Multiple Fluxional Processes in Chiral (Pentaphenylcyclopentadienyl)iron Complexes: X-ray Crystal Structure of $(C_5Ph_5)Fe(CO)(PMe_3)(HC{=}O)$ and the Barriers to Aryl, Phosphine, and Tripodal Rotation in $(C_5Ph_5)Fe(CO)(PMe_2Ph)C(O)Et$

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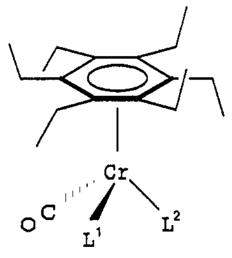
The X-ray crystal structure of $(C_5Ph_5)Fe(CO)(PMe_3)(HC{=}O)$ (**5**) reveals that the phenyl rings adopt a paddle-wheel orientation with an average tilt of 50° relative to the plane of the five-membered ring. **5** crystallizes in the monoclinic space group $I2/a$ with a = 24.159(8) Å, b = 12.868(7) Å, c = 25.861(9) Å, β = 93.95(5)°, V = 8021(1) Å^3, and Z = 8. ^{13}C and ^{31}P variable-temperature NMR spectra of the sterically crowded molecule $(C_5Ph_5)Fe(CO)(PPhMe_2)C(O)Et$ reveal the presence of two fluxional processes. When rotation of the chiral tripod becomes slow on the NMR time scale, the 5-fold degeneracy of the cyclopentadienyl ring carbons is split. Moreover, slowed rotation of either the peripheral phenyl rings or the phosphine ligand can give rise to a mixture of diastereomers. The barriers for these two processes (8.7 ± 0.3 and 11.7 ± 0.3 kcal mol^{-1}, respectively) demonstrate that the two types of fluxional behavior are not correlated.

Introduction

Fluxional processes in organometallic systems are frequently hidden and can only be detected when the symmetry of the system is judiciously broken.[1] Typically, in (hexaethylbenzene)$Cr(CO)_3$ (**1**), the slowed rotation of the ethyl groups at low temperature is readily detectable by NMR since the proximal and distal ethyl substituents are readily differentiable in either the ^{13}C or ^1H regimes.[2,3]



1 : $L^1 = L^2 = CO$

2 : $L^1 = CS$; $L^2 = NO^+$

In contrast, one cannot probe whether the ML_3 moiety can rotate slowly on the NMR time scale since the molecule has effective C_{3v} symmetry whether the tripod spins or not; thus, one cannot measure such barriers by line-broadening techniques. It is necessary to break the symmetry, as in the chiral molecule $[(C_6Et_6)Cr(CO)(CS)(NO)]^+$ (**2**); at low temperature one can see six different ring carbons (and also six CH_3 and six CH_2 environments).[4] Similarly, the barrier to migration of the diphenylarsino terminus from one cobalt vertex to another in $(Ph_2AsCH_2CH_2PPh_2)Co_3(CO)_7CR$ (**3**), as shown in Figure 1, can only be measured when the molecular symmetry is reduced. This has been accomplished either by using a chiral capping group (*e.g.* menthyl) and observing two ^{31}P signals[5] or by incorporating potentially diastereotopic probes into the system, (*e.g.* R = isopropyl), which gives two methyl signals when interconversion of the two enantiomers is slow.[6]

Chirality can arise in various guises in organometallic systems. One manifestation which is of current interest involves metallocenic chirality brought about by the clockwise or counterclockwise arrangement of the substituents on the cyclopentadienyl rings.[7] A beautiful example is the pentaisopropylcobaltocenium cation **4** reported by Astruc *et al.*[8] In this system the diastereotopic methyls of the isopropyl groups are equilibrated *via*

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[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1993.

[1] For a selection of recent examples see: (a) D'Agostino, M. F.; McGlinchey, M. J. *Polyhedron* **1988**, *7*, 807. (b) Clark, D. T.; Sutin, K. A.; Perrier, R. E.; McGlinchey, M. J. *Polyhedron* **1988**, *7*, 2297.

[2] Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073.

[3] McGlinchey, M. J.; Bougeard, P.; Sayer, B. G.; Hofer, R.; Lock, C. J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 789.

[4] Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; Top, S.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 1177.

[5] Clark, D. T.; Sutin, K. A.; McGlinchey, M. J. *Organometallics* **1989**, *8*, 155.

[6] Sutin, K. A.; Kolis, J. W.; Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Quilliam, M. A.; Faggiani, R.; Lock, C. J. L.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **1987**, *6*, 439.

[7] (a) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151. (b) Mislow, K. *Chimia* **1986**, *40*, 395. (c) Schuster, I. I.; Weissensteiner, W.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 6661.

[8] Gloaguen, B.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 4607.

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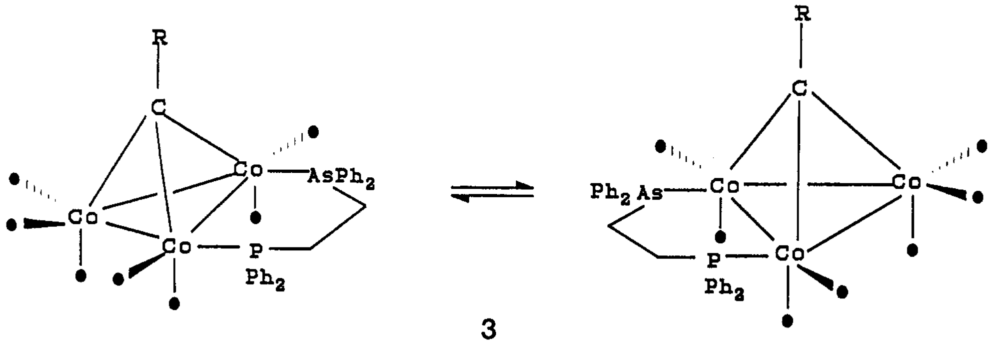

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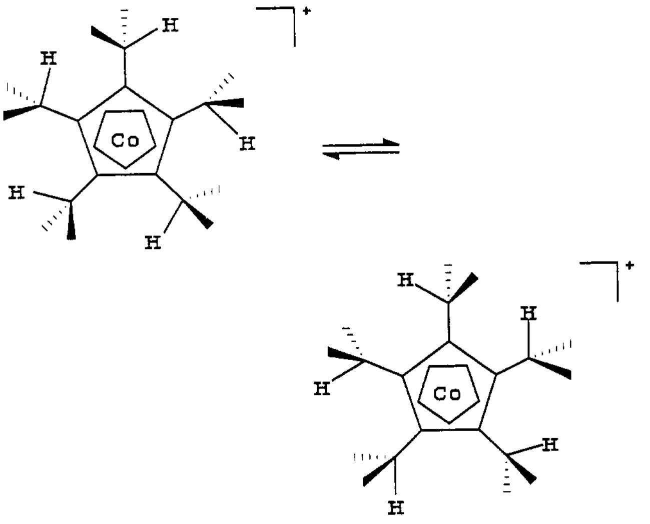
Figure 1. Racemization of an arphos cluster via migration of a diphenylarsino moiety.



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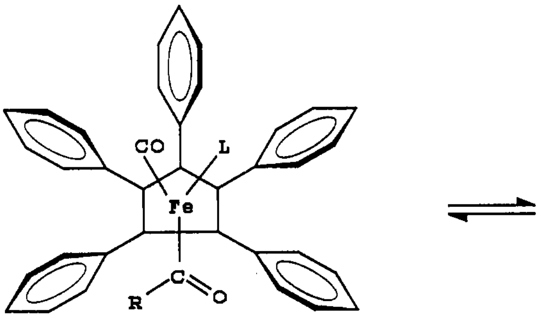

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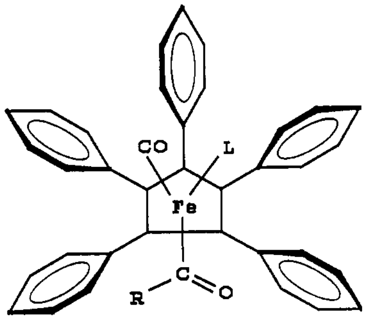

b

5: R = H; L = PMe$_3$

6: R = Me; L = PMe$_2$Ph

rotations of the five substituents; this process, for which $\Delta G^{\ddagger}_{338}$ = 17 kcal mol^{-1}, has the consequence of interconverting the enantiomers of **4**. Such chirality is also found in (pentaphenylcyclopentadienyl)metal complexes since the aryl rings can be canted in either a clockwise or counterclockwise manner.[9]

We here discuss molecular systems in which multiple fluxional processes can arise when a pentaphenylcyclopentadienyl ligand is bonded to a chiral tripod. (C_5Ph_5)Fe(CO)(HC=O)(PMe$_3$) (**5**) and (C_5Ph_5)Fe(CO)(EtC=O)(PMe$_2$Ph) (**6**) have recently been synthesized, and the chiral nature of the C_5Ph_5 ligand has been established in the solid state. This is evident from the IR spectrum, which exhibits two ν_{CO} peaks in the terminal carbonyl region, and also from the complexity of the CPMAS ^{13}C NMR spectrum of **6**, which exhibits five cyclopentadienyl ring-carbon resonances for *each* diastereomer.[10] We now describe some variable-temperature NMR experiments designed to probe the molecular dynamics of such molecules.

Results and Discussion

Organo-transition-metal complexes containing the pentaphenylcyclopentadienyl ligand have attracted attention[11] as alternatives to the analogous C_5Me_5 systems.[12] Not only do they provide a ligand which enhances the reactivity of the metal center toward dissociative replacement of carbonyls but they also have the potential to adopt a favored chiral conformation.[13] To this end, it is important to establish the factors controlling the rates of enantiomerization (or diastereomerization) of such molecules.

X-ray Crystallography. Orange crystals of (C_5Ph_5)Fe(CO)(HC=O)(PMe$_3$) (**5**), formed by diffusion of pentane into a toluene solution of the formyl complex at −20 °C, were suitable for X-ray diffraction, and top and side views of the resulting molecular structure are shown in Figure 2. The phenyl rings adopt a paddle-wheel orientation and are tilted relative to the plane of the five-membered ring through angles ranging from 42.9 to 53.5° (average of 50.1°). These peripheral rings adopt a compromise between the sterically favored orthogonal orientation and the completely coplanar rotamer, which would maximize conju-

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[9] (a) Chambers, J. W.; Baskar, A. J.; Bott, S. G.; Atwood, J. L.; Rausch, M. *Organometallics* **1986**, *5*, 1635. (b) Field, L. D.; Hambley, T. W.; Lindall, C. M.; Masters, A. F. *Polyhedron* **1989**, *8*, 2425.

[10] (a) Brégaint, P.; Hamon, J.-R.; Lapinte, C. *J. Organomet. Chem.* **1990**, *398*, C25. (b) Brégaint, P.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1992**, *11*, 1417.

[11] Connelly, N. G.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1989**, 283 and references therein.

[12] (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Marks, T. J. *Science* **1982**, *217*, 989.

[13] Adams, H.; Bailey, N. A.; Browning, A. F.; Ramsden, J. A.; White, C. *J. Organomet. Chem.* **1990**, *387*, 305.

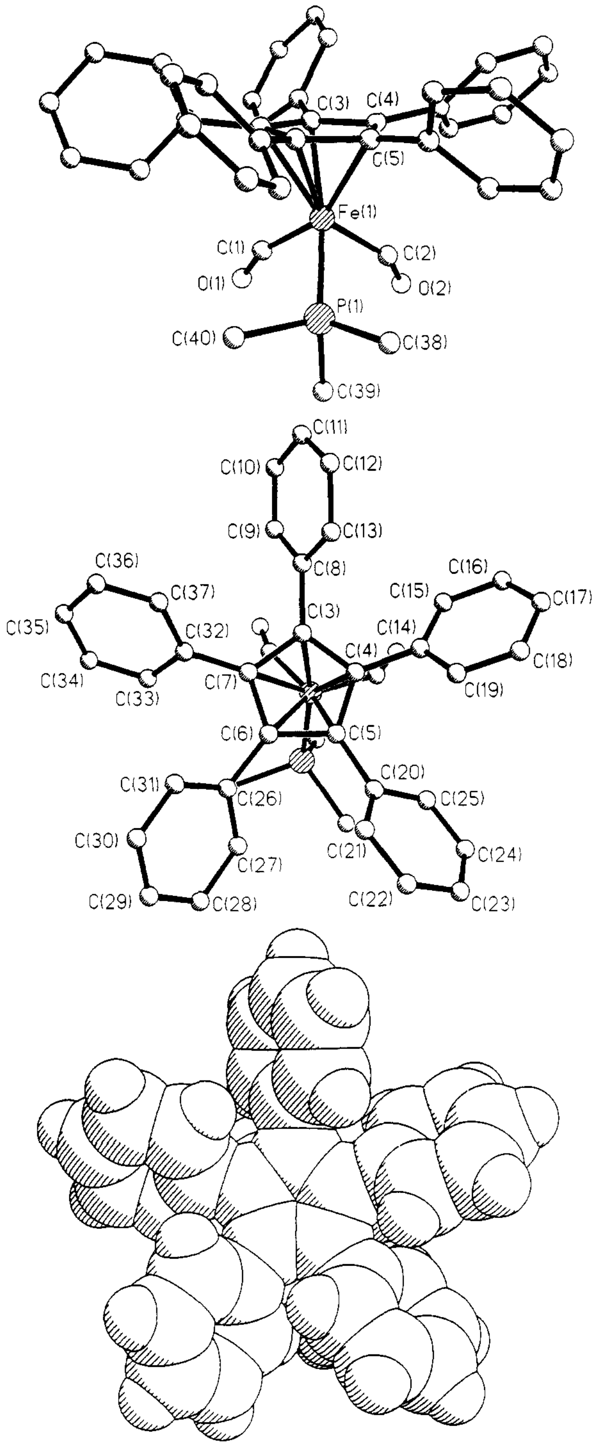

Figure 2. Views of $(C_5Ph_5)Fe(CO)(HC{=}O)(PMe_3)$ (**5**) showing (a, top) the atom-numbering scheme for the tripod, (b, middle) the atom-numbering scheme for the phenyl rings, and (c, bottom) a space-filling model depicting the canted nature of the array of peripheral phenyl rings.

gation but yield unacceptably short H···H distances. Such a geometry has been previously observed in other half-sandwich complexes, *e.g.*, $(C_5Ph_5)Co(CO)_2$,[9a] $(C_5Ph_5)Fe(CO)_2Br$,[9b] and $(C_5Ph_5)Ru(PPh_3)(CO)Br$.[13] This phenomenon confers a chiral array on the pentaphenylcyclopentadienyl ligand. The two opposite clockwise and counterclockwise chiral forms are clearly observed in the unit cell and are arranged with respect to the inversion center.

There is a minor disorder problem associated with the presence of toluene and methanol molecules in the crystal lattice; this results in convergence at $R = 0.084$ and limits the overall precision of the X-ray measurements. This disorder is also apparent in the Fe-bonded CO and CHO moieties, which manifest themselves as two similar and virtual fragments intermediate in structure between standard carbonyl and formyl groups. This is not to suggest that the CO and CHO groups have unusual geometries, merely that the crystal packing is controlled primarily by the orientations of the C_5Ph_5 moieties rather than the configuration at the metal atom. This result is readily rationalizable in terms of a statistical distribution (without any correlation with the inversion center) of the chiral *R* and *S* tripods.

^{13}C NMR. Overall, the crystallographic and spectroscopic data unambiguously establish that the complexes **5** and **6** both possess a chiral tripod which, together with the clockwise or counterclockwise canting of the peripheral phenyl rings of the C_5Ph_5 ligand, yields a diastereomeric mixture. These criteria are also satisfied in $(C_5Ph_5)Ru(PPh_3)(CO)Br$, but to our knowledge, no variable-temperature NMR data are available for this molecule.[13]

In the uncomplexed ligand C_5Ph_5, free rotation or even hindered rotation of the phenyl rings imparts effective D_{5h} symmetry; in contrast, hindered libration imposes cyclic directionality on the ring and the effective symmetry is D_5. Furthermore, placement of an organometallic fragment on one face of the C_5 ring not only lowers the maximum symmetry to C_{5v} but, in principle, also allows the detection of slowed phenyl rotation since each aryl ring would have a proximal and a distal edge with respect to the metal. Moreover, in the eventuality of slowed rotation about the C_5–metal axis, use of a chiral organometallic fragment would render inequivalent the cyclopentadienyl ring carbons. In the limit, if both tripodal and phenyl rotation are slowed on the NMR time scale, all 30 phenyl ring carbons in *each* diastereomer can become nonequivalent.

At room temperature the peripheral phenyls in **6** must be undergoing rapid ring rotation, since one sees only a single ^{13}C NMR resonance for the *ortho* and also for the *meta* environments. However, it is apparent from Figure 3 that tripodal rotation can be slowed on the NMR time scale; the room-temperature ^{13}C singlet for the cyclopentadienyl ring nuclei in **6** is split into five peaks (two of which overlap) at 173 K. Simulation of this fluxional process is nontrivial!

The connectivity pattern of the ^{13}C resonances in the five-membered ring is, of course, unknown and would require an exceedingly time-consuming two-dimensional double-quantum INADEQUATE spectrum[14] to establish which carbons are contiguous. Such an experiment would, of course, need to be carried out at −100 °C and is simply not a viable option without ^{13}C enrichment of the C_5 ring carbons. Fortunately, however, the number of possible permutations can readily be reduced to a manageable number. Starting arbitrarily from the lowest field resonance A, one must deduce which of the higher field carbon peaks, which we label successively B–E, are contiguous to A. Because of the cyclic nature of the ligand, the 24 possibilities are immediately reducible to 12: thus, A → B → C → D → E is indistinguishable from A → E → D → C → B. Furthermore, two of the five ring carbons, *viz.* B and C, are isochronous: for example, A → D → B → E

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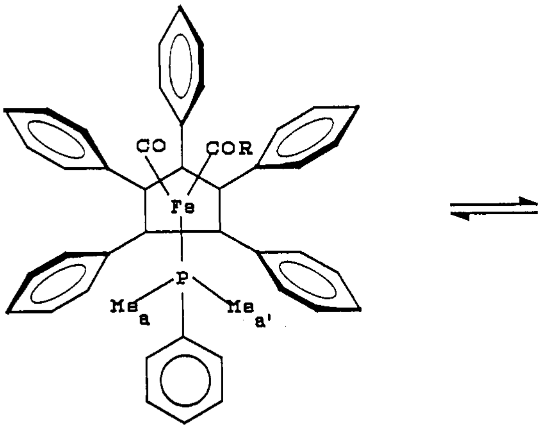
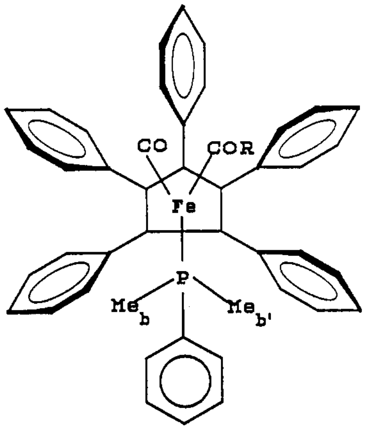
(14) Bax, A.; Freeman, R.; Frenkiel, T. A.; Levitt, M. H. *J. Magn. Reson.* 1981, *43*, 478.

→ C is indistinguishable from A → D → C → E → B. Analogously, we can combine all other sequences in which sites B and C can be interchanged. Of the six remaining permutations, only one exchange matrix gives peak coalescence behavior in accord with the experimental spectra. The resulting Arrhenius plot yields an activation energy for the tripodal rotation process of 8.7 ± 0.3 kcal mol^{-1}.

In order to determine whether the tripodal rotation is correlated with phenyl rotation, it is necessary to incorporate a probe for the latter fluxional process. As mentioned previously, the ^{1}H and ^{13}C resonances of the peripheral phenyl rings in **6** are very severely overlapped at low temperature even when using an 11.7 T magnet (500 MHz for protons, 125 MHz for carbons) and attributions of peaks to *ortho* or *meta* environments cannot be made with any confidence. One might envision taking advantage of the different ^{31}P shifts for the two diastereomers **6a** and **6b**, to follow the rate of interconversion between these molecules. However, uncertainties in line widths lead to unrealistically large error values in the simulations. Nevertheless, it is clear from the ^{31}P spectra over the range 183–153 K that the ratio of diastereomers changes quite markedly with temperature. This ratio can be determined directly from the phosphorus-31 spectrum at low temperature and ranges from 80/20 at 153 K to 75/25 at 173 K; the ^{31}P chemical shift at 300 K corresponds to a weighted average such that the diastereomers are in a 65/35 ratio. In such cases, evaluation of the activation energy barrier requires a knowledge of both the rate constant and the equilibrium constant at each temperature.[15] These changing diastereomer ratios are also evident in the ^{13}C variable-temperature spectra, which exhibit pairs of resonances for the terminal carbonyls (Fe–*C*O) and also for the propionyl carbonyl ligands (Fe–*C*O–Et).



6a



6b

The most convenient probes, however, are the CH_3 groups in the Me_2PPh ligand. These diastereotopic methyls give rise to two phosphorus-coupled doublets at room temperature when the only source of chirality is the iron atom, which, of course, bears four different substituents. However, as the temperature is lowered and the fluxional process slows on the NMR time scale, there develop two pairs of methyl resonances. In accord with the unequal populations of the diastereomers, we see a large pair of methyl resonances and a less intense pair of peaks, as shown in Figure 4. Simulations reveal that the more shielded methyl in the minor diastereomer exchanges with the lower field methyl in the major diasteromer and *vice versa*. Taking into account the temperature dependence of the equilibrium constant, one can extract an activation energy barrier of 11.7 ± 0.3 kcal mol^{-1}. This value is significantly different from the 8.7 kcal mol^{-1} value obtained for tripodal spinning and indicates that the two fluxional processes are not correlated. Such behavior is reminiscent of the extensively studied (hexaethylbenzene)-ML_3 systems, in which tripodal rotation ($\Delta G^{\ddagger} \approx 9.5$ kcal mol^{-1}) is considerably more facile than is ethyl rotation, for which $\Delta G^{\ddagger} \approx 11.5$ kcal mol^{-1}.[2,4,16]

In an attempt to generate another $(C_5Ph_5)FeL^1L^2L^3$ system containing an even more bulky chiral tripod, $(C_5Ph_5)Fe(CO)_2Br$ was treated with trimethyl phosphite so as to replace a carbonyl and thus obtain $(C_5Ph_5)Fe(CO)(Br)P(OMe)_3$ (**7**). However, the isolated product was not **7** but rather the result of an Arbuzov reaction in which initial displacement of the bromide occurred; subsequent attack by Br^- led to formation of bromomethane and the phosphonate complex **8**, as shown in Figure 5. Such a reaction is not unprecedented; Haines reported in 1971 that treatment of $(C_5H_5)Fe(CO)_2Cl$ with phosphites yields a mixture of products resulting from both CO displacement and from Arbuzov reactions.[17] Clearly, in the $(C_5Ph_5)Fe(CO)_2Br$ case, the latter process predominates.

At this point one must reflect on the possible implications of incorporating the phosphine $PR'R''_2$ into a system of the type $(C_5Ph_5)MLL'L''$. The two R″ substituents will, of course, be diastereotopic, but they may also introduce an extra potential source of asymmetry. Indeed, recent reports[18,19] of hindered rotation about metal–phosphine bonds raise the question as to whether one is really detecting slowed phenyl libration in the pentaphenylcyclopentadienyl ligand; that is, does the dimethylphenylphosphine merely act as an innocent probe

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[15] For a recent example, see: Tondu, S.; Jaouen, G.; Malisza, K. L.; D'Agostino, M. F.; McGlinchey, M. J. *Can. J. Chem.* **1992**, *70*, 1743.

[16] (a) McGlinchey, M. J. *Adv. Organomet. Chem.* **1992**, *34*, 285. (b) Nambu, M.; Siegel, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 3675. (c) Downton, P. A.; Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1990**, *111*, 27. (d) Kilway, K. V.; Siegel, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 2332. (e) Nambu, M.; Hardcastle, K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 369. (f) Kilway, K. V.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 255. (g) Kilway, K. V.; Siegel, J. S. *Organometallics* **1992**, *11*, 1426.

[17] Haines, R. J.; Du Preez, A. L.; Marais, I. L. *J. Organomet. Chem.* **1971**, *28*, 405.

[18] (a) Chudek, J. A.; Hunter, G.; Mackay, R. L.; Fäber, G.; Weissensteiner, W. *J. Organomet. Chem.* **1989**, *377*, C69. (b) Chudek, J. A.; Hunter, G.; Mackay, R. L.; Kremminger, P.; Weissensteiner, W. *J. Chem. Soc., Dalton Trans.* **1991**, 3337.

[19] Howell, J. A. S.; Palin, M. G.; McArdle, P.; Cunningham, D.; Goldschmidt, Z.; Gottlieb, H. E.; Hezroni-Langerman, D. *Organometallics* **1993**, *12*, 1694.

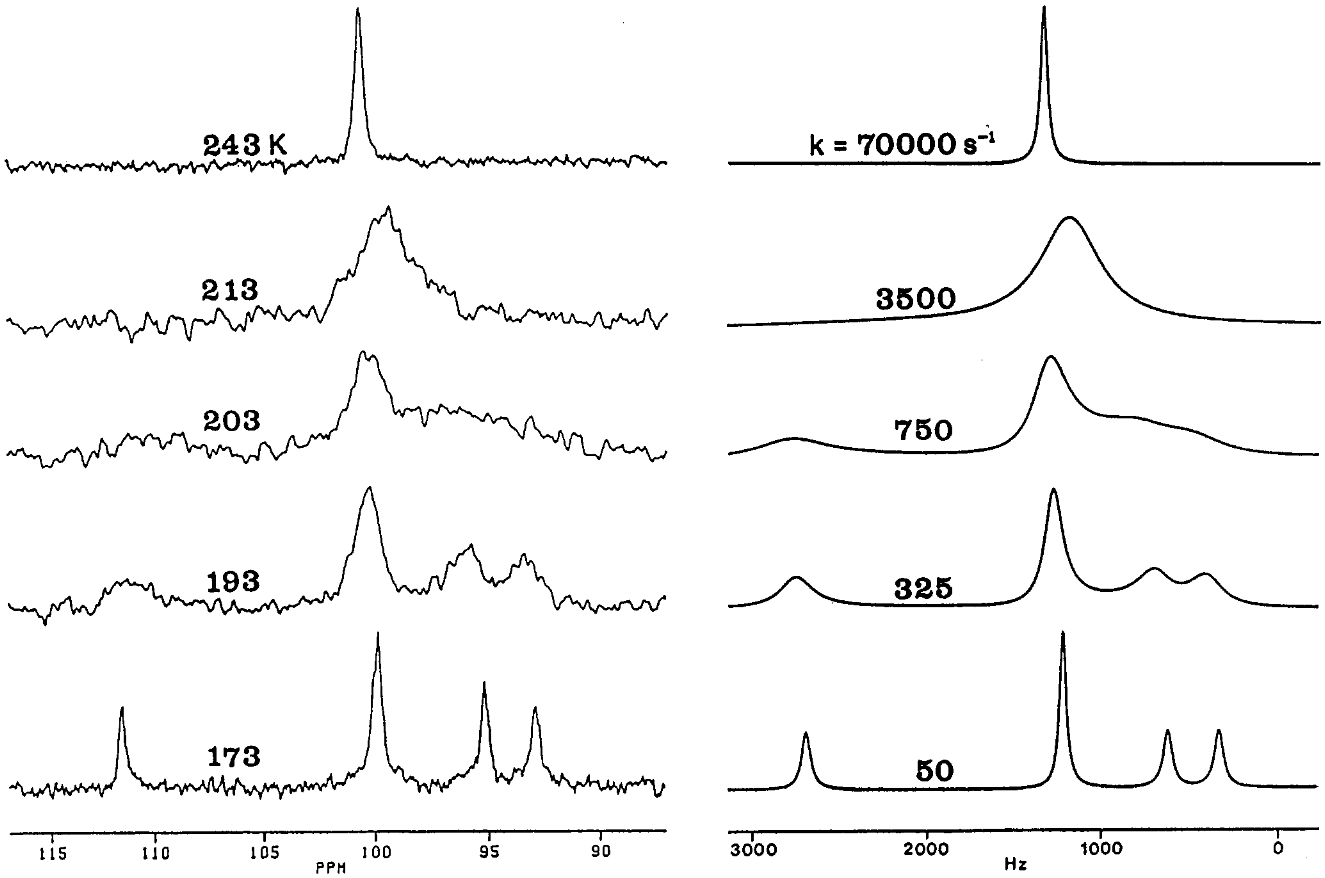
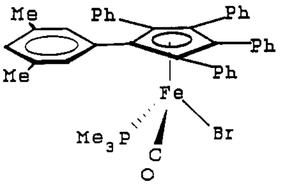


Figure 3. Experimental (left) and simulated (right) variable-temperature 125.7-MHz ^{13}C NMR spectra of $(C_5Ph_5)Fe(CO)(EtC{=}O)(PMe_2Ph)$ (**6**) in the cyclopentadienyl ring region.

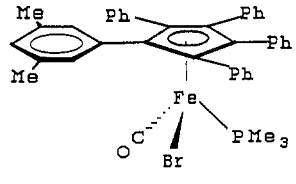
for inversion of the chirality of the C_5Ph_5 moiety, or can the $PPhMe_2$ ligand also give rise to different conformers at low temperature?

Hunter has detected a barrier of ~9 kcal mol^{-1} for rotation about the triphenylphosphine–chromium axis in $(C_6R_6)Cr(CO)_2PPh_3$ (R = Me, Et, Pr),[18] and Howell has very recently discussed the hindered rotation of the tri-*o*-tolylphosphine ligand in a related series of chromium complexes.[19] We note also that the X-ray crystal structure of $(C_5Ph_5)Ru(PPh_3)(CO)Br$ revealed that one of the phenyls of the C_5Ph_5 ring did not adopt the normal propeller twist of 50–60° but instead made a dihedral angle of only 26° with the C_5 ring plane.[13] The authors speculated that rotation of the peripheral rings of the C_5Ph_5 propeller might be restricted by the bulk of the triphenylphosphine group. However, no mention was made of hindered rotation about the C_5–Ru axis.

Although our X-ray crystal structure of $(C_5Ph_5)Fe(CO)(HC{=}O)(PMe_2Ph)$ (**5**) reveals no particular steric problems arising from the presence of the $PPhMe_2$ group, one might still attribute the splitting of the Me_2P fragment (from two ^{13}C methyl signals at room temperature to four at −100 °C) to hindered phosphine rotation rather than to slowed libration of the phenyls in the C_5 ring. In an attempt to clarify this point, we prepared $(C_5Ph_4\text{-}m\text{-}C_6H_3Me_2)Fe(CO)(PMe_3)Br$ (**9**), which possesses a small symmetrical phosphine but where the C_5Ar_5 ring bears a *m*-xylyl substituent such that the ring edges are potentially differentiable and could give rise to proximal and distal methyl resonances. The cyclopentadienyl ring carbons in **9** are, of course, nonequivalent even under conditions of rapid rotation of the chiral $Fe(CO)(PMe_3)Br$ tripod, but at −100 °C, it is apparent that tripodal rotation has slowed to give major and minor rotamers, exemplified by **9a** and **9b**, each of which exhibits five ^{13}C resonances. However,



9a



9b

the methyl resonance in the *m*-xylyl ring remains unsplit. One can conclude that either use of the relatively nonbulky Me_3P does not gate the phenyl rotations or the ^{13}C chemical shift difference between proximal and distal methyls is too small to be observed in solution. Thus, at present, one cannot state unequivocally that the phosphine rotation and the ability of the peripheral phenyls to spin are correlated. To clarify these points, it will be necessary to incorporate into the C_5Ar_5 system bulkier substituents, as in $C_5(m\text{-}C_6H_3Me_2)_5$, and also to differentiate between ring edges by use of probes, such as ^{19}F, which have larger chemical shift ranges than do ^{1}H or ^{13}C nuclei. These will be the subject of future reports.

The results of these experiments should be placed in context with other relevant studies. The fluxional behavior of polyaryl systems of the Ph_nZX type has prompted much thoughtful discourse and numerous elegant experiments.[20] A particular focus of the molecular dynamics involves the question of correlated motions versus the uncorrelated

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[20] (a) Mislow, K.; Gust, D.; Finocchiaro, P.; Boettcher, R. J. *Top. Curr. Chem.* **1974**, *47*, 1. (b) Mislow, K. *Chemtracts*: *Org. Chem.* **1989**, *2*, 151.

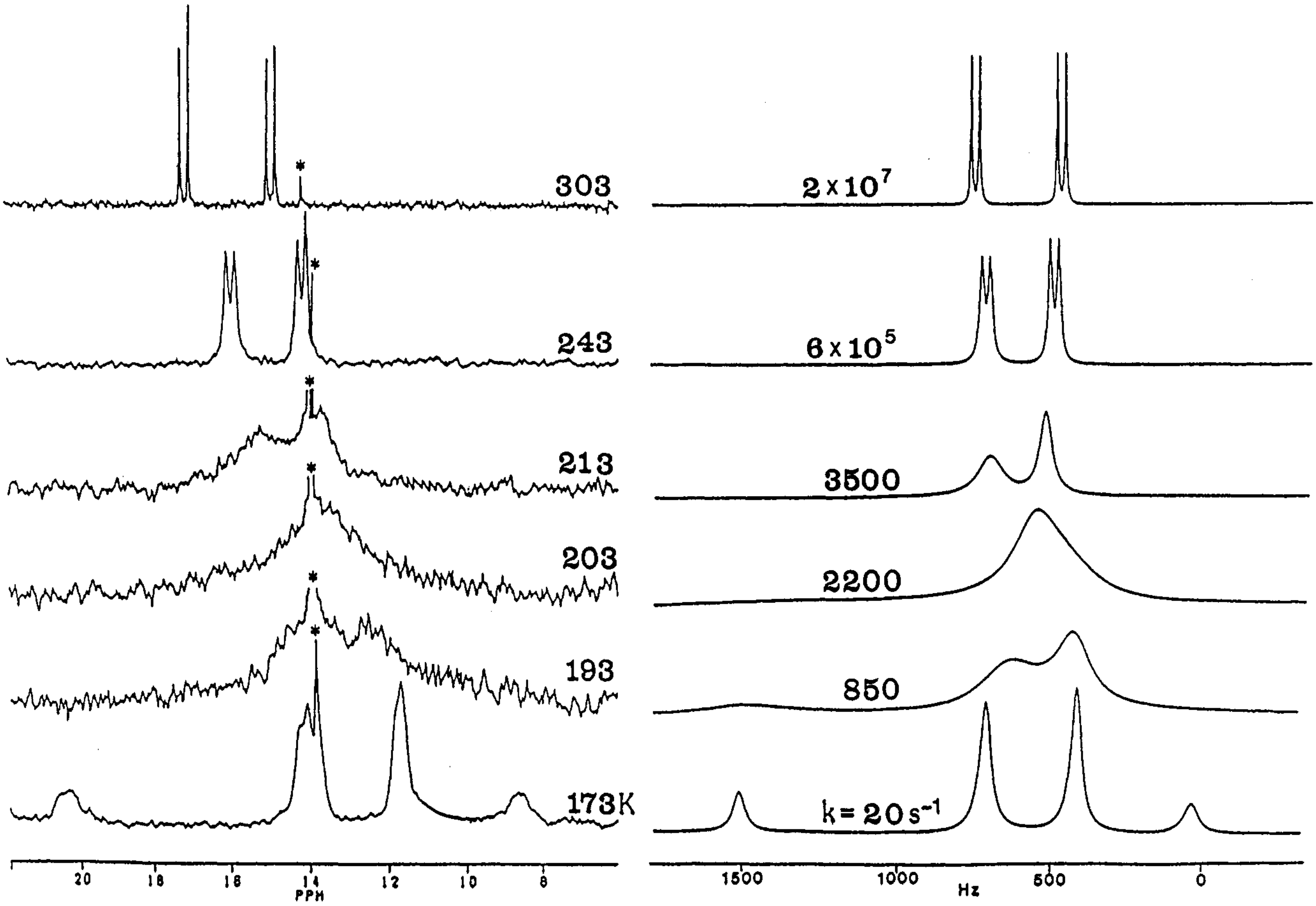

Figure 4. Experimental (left) and simulated (right) variable-temperature 125.7-MHz ^{13}C NMR spectra of (C_5Ph_5)Fe(CO)(EtC=O)(PMe_2Ph) (**6**) in the dimethylphosphino region. (A small impurity is marked by an asterisk.)

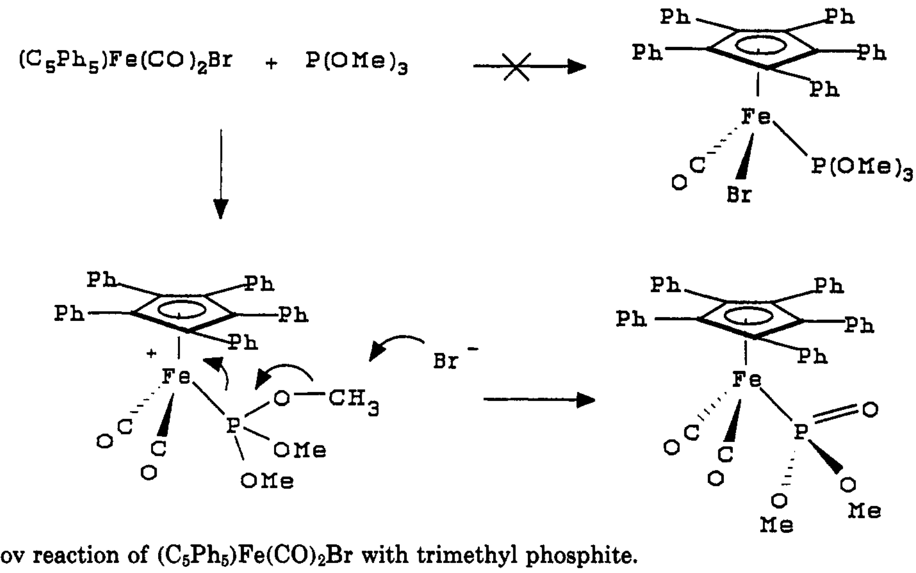

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Figure 5. Arbuzov reaction of (C_5Ph_5)Fe(CO)$_2$Br with trimethyl phosphite.

rotation of a single ring at any one time. For example, in hexaphenylbenzene one could envisage all six peripheral rings turning in a concerted manner so as to interchange the ring edges with respect to one face of the central arene, as in Figure 6.

In fact, an ingenious set of variable-temperature NMR experiments in which edges were labeled with relatively bulky substituents does not support such a view and instead points to a scenario in which uncorrelated peripheral aryl ring rotation occurs.[21] Crystallographic data on hexaphenylbenzene reveal that, in the solid state at least, the exterior rings are not oriented in a perpendicular fashion with respect to the central one but rather are canted; thus, for an unsubstituted peripheral phenyl ring the local symmetry is C_2.[22] Nevertheless, the fluxional properties of such molecules in solution can be satisfactorily accounted for by treating these rings as being orthogonal to the central ring on the NMR time scale.[23] In (C_6Ph_6)Cr(CO)$_3$ (**10**) each phenyl ring as well as the π-complexed moiety shows only one *ortho* and one *meta*

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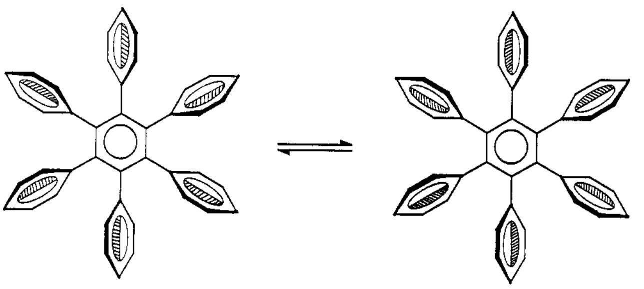
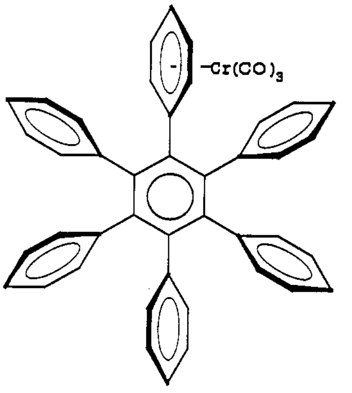


Figure 6. Concerted rotation of all six peripheral phenyl rings in hexaphenylbenzene.



10

^{13}C resonance even at the lowest accessible temperature.[24] It is therefore noteworthy that in the (pentaphenylcyclopentadienyl)iron complexes discussed here we have evidence which may suggest that the peripheral phenyl rings are indeed canted and are not orthogonal to the central ring on the NMR time scale.

The subtle interplay between ring substituents and π-complexed organometallic fragments is well illustrated by the molecules [C$_6$(SiMe$_2$H)$_6$]Cr(CO)$_3$,[7c] [C$_5$(*i*-Pr)$_5$]CoCp$^+$,[8] and [C$_5$(*i*-Pr)$_5$]Mo(CO)$_3$Me,[25] which are sterically congested, and [C$_5$(SiMe$_2$H)$_5$]Mn(CO)$_3$, which is not.[26] Moreover, in (Ph$_3$SiOH)[Cr(CO)$_3$]$_3$ the three π-complexed phenyl rings spin freely (on the NMR time scale) about the silicon–*ipso*-carbon bond; in contrast, when the rings have shorter bonds to the central atom, as in (Ph$_3$COH)Cr(CO)$_3$, the NMR spectrum clearly shows temperature-dependent behavior.[27]

Experimental Section

All manipulations were carried out under an inert atmosphere, using freshly dried solvents. ^{1}H and ^{13}C NMR spectra were recorded in CD$_2$Cl$_2$ on a Bruker AM-500 spectrometer operating at 500 and 125.7 MHz, respectively. Fast atom bombardment (FAB) mass spectra were obtained on a VG ZAB-E spectrometer. 3-Nitrobenzyl alcohol was used as the sample matrix, and xenon was the bombarding species (8 keV).

The complexes 5 and 6 were prepared as described previously.[10]

Table 1. Structure Determination Summary

empirical formula	C$_{40}$H$_{35}$FeO$_2$P·C$_7$H$_8$·CH$_3$OH
color, habit	orange prism
cryst size (mm)	0.12 × 0.22 × 0.35
cryst syst	monoclinic
space group	*I*2/*a*
unit cell dimens	a = 24.159(6) Å b = 12.868(7) Å c = 25.861(9) Å β = 93.95(5)°
V (Å^3)	8021(1)
Z	8
fw	758.7
density (calcd) (Mg/m^3)	1.27
abs coeff (cm^{-1})	7.6
F(000)	3192
temp (K)	140
2θ range (deg)	2.0–50.0
scan type	$\omega/2\theta$
index ranges	$0 \le h \le +25, 0 \le k \le +13, -27 \le l \le +27$
no. of rflns collected	5326
no. of indep rflns	1774 ($I \ge 3\sigma(I)$)
abs cor	n/a
weighting scheme	$w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o{}^2)^2]^{-1/2}$
no. of params refined	434
final R indices	R = 8.9%, R_w = 8.4%

(η^5-C$_5$Ph$_5$)Fe(CO)$_2$[P(O)(OMe)$_2$] (8). (η^5-C$_5$Ph$_5$)Fe(CO)$_2$Br (0.480 g, 0.75 mmol) was dissolved in benzene (10 mL) and the solution treated with P(OMe)$_3$ (0.127 g, 1.0 mmol), by use of a syringe. The mixture was heated under reflux for 24 h, during which time the solution became purple. The solvent and excess trimethyl phosphite were removed under reduced pressure, and the resulting dark green solid was dried under high vacuum. Subsequent flash chromatography (toluene/acetone) or recrystallization from toluene/acetone yielded (η^5-C$_5$Ph$_5$)Fe(CO)$_2$[P(O)(OMe)$_2$] (8; 0.195 g, 0.29 mmol; 39%). IR (CH$_2$Cl$_2$): ν_{CO} at 2030 and 1983 cm^{-1}. ^{13}C NMR (CD$_2$Cl$_2$, at 300 K; δ): 213.2, d, J(^{13}C–^{31}P) = 45.9 Hz, Fe(*C*O); 132.7, 129.9, 128.7, 127.7, phenyl *C*'s; 104.0, cyclopentadienyl *C*'s; 62.5, *C*H$_3$O's. ^{13}C NMR (CD$_2$Cl$_2$; at 158 K): the resonance at δ 104.0 has disappeared to yield peaks at δ 107.6 (2C), 100.2 (1C), 98.5 (1C), 97.6 (1C). ^{31}P NMR (CH$_2$ClCH$_2$Cl; δ): 116.4 (relative to external 85% H$_3$PO$_4$). Mass spectrum (FAB; m/z (%)): 667 (77) ([M + H]$^+$), 579 (23) ([M − 2CO − MeO]$^+$), 532 (29) ([C$_5$Ph$_5$FeOMe]$^+$), 501 (100) ([C$_5$Ph$_5$Fe]$^+$), 365 (28), 289 (45).

(η^5-C$_5$Ph$_4$-*m*-C$_6$H$_3$Me$_2$)Fe(CO)(PMe$_3$)Br (9) was prepared in a fashion entirely analogous to that for (η^5-C$_5$Ph$_5$)Fe(CO)(PMe$_3$)Br, but C$_5$Ph$_5$Br was replaced by C$_5$Ph$_4$(*m*-C$_6$H$_3$Me$_2$)Br; this latter ligand is trivially synthesized from C$_5$Ph$_4$(*m*-C$_6$H$_3$Me$_2$)OH made from (3,5-dimethylphenyl)magnesium bromide and commercially available tetraphenylcyclopentadienone.

X-ray Crystallography. Data were collected at 140 K on a CAD4 Enraf-Nonius diffractometer with graphite-monochromated Mo Kα radiation. Numbers related to data collection appear in Table 1. The cell parameters were obtained by fitting a set of 25 high-θ reflections. The structure was originally solved in the monoclinic space group *C*2/*c* with a = 36.585(6) Å, b = 12.868(7) Å, c = 21.159(9) Å, β = 135.15°, V = 8021 Å^3, Z = 8, R = 0.089, and R_w = 0.085. However, it is possible to transform this cell into the nonstandard space group *I*2/*a* with a = 24.159(8) Å, b = 12.868(7) Å, c = 25.861(9) Å, β = 93.95(5)°, V = 8021 Å^3, Z = 8, R = 0.089, and R_w = 0.084. This leaves the structure unchanged. The atomic coordinates listed in Table 2 are for the nonstandard cell *I*2/*a*, but those derived from the *C*2/*c* space group appear at Table S-6 in the supplementary material.

After Lorentz and polarization corrections (no absorption correction) the structure was solved with a Patterson map, which revealed the iron atom. The remaining non-hydrogen atoms of the structure were found after scale factor refinement and Fourier differences. After isotropic refinement (R = 0.12) the first solvent molecule (toluene) appeared; subsequent refinement revealed a

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Table 2. Atomic Coordinates for $(C_5Ph_5)Fe(CO)(CHO)(PMe_3)$ (5)

atom	x	y	z	B (Å^2)
Fe	–0.00904(9)	0.0359(2)	–0.17872(8)	2.65(4)
P	–0.0749(2)	0.0309(5)	–0.2420(2)	4.2(1)
O1	0.0358(7)	0.195(1)	–0.2369(6)	11.9(5)
O2	0.0576(5)	–0.063(1)	–0.2503(6)	9.5(5)
C1	0.0153(8)	0.147(2)	–0.2093(7)	4.9(5)
C2	0.0287(6)	–0.051(2)	–0.2195(8)	5.1(5)
C3	0.0384(6)	0.057(1)	–0.1083(6)	2.5(3)
C4	0.0224(6)	–0.049(1)	–0.1115(6)	3.1(4)
C5	–0.0356(5)	–0.055(1)	–0.1138(5)	2.1(3)
C6	–0.0565(5)	0.050(1)	–0.1079(5)	2.6(3)
C7	–0.0107(6)	0.119(1)	–0.1047(6)	2.8(4)
C8	0.0975(6)	0.096(1)	–0.0975(6)	3.1(4)
C9	0.1208(7)	0.176(1)	–0.1245(7)	4.1(4)
C10	0.1732(7)	0.205(2)	–0.1093(9)	5.9(6)
C11	0.2029(7)	0.159(2)	–0.0684(8)	5.7(5)
C12	0.1815(7)	0.083(1)	–0.0375(7)	3.7(4)
C13	0.1279(6)	0.049(1)	–0.0528(6)	3.5(4)
C14	0.0602(6)	–0.140(1)	–0.1065(5)	2.3(3)
C15	0.1087(6)	–0.145(1)	–0.1323(6)	2.7(4)
C16	0.1447(6)	–0.227(1)	–0.1273(7)	3.8(4)
C17	0.1328(7)	–0.305(1)	–0.0918(7)	3.8(4)
C18	0.0843(7)	–0.303(1)	–0.0651(8)	4.4(5)
C19	0.0492(6)	–0.219(1)	–0.0725(6)	2.4(3)
C20	–0.0707(6)	–0.148(1)	–0.1123(6)	2.3(3)
C21	–0.1029(6)	–0.166(1)	–0.0729(6)	2.9(4)
C22	–0.1331(7)	–0.260(1)	–0.0688(8)	4.1(4)
C23	–0.1259(7)	–0.337(1)	–0.1066(9)	5.0(5)
C24	–0.0931(8)	–0.317(1)	–0.1458(7)	4.3(5)
C25	–0.0654(6)	–0.228(1)	–0.1497(6)	3.0(4)
C26	–0.1148(6)	0.079(1)	–0.0988(5)	1.9(3)
C27	–0.1611(6)	0.038(1)	–0.1255(6)	3.4(4)
C28	–0.2156(6)	0.060(1)	–0.1093(7)	3.6(4)
C29	–0.2211(7)	0.125(1)	–0.0711(7)	3.5(4)
C30	–0.1764(7)	0.164(1)	–0.0430(7)	3.9(4)
C31	–0.1230(6)	0.142(1)	–0.0572(6)	2.6(3)
C32	–0.0135(6)	0.232(1)	–0.0966(7)	3.0(4)
C33	–0.0487(7)	0.296(1)	–0.1285(7)	3.8(4)
C34	–0.0513(8)	0.400(1)	–0.1170(7)	4.1(5)
C35	–0.0186(8)	0.445(1)	–0.0785(7)	4.8(5)
C36	0.0157(8)	0.386(2)	–0.0442(7)	4.9(5)
C37	0.0206(6)	0.277(1)	–0.0574(6)	3.2(4)
C38	–0.1184(8)	–0.084(1)	–0.2497(7)	4.8(5)
C39	–0.0520(9)	0.040(2)	–0.3054(7)	6.9(6)
C40	–0.1240(7)	0.139(2)	–0.2413(7)	4.9(5)
C41	–0.206(1)	–0.493(3)	–0.230(1)	8.5(9)*
C42	–0.198(2)	–0.605(3)	–0.222(2)	11(1)*
C43	–0.209(2)	–0.650(3)	–0.180(2)	11(1)*
C44	–0.234(1)	–0.599(3)	–0.141(1)	9(1)*
C45	–0.249(2)	–0.498(3)	–0.154(2)	10(1)*
C46	–0.233(1)	–0.446(3)	–0.197(1)	8.3(9)*
C47	–0.191(2)	–0.423(4)	–0.269(2)	12(1)*
O′	–0.172(2)	–0.539(4)	–0.022(2)	13(1)*
C′	0.256(4)	0.003(6)	–0.524(3)	17(3)*

[a] Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $(C_5Ph_5)Fe(CO)(CHO)(PMe_3)$ (5)

C3–C4	1.42(3)	Fe–P	2.203(6)
C4–C5	1.40(2)	Fe–C1	1.75(3)
C5–C6	1.46(2)	Fe–C2	1.82(3)
C6–C7	1.41(2)	Fe–C3	2.10(2)
C7–C3	1.43(2)	Fe–C4	2.15(2)
C3–C8	1.52(2)	Fe–C5	2.18(2)
C4–C14	1.49(2)	Fe–C6	2.22(2)
C5–C20	1.47(2)	Fe–C7	2.19(2)
C6–C26	1.49(2)	P–C38	1.82(2)
C7–C32	1.48(2)	P–C39	1.77(2)
C1–O1	1.09(3)	P–C40	1.83(2)
C2–O2	1.11(3)		
P–Fe–C1	86.4(8)	C4–C3–C7	108(2)
P–Fe–C2	85.2(7)	C4–C3–C8	125(2)
P–Fe–C3	165.9(5)	C7–C3–C8	125(2)
P–Fe–C4	141.5(6)	C3–C4–C5	109(2)
P–Fe–C5	108.7(5)	C3–C4–C14	126(2)
P–Fe–C6	103.1(4)	C5–C4–C14	125(2)
P–Fe–C7	127.3(5)	C4–C5–C6	108(2)
Fe–P–C38	119.1(7)	C4–C5–C20	128(2)
Fe–P–C39	115.5(8)	C6–C5–C20	123(1)
Fe–P–C40	114.0(8)	C5–C6–C7	108(1)
C38–P–C39	100(1)	C5–C6–C26	126(2)
C38–P–C40	105(1)	C7–C6–C26	126(2)
C39–P–C40	102(1)	C3–C7–C6	107(2)
Fe–C1–O1	160(3)	C3–C7–C32	127(2)
Fe–C2–O2	150(3)	C6–C7–C32	126(2)

second solvent (methanol). After anisotropic refinement of all non-hydrogen atoms ($R = 0.92$), some hydrogens were located from the Fourier difference map; the remaining hydrogens were placed in idealized positions and allowed to ride on the relevant carbons. The whole structure was refined by the full-matrix least-squares technique. Atomic scattering factors are from ref 28. Calculations were performed on a Digital PDP 11/60 computer with the SDP package[29] and on a Digital MicroVAX 3100 computer with the MOLEN package.[30] Diagrams were obtained by using the SHELXTL program library.[31]

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Supplementary Material Available: Tables of positional parameters for H atoms, thermal parameters, and bond lengths and angles for molecule 5 and also of atomic coordinates for 5 in the standard space group $C2/c$ (10 pages). Ordering information is given on any current masthead page.

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