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Rotational Isomerism in the Compounds η^5-$C_5H_5FeCOLCH_2R$

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Abstract: A series of compounds η^5-$C_5H_5Fe(CO)_2CH_2R$ and η^5-$C_5H_5FeCOLCH_2R$ (L = phosphorus donor; R = Ph, $SiMe_3$, 1-naphthyl) have been prepared and characterized. Ir spectra in the carbonyl stretching region indicate rotational isomerism about the iron-alkyl bonds in both types of compounds, while ^1H NMR spectra show that interconversion between rotamers in both systems is rapid on the NMR time scale. Variable-temperature NMR studies of the tertiary phosphine derivatives suggest that steric considerations determine the rotamer preferences, and that the stablest rotamer is that in which the bulky η^5-C_5H_5 is gauche to both methylene hydrogen atoms.

In recent years, there has been a number of reports of conformational isomerism resulting from restricted rotation about single bonds in organotransition metal chemistry. Among the earliest of these were suggestions that compounds of the type η^5-$C_5H_5Fe(CO)_2MX_2R$ (M = Si, Ge; X = Cl, Br, I; R = alkyl) exist in solution as mixtures of rotational isomers with respect to the iron–M bond.[1-4] Conclusions were based on the observations of four strong carbonyl stretching bands in the ir spectra of the compounds. Similar behavior has been observed for series of methylthio-bridged[5] and metal-metal bonded[6] bimetallic carbonyl complexes.

Nuclear magnetic resonance evidence has been presented for restricted rotation about phosphorus-metal[7-9] and phosphorus-carbon[10] bonds in complexes of tertiary phosphines containing the bulky *tert*-butyl group, although similar claims for the compounds *trans*-$PdCl_2[PPh(CH_2Ph)_2]_2$[11] and $M(CO)_3[\eta^6$-*o*-$MeC_6H_4)P($*o*-tolyl$)_2]$[12] (M = Cr, Mo) are open to alternative interpretations. In the former case, although the observation of a quartet of triplets for the benzylic methylene resonance was taken as evidence for restricted rotation about the phosphorus–methylene bonds,[11] it has been pointed out that the methylene protons are magnetically nonequivalent even if rotation about the phosphorus-carbon is rapid on the NMR time scale, thus explaining the unexpected multiplicity of lines.[13] In the case of the π-arene complex, the presence of separate resonances for the methyl groups of the two noncoordinated tolyl groups was taken as evidence for restricted rotation about the phosphorus-aryl bonds, although again the two groups are magnetically nonequivalent in any case.[14]

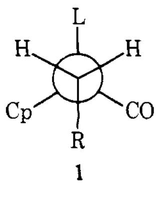
Restricted rotation about transition metal-carbon σ bonds has been reported for a variety of systems and is of obvious interest in view of the importance of alkylmetal compounds in, for instance, many catalytic processes. The presence of rotational isomers in solutions of the alkyl compounds $RCOCo(CO)_3L$[15,16] ($R = CH_2F, CHF_2$; $L = PPh_3, P(OPh)_3$), and $(HBpz_3)(COMe)(CO)_2Fe$[17] has been inferred from the presence of a doubling of bands in the carbonyl stretching region of the high resolution ir spectra of these compounds. In each case, only one set of time-averaged resonances was observed in the NMR spectrum, suggesting that the barriers to rotation in these compounds are very low (<10 kcal mol^{-1}).[17]

Similar observations have been made for a series of carbene complexes of the general formula $(\eta^6\text{-arene})Cr(CO)_2[C(OMe)Ph]$, for each of which four carbonyl stretching bands were observed;[18] again only time-averaged NMR spectra were observed, although restricted rotation on the NMR time scale has recently been reported for rhodium-carbene complexes such as *trans*-$RhClCO[C\overline{N(Et)CH_2CH_2N}(Et)]_2$[19] and $RhClCO(PPh_3)[C\overline{N(Et)CH_2CH_2N}(Et)]$.[19] It is not clear whether the origins of the barriers to rotation are steric in nature or reflect partial metal-carbon double-bond character.

Barriers to rotation of coordinated alkyl groups have been measured for the compound $MeMn(CO)_5$[20] and $(\eta^5\text{-}C_5H_5)_3UCHMe_2$.[21] For the former, vibrational spectroscopy suggested a barrier of 2.7 ± 0.5 kcal mol^{-1} in C_2Cl_4 solution while, for the latter, nmr spectroscopy suggested a barrier of 10.5 ± 0.5 kcal mol^{-1} in dimethyl ether-toluene solution. Similarly, the barrier to rotation must be small for the compound $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$,[22] for which four carbonyl stretching bands in the ir spectrum but only one set of resonances in the NMR spectrum are observed. The barrier to rotation about the iridium-C_6F_5 bond of the compounds $IrHX(C_6F_5)(CO)(PPh_3)_2$ (X = Cl, Br)[23] must be substantial, as all five fluorine atoms are magnetically nonequivalent.

We have recently utilized ^1H and ^{19}F NMR data[24-26] to demonstrate hindered rotation about the metal-carbon σ bonds in complexes of the types $\eta^5\text{-}C_5H_5NiPPh_3R$,[24] $\eta^5\text{-}C_5H_5NiPPh_3R_F$,[26] $\eta^5\text{-}C_5H_5FeCOLR_F$,[26] and $\eta^5\text{-}C_5H_5CoILR_F$[25] (R = primary and secondary alkyl groups; $R_F = C_2F_5, CF(CF_3)_2$; L = tertiary phosphine or phosphite). In all cases the barriers to rotation were sufficiently small that only time-arranged NMR were observed, but variable-temperature NMR studies showed quite clearly that the $\eta^5\text{-}C_5H_5$ group and bulky phosphines can present significant rotational barriers to coordinated alkyl groups and can also force the latter to favor a particular conformation.

Implicit in the arguments presented[24] was the prediction that primary alkyl compounds of the type $\eta^5\text{-}C_5H_5FeCOLCH_2R$ can exist as three staggered rotamers, **1**, **2**, and **3**, and that, of these, **3** should be the most stable and **2** the least. We now present data testing this hypothesis for a series of such complexes with varying stereochemical requirements for L and R. A preliminary account of some of this work has appeared.[27]



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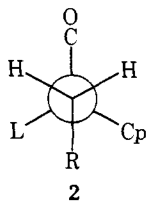

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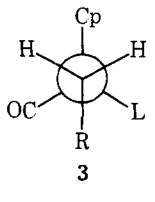

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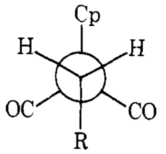
Table I. Infrared Frequencies and Band Half-Widths for the ν_{CO} Vibrations of the Compounds $\eta^5\text{-}C_5H_5Fe(CO)_2X$ (Petroleum Ether Solutions)

X	ν_{CO}, cm^{-1} [a]	$\Delta\nu_{1/2}$, cm^{-1}
Br	2052 (s)	9
	2011 (s)	9
I	2042 (s)	9
	2002 (s)	10
Me	2013	6
	1960	7.5
CH_2Ph	2012 (sh), 2010 (s)	6[b]
	1962 (sh), 1958 (s)	8[b]
CH_2CH_2Ph[c]	2011.5 (s), 2009 (sh)	6.5[b]
	1958 (s), 1956 (sh)	7.5[b]
CH_2SiMe_3	2012 (s)	7[b]
	1961.5 (s), 1958 (sh)	9[b]
CH_2Naph	2008 (ms), 2006 (s)	
	1965 (s), 1958.5 (s)	

[a] s = strong; sh = shoulder; ms = medium strong. [b] In these cases, the estimated band half-width is actually the sum of overlapping lines. [c] D. Slack and M. C. Baird, unpublished results.

Results and Discussion

Dicarbonyl Compounds. Table I lists ir data for the compounds $\eta^5\text{-}C_5H_5Fe(CO)_2X$ ($X = Br, I, CH_3, CH_2Ph, CH_2CH_2Ph, CH_2SiMe_3, CH_2\text{-}Naph$). Rotational isomerism is impossible for the first three, and only two carbonyl stretching bands (A′ and A″) are expected. By analogy with compounds of the type $\eta^5\text{-}C_5H_5Fe(CO)_2MX_2R$,[1-4] however, two rotamers **4** and **5** and, therefore, four carbonyl stretching bands are expected for the primary alkyl compounds.



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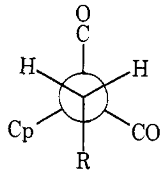

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Although in principle it should be possible to assign the observed carbonyl stretching bands to either **4** or **5** using ^{13}C satellites,[4] we have not done so. We note, however, that visual comparisons of the intensities of the carbonyl stretching bands suggest that the two rotamers of the primary alkyl compounds are more equally populated[28] than are the two rotamers of compounds of the type $\eta^5\text{-}C_5H_5Fe(CO)_2MX_2R$ (M = Si, Ge).[3,4] Furthermore the ratios of the intensities of the two modes for each rotamer appear in all cases to be slightly greater than unity, suggesting a fairly constant geometry for the $Fe(CO)_2$ grouping (i.e., a bond angle of about 93-95°) as has been observed for a variety of compounds of this type.[29,30]

Finally we note that the variation in bandwidths of the compounds in Table I is very small, the alkyl compounds perhaps exhibiting slightly narrower lines than do the halide compounds. Although it is expected that the carbonyl stretching bands for petroleum ether solutions should be narrower than has been observed for chloroform solutions,[28] it is surprising that the spectra of the alkyl compounds exhibit narrower lines than do spectra of the halide compounds. In the more polar chloroform, solvent interactions with the FeCO dipoles cause a large reversal of this trend.[30]

Table II. Infrared Frequencies and Band Half-Widths of the ν_{CO} Vibrations of the Compounds η^5-$C_5H_5FeCOLCH_2R$ (Petroleum Ether Solutions)

R	L	ν_{CO}, cm^{-1} [a]	$\Delta\nu_{1/2}$, cm^{-1}
Ph	$P(OMe)_3$	1937 (s), 1928 (s)	19–20 (each band)
Ph	PMe_2Ph	~1925 (sh), 1915 (s)	16
Ph	$PMePh_2$	~1925 (sh), 1916 (s)	11
Ph	PPh_3	~1925 (sh), 1917 (s)	15
$SiMe_3$	$P(OMe)_3$	1938 (s), 1928 (s)	~15 (each band)
$SiMe_3$	PPh_3	~1922 (sh), 1915.5 (s)	10
Naph	$P(OMe)_3$	1936 (s), 1928 (s)	~19 (each band)
Naph	PPh_3	~1930 (w, sh), ~1923 (sh) 1916 (s)	19

[a] s = strong, w = weak, sh = shoulder.

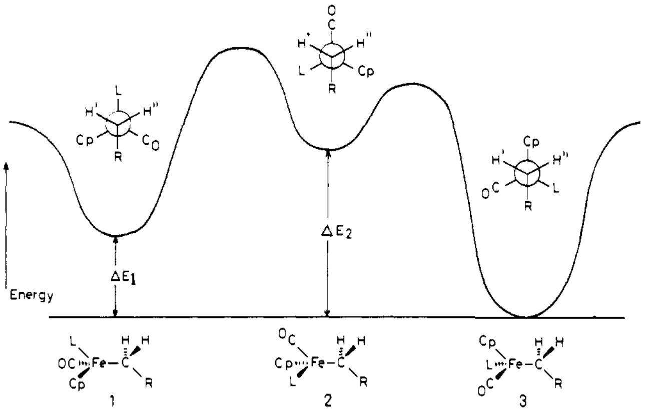


Figure 1. Qualitative potential-energy diagram for the staggered rotamers of η^5-$C_5H_5FeCOLCH_2R$.

Monocarbonyl Compounds. Table II lists ir data for compounds of the type η^5-$C_5H_5FeCOLCH_2R$ (L = phosphorus donor; R = Ph, $SiMe_3$, 1-naphthyl). As can be seen, the spectra are in many cases surprisingly complex. If a "normal" bandwidth is assumed to be about 8 cm^{-1}, as it is for the dicarbonyl compounds (see above) and for the compound η^5-$C_5H_5FeCO(PPh_3)CF(CF_3)_2$,[26] then each spectrum clearly contains at least two components.

Assignment of the bands to specific rotamers is, unfortunately, impossible. In addition to rotational isomerism about the iron-carbon bonds, as represented by **1**, **2**, and **3**, conformational isomerism of the coordinated phosphorus donors is also possible in most cases.[25,26] Thus, for instance, since a coordinated triphenylphosphine can assume two senses of twist (right- and left-handed propellers), six conformational isomers of the triphenylphosphine complexes are possible. Even more complicated behavior is suggested by the relatively broad, non-Lorentzian bands in the spectra of the trimethyl phosphite complexes. Space-filling molecular models suggest that rotational isomerism about both the phosphorus-oxygen and the oxygen-carbon bonds can occur, increasing the number of possible conformational isomers. In support of this hypothesis, we find that the ir spectrum of η^5-$C_5H_5FeCO[P(OMe)_3]I$[31] in petroleum ether consists of two broad ($\Delta\nu_{1/2} \sim$ 12–13 Hz) bands of unequal intensity at 1980.5 (ms) and 1968 (s) cm^{-1}.

The NMR spectra of these compounds are much more informative than are the ir spectra. Room temperature NMR data are listed in Table III. In all cases, the iron atoms are chiral, the methylene protons are therefore diastereotopic, and the ^1H NMR spectra in the methylene regions exhibit typical ABX-type octets (X = ^{31}P).[32] The methylene proton NMR parameters listed in Table III were calculated using standard procedures,[33] identification of the correct solution being achieved using double resonance procedures based on population transfer.[34] Both J_{AX} and J_{BX} have the same sign for several of the compounds and, for reasons outlined previously,[27] we believe that all $^3J_{PH}$ in the iron compounds are positive, and that trans couplings are larger than gauche.

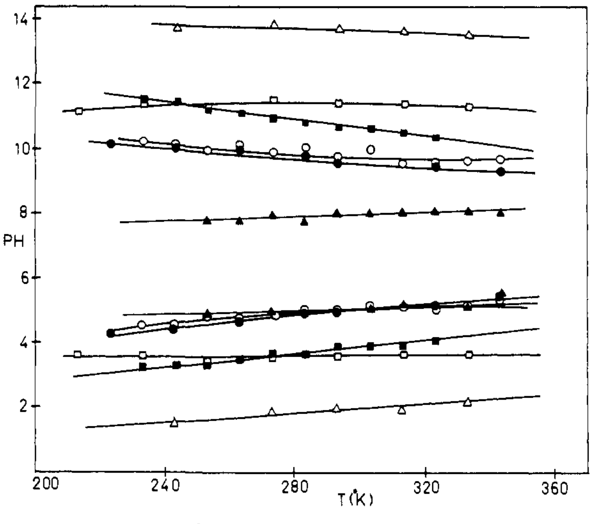


Figure 2. Variation of $^3J_{PH}$ with temperature for the compounds η^5-$C_5H_5FeCOPPh_3CH_2SiMe_3$ (△), η^5-$C_5H_5FeCOP(OMe)_3CH_2SiMe_3$ (□), η^5-$C_5H_5FeCOPPh_3CH_2Ph$ (■), η^5-$C_5H_5FeCOPMePh_2CH_2Ph$ (○), η^5-$C_5H_5FeCOPMe_2PhCH_2Ph$ (▲), and η^5-$C_5H_5FeCOP(OMe)_3CH_2Ph$ (●).

Because of the chiral iron atom, each of the three staggered rotamers **1**, **2**, and **3** should be of different energy. Figure 1 shows qualitatively the potential energy of the system assuming, as suggested previously,[24] that **3** is the stablest and **2** the least stable rotamer. The relative energies of the rotamers can then be defined by setting $\Delta E_1 = E_1 - E_3$ and $\Delta E_2 = E_2 - E_3$.

The observation of only one set of resonances in the NMR spectrum of each compound suggests either that only one rotamer is populated (because of high energy barriers and/or large values of ΔE_1 and ΔE_2), or that the barriers to rotation about the iron-carbon bonds are sufficiently low that interconversion between rotamers is rapid on the NMR time scale, and that time-averaged spectra are being observed. If the former were true, the NMR parameters should be essentially independent of temperature; if the latter were true, the relative rotamer populations and, hence, the nmr parameters, should vary with the temperature.

Figure 2 illustrates the variation of J_{AX} and J_{BX} with temperature of the benzyl and trimethylsilylmethyl complexes.[35] As can be seen, the vicinal phosphorus-hydrogen coupling constants in all cases vary smoothly with temperature, J_{AX} and J_{BX} generally diverging as the temperature decreases. Thus clearly the relative rotamer populations are changing with temperature. Furthermore it would seem that the stablest (low temperature) rotamer is one which has quite different phosphorus-hydrogen coupling constants, consistent with the suggestion made above that **3** is the low energy conformation. Although sufficiently low temperatures to achieve the slow exchange limit could not be reached, extrapolations of the data to 0 K suggest that gauche coupling constants, J_g, and trans coupling constants, J_t, are about 0 ± 1 and 17 ± 1 Hz, respectively, for these compounds.

Although the extrapolations are extremely crude, the values suggested are very similar to those found for the nickel compounds, η^5-$C_5H_5NiPPh_3R$[24] (J_g = −0.6 Hz, J_t = 18.0 Hz), and predict reasonably well the phosphorus-hydrogen coupling constants of the corresponding methyl compounds, which should be an average of two gauche and

Table III. NMR Data for the Compounds η^5-$C_5H_5FeCOLCH_2R$ at 298 K

R	L	τ_A[a]	τ_B[a]	J_{AB}, Hz[a]	J_{AX}, Hz[a]	J_{BX}, Hz[a]	τ_{Cp} (J_{HP}, Hz)[b]	Remarks[b]
Ph	$P(OMe)_3$	7.58	8.02	8.4	5.0	9.6	5.73 (1)	τ 6.42 (d, J_{PH} = 11 Hz; OMe) τ 2.95 (m, Ph)
Ph	PMe_2Ph	7.63	8.31	8.5	5.0	8.0	6.02 (1.5)	τ 2.91 (m, CPh), τ 2.58 (m, PPh) τ 8.43 (d, J_{PH} = 8.5 Hz, Me) τ 8.15 (d, J_{PH} = 8.5 Hz, Me)
Ph	$PMePh_2$	7.65	8.38	8.2	5.1	9.9	5.95 (1)	τ 2.99 (m, CPh), τ 2.65 (m, PPh)
Ph	PPh_3	7.44	8.26	8.1	3.9	10.7	5.93 (1)	τ 2.98 (m, CPh), τ 2.65 (m, PPh)
$SiMe_3$	$P(OMe)_3$	10.50	11.22	11.9	3.6	11.4	5.63 (<1)	τ 10.1 (s, SiMe) τ 6.56 (d, J_{PH} = 11 Hz, OMe)
$SiMe_3$	PPh_3	10.19	11.20	11.9	2.0	13.7	5.83 (1)	τ 10.1 (s, SiMe) τ 2.72 (m, Ph)
Naph	$P(OMe)_3$	6.98	7.60	8.6	5.5	9.0	5.83 (1.5)	τ 6.34 (d, J_{PH} = 11.5 Hz, OMe) τ 2.63 (m, Naph)
Naph	PPh_3	7.01	7.88	8.5	7.2	7.4	6.05 (1)	τ 2.58 (m, Ph + Naph)

[a] In CH_2Cl_2. [b] In $CDCl_3$. [c] s = singlet, d = doublet, m = multiplet.

one trans coupling constants. Thus we find that $^3J_{PH}$ for η^5-$C_5H_5FeCOPPh_3Me$[36] is 6.5 Hz, consistent with J_g = 1 Hz and J_t = 17.5 Hz. Substituent effects will cause small variations in vicinal coupling constants between different compounds and, not surprisingly,[37] we find that the compounds η^5-$C_5H_5FeCO[P(OPh)_3]Me$[38] and η^5-$C_5H_5FeCO[P(OMe)_3]Me$,[38] with the more electronegative phosphites, exhibit lower averaged phosphorus-hydrogen coupling constants, 5.6 and 4.8 Hz, respectively. Even these are consistent with the range of values of J_g and J_t discussed above, however, and it seems reasonable to suggest that J_g and J_t remain essentially constant for each rotamer of the tertiary phosphine complexes.

Table IV lists, for several of the compounds studied, the room temperature mole fractions, n_1, n_2, and n_3, of rotamers **1**, **2**, and **3**, respectively, calculated assuming constant gauche angles of 60°[39] for all rotamers of all compounds and constant values of J_g = 1 Hz and J_t = 17.5 Hz for all rotamers of all compounds. Although the assumptions made are definitely not above suspicion, especially for the trimethyl phosphite complexes (see above), the data in Table IV probably give "ball-park" estimates of the rotamer populations. Thus, as expected, rotamer **3** is in all cases most heavily populated and, although the relative populations of **1** and **2** for complexes of the smaller phosphorus donors are somewhat closer than might have been expected, it is interesting to note that **2** is virtually unpopulated in the case of the very crowded η^5-$C_5H_5FeCOPPh_3CH_2SiMe_3$.

Although the barriers to rotation about the iron-carbon bonds are too low to permit observation of the spectra of the separate rotamers and thus to permit calculation of their relative energies, a mathematical formalism has been developed by Gutowsky et al.[40] which should in principle make possible calculation of ΔE_1 and ΔE_2 from the observed time-averaged data. In terms of Figure 1, for H′ and H″

$$\langle J_{PH}\rangle_{obsd} = \frac{J_1\exp(-\Delta E_1/RT) + J_2\exp(-\Delta E_2/RT) + J_3}{\exp(-\Delta E_1/RT) + \exp(-\Delta E_2/RT) + 1} \quad (1)$$

where J_1, J_2, J_3 are $^3J_{PH'}$ or $^3J_{PH''}$ for rotamers **1**, **2**, and **3**, respectively.

A search of the literature produced very few critical discussions of the Gutowsky treatment, which requires that the temperature dependence of changes in the rotamer energy differences and in the individual rotamer vicinal coupling constants be negligible, and that the rotamer entropy differences be essentially zero. Tests of the Gutowsky approach appear to deal exclusively with haloethanes[41-43] and come to quite different conclusions about its usefulness. It would appear, however, that temperature-dependent molecular electric field interactions of the solvent with molecules such as the haloethanes, which exhibit large bond dipole moments, can have a serious effect on rotamer populations.[42,43]

Table IV. Rotamer Populations at 298° for the Compounds η^5-$C_5H_5FeCOLCH_2R$

Compd	n_1[a]	n_2	n_3
R = Ph; L = $P(OMe)_3$	0.24	0.24	0.52
R = Ph; L = PMe_2Ph	0.34	0.24	0.42
R = Ph; L = $PMePh_2$	0.21	0.25	0.54
R = Ph; L = PPh_3	0.23	0.18	0.59
R = $SiMe_3$; L = $P(OMe)_3$	0.21	0.16	0.63
R = $SiMe_3$; L = PPh_3	0.17	0.06	0.77

[a] The values of n_1, n_2, and n_3 were calculated on the basis that $n_1 + n_2 + n_3 = 1$ and that, for both H′ and H″, $n_1J_1 + n_2J_2 + n_3J_3 = \langle J_{PH}\rangle_{obsd}$.

In spite of the above possible shortcomings, the Gutowsky treatment does appear to work for a number of compounds[42,43] and thus should be valid for compounds of the type studied here, which probably exhibit quite low bond dipole moments for all configurations[44,45] and which, therefore should be relatively unaffected by temperature-dependent electric fields. In agreement with these assumptions, we find that the compound η^5-$C_5H_5FeCOPPh_3CH_2Ph$ exhibits only small changes in vicinal phosphorus-hydrogen coupling constants (allowing for experimental error) in solvents of widely varying dielectric constants, CS_2, C_6H_6, CH_2Cl_2, and 2:1 CD_3CN-CH_2Cl_2.

In the limit of high temperatures and/or small values of ΔE_1 and ΔE_2, the exponential terms of eq 1 approach unity and thus, at infinite temperature, the observed values of $^3J_{PH'}$ and $^3J_{PH''}$ of a compound should converge to the value of $(2J_g + J_t)/3$, i.e., approximately the value of the corresponding methyl derivative.

Figure 3 illustrates plots of $^3J_{PH'}$ and $^3J_{PH''}$ for the benzyl and trimethylsilylmethyl complexes vs. T^{-1}; as can be seen, the two coupling constants for each benzyl complex do converge at about $T = \infty$. Considering the assumption of negligible substituent effects and the length of the extrapolation, the points of convergence are in good agreement with the value of $^3J_{PH}$ of η^5-$C_5H_5FeCOPPh_3CH_3$[46] (6.5 Hz).

The lack of significant convergence in the case of the trimethylsilylmethyl complexes suggests that, over the temperature range studied, not all three rotamers are significantly populated. This conclusion is in agreement with the rotamer population data discussed above. On the other hand, the variation in $|^3J_{PH'} - {}^3J_{PH''}|$, i.e., η^5-$C_5H_5FeCOPPh_3CH_2SiMe_3$ > η^5-$C_5H_5FeCOPPh_3CH_2Ph$ > η^5-$C_5H_5FeCOPMePh_2CH_2Ph$ > η^5-C_5H_5FeCOP-

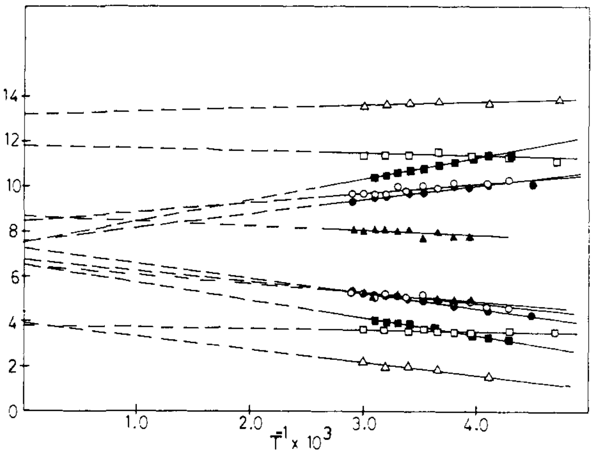


Figure 3. Variation of $^3J_{PH}$ with T^{-1} for the compounds η^5-$C_5H_5FeCOPPh_3CH_2SiMe_3$ (△), η^5-$C_5H_5FeCOP(OMe)_3CH_2SiMe_3$ (□), η^5-$C_5H_5FeCOPPh_3CH_2Ph$ (■), η^5-$C_5H_5FeCOPMePh_2CH_2Ph$ (○), η^5-$C_5H_5FeCOPMe_2PhCH_2Ph$ (▲), and η^5-$C_5H_5FeCOP(OMe)_3CH_2Ph$ (●).

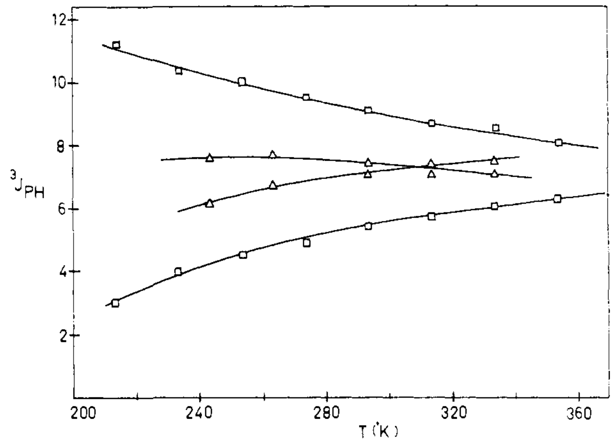


Figure 4. Variation of $^3J_{PH}$ with temperature for the compounds η^5-$C_5H_5FeCOPPh_3CH_2Naph$ (△) and η^5-$C_5H_5FeCOP(OMe)_3CH_2Naph$ (□).

Table V. Values of ΔE_1 and ΔE_2 for the Compounds η^5-$C_5H_5FeCOLCH_2R$

Compd	ΔE_1, cal mol^{-1}	ΔE_2, cal mol^{-1}
R = Ph; L = PMe_2Ph	180	330
R = Ph; L = $PMePh_2$	480	480
R = Ph; L = PPh_3	550	700
R = $SiMe_3$; L = PPh_3	900	1500

Me_2PhCH_2Ph, reflects the expected order of decrease in steric requirements of the ligands in the orders CH_2SiMe_3 > CH_2Ph and PPh_3 > $PMePh_2$ > PMe_2Ph.[47] If, as seems likely,[24,26] the steric requirements of the ligands govern the relative rotamer populations, then decreasing the degree of crowding around the metal atom should result in decreases in ΔE_1 and/or ΔE_2 and, hence, in an increase in the populations of the less stable rotamers. This increase should be reflected in the time-averaged NMR spectra as a decrease in $^3J_{PH'}$ and an increase in $^3J_{PH''}$, as is observed.

Estimates of ΔE_1 and ΔE_2 for the phosphine complexes were made using eq 1 and substituting 1 or 17.5 Hz as appropriate for J_1, J_2, and J_3. Values of ΔE_1 and ΔE_2 were varied in each case until a good fit with the experimental data over the temperature range studied was obtained. The results are listed in Table V. Although, as stated above, several assumptions are made in using eq 1, the fact that two coupling constants were found to fit the data over a range of approximately 100° in each case suggests that the results may be regarded with some confidence. Surprisingly, the rotamer energy differences appear to be very similar to those of a variety of 1,2-disubstituted ethanes.[37]

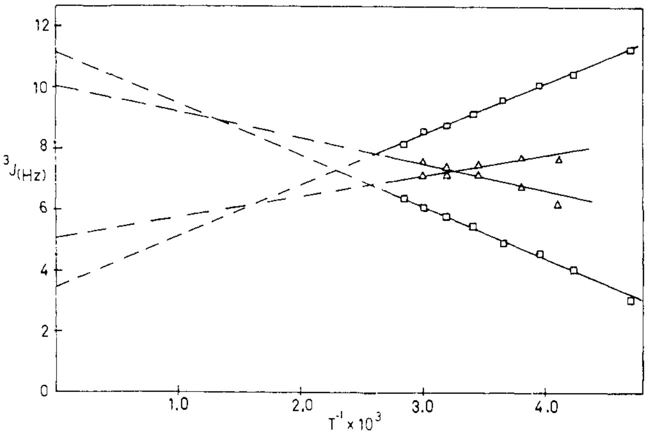
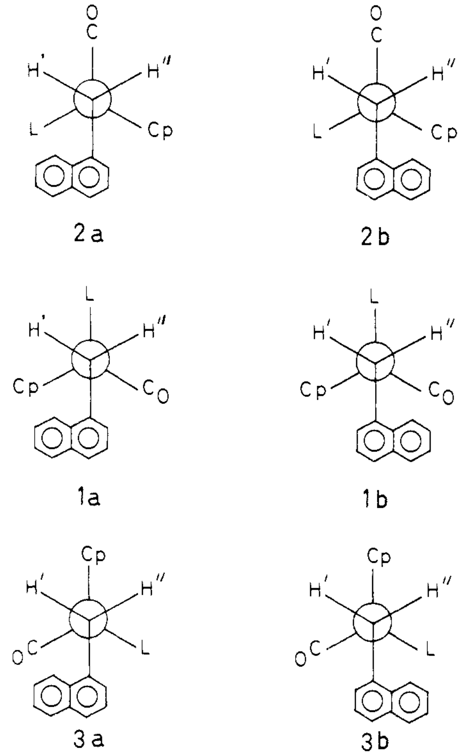


Figure 5. Variation of $^3J_{PH}$ with T^{-1} for the compounds η^5-$C_5H_5FeCOPPh_3CH_2Naph$ (△) and η^5-$C_5H_5FeCOP(OMe)_3CH_2Naph$ (□).



2a 2b

1a 1b

3a 3b

Figure 6. Staggered rotamers for the compounds η^5-$C_5H_5FeCOLCH_2Naph$.

The variation of J_{AX} and J_{BX} with temperature for the naphthylmethyl compounds is shown in Figure 4. As can be seen, the two coupling constants of the triphenylphosphine derivative cross at about 307°; a plot of J_{AX} and J_{BX} vs. T^{-1} for the trimethyl phosphite compound suggests that they also would cross at about 440 K (Figure 5).

The observed cross-overs cannot be rationalized in terms of a Boltzmann distribution over three rotamers such as **1**, **2**, and **3**; as explained above, J_{AX} and J_{BX} for each compound should only converge at higher temperatures. Instead, consideration must be taken of the fact that a coordinated naphthylmethyl group is highly asymmetric and may take either of two orientations for each of **1**, **2**, and **3**, as shown in Figure 6 (space-filling models suggest that the in-

Table VI. Analytical and Physical Data on the Compounds η^5-$C_5H_5FeCOLCH_2R$

Compd			Analysis		Necessary irradiation time, hr[a]
R	L	Mp, °C	Calcd	Found	
Ph	PPh_3	120–123	C, 74.11; H, 5.43	C, 74.95; H, 5.77	3
Ph	$PMePh_2$	34–37	C, 70.91; H, 5.73	C, 71.07; H, 5.96	6
Ph	PMe_2Ph	Oil	C, 66.72; H, 6.08	C, 66.20; H, 6.22	36
Ph	$P(OMe)_3$	Oil	C, 52.79; H, 5.77	C, 52.79; H, 6.01	24
$SiMe_3$	PPh_3	132–135	C, 67.46; H, 6.28	C, 66.84; H, 6.30	3
$SiMe_3$	$P(OMe)_3$	Oil	C, 43.33; H, 7.01	C, 42.89, H, 6.72	24
Naph	PPh_3	128–132	C, 76.09; H, 5.30	C, 74.94; H, 5.14	3
Naph	$P(OMe)_3$	Oil	C, 57.98; H, 5.61	C, 59.89; H, 5.62	24

[a] Yields in the irradiation step were 60–70%.

termediate orientation, in which the naphthyl rings bisect the H′CH″ angle, is relatively strained). Thus the naphthylmethyl compounds can exist in six rather than three conformations.

In order to explain the observed cross-overs, it is necessary to postulate decreasing steric interactions of the 7- and 8-positions of the naphthyl rings with the other ligands on the iron in the order η^5-C_5H_5, PR_3 > CO.[24-26] Thus there would be a twist of the iron–carbon bonds away from the normal staggered angles (~60°) in order to alleviate the added strain, an effect which should be most noticeable in conformations **1a** and **3b.**

The relationship between $^3J_{PH}$ and the dihedral angle ϕ is normally of the form:[24]

$$^3J = K_1 \cos^2 \phi + C \qquad 0 < \phi < 90° \tag{2}$$

$$^3J = K_2 \cos^2 \phi + C \qquad 90° < \phi < 180° \tag{3}$$

where $C \lesssim 0$ and $K_2 \gtrsim K_1$. Assuming $K_1 = K_2 = K$, and that $^3J = 1$ Hz when $\phi = 60°$, 17.5 Hz when $\phi = 180°$, then $K = 22$ and $C = -4.5$. Approximate "corrected" values of $^3J_{PH'}$ and $^3J_{PH''}$ can then be calculated for **1a** and **3b** for any angle of twist away from the "normal" staggered angle. Taking such "corrected" values calculated on the basis of a 20° twist for **1a** and **3b,** but "normal" dihedral angles for the remaining conformations, and averaging the six coupling constants for each of H′ and H″, the resulting values agree reasonably well with the extrapolated values at $T = \infty$ (Figure 5). Furthermore, the fact that the vicinal coupling constants of the triphenylphosphine complex cross at a lower temperature than those of the trimethyl phosphite complex can also be rationalized, as the angle of twist would be greater for the complex containing the larger phosphorus donor, and thus the deviation from "normal" coupling constants would be greater.

The model used is admittedly very crude but is the only one we are aware of which qualitatively reproduces the data illustrated in Figure 5.

Experimental Section

NMR spectra were run on a Bruker HX-60 spectrometer equipped with a variable-temperature probe. The temperature controller was checked with methanol at 213 and 313 K and was accurate to ±1°. In the case of the compound η^5-$C_5H_5FeCOPMe_2PhCH_2Ph$, part of the methylene octet was obscured by the stronger methyl resonances, and the positions of the hidden lines were determined using INDOR techniques.

NMR samples were prepared under nitrogen in degassed solvents immediately prior to running the spectra.

Infrared spectra were obtained on a Perkin-Elmer 180 instrument using standard double-beam techniques with CsI cells. Spectra were calibrated with HCl and water and are believed correct to ±0.2 cm^{-1}.

$[\eta^5$-$C_5H_5Fe(CO)_2]_2$ and 1-(chloromethyl)naphthalene were purchased from commercial sources and used without further purification. The phosphines were also obtained commercially and were checked for purity by ^1H NMR spectroscopy. PPh_2Me and $PPhMe_2$ were handled under nitrogen. Trimethyl phosphite was prepared by reacting PCl_3 with methanol.[48] The compound (bp 109–112°) was obtained pure as shown by ^1H NMR spectroscopy. Tetrahydrofuran was distilled under N_2 from a blue solution of sodium benzophenone ketal prior to use. Petroleum ether (bp 30–50°) was used without further purification.

η^5-$C_5H_5Fe(CO)_2CH_2Ph$[49] and η^5-$C_5H_5Fe(CO)_2CH_2SiMe_3$[50] were prepared by reported procedures.

η^5-$C_5H_5Fe(CO)_2CH_2C_{10}H_7$. The reaction of η^5-$C_5H_5Fe(CO)_2Na$[51] with slight excess of 1-(chloromethyl)naphthalene in dry THF gave the new compound η^5-$C_5H_5Fe(CO)_2CH_2C_{10}H_7$. After stirring for 1 hr, the THF was removed in vacuo, and unreacted $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ and $C_{10}H_7CH_2Cl$ were removed by repeated extraction with petroleum ether. The pure compound (yield 85%) was obtained by recrystallization from 1:1 $CHCl_3$–hexane (mp 144–146°). The compound is slightly soluble in petroleum ether and very soluble in polar solvents. Solutions of η^5-$C_5H_5Fe(CO)_2CH_2C_{10}H_7$ decompose rapidly in air but, in the solid form, the compound is stable for several months. The NMR spectrum ($CDCl_3$ with Me_4Si lock) showed resonances at τ 6.83 (singlet, CH_2), 5.33 (singlet, C_5H_5), and 2.66 (multiplet, $C_{10}H_7$).

Anal. Calcd for $C_{18}H_{14}O_2Fe$: C, 67.94; H, 4.44. Found: C, 68.14; H, 4.40.

η^5-$C_5H_5Fe(CO)LCH_2R$. The phosphine and phosphite substituted complexes were prepared by irradiating a petroleum ether solution of η^5-$C_5H_5Fe(CO)_2CH_2R$ with a slight excess of ligand in a Pyrex flask with a Hanovia lamp at a distance of 10–15 cm. After the reaction was essentially completed (see Table VI for time), the solution was passed through an alumina column under nitrogen. The unreacted starting materials were eluted with 10% CH_2Cl_2–petroleum ether, the products with 50% CH_2Cl_2–petroleum ether. The solvent was removed under vacuum, and the product was recrystallized when possible. Several of the products were isolated as apparently rather thermally unstable oils. Although most of the compounds could be kept indefinitely at −20° under nitrogen, they decomposed slowly at room temperature. The formulations were verified in all cases by the NMR, ir, and mass spectra; the observation of molecular ions in many of the latter was very useful, as the compounds which yielded the best mass spectra were generally those compounds which were least stable. The compounds η^5-$C_5H_5FeCOPPh_3CH_2R$ (R = Ph,[32] $SiMe_3$[52]) have been reported previously. Analytical data and other details are listed in Table VI.

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Factors Controlling Association of Magnesium Ion and Acyl Phosphates[1]

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Abstract: The binding of magnesium ion to acetyl phosphate, acetonylphosphonate, and related compounds was examined by potentiometric and spectrophotometric procedures. The free energy of binding of magnesium ion to these compounds follows a linear correlation with the basicity of the compounds. However, the lack of correlation between the first and second proton dissociation constants (free energies) and the unique deviation of phosphate ion from the correlation of basicity and affinity indicate that factors other than inductive effects are of significance. One major factor suggested is relative solvation of various species. The value obtained for the binding constant of magnesium ion and acetyl phosphate dianion at high ionic strength (30°, pH 8) is 6 M^{-1}. This is in close agreement with a corrected value extrapolated from kinetic results by Oestreich and Jones. The value had been disputed by other workers. Infrared and phosphorus NMR spectroscopic data are presented which indicate that consideration of protonation state simplifies interpretation of carbonyl absorption position in the infrared and phosphorus NMR chemical shift effects due to magnesium ion. It is proposed that the failure of magnesium ion to catalyze many nonenzymic reactions is consistent with the control function of enzymic catalysis. It is suggested that, by minor perturbation of the dominant form of complexation, enzymic binding can bring about observed catalytic patterns.

The role of magnesium ion in the reactions of phosphates in aqueous solution is of particular interest because of the large number of cases of enzymatic catalysis which involve magnesium.[3] Hydrated magnesium ion alone does not compare in effectiveness as a catalyst for phosphate transfer with the combination of an enzyme and magnesium ion and may even hinder reaction.[3,4] It would appear that, if magnesium ion is to participate in enzymic catalysis, it must be involved in a way that differs in some respects from the nonenzymic case. However, since in many cases the magnesium ion becomes associated with the enzyme as a complex of the substrate,[5] one might expect that the catalytically relevant mode of binding between metal ion and substrate can be brought about as a perturbation of the mode in bulk solution. The association of magnesium ion with biologically important phosphate compounds has been studied extensively,[6-11] resulting in uncertainty in conclusions about the details of coordination to complex substrates.[12] Most of the uncertainty arises because there are many possibilities which are difficult to distinguish by conventional physical methods. Similar problems exist for acyl phosphates,[10,13] which are biological phosphate derivatives of much simpler