J. Am. Chem. Soc. 1991, 113, 2854-2861

Conformational Analysis and Dynamics of the Triphenylphosphine Ligand in $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_3]$

Stephen G. Davies,*[†] Andrew E. Derome,[†] and John P. McNally[‡]

Contribution from the Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, United Kingdom, and BP Research Centre, Chertsey Road, Sunbury-on-Thames TW16 7LA, United Kingdom. *Received July 31, 1990*

Abstract: Conformational analyses are reported on the chiral iron acetyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe]$ (**1**) and the two fluorinated derivatives, $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(3,5\text{-}C_6H_3F_2)_3\}COCH_3]$ (**2**) and $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(C_6F_5)Ph_2\}COCH_3]$ (**3**), to characterize the dynamic processes of the triphenylphosphine ligand. Calculations indicate that rotation of the phenyl rings about the P–C_{ipso} bonds within **1** are facile ($\Delta G^{\ddagger}_{calc}$ = 5 kcal mol^{-1}), and a correlated cog-like rotation of the three rings is identified as a low-energy pathway for ring flip. A higher energy phosphine rotational process about the P–Fe bond is also identified for **1** ($\Delta G^{\ddagger}_{calc}$ = 12 kcal mol^{-1}) which requires correlated motion of the phenyl rings about the P–C_{ipso} bonds to minimize steric interactions with the congested metal center. Similar dynamic properties of the triphenylphosphine ligand in the partially fluorinated derivatives **2** and **3** are also predicted. Variable-temperature $^{13}C\{^1H\}$ NMR spectroscopic studies on **1** corroborate the molecular modelling predictions on the dynamic processes of the triphenylphosphine ligand: line-shape analyses on the aromatic subspectra were employed to determine an activation energy for phosphine rotation about the P–Fe bond, $\Delta G^{\ddagger}_{exp}$ = 10.3 ± 0.1 kcal mol^{-1}, whereas phenyl ring rotation about P–C_{ipso} was found to be rapid on the NMR time scale down to −90 °C. Similar variable-temperature $^{19}F\{^1H\}$ NMR spectroscopic studies and line-shape analyses on **2** found $\Delta G^{\ddagger}_{exp}$ = 10.8 ± 0.1 kcal mol^{-1} for rotation of the phosphine about the P–Fe bond, and no evidence for arrest of phenyl ring rotation down to −90 °C could be found. A full line-shape analysis of the $^{19}F\{^1H\}$ NMR spectrum of **3** clearly indicates that phenyl ring rotation is rapid at ambient temperature, in complete agreement with the conformational analysis.

Introduction

The fragment $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ is an effective chiral auxiliary for a wide variety of reactions of attached acyl ligands.[1] Empirically this stereocontrol has been described in terms of the chiral auxiliary orienting the acyl ligand to lie with the acyl oxygen anti to the carbon monoxide while the triphenylphosphine shields one face.[2,3] Although this naive interpretation allowed the easy and reliable prediction of stereoselective reactions, a more sophisticated conformational analysis for the chiral auxiliary was warranted. Extended Hückel and ab initio SCF MO calculations, the latter based on suitably simplified derivatives of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_3]$ (**1**), supported these empirical observations and revealed that the conformational preference for the acetyl oxygen to lie anti to the carbon monoxide was due to steric interactions with an ortho hydrogen on one of the phenyl rings of the triphenylphosphine with concomitant shielding of one face of the acetyl ligand by a second phenyl group.[2b] Subsequently, molecular modelling techniques were used to study **1** in detail, and the influence of triphenylphosphine on acyl ligand conformations was generalized for all classes of η^1-acyl complexes.[3]

These conformational analyses were based on a static model of the triphenylphosphine ligand. Although many theoretical and experimental studies of phosphines and phosphonium salts, etc., have been undertaken by Mislow and others,[4,5] much less is known about the dynamic behavior of the triphenylphosphine ligand in organometallic species.[6] The observation of two ν(CO) absorption bands in the solution IR spectra for complexes of the form $[(\eta\text{-}C_5R_5)M(CO)(PPh_3)X]$ has been attributed to the existence of more than one possible conformation of the PPh_3 ligand,[6a,f,h] but unfortunately, no further characterization of the phenomenon was possible. Similarly, the identification of two ν(NN) absorption bands in the IR spectra of $[(\eta\text{-}C_5Me_5)Re(CO)(PPh_3)(N_2)]$ has recently been suggested by Klahn and Sutton as indicative of conformational isomerism of the phosphine.[6a] Variable-temperature NMR studies have been more successful in characterizing the dynamic processes of coordinated triphenylphosphine, and estimated energy barriers to M–P bond rotation have been reported for several organometallic complexes.[6b-g]

We describe here our investigations of the dynamic properties of the triphenylphosphine ligand within the acetyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_3]$ (**1**). Our investigations utilize a combination of variable-temperature multinuclear NMR spectroscopy and computer-aided molecular modelling techniques

---

[†] The Dyson Perrins Laboratory.

[‡] BP Research Centre.

(1) (a) Davies, S. G.; Dordor-Hedgecock, I. M.; Easton, R. J. C.; Preston, S. C.; Sutton, K. H.; Walker, J. C. *Bull. Soc. Chim. Fr.* **1987**, 608–630. (b) Davies, S. G. *Pure Appl. Chem.* **1988**, *60*, 13–20. (c) Davies, S. G.; Bashiardes, G.; Beckett, R. P.; Coote, S. J.; Dordor-Hedgecock, M.; Goodfellow, C. L.; Gravatt, G. L.; McNally, J. P.; Whittaker, M. *Philos. Trans. R. Soc. London, Ser. A* **1988**, *326*, 619–631. (d) Davies, S. G. *Aldrichimica Acta* **1990**, *23*, 31–37.

(2) (a) Davies, S. G.; Blackburn, B. K.; Whittaker, M. *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amerstadam, 1989; Vol. 3, pp 141–223. (b) Davies, S. G.; Seeman, J. I.; Williams, I. H. *Tetrahedron Lett.* **1986**, *27*, 619–622.

(3) Davies, S. G.; Blackburn, B. K.; Sutton, H.; Whittaker, M. *Chem. Soc. Rev.* **1988**, *17*, 147–179.

(4) For reviews, see: (a) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26–33. (b) Mislow, K.; Gust, D.; Finocchiaro, R. J.; Boettcher, R. J. *Top. Curr. Chem.* **1974**, *47*, 1–28. (c) Mislow, K. *Pure Appl. Chem.* **1971**, *25*, 549–562.

(5) A representative, but not comprehensive, list of publications in this area includes: (a) Wille, E. E.; Stephenson, D. S.; Capriel, P.; Binsch, G. *J. Am. Chem. Soc.* **1982**, *104*, 405–415. (b) Bye, E.; Schweizer, B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 5893–5898. (c) Dougherty, D. A.; Mislow, K.; Whangbo, M.-H. *Tetrahedron Lett.* **1979**, *25*, 2321–2324. (d) Kost, D.; Cozzi, F.; Mislow, K. *Tetrahedron Lett.* **1979**, *22*, 1983–1986. (e) Baxter, S. G.; Dougherty, D. A.; Hummel, J. P.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 7795–7798. (f) Brock, C. P.; Ibers, J. A. *Acta Crystallogr.* **1973**, *B29*, 2426. (g) Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535–1547. (h) Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535–1547. (i) Rauk, A.; Andose, J. D.; Frick, W. G.; Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6507–6515. (j) Mislow, K.; Baechler, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 773–774. (k) Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 4758–4759. (l) Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 3090–3093. (m) Farnham, W. B.; Herriott, A. W.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 6878–6879. (n) Halpern, E. J.; Mislow, K. *J. Am. Chem. Soc.* **1967**, *89*, 5221–5228.

(6) (a) Klahn, A. H.; Sutton, D. *Organometallics* **1989**, *8*, 198–206. (b) Hunter, G.; Weakley, T. J. R.; Weissensteiner, W. *J. Chem. Soc., Dalton Trans.* **1987**, 1545. (c) Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376–2388. (d) Docherty, J. B.; Rycroft, D. S.; Sharp, D. W. A.; Webb, G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 336–337. (e) Faller, J. W.; Johnson, B. V. *J. Organomet. Chem.* **1975**, *96*, 99–113. (f) Stanley, K.; Zelovka, R. A.; Thomson, J.; Fiess, P.; Baird, M. C. *Can. J. Chem.* **1974**, *52*, 1782. (g) Brown, J. M.; Mertis, K. *J. Organomet. Chem.* **1973**, *47*, C5. (h) Brown, D. A.; Lyons, H. J.; Manning, A. R. *Inorg. Chim. Acta* **1970**, *4*, 428.

0002-7863/91/1513-2854$02.50/0

on the complexes [(η^5-C_5H_5)Fe(CO)(L)$COCH_3$] with L = PPh_3 (**1**), P(3,5-$C_6H_3F_2$)$_3$ (**2**), and $PPh_2(C_6F_5)$ (**3**) to define the motions of the triphenylphosphine and its interactions with the acetyl ligand within **1**. Prior to this work, Ojima and Kwon[7] have proposed an alternative conformational and dynamic model for complex **3**, and their data are extended and reinterpreted.

Results and Discussion

Free triphenylphosphine possesses three rotational degrees of freedom, namely, rotation about the three P–C_{ipso} bonds. As has been well documented, the three phenyl rings of triphenylphosphine prefer, for steric reasons, to adopt a chiral propeller-like conformation with either a clockwise or anticlockwise screw configuration.[5a] The motions of the three phenyl rings are not completely independent, and interconversion of the two enantiomeric rotor configurations, or indeed full rotation about any P–C_{ipso} bond, requires a cooperative sequence of motions of the other two rings. Nonetheless, at ambient temperature the phenyl rings of triphenylphosphine are freely rotating, and the energy barrier to racemization is relatively low, as is the barrier to full rotation about the P–C_{ipso} bonds. In a conformational analysis study of free triphenylphosphine, Brock and Ibers estimated both barriers to be less than 2 kcal mol^{-1}.[5f]

On coordination of triphenylphosphine to a chiral metal center as in **1**, the two degenerate enantiomeric rotor configurations become diastereomeric. Rotation about the P–Fe bond adds an additional degree of freedom to the coordinated triphenylphosphine, and, if there were no interactions between the phosphine and the rest of the complex, then its complicated "whirling dervish" motion, as seen for the free phosphine, would be completely unconstrained. However, a cursory glance at a space filling model of **1** suggests that a number of constraints on the rotational freedom of the triphenylphosphine are sterically imposed. In fact, a survey[2,3] of all relevant crystal structures reveals that the acyl complexes [(η^5-C_5H_5)Fe(CO)(PPh_3)COR] are all of the diastereoisomer with the *R* configuration at iron and a clockwise screw for the triphenylphosphine ligand (or *S* at iron with an anticlockwise screw), suggesting that at least in the solid state this combination is thermodynamically the most stable.

(i) Molecular Modelling Studies on [(η^5-C_5H_5)Fe(CO)(PPh_3)COMe]. Molecular modelling studies using the CHEMX package,[8] which employ van der Waals and electrostatic interaction energy calculations on conformations generated by simple rigid rotor rotations about all appropriate single bonds, have proven remarkably successful in determining the accessible conformational space for a variety of iron acetyl complexes.[2,3,9] The triphenylphosphine ligand with only four degrees of rotational freedom seemed ideally suited for a similar computer-aided modelling analysis, with the aim in this case to determine the lowest energy conformation and dynamic processes of the ligand.

The iron acetyl complex **1** has a geometry about iron close to octahedral with the cyclopentadienyl ligand occupying three of the coordination sites. It is configurationally stable in solution, and phosphine dissociation is not a significant process at ambient temperature.[10] The modelling calculations were therefore limited to include only intramolecular dynamic processes with all atoms directly bound to iron remaining fixed. The single-crystal X-ray structure of **1** (Figure 1) was used as a starting point for all of the calculations conducted.[11] Our initial studies focused on determining the thermodynamically preferred conformation of the triphenylphosphine ligand in **1**. This is achieved in several ways, the simplest of which was to orient the three phenyl rings so that they were vertical[12] (and thus were not biased to one helical form over the other) and then allow the molecule to "relax" by minimizing van der Waals and electrostatic interactions through independent rotations about all appropriate bonds in the molecule. This calculation yielded a structure for **1** essentially identical with the solid-state conformation, with the same helical sense of the phosphine (clockwise screw for the *R* enantiomer) and disposition of the three phenyl rings with respect to the iron center, that is, with the carbon monoxide ligand staggered with respect to two of the P–C_{ipso} bonds. To prove that this conformation was indeed the lowest possible rather than a local minimum on what is a complicated conformation-energy surface, the three P–C_{ipso} bonds and P–Fe bond were independently driven through 180° and 120°, respectively, with concomitant minimization about all appropriate bonds at each conformation. This more rigorous (and considerably longer) calculation gave the same lowest energy conformation, although other conformers only slightly higher in energy were identified (vide infra). It appears that the solid-state conformation of **1** as determined from the crystal structure is not significantly influenced by "solid-state interactions", and our calculations indicate that this is certainly one of the lowest energy conformations, at least in nonpolar solutions.

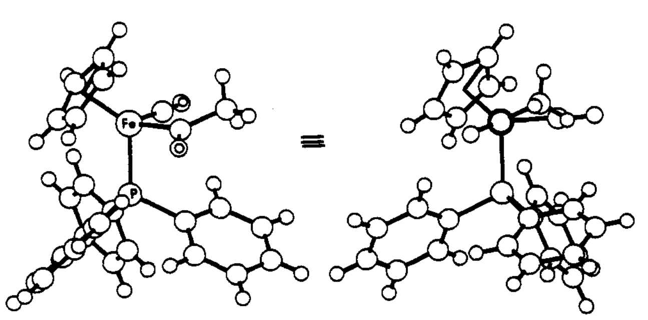

Figure 1. X-ray crystal structure of (*R*,*S*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)-$COCH_3$] (*R* enantiomer shown). Second view looking down the acyl C–Fe bond.

Upon confirming that the X-ray crystal structure of **1** does represent a realistic low-energy solution conformation, the identification and characterization of kinetically accessible dynamic processes of the triphenylphosphine ligand were initiated. As well as containing information concerning the lowest energy conformations of the triphenylphosphine ligand, calculations such as the one described above can also be used to evaluate low-energy dynamic processes. Starting with the crystal structure conformation of **1**, Figure 2 shows the calculated lowest energy pathway for a 120° rotation about the phosphorus–iron bond in a sequence of 5° increments (only every fourth optimized conformer is shown). Each phenyl ring undergoes a "rollercoaster"-type motion as it swings around the molecule, being forced to lie almost flat under the acyl and CO ligands, but relaxing to a nearly vertical orientation in the open space between the carbonyl and cyclopentadienyl ligands. The rotational energy, as calculated from steric and electrostatic interactions only and not allowing for bond stretching and bending terms, is 12 kcal mol^{-1}. Because of the necessary constraints imposed in the study, this energy can be considered an upper limit. The calculations also establish that neither helicity reversal nor phenyl ring rotations are *necessary* conditions for a low-energy rotational process about the iron–phosphorus bond, but they do not eliminate the possibility of other low-energy rotation pathways which incorporate these elements.

Low-energy processes for phenyl ring rotations were identified and evaluated next. Figure 3 shows the calculated lowest energy pathway for driving one phenyl ring through 180° in 5° increments (only every sixth conformation is shown) with minimization of each conformer by rotating about the remaining two P–C_{ipso} bonds, the P–Fe bond, the acyl–Fe bond, and the axis through the centroid of the cyclopentadienyl ring and iron. Since only the lowest energy *kinetic* pathways for ring rotations are of interest, the atomic

---

(7) Ojima, I.; Kwon, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 5617–5621.

(8) CHEMX, developed and distributed by Chemical Design Ltd., Oxford, U.K.

(9) Davies, S. G.; Bashiardes, G.; Coote, S. J.; Goodfellow, C. L.; McNally, J. P. *New Aspects of Organic Chemistry*; Yoshida, Z., Shiba, T., Ohshiro, Y., Eds.; VCH: Basel, 1990; Vol. 1, pp 81–111.

(10) A stirred THF solution of **1** at 20 °C in the presence of 10 equiv of PMe_3 shows no exchange of phosphine over a 1-week period.

(11) Bandy, J. A.; Davies, S. G.; Prout, K. Unpublished data. For data on the *S*-enantiomer see: Bernal, I.; Brunner, H.; Muschiol, M. *Inorg. Chim. Acta* **1988**, *142*, 235.

(12) Horizontal is defined by the plane through iron orthogonal to the Fe–P bond, and therefore vertical is any plane parallel to the Fe–P bond.

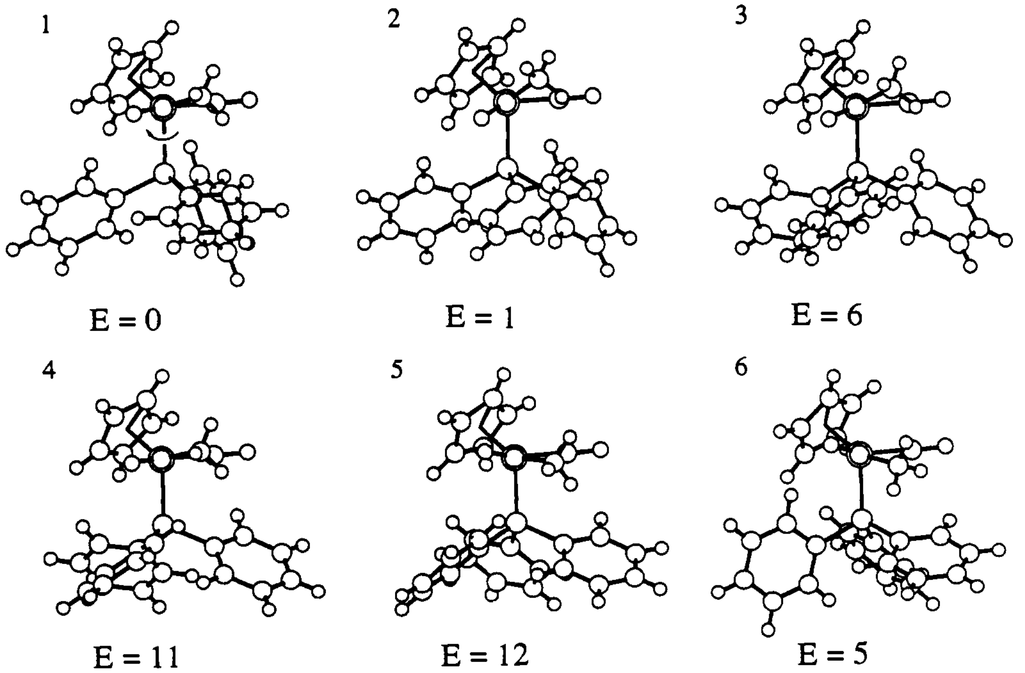

Figure 2. Lowest energy pathway for a 120° rotation about the P–Fe bond of complex **1**. The views depict incremental rotations of 20° in the direction shown, and energies (in kcal mol^{-1}) are relative to the crystal structure geometry seen in frame 1.

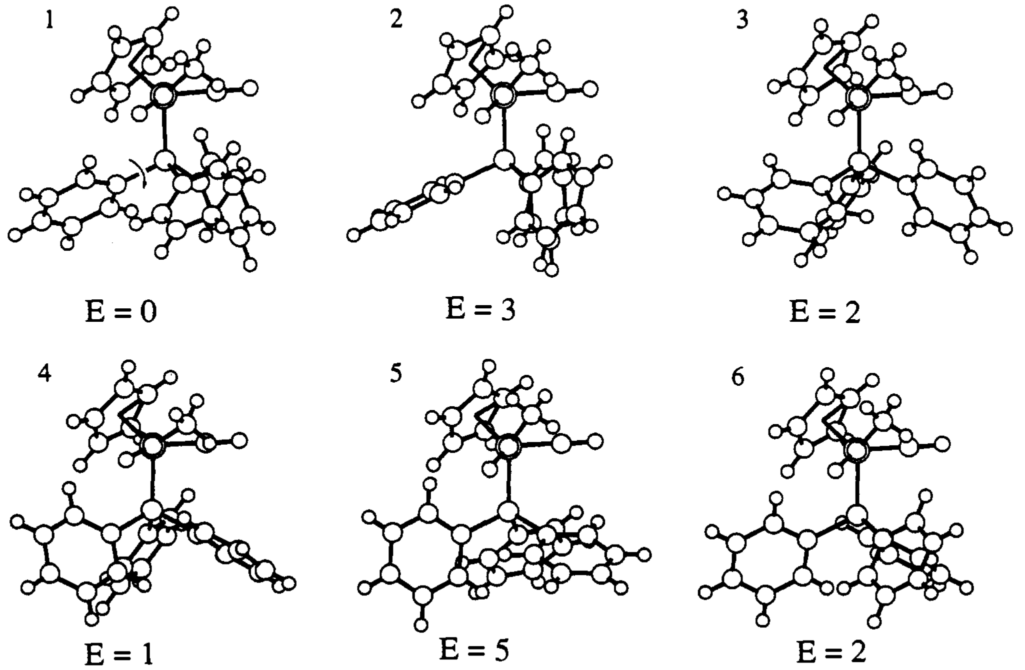

Figure 3. Lowest energy pathway for a 180° rotation about a C_{ipso}–P bond of complex **1**. The views depict incremental rotations of 30° in the direction shown. Energies (in kcal mol^{-1}) are relative to the conformer seen in frame 1, which has undergone a 10° rotation about the C_{ipso}–P bond from the crystal structure geometry (thus allowing for the inclusion in the figure of the highest energy conformer found in the calculation frame 5).

coordinates of each optimized conformer were used for the starting geometry of the next conformer, but for the further rotation of the chosen phenyl ring by 5°. This ensured that each optimized conformer on the lowest energy pathway was kinetically accessible from the previous one. Significantly, after driving the chosen ring the full 180°, the other two rings had also rotated 180°, yielding a conformation of the phosphine equivalent to the original. The motions of the three rings are therefore correlated in this low-energy rotation pathway like cogs on a mechanical gear.[13] As can be seen in Figure 3, phosphine helicity inversion can best be described as a sequence of two-ring and one-ring flips, using the nomenclature of Kurland.[14] The calculated highest energy conformations have one ring in a near-vertical orientation while the other two rings are nearly flat and orthogonal to the P–Fe bond (Frame 5). The meshing of the three rings is not very efficient, however, and "slipped cog" rotations (i.e., rotation of two rings by 180° without net rotation of the third ring) can occur with only minimal investments of energy relative to the correlated rotational process.

The calculated rotational energy about any of the P–C_{ipso} bonds is ca. 5 kcal mol^{-1}. It was surprising to find that the conformational calculations predict rotation about the P–C_{ipso} bonds which is considerably more facile than rotation about the P–Fe bond.

---

[13] For an excellent discussion on dynamic gearing at the molecular level, see: Iwamura, H.; Mislow, K. *Acc. Chem. Res.* **1988**, *21*, 175–182 and references within.

[14] Kurland, R. J.; Schuster, I. I.; Colter, A. K. *J. Am. Chem. Soc.* **1965**, *87*, 2279.

Space-filling models of the iron acetyl complex **1** show the iron center to be very congested and might lead one to the erroneous conclusion that rotation of a phenyl ring of the phosphine through the vertical is *necessarily* a high-energy process. Exhaustive conformational searches including the one above reveal that the triphenylphosphine can take advantage of the inhomogeneity of the steric congestion about the iron center and that low-energy pathways for ring rotations do exist which rely on relatively small but important oscillations around the P–Fe bond (±45°) to help "slip" the phenyl rings between the other ligands bound to the iron.

The acetyl ligand is shown by these calculations to have considerable flexibility during the dynamic processes of the triphenylphosphine ligand, much more so than found when modelling with a *static* phosphine. The acetyl oxygen, however, is always constrained to lie between the triphenylphosphine and cyclopentadienyl ligands in the lowest energy paths for both P–Fe and P–C_{ipso} rotations,[15,16] i.e., with the methyl group always lying syn to the carbon monoxide.

The calculations predict a slight energetic preference for the right-hand screw helicity for the *R* enantiomer of **1**, as found in the crystal structure. The difference in energy between the right- and left-hand screw configurations (frames 1 and 4 of figure 3, respectively) is only found to be 1 kcal mol^{-1}, however, and the ability of the steric interaction calculations to discern differences in conformational energy at this level must be questioned. What is clearly shown by the modelling study is that helicity reversal is a relatively low-energy process (calculated as ~3 kcal mol^{-1}) occurring through a two-ring flip mechanism as seen in the first four frames of Figure 3. The facility of this conversion between helical rotor forms would account for the lack of observation of conformational diastereomers by ^{1}H and ^{31}P NMR spectroscopy in literally hundreds of iron acyl derivatives.

(ii) Variable-Temperature ^{13}C NMR Spectroscopic Studies of [(η^5-C_5H_5)Fe(CO)(PPh$_3$)COCH$_3$] (1). Variable-temperature ^{13}C{^{1}H} NMR spectroscopic studies on **1** provided a means to verify experimentally some of the conclusions formed in the molecular modelling studies described above of the dynamic processes of the triphenylphosphine ligand. The room-temperature ^{13}C{^{1}H} spectra of **1** and indeed all other derivatives [(η^5-C_5H_5)Fe(CO)(PPh$_3$)-COR] show a similar set of three doublets and one singlet attributed to the triphenylphosphine ligand and easily assigned by P couplings and chemical shift as the ipso (J_{P-C} = 42.2 Hz), ortho (J_{P-C} = 9.5 Hz), para (J_{P-C} = 0.0 Hz), and meta (J_{P-C} = 9.5) carbons of the three aromatic rings (downfield to upfield). The observation of only four chemically inequivalent carbon resonances in all of these complexes immediately confirms that the triphenylphosphine ligand is indeed dynamic on the NMR time scale at ambient temperature. Rapid rotation about both the P–Fe and three P–C_{ipso} bonds must be invoked to account for the equivalence of all the ipso, ortho, meta, and para sets of carbons. A static structure of the triphenylphosphine ligand attached to the chiral iron center would result in all 18 carbon atoms of the phenyl rings being chemically inequivalent. If only rotation about the P–Fe bond were rapid, then all three rings would be equivalent, but the ortho and meta positions within each ring would not be, resulting in an anticipated observation of six resonances. Alternatively, if only rotation about the three P–C_{ipso} bonds were rapid at room temperature, then each ring would be chemically inequivalent, but the ortho and meta positions within each ring would be averaged, resulting in 4 resonances per ring and 12 resonances in total. Thus on cooling, if the rotation about the P–Fe bond becomes slow on the NMR time scale, each original resonance observed in the ambient spectrum will split into three, whereas if rotation about each P–C_{ipso} becomes slow, then the ortho and meta resonances will split into two whereas the ipso and para resonances will not split. The utility of low-temperature ^{13}C NMR studies in exploring the rotational processes of coordinated triphenylphosphine ligands has recently been demonstrated by Hunter et al. in their study of (η^6-arene)Cr(CO)$_2$(PPh$_3$) derivatives.[6b]

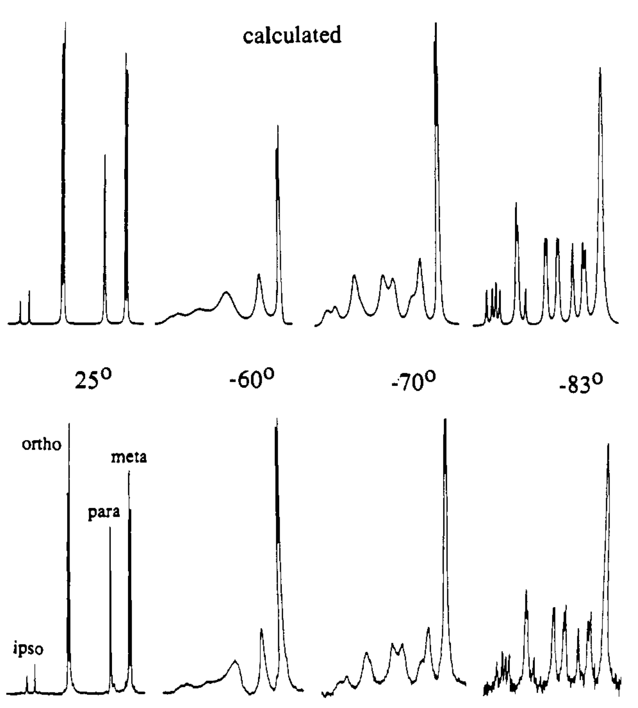

Figure 4. Variation in the aromatic region of the ^{13}C{^{1}H} NMR spectra of complex **1** upon cooling from 25 to −83 °C. Calculated spectra from line-shape analyses of the phenyl ring exchange process (see Table I) are shown above.

Table I. Phenyl Ring Exchange Rates Determined at Four Temperatures for Complex **1** by Line-Shape Analysis[a]

temp (K)	exchange rate k (s^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})
233	1000	10.3 ± 0.1
223	400	10.2 ± 0.1
213	150	10.2 ± 0.1
203	25	10.4 ± 0.1

[a] Gibbs free energies determined from exchange rates using the Eyring equation: $k = (\kappa T/h)\exp(-\Delta G^{\ddagger}/RT)$.

Upon cooling, the aromatic region of **1** becomes complex with the ipso, ortho, and para resonances broadening and eventually separating at −83 °C into three resonances for each position, with appropriate phosphorus coupling (Figure 4). The meta peak begins to broaden at −70 °C, but no separate resonances were resolved down to −90 °C. As each resonance clearly splits to three upon cooling, it is apparent that rotation about the P–Fe bond has been arrested, but P–C_{ipso} rotations are still rapid on the NMR time scale.[17] Line-shape analyses on the ^{13}C{^{1}H} NMR aromatic subspectra were used to determine the exchange rate (k) at four temperatues (Table I). These data were then used to evaluate $\Delta S^{\ddagger} = 0$ and $\Delta G^{\ddagger} = \Delta H^{\ddagger} = 10.3 \pm 0.1$ kcal mol^{-1}. The cyclopentadienyl and methyl carbon resonances showed no observable broadening down to −90 °C. All changes in the appearance of the spectrum were completely reversed upon warming.

Jones and Feher conducted band-shape analysis of variable-temperature NMR data and spin population transfer experiments to calculate $\Delta H^{\ddagger} = 15.7 \pm 0.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.8 \pm 0.2$ eu for Rh–P rotation in [(η-C_5Me_5)RhBr(C_6D_5)P(p-tol)$_3$], and $\Delta H^{\ddagger} = 14.3 \pm 0.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = 1.8 \pm 1.2$ eu for Rh–P rotation in [(η-C_5Me_5)RhBr$_2$P(p-tol)$_3$].[6c] The activation energies

---

(15) Although the lowest energy conformation of the acyl ligand has the acyl oxygen anti to the carbonyl ligand, our studies indicate that the syn conformer is kinetically accessible. This topic is discussed in more detail in another paper.[16]

(16) Davies, S. G.; McNally, J. P. Manuscript in preparation.

(17) It is conceivable that rotations about the three P–C_{ipso} bonds have also been arrested, but the magnetic environments of the resulting inequivalent ortho and meta positions of each ring are degenerate. The highly anisotropic nature of the chiral iron center, however, makes it very unlikely that accidental equivalence would be observed for all six pairs of resonances.

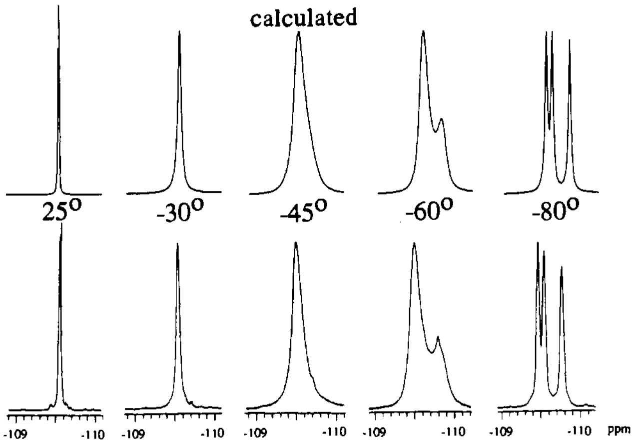

Figure 5. Variable-temperature $^{19}F\{^1H\}$ NMR spectra of complex **2**. Calculated spectra from line-shape analyses of the phenyl ring exchange process (see Table II) are shown above.

calculated for these rhenium complexes, which have a similar coordination geometry to the iron acetyls, is most likely a consequence of increased steric repulsion between the aryl rings and the methyl groups of the permethylated cyclopentadienyl ring. In contrast, Faller and Johnson estimate an upper limit of only 8.0 kcal mol^{-1} for the Fe–P rotation barrier in $[(\eta\text{-}C_5H_5)Fe(CO)(CN)PPh_3]$,[6e] which has less steric congestion about the metal than in the iron acetyls.

The conclusions from the variable-temperature ^{13}C NMR experiments are in agreement with the molecular modelling studies which indicate that rotation about the P–Fe bond is a higher energy process than rotation about the P–C$_{ipso}$ bonds, but that both processes are rapid at ambient temperature. The agreement between the calculated value for rotation about P–Fe (ca. 12 kcal mol^{-1}) and the experimental value (ca. 10 kcal mol^{-1}) is quite remarkable considering the simplicity of the modelling calculations. It would suggest that little stretching of the P–Fe bond, or bending of the C$_{ipso}$–P–Fe angles is necessary to facillitate the revolution of the PPh$_3$ under the sterically crowded iron center.

(iii) Variable-Temperature ^{19}F NMR Spectroscopic Analysis of $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(3,5\text{-}C_6H_3F_2)_3\}COCH_3]$ (2). In order to probe further the dynamic properties of the triphenylphosphine ligand in the acetyl complex **1**, the novel meta-perfluorinated triphenylphosphine derivative $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(3,5\text{-}C_6H_3F_2)_3\}COCH_3]$ (**2**) was prepared. This complex should have very similar steric properties to **1** with the small fluorine atoms situated on the meta positions of the phenyl rings where they should not influence significantly the dynamic processes of the ligand. The ^{19}F NMR spectrum of **2**, however, should simplify interpretation of fluxional processes since arrest of all motion of the triarylphosphine ligand on the NMR time scale will give rise to six separate fluorine resonances (as compared to the 18 possible ^{13}C resonances for **1**). Freezing out of only the P–Fe rotation should result in the observation of three ^{19}F resonances, whereas freezing out of only the three P–C$_{ipso}$ rotations should give two resonances.

The synthesis of complex **2** was conducted in two steps. Photolysis of a tetrahydrofuran/cyclohexane (2:1) solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_3)]$ and $P(3,5\text{-}C_6H_3F_2)_3$ gave $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(3,5\text{-}C_6H_3F_2)_3\}(CH_3)]$ in good yield. Carbonylation of this intermediate with concomitant carbon monoxide insertion by pressurizing under 4.2 atm of carbon monoxide in the presence of 1 equiv of boron trifluoride gave the product **2** in moderate yield.

The room-temperature $^{19}F\{^1H\}$ NMR spectrum of complex **2** shows, as anticipated, a single fluorine doublet ($J_{P\text{-}F}$ = 4.6 Hz). The observation of a clean septet ($J_{P\text{-}F}$ = 4.6 Hz) in the $^{31}P\{^1H\}$ spectrum confirms that the doublet arises from phosphorus coupling. As the probe is cooled, the fluorine doublet broadens with loss of observable splitting, and eventually resharpens as three singlets at −90 °C. The line widths of the three resonances at this temperature precluded the observation of phosphorus coupling, but presumably this would have reappeared at a lower temperature. The observation of only three singlets again indicates that P–Fe rotation has been stopped, but P–C$_{ipso}$ rotations are still rapid on the NMR time scale. Figure 5 shows the variable-temperature $^{19}F\{^1H\}$ NMR spectrum for **2** together with the calculated spectra based on the arrest of rotation about the P–Fe bond but with continued rapid rotation about the C$_{ipso}$–P bonds.

Table II. Phenyl Ring Exchange Rates Determined at Four Temperatures for Complex **2** by Line-Shape Analyses[a]

temp (K)	exchange rate k (s^{-1})	$\Delta G^‡$ (kcal mol^{-1})
243	1000	10.8 ± 0.1
228	200	10.8 ± 0.1
213	40	10.8 ± 0.1
193	1.5	11.0 ± 0.1

[a] Gibbs free energies determined using the Eyring equation.

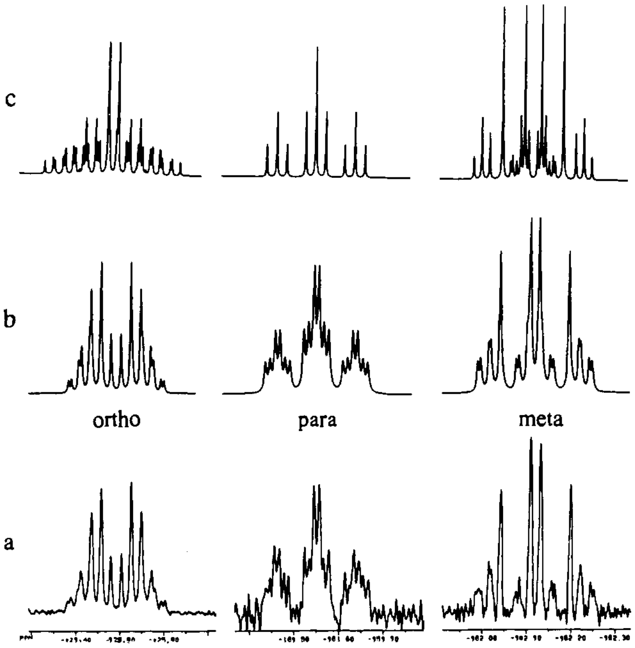

Figure 6. (a) $^{19}F\{^1H\}$ NMR spectrum of complex **3**. (b) Calculated spectrum assuming rapid rotation about the C$_{ipso}$–P bond and a corresponding AA′MM′QX spin system (see text). (c) Calculated spectrum assuming no rotation about the C$_{ipso}$–P bond using the coupling constants proposed by Ojima and Kwon (see text).

Line-shape analyses were possible at four temperatures (Table II) from which $\Delta S^‡$ was evaluated to be essentially zero as for the nonfluorinated complex **1**, and $\Delta G^‡ = \Delta H^‡ = 10.8 \pm 0.1$ kcal mol^{-1}. The similarity of the experimentally derived P–Fe rotation energies for the meta-perfluorinated complex **2** and the nonfluorinated complex **1** ($\Delta G^‡$ = 10.3 kcal mol^{-1}) support the original assertion that the small fluorine atoms would not significantly influence the energetics of phosphine dynamic processes.

(iv) NMR Studies of $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(C_6F_5)(C_6H_5)_2\}COCH_3]$. A recent report by Ojima and Kwon[7] which discusses the dynamic processes of the phosphine ligand of $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(C_6F_5)(C_6H_5)_2\}COCH_3]$ (**3**) postulated motions of this pentafluorinated derivative which are fundamentally different from the ones elaborated above. In particular, the calculated and experimentally verified facility for rotations about the P–C$_{ipso}$ bonds in the iron acetyl complex **1**, and the fluorinated derivative **2**, was inconsistent with Ojima and Kwon's analysis of the dynamic processes of the pentafluorinated complex **3** in which rotation about the P–C$_{ipso}$ bond of the perfluorinated phenyl ring *does not* occur at ambient temperature, and, furthermore, it is implied that this rotational process is slow on the NMR time scale even at 100 °C.[7] Figure 6a shows the $^{19}F\{^1H\}$ NMR spectrum of **3** in CDCl$_3$. Ojima and Kwon interpreted the complex multiplet centered at −125.5 ppm in CDCl$_3$ as overlapping resonances for *diastereotopic ortho* fluorines. If the two ortho fluorines are indeed diastereotopic, and therefore chemically inequivalent, then rapid rotation of the pentafluorophenyl ring on the NMR time scale cannot be occurring as this process would *necessarily* render the ortho (and meta) positions of the ring chemically equivalent. We believe, however, that this assignment of the $^{19}F\{^1H\}$ NMR spectrum of **3** is incorrect and that the spectrum in fact derives from the AA′MM′QX spin system due to the phosphorus (X), ortho fluorines which are chemically equivalent (but magnetically inequivalent AA′), magnetically inequivalent meta fluorines (MM′), and the para fluorine (Q). This system gives a familiar type AA′XX′ pattern, but with further first-order splittings by the two extra nuclei, and can only arise if rotation about the $P\text{–}C_{ipso}$ bond of the pentafluorophenyl is rapid on the NMR time scale.

Direct analysis of the fluorine spectrum for complex **3** is impractical because of the lack of resolution of some of the weak lines, but it is possible to proceed by comparison with the spectrum of the free ligand $(C_6H_5)_2(C_6F_5)P$.[18,19] Analysis by standard methods (see Experimental Section) yields the following parameters for this compound: $J_{AX} = J_{A'X} = 38.3$ Hz; $J_{MX} = J_{M'X} = 0.0$ Hz; $J_{QX} = 0.6$ Hz; $J_{AA'} = 1.4$ Hz; $J_{AM} = J_{A'M'} = -23.9$ Hz; $J_{AM'} = J_{A'M} = 9.5$ Hz; $J_{AQ} = J_{A'Q} = 4.1$ Hz; $J_{MM'} = 4.3$ Hz; $J_{MQ} = J_{MQ'} = -20.6$ Hz. Comparison with the complex **3** indicates that the principal change on complexation is a reduction in the ortho F–P coupling to ca. 5 Hz; with minor adjustments to the other parameters, a good match between simulated and observed spectra is obtained as follows: $J_{AX} = J_{A'X} = 5.4$ Hz; $J_{MX} = J_{M'X} = 0.0$ Hz; $J_{QX} = 2.5$ Hz; $J_{AA'} = 1.4$ Hz; $J_{AM} = J_{A'M'} = -24.3$ Hz; $J_{AM'} = J_{A'M} = 8.2$ Hz; $J_{AQ} = J_{A'Q} = 5.3$ Hz; $J_{MM'} = 5.7$ Hz; $J_{MQ} = J_{MQ'} = -20.6$ Hz. The calculated phosphorus coupling to the ortho fluorines ($J_{Po\text{-}F} = 5.4$ Hz) and para fluorines ($J_{Pp\text{-}F} = 2.5$ Hz) was experimentally verified by the observation of a doublet of triplets in the ^{31}P NMR spectrum of **3** with $J_{Po\text{-}F} = 6.2$ Hz and $J_{Pp\text{-}F} = 2.5$ Hz. The predicted spectrum of complex **3** based on rapid rotation of the perfluorinated phenyl ring and using the coupling constants described above is shown in Figure 6b.

The $^{19}F\{^1H\}$ NMR spectrum of **3** is only consistent with chemically equivalent ortho and meta fluorines, since any further reduction in symmetry leads to greater complexity. For instance, Ojima and Kwon's proposed model has zero coupling to phosphorus, $J_{o\text{-}o} = 10.6$ Hz, $J_{o\text{-}p} = 5.3$ Hz, $J_{o\text{-}m} =$ (presumably −)21.2 Hz, other couplings not stated and hence assumed equal to those of the free phosphine, chemical shift differences between presumed diastereotopic ortho fluorines not stated, but implied to be ca. 20 Hz, and meta fluorines presumed chemically equivalent. These parameters yield the simulated spectrum of Figure 6c. The ^{19}F NMR data for **3**, therefore, clearly indicates that rotation of the pentafluorophenyl group is rapid at room temperature.

The $^{13}C\{^1H\}$ NMR spectrum of complex **3** taken in $CDCl_3$ at ambient temperature is in full agreement with the conclusions of the ^{19}F NMR spectrum analysis. Although the carbon resonances for the perfluorinated phenyl ring are complex owing to extensive phosphorus and fluorine couplings, only three multiplets are observed for the ortho, meta, and para positions. This suggests that the two ortho carbons and the two meta carbons are chemically equivalent, which can only be true if the pentafluorinated phenyl is rapidly rotating on the NMR time scale. The ^{13}C spectrum also shows only one ortho and one meta resonance for each diastereotopic nonfluorinated phenyl ring which confirms that these two phenyl rings are also rotating rapidly at room temperature, as anticipated.

A second conclusion of the Ojima and Kwon analysis of the dynamic behavior of complex **3** is that rotation about the Fe–P bond is fixed at 25 °C. Unfortunately, the pentafluorinated triphenylphosphine is a poor ligand for the analysis of dynamic processes about the P–Fe bond; since the phosphine does not have 3-fold rotational symmetry, the three possible staggered conformers of the phosphine with respect to the iron center are not necessarily degenerate in energy. Consequently, one cannot readily distinguish by NMR spectroscopy a situation in which the phosphine has been frozen into one and only one low-energy rotamer, which Ojima and Kwon postulate has occurred in complex **3**, from the other dynamic extreme in which rotation about the P–Fe bond is rapid on the NMR time scale. In light of our conclusions for the dynamic processes of complexes **1** and **2**, which clearly indicate that rapid rotation about the P–Fe bond is occurring at ambient temperatures, it is unlikely that the perfluorination of one phenyl ring would cause such a drastic change in the energetics of rotation about the P–Fe bond, and we believe, therefore, that rapid rotation about this bond at ambient temperature is the most logical conclusion.

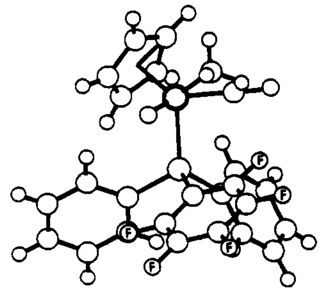

Figure 7. Calculated lowest energy conformer of complex 3.

Conformational analyses on complex **3** similar to those which proved successful in predicting the dynamic processes of the parent acetyl complex **1** support this prediction. The calculations, based on steric interactions only, indicate that the rollercoaster rotation about the Fe–P bond allows the interchange of all three possible rotamer forms of the $PPh_2(C_6F_5)$ ligand with respect to the iron center of **3** with an energy barrier calculated to be 16 kcal mol^{-1} compared to the value of 12 kcal mol^{-1} found for **1**. Again this energy barrier must be considered an upper limit for steric interactions as no account is made of possible bond stretching and bending, which will undoubtedly be more important for the fluorine-substituted phosphine. Nonetheless, interconversion of rotamers is calculated to be ca. 10 s^{-1} at 25 °C for this energy barrier, which is at odds with the proposal that the sharp $^{19}F\{^1H\}$ NMR spectrum of **3** is indicative of a *static* and singly occupied phosphine rotamer. The calculations also clearly establish that there is no substantial steric preference between the three staggered rotamers of the phosphine with respect to the Fe centers, as there must be if the NMR data for this complex are to be interpreted in terms of a singly occupied rotamer. It has been proposed[7] that an electron donor–acceptor-type interaction is formed between the acetyl oxygen and the perfluorinated ring in the rotamer which places the ring adjacent to the acetyl ligand, and this electronic interaction *cannot* be accounted for in molecular mechanics calculations such as the ones we have applied. However, if this interaction were energetically significant, then rotation of the perfluorinated ring, which would necessarily break the interaction twice per revolution, would not occur. The clear NMR evidence for rapid rotation of this ring discussed above leads to the conclusion that a charge-transfer interaction, if it exists, is not a significant influence on the dynamic processes of **3** at ambient temperature.

The conformational calculations also clearly show that on steric grounds helical configurations of the phosphine are lowest in energy, with both the clockwise and anticlockwise screw conformations calculated to be within 1 kcal mol^{-1}, similar to that found for the parent acetyl **1**. The calculated lowest energy conformation for **3** is shown in Figure 7. In contrast, Ojima and Kwon propose that conformations of **3** based on a clockwise propeller structure for the phosphine "severely suffer from steric conflicts with other ligands, e.g., Cp, acetyl, and CO". The "most favorable" and hence lowest energy conformation proposed by these authors for **3** is shown in Figure 8 and is similar to the transition state for a two-ring flip helical inversion process with the two unsubstituted phenyl rings in near-vertical orientations. Steric interaction calculations conducted on this conformation, in which we constrain the perfluorinated ring to lie flat (that is,

---

[18] Which in the $^{19}F\{^1H\}$ NMR spectrum also exhibits the expected AA′MM′QX coupling pattern due to rapid rotation about all $P\text{–}C_{ipso}$ bonds.[20]

[19] Hogben, M. G.; Graham, W. A. G. *J. Am. Chem. Soc.* **1969**, *91*, 283–291.

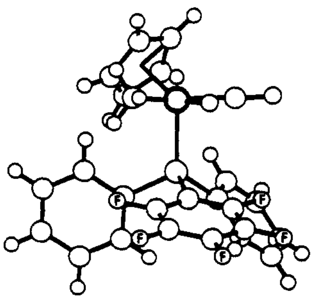

Figure 8. Lowest energy conformation for complex **3** proposed by Ojima and Kwon.

with the torsion angle $C_{ortho}-C_{ipso}-P-Fe = 90°$) and the methyl group to lie anti to the carbonyl, but allowed rotations about both unsubstituted phenyl rings and the P–Fe bond found that the lowest energy conformation under these constraints was 5 kcal mol^{-1} higher than that shown in Figure 7.

The fourth point in which we disagree with the dynamic model of Ojima and Kwon concerns their conclusion that the two unsubstituted phenyl rings in complex **3** undergo correlated rotation *independent* of the perfluorinated ring which can be frozen out on the NMR time scale below −60 °C. In light of the conclusive proof that the perfluorinated ring is rotating rapidly at ambient temperature, the need to invoke independent rotation of the two unsubstituted rings becomes unnecessary since a completely correlated rotation of all three rings similar to that described for the parent acetyl complex **1** would be anticipated. Furthermore, modelling calculations on this process which incorporate the constraint on the perfluorinated ring to lie flat clearly indicate that severe ortho–ortho interactions between the fluorinated and unfluorinated rings arise upon independent rotation of the unsubstituted rings which completely rule out such a motion.

Ojima and Kwon propose that changes in the shape and positions of the complex aromatic multiplets observed in the ^1H NMR spectrum of complex **3** upon cooling to −100 °C can be attributed to the freezing out of phenyl ring rotations. The lack of evidence for arrest of ring rotations in the similar complexes **1** and **2** at low temperature leads us to the conclusion that a more reasonable interpretation of these data is that rotation about the P–Fe bond is slowing on the NMR time scale, as found in complexes **1** and **2**, and that resonances for three distinct rotamers of the phosphine are resolving. The broadening of ortho, meta, and para ^{13}C resonances for the two unsubstituted phenyl rings of **3** upon cooling to −90 °C is in accord with this interpretation. Note that if the broadening observed in the ^{13}C spectrum were only a result of the slowing of phenyl ring rotation, then the para carbon resonances would be expected to remain sharp, and only the ortho and meta positions would broaden. No observable difference in the degree of broadening for the para peaks was observed. As discussed above, the population of the three rotamers need not be equal for this complex, and this factor, together with further possible perturbations in the spectrum from dynamic processes of the acetyl ligand discussed by Ojima and Kwon would account for the complexity of the cooled spectrum of **3** in comparison to the readily interpreted low-temperature spectra of complexes **1** and **2**.

Conclusions

A combination of molecular modelling calculations and NMR spectroscopic studies have proven remarkably effective at qualitative and quantitative elucidation of the intimate dynamic processes of the triphenylphosphine ligand in the chiral iron acyl complex **1** and the fluorinated derivatives **2** and **3**. The studies have revealed the following.

Rotation of the phenyl rings about the $P-C_{ipso}$ bond is facile with $\Delta G^{\ddagger}_{calc} = 5$ kcal mol^{-1} for **1**. Low-temperature NMR studies fail to observe arrest of the rotation down to −90 °C.

The mechanism of phenyl ring rotation is complex and requires concerted motion of all three phenyls and an oscillation about the P–Fe bond. The calculated lowest energy pathway for phenyl ring flip involves consecutive rotation of the other two rings in a cog-like fashion. "Slipped-cog" rotations in which one phenyl ring does not flip with the other two can occur with only slightly higher energetic paths.

Rotation about the P–Fe bond is a considerably higher energy process, but still rapid at ambient temperature; $\Delta G^{\ddagger}_{calc} = 12$ kcal mol^{-1}, $\Delta G^{\ddagger}_{exp} = 10.3 \pm 0.1$ kcal mol^{-1} for **1**.

The mechanism of phosphine rotation again is calculated to involve concerted motion of the three phenyl rings which must dip flat under the acyl and carbonyl ligands, and then open to a nearly vertical orientation in the space between the CO and cyclopentadienyl ligands.

The acyl ligand is calculated to have considerably more rotational flexibility about the C–Fe bond than observed for similar calculations with a static phosphine. The acyl oxygen, however, is still confined to lie in the spatial quadrant between the PPh_3 and cyclopentadienyl ligands, anti to CO. Our explanation of the stereoselectivity of reactions on the acyl fragment which relies on the anti nature of the acyl oxygen and CO ligand are thus qualitatively unaffected by the dynamic properties of the phosphine ligand.

The particular success of the molecular modelling efforts in this study serves to underline the value of simple steric and electrostatic interaction calculations as a mechanistic tool in organometallic chemistry. Further efforts to evaluate conformational and dynamic processes of phosphine complexes with the aid of molecular modelling are currently underway.

Experimental Section

General. ^1H NMR spectra were recorded on a Bruker WH-300 spectrometer at 300.13 MHz and referenced to residual protio solvent with chemical shifts being reported as δ ppm from TMS. ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded on a Bruker AM-250 spectrometer at 62.90 MHz (referenced to TMS), 101.26 MHz (externally referenced to triethyl phosphate in D_2O), and 235.35 MHz (externally referenced to $CFCl_3$), respectively. Mass spectra were recorded on a V.G. micromass ZAB 2F instrument using EI and FD techniques. IR spectra were recorded on a Perkin-Elmer 1710. Elemental analyses were performed by the Dyson Perrins Analytical Service.

All reactions and purifications involving organometallic species were performed under nitrogen atmosphere using standard vacuum-line techniques. Tetrahydrofuran was died over sodium benzophenone ketyl and distilled. Dichloromethane was dried over calcium hydride and distilled. Hexane refers to that fraction boiling between 67 and 70 °C. The phosphines $P(3,5\text{-}C_6H_3F_2)_3$ and $PPh_2(C_6F_5)$ were prepared in standard fashion[20] from PCl_3 and $3,5\text{-}C_6H_2F_2Li$, and PPh_2Cl and C_6F_5Li, respectively. $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(C_6F_5)(C_6H_5)_2\}COCH_3]$ (**3**) was prepared following the procedure of Ojima and Kwon.[7]

Molecular Modelling Calculations. All molecular modelling calculations were conducted using the CHEMX modelling package[9] on a Vaxstation 3520. The van der Waals interaction potential within the software package is that of Del Re et al.[21] and takes the form:

$$V(\text{pot}) = A\exp(-Br)/r^D - C/r^6$$

In all calculations, steric contributions to V(pot) from the iron atom were not included because of lack of adequate parameterization. For the calculations conducted, however, steric influences of the Fe center on phosphine dynamic processes are considered to be negligible. The cyclopentadienyl ligand was treated as a rigid body and rotated about the axis from the centroid of the C5 ring to the Fe atom. Bond lengths for the C–F (1.340 Å), C_{ipso}–P (1.847 Å), and P–Fe (2.273 Å) bonds for complex **3** (for which no crystal structure was available) were taken from a statistical compilation of bond lengths determined by X-ray and neutron diffraction.[22] Rotational conformers were generated by incrementally revolving one or more bonds independently through 360° or a symmetry reduction fraction of 360° (i.e., 180° for a phenyl ring). The summation of electrostatic and van der Waals energy was minimized for each conformation by independent rotations about all other single bonds

---

(20) Wakefield, B. J. *Organolithium Methods*; Academic Press: London, 1988; Chapter 14.3 and references therein.

(21) Del Re, G.; Gavuzzo, E.; Giglio, E.; Lelj, F.; Mazza, F.; Zappia, V. *Acta Crystallogr.* **1977**, *B33*, 3289.

(22) (a) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc. Perkin Trans. 2* **1987**, S1. (b) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

J. Am. Chem. Soc. **1991**, *113*, 2861–2865

(except those to hydrogen) within the molecule.

NMR Simulations and Analyses. The $^{19}F\{^1H\}$ spectrum of $P(C_6F_5)Ph_2$ was analyzed by iterative least-squares fitting using the program UEA/NMR II[23] running on a SUN-4/260. The best fit to the spectrum of **3** was then obtained by manual adjustment of the appropriate parameters, and direct comparison between the simulated and experimental spectra. Dynamic NMR spectra were simulated using the DNMR3 program,[24] modified to permit calculation of spectra as a sum of several independent exchanging systems.

Preparation of $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(3,5\text{-}C_6H_3F_2)_3\}COMe]$ (2). A deoxygenated solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Me]$ (0.69 g, 3.6 mmol) and $P(3,5\text{-}C_6H_3F_2)_3$ (1.3 g, 3.6 mmol) in tetrahydrofuran/cyclohexane (2:1) was photolyzed with a Hanovia 125-W medium-pressure Hg arc lamp for 5.5 h. Volatiles were removed from the resulting red solution under vacuum to yield a red oil which was shown by ^1H NMR to be an 8:3 mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(3,5\text{-}C_6H_3F_2)_3\}Me]$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Me]$ (the methyl resonance for the phosphinated derivative showing characteristic coupling to phosphorus $J_{P\text{-}H} = 8$ Hz). The oil was taken up in 35 mL of THF and after addition of 1 equiv of $BF_3{\cdot}Et_2O$ (43 μL, 3.6 mmol) charged to a Fisher–Porter bottle and pressurized with CO (120 psi) for 3 days. The vessel was then depressurized and of 50 mL/H_2O added. The mixture was extracted with dichloromethane (3 × 50 mL) and dried over Na_2SO_4; volatiles were removed under vacuum to give a red brown oil. Chromatography on Grade I alumina with CH_2Cl_2–hexane allowed facile separation of the less polar starting material and methyl intermediate $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(3,5\text{-}C_6H_3F_2)_3\}Me]$ from the carbonyl inserted product. Collection of the final orange band and removal of solvent under vacuum gave analytically pure **2** (0.41 g, 0.72 mmol, 20%) as a bright orange foam. The collected starting material and phosphine exchanged methyl intermediate could be effectively recycled through the procedure. Anal. Calcd for $C_{26}H_{17}F_6Fe_1O_2P_1$: C, 55.55; H, 3.05. Found: C, 55.70; H, 4.23. IR (CH_2Cl_2): ν_{max} 1928 (CO), 1608 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.85–7.1 (9 H, m, $C_6H_3F_2$), 4.49 (5 H, d, $J = 1.3$ Hz, C_5H_5), 2.47 (3 H, s, CH_3). $^{13}C\{^1H\}$ ($CDCl_3$): δ 272.51 (d, $J_{P\text{-}C} = 22.5$ Hz, C≡O), 219.27 (d, $J_{P\text{-}C} = 30.0$ Hz, C=O), 162.73 (d of d of d, $J_{C\text{-}F} = 253.7$ Hz, $J_{C\text{-}F} = 16.5$ (11.8) Hz, $J_{C\text{-}P} = 11.8$ (16.5) Hz, C_{meta}). 139.64 (d of t, $J_{C\text{-}P} = 40.8$ Hz, $J_{C\text{-}F} = 6.7$ Hz, C_{ipso}), 116.00 (d of d, $J_{C\text{-}F} = 26.1$ Hz, $J_{C\text{-}P} = 11.3$ Hz, C_{ortho}), 106.41 (t, $J_{C\text{-}F} = 25.3$ Hz, C_{para}), 85.26 (s, C_5H_5), 52.03 (s, CH_3). $^{19}F\{^1H\}$ ($CDCl_3$): δ −109.53 (d, $J_{P\text{-}F} = 4.6$ Hz). Mass spectral analysis: $m/z = 562$.

Acknowledgment. We thank BP International Ltd. for a Venture Research Award.

---

[23] Loomes, D. J.; Harris, R. K.; Anstey, P. *The NMR Program Library*; SERC Daresbury Laboratory: Warrington, UK.

[24] Stephenson, D. S.; Binsch, G. *J. Magn. Reson.* **1978**, *32*, 141.

Cupric Ion Location and Adsorbate Interactions in Cupric Ion Exchanged H-SAPO-5 Molecular Sieve As Determined by Electron Spin Resonance and Electron Spin Echo Modulation Spectroscopies

Xinhua Chen and Larry Kevan*

Contribution from the Department of Chemistry, University of Houston, Houston, Texas 77204-5641.

Received September 24, 1990

Abstract: Locations of Cu^{2+} ions exchanged into H-SAPO-5 and interactions of Cu^{2+} ions with water, ammonia, and methanol have been investigated by electron spin resonance and electron spin echo modulation techniques. It has been determined that Cu^{2+} ions locate at a position inside a 12-ring channel, close to the center of a 6-ring window in hydrated, ammonia-adsorbed, and methanol-adsorbed CuH-SAPO-5 samples. The Cu^{2+} ion directly coordinates to three framework oxygens in all systems studied; it also directly coordinates to three water molecules in the hydrated sample and to three ammonia molecules in the ammonia-adsorbed sample. In methanol-adsorbed samples, the Cu^{2+} ion directly coordinates to two methanol molecules and indirectly coordinates to one methanol molecule at a greater distance. The more bulky size of methanol molecules compared to water and ammonia is likely the cause of fewer methanol molecules directly coordinated to Cu^{2+}.

Introduction

Silicoaluminophosphate (SAPO) molecular sieves form a new class of microporous crystalline materials comparable to the well-known zeolites, or aluminosilicate molecular sieves. Zeolites, which have been widely used for adsorption and catalysis, have pores or channels formed by aluminum and silicon tetrahedra linked by oxygen bridges. Substitution of other elements for Al and/or Si in the molecular sieve framework can yield various kinds of new materials. In 1982, Wilson et al. reported the synthesis of aluminophosphate ($AlPO_4$) molecular sieves.[1,2] The structures of $AlPO_4$ molecular sieves include novel structure types, such as $AlPO_4$-5, as well as structure types analogous to certain zeolites, such as $AlPO_4$-37 (faujasite structure). In 1984, Lok et al. reported the synthesis of SAPO molecular sieves,[3,4] which can be viewed as silicon-substituted $AlPO_4$. The numbering of structure types of SAPO follows that of $AlPO_4$, so that SAPO-5 denotes the SAPO molecular sieve that possesses the same framework structure as $AlPO_4$-5.

The SAPO-5 molecular sieve is composed of 4-ring, 6-ring, and 12-ring straight channels, which are interconnected by 6-ring windows (Figure 1). Because the SiO_2 tetrahedron is electrically neutral and, in SAPO-5, the number of AlO_2^- tetrahedra is slightly greater than the PO_2^+ tetrahedra, the SAPO-5 framework is slightly negatively charged.[5] The framework negative charges are balanced by H^+ ions and the cationic form of the templating agent in the as-synthesized SAPO-5 and by H^+ ions only in H-SAPO-5, the calcined form of SAPO-5. H^+ ions in H-SAPO-5

---

[1] Wilson, S. T.; Lok, B. M.; Flanigen, E. M. U.S. Patent 4310440, 1982.

[2] Wilson, T. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146–1147.

[3] Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannan, T. R.; Flanigen, E. M. U.S. Patent 4440871, 1984.

[4] Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1984**, *106*, 6092–6093.

[5] Flanigen, E. M.; Lok, B. M.; Patton, R. L.; Wilson, S. T. In *New Developments in Zeolite Science and Technology*; Murakami, Y., Iijima, A., Ward, J. W., Eds.; Proceedings of the 7th International Zeolite Conference; Elsevier: Amsterdam, 1986; pp 103–112.

0002-7863/91/1513-2861$02.50/0