_3)$ (R = Et, *n*-Pr), in which the PPh_3 assumes the staggered conformation mentioned above and the arene ligands assume conformations in which all six alkyl groups R are oriented distally with respect to the chromium atom.

Analyses of the NMR data resulted in estimations of the barriers to rotation of the PPh_3 in the compound $(\eta^6\text{-}C_6Me_6)Cr(CO)_2PPh_3$.[11] Hunter et al. found $\Delta H^{\ddagger}_{200}$ and $\Delta G^{\ddagger}_{200}$ for the rotation of PPh_3 to be 6.74 ± 0.72 and 9.19 ± 0.72 kcal mol^{-1}, respectively. In view of an apparent correlation between the barriers to PPh_3 rotation and the extent of alkyl substitution on the arene ring, it was thought that the bulky phosphine and arene ligands might act as pairs of meshed gears. However, decoalescence of the carbonyl carbon resonances, of the arene carbon atom resonances, and of the pairs of ortho and meta resonances of the individual phenyl groups could in no case be observed. It was therefore suggested that both arene ring and phenyl ring rotations occur at significantly faster rates than does PPh_3 rotation and thus that the ligand substituents do not intermesh as cogs in a pair of gears.

Optimization of the geometry of $(\eta^6\text{-}C_6Me_6)Cr(CO)_2PPh_3$ using MMX resulted in a structure remarkably similar to those reported previously for $(\eta^6\text{-}C_6Et_6)Cr(CO)_2PPh_3$ and $(\eta^6\text{-}C_6Pr_6)Cr(CO)_2PPh_3$.[11] Important structural data are listed in Table I, and as with $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$, the calculated bond lengths and angles and (arene centroid)–Cr–P–C(ipso) and Cr–P–C(ipso)–C(ortho) torsional angles (Table I) are reasonably similar to those observed

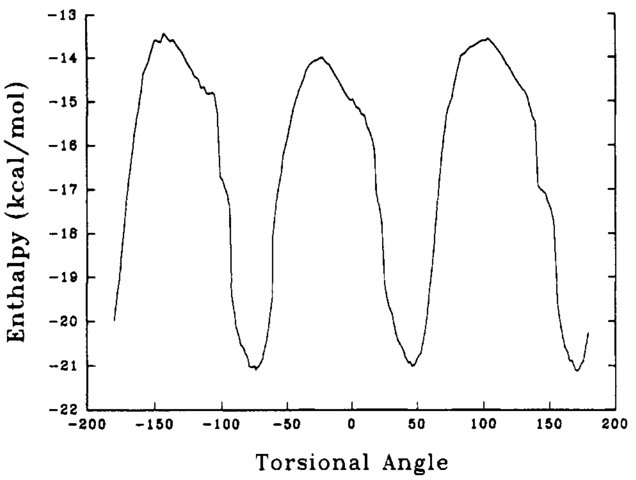

Figure 2. Conformational energy profile for rotation of PPh_3 in the compound (η^6-C_6Me_6)Cr$(CO)_2(PPh_3)$.

previously in crystal structures of the similar complexes (η^6-C_6Et_6)Cr$(CO)_2PPh_3$ and (η^6-C_6Pr_6)Cr$(CO)_2PPh_3$.[11]

As with (η^6-C_6H_6)Cr$(CO)_2PPh_3$, the PPh_3 in (η^6-C_6Me_6)Cr$(CO)_2PPh_3$ was forced to rotate by driving one of the OC–Cr–P–C(ipso) dihedral angles in the clockwise direction. The conformational energy profile for PPh_3 rotation in (η^6-C_6Me_6)Cr$(CO)_2PPh_3$ was computed for the system, and the resulting conformational energy profile is shown in Figure 2. During the PPh_3 rotation, the three phenyl groups rotated, essentially in concert and all in the same direction, although a C_3-like structure was never achieved; a full 360° rotation of the PPh_3 resulted in the system returning to the original configuration. The calculated barrier for PPh_3 rotation is about 7.3 kcal mol^{-1}, in impressive agreement with the experimental value of $\Delta H^{\ddagger}$ for this compound (6.74 ± 0.72 kcal mol^{-1}).[11] Interestingly, and apparently contrary to the conclusion that PPh_3 and arene rotations are unsynchronized,[11] the C_6Me_6 ligand was found to rotate by about 60° about the Cr–arene axis for each 120° rotation of the PPh_3. Thus the motions of the two ligand groups do seem to be essentially concerted.

This conclusion apparently contradicts the experimental NMR results, which were taken to suggest that arene rotation is much more facile than PPh_3 rotation[11] (see above). However, for an intramolecular, two-site exchange of the type under consideration here, the rate constant at the coalescence temperature is proportional to the frequency separation of the resonances of the nuclei undergoing exchange.[15] Thus a closely spaced pair of exchanging resonances will coalesce at a lower temperature than a widely spaced pair of resonances exchanging with the same rate constant. This is clearly illustrated in the variable-temperature NMR spectra of (η^6-C_6Me_6)Cr$(CO)_2PPh_3$, for which the coalescence temperature of the ipso carbon resonances ($\Delta\delta$ 6.13 ppm) is much higher than that of the ortho carbon resonances ($\Delta\delta$ 2.25 ppm).[11a] Therefore, if the individual chemical shifts of the arene and carbonyl carbon resonances were to differ by significantly less than those of the phenyl carbons, then the arene rings could indeed be rotating synchronously with the PPh_3 without decoalescence being observed.

That this rationale may indeed be valid is suggested by a recent variable-temperature NMR study of the three complexes (η^6-C_6Et_6)Cr$(CO)_2$CS, [(η^6-C_6Et_6)Cr$(CO)_2$NO]$^+$, and [(η^6-C_6Et_6)Cr(CO)(CS)(NO)]$^+$.[16] Although the low-temperature, limiting $^{13}C\{^1H\}$ spectra show that the arene ligands of all three complexes adopt 1,3,5-distal-2,4,6-proximal arrangements of ethyl groups, with arene carbon chemical shifts of the distal and proximal groupings differing by 6–8 ppm, the arene carbon chemical shifts *within* each trio differ by 2 ppm or less. The carbonyl carbon chemical shift differences are comparable, and thus the differences in the arene and carbonyl carbon resonances of (η^6-C_6Me_6)Cr$(CO)_2PPh_3$ may indeed be negligibly small.

However, we also note that the calculated barriers to PPh_3 rotation in (η^6-C_6H_6)Cr$(CO)_2PPh_3$ and (η^6-C_6Me_6)Cr$(CO)_2PPh_3$ are disconcertingly similar. Thus the apparent experimental correlations between the size of arene ring and the barrier to PPh_3 rotation[11] do not appear to be reflected in the MMX calculations. However, the observed differences in coalescence temperatures reflect differences in $\Delta G^{\ddagger}$, not $\Delta H^{\ddagger}$ alone, and as Allinger et al.[17] have shown, entropy contributions can become quite significant at the tops of rotational barriers of sterically congested molecules. In the systems under consideration here, significant decreases in methyl and arene rotation at the maxima in the PPh_3 rotational energy profile may well result in an increase in the overall free energy barriers which would be more significant for the η^6-C_6Me_6 compound. Thus, while $\Delta S^{\ddagger}$ for PPh_3 rotation in (η^6-C_6Me_6)Cr$(CO)_2PPh_3$ is about −12 cal mol^{-1} K^{-1},[11] it is presumably much nearer zero for rotation of PPh_3 in (η^6-C_6H_6)Cr$(CO)_2PPh_3$. Apparently strengthening this argument, we find that PPh_3 rotation in (η^6-C_6H_6)Cr$(CO)_2PPh_3$ does not force the benzene ring to rotate. The latter merely oscillates ±15° about the 6-fold axis but within the potential well.

Finally, as noted above for the η^6-C_6H_6 analogue, the barriers to PPh_3 rotation shown in the conformational energy profile of (η^6-C_6Me_6)Cr$(CO)_2PPh_3$ are not symmetric and do not correspond with the exact eclipsing of a phenyl group with any particular ligand. As suggested above, a rationale for this observation lies in the fact that it is the phenyl ortho CH groups which interact most strongly with the other ligands[13] and, as the phenyl groups are twisted with respect to the P–Cr axis,[12] maximum steric interactions between the phenyl groups and the other ligands occur when the relevant torsional angles are significantly different from zero.

Detailed consideration of the phenyl group rotations with the conformational energy profile of Figure 2 shows that the total potential energy rises smoothly as the phenyl rings approach the other ligands and begin to twist in order to ameliorate the growing strain. Each of the 3-fold barriers in the conformational energy plot diplays a maximum corresponding to a concerted interaction of the three phenyl groups with the other three ligands. In addition, each barrier also displays two sharp decreases in energy which appear to correspond to sudden twisting of phenyl rings as first one and then another passes a CO group. Similar abrupt decreases in energy were noted in the conformational energy profile of (η^6-C_6H_6)Cr$(CO)_2PPh_3$, and again the ortho phenyl hydrogen atoms were found to sweep to ≈0.9 and ≈0.8 Å, respectively, less than the sums of the van der Waals radii of the phenyl hydrogen atoms on one hand and the carbonyl carbon and the arene methyl hydrogen atoms on the other.

Triphenylphosphine Rotation in (η^5-C_5H_5)Fe(CO)(PPh_3)R (R = H, Me, Et, CH_2Ph, CH_2SiMe_3, COMe). We have previously dealt at length with con-

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Table II. Torsional Angles (deg) of the Compounds (η^5-C_5H_5)Fe(CO)(PPh_3)R (R = H, Me, Et, CH_2Ph, CH_2SiMe_3, COMe) in Their Optimized Structures (Experimental Crystallographic Data in Parentheses)

R	α1	α2	α3	τ1	τ2	τ3
H	29.1	145.6	269.9	72.7	35.6	19.9
Me	30.3	153.4	270.5	72.9	50.2	2.3
Et[18c]	40.3 (37.3)	161.9 (158.0)	282.4 (278.7)	72.3 (72.3)	47.1 (36.2)	0.9 (−0.5)
CH_2Ph	41.9	163.5	283.8	69.2	56.3	2.6
CH_2SiMe_3[18c]	43.2 (39.7)	164.9 (161.4)	284.1 (280.1)	66.3 (54.4)	62.9 (53.3)	1.3 (16.3)
COMe[18a]	28.5 (24.5)	152.0 (147.4)	268.5 (264.9)	60.1 (58.1)	63.2 (77.3)	25.2 (15.6)

formational preferences and barriers to rotation of alkyl and acyl ligands in these and similar complexes.[9] While we deferred detailed discussion of conformational preferences and barriers to rotation of the coordinated PPh_3 to the present paper, we did describe relevant IR and variable-temperature ^1H and $^{13}C\{^1H\}$ NMR experiments which suggested that PPh_3 may coordinate to a chiral iron atom center in both propeller-like conformations and that M $\rightleftarrows$ L interconversion is rapid on the ^1H and ^{13}C NMR time scale for each compound at room temperature, but that the compounds exhibit a preference, which decreases as R becomes smaller, for one diastereomer over the other. (It has in fact been shown elsewhere[8l] that the *S*-enantiomers of the chiral iron moieties exhibit a preference for the M conformation of the PPh_3.) We also demonstrated that PPh_3 rotation is rapid on the ^1H and ^{13}C NMR time scales for all of the compounds at room temperature but can be slowed at low temperatures when R = MeCO such that, as with the chromium compounds discussed above, ^{13}C resonances of the individual phenyl groups may be resolved. Similar results had been reported by Davies et al. for (η^5-C_5H_5)Fe(CO)(PPh_3)COMe,[8k] line shape analysis of the variable-temperature $^{13}C\{^1H\}$ NMR spectrum suggesting that the barrier to PPh_3 rotation is 10.3 kcal mol^{-1}, similar to the barrier to PPh_3 rotation (12 kcal mol^{-1}) calculated using Chem-X.

Since the structures of these molecules have been optimized previously,[9] we have now utilized MMX only to calculate barriers to rotation of the coordinated PPh_3. Rotation of the latter was induced by driving the OC–Fe–P–C(ipso) dihedral angles, structural data typical of this type of compound being utilized.[9,18] As anticipated, the coordinated PPh_3 assumes in each case a structure analogous to A, with torsional angles as listed in Table II. In the cases of (η^5-C_5H_5)Fe(CO)(PPh_3)Et, (η^5-C_5H_5)Fe(CO)(PPh_3)CH_2SiMe_3, and (η^5-C_5H_5)Fe(CO)(PPh_3)COMe (two isomorphs), for which crystallographic data are available,[18] the agreement is particularly gratifying.

As with the compound (η^6-C_6H_6)Cr(CO)$_2$$PPh_3$, the calculations on the iron compounds suggest that PPh_3 prefers to rotate in the direction which will permit the phenyl groups to approach the other ligands in a face-on rather than an edge-on fashion, and that forced rotation in an edge-on fashion results in a change in the helical conformation of the PPh_3. However, in contrast to the situation with the achiral (at metal) chromium compounds, calculations on the chiral iron compounds suggest that the barriers to rotation of the M and P conformations in the directions which permit face-on interactions with the other ligands (counterclockwise and clockwise, respectively) differ significantly.

These results are to be anticipated in principle, since the three phenyl groups are inequivalent at any particular PPh_3 orientation during both clockwise and counterclockwise rotation of the PPh_3. Thus the overall van der Waals repulsions between phenyl groups and between phenyl groups and other ligands will be different at each stage of the rotation process. We present in Table III the steric barriers computed in each case, and note that the barriers generally increase as R becomes larger. We also note that the steric barriers for the diastereomers of (η^5-C_5H_5)Fe(CO)(PPh_3)COMe are very similar to the barrier determined experimentally.[8k]

Table III. Calculated Barriers (kcal mol^{-1}) to PPh_3 Rotation in the Compounds (*S*)-(η^5-C_5H_5)Fe(CO)(PPh_3)R

R	PPh_3 rotor	barrier
H	M	3.8
	P	5.2
Me	M	8.6
	P	9.0
Et	M	9.3
	P	9.6
CH_2Ph	M	10.6
	P	8.8
COMe	M	11.1
	P	11.1

Table IV. $^{13}C\{^1H\}$ Spin–Lattice Relaxation Times (s) for the Phenyl Carbon Atoms of PPh_3 and (η^5-C_5H_5)Fe(CO)(PPh_3)COMe

T_1 data	PPh_3	(η^5-C_5H_5)Fe(CO)(PPh_3)COMe
T_1 (ortho)	3.93	1.22
T_1 (meta)	4.05	1.22
T_1 (para)	2.53	1.08
T_1 (ortho)/T_1 (para)	1.55	1.13
T_1 (meta)/T_1 (para)	1.60	1.13

Davies et al. have also carried out Chem-X calculations of phenyl rotation in (η^5-C_5H_5)Fe(CO)(PPh_3)COMe,[8k] finding a barrier to rotation of about 5 kcal mol^{-1}. This result is in accord with the observation that phenyl rotation must remain facile at even the lowest temperature reached in the NMR study and is generally consistent with observations on the arenechromium system, described above.

We have not attempted to replicate this calculation using MMX, since it was realized that different results would likely be obtained on forcing the rotation of each of the three phenyl groups, clockwise and counterclockwise, in each of the possible diastereomers. As described below, however, we have calculated a barrier to phenyl rotation of 0.8 kcal mol^{-1} for the free ligand, for which phenyl rotation should be more facile. That the latter point is valid has also been shown by comparisons of the spin-lattice (T_1) relaxation measurements of the phenyl ^{13}C resonances of free PPh_3 and (η^5-C_5H_5)Fe(CO)(PPh_3)COMe. Preferential rotation about the C(ipso)–C(para) axis of a monosubstituted phenyl group is known to result in the off-axis ortho and meta carbon atoms relaxing at rates significantly slower than that of the para carbon atom.[19]

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Thus the ratios T_1(ortho,meta)/T_1(para) for a series of comparable compounds can provide a measure of the relative rates of rotation about this axis, the ratio declining from $\gg 1$ for cases of highly anisotropic motion to ≈ 1 where no preferential rotation along the C_1–C_4 axis occurs. We have therefore carried out $^{13}C\{^1H\}$ T_1 measurements at room temperature for both free PPh_3 and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ in $CDCl_3$, with results as shown in Table IV.

As can be seen, the ratios T_1(ortho,meta)/T_1(para) decrease very significantly from about 1.6 to 1.1 on going from free PPh_3 to $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$, in spite of the more rapid tumbling of the smaller free ligand, evidenced by its generally larger T_1 values. This result provides experimental evidence that phenyl rotation is indeed less facile in the iron complex and, presumably, that the barrier to phenyl rotation increases on coordination of the PPh_3.

Phenyl Rotation in PPh_3: Phenyl and PPh_3 Rotation in $Ni(CO)_3PPh_3$. For purposes of comparison, we have also utilized MMX to optimize the structures of free PPh_3 and the relatively uncrowded compound $Ni(CO)_3PPh_3$ and to calculate the barriers to phenyl rotation in both and PPh_3 rotation in the latter. When the position of the lone pair is defined as the normal to the plane of the three ipso carbon atoms, the crystallographically determined (lone pair)–P–C(ipso)–C(ortho) torsional angles (τ) are found to be 25, 27, and 59°[20b] in free PPh_3. In reasonable agreement, a structure built utilizing the normal PCMODEL input routines and assuming an approximate propeller shape exhibited, on minimization, torsional angles τ of 30, 37, and 48°; however, a survey of the conformational energy profile utilizing the dihedral driver to force the rotation of one ring demonstrated several local minima differing by <0.4 kcal mol^{-1}. It has been suggested that the conformations of $OPPh_3$ and $SPPh_3$ in the solid state are determined by inter- rather than intramolecular interactions,[13] and the same is presumably true for PPh_3. Phenyl rotation in free PPh_3 was found to involve a two-ring flip mechanism,[12a,b] the calculated barrier being ≈0.8 kcal mol^{-1}; no experimental data are available.

Although the crystal structure of $Ni(CO)_3PPh_3$ does not appear to have been published, we find a calculated structure very similar to those of the isoelectronic compounds $Mn(NO)_3PPh_3$, $Co(CO)_2(NO)PPh_3$, and $Fe(CO)(NO)_2PPh_3$.[13] Thus the PPh_3 ligand of $Ni(CO)_3PPh_3$ assumes a somewhat distorted structure in which the three phenyl groups are twisted at metal–P–C(ipso)–C(ortho) torsional angles τ of about 29, 48, and 45°, compared with 45 ± 9° for the manganese, cobalt, and iron analogues. The calculated barriers to PPh_3 and phenyl rotation are 2.4 and 3.6 kcal mol^{-1}, respectively, the former, as anticipated, being significantly less than the barriers found for the sterically more crowded η^6-arene and $\eta^5\text{-}C_5H_5$ complexes. Also as anticipated, the barrier to phenyl rotation in $Ni(CO)_3PPh_3$ is intermediate between the barrier calculated for free PPh_3 and that estimated above for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$.

Summary. We have found that the MMX methodology permits highly accurate estimates of the steric barriers to PPh_3 rotation in the compounds $(\eta^6\text{-}C_6Me_6)Cr(CO)_2PPh_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$. In addition, MMX also seems quite capable of determining the torsional angles associated with the coordinated phosphines.

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