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XIX*. LANTHANIDE SHIFT REAGENT STUDIES OF ROTATIONAL BARRIERS AND PREFERRED ORIENTATIONS IN PHOSPHINE DERIVATIVES OF CYCLOPENTADIENYL COMPLEXES OF IRON AND NICKEL

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Summary

The series of compounds, η^5-$C_5H_5FeCOCNL$ (L = PPh_3, PPh_2Me, $PPhMe_2$ and PMe_3) and η^5-$C_5H_5NiCNPPh_3$, has been prepared and characterized. Addition of the shift reagent $Eu(fod)_3$ produces downfield shifts and first order coupling patterns in ^1H and ^{13}C NMR spectra and allows the determination of conformational effects and rotational barriers. Evidence for preferred conformations in η^5-$C_5H_5FeCOCNPPh_2Me$ and η^5-$C_5H_5FeCOCNPPhMe_2$ resulting from rotation about the Fe—P bond is presented. Conformations in which the phenyl rings are oriented adjacent to the cyclopentadienyl ligand appear to be favored. Maximum barriers to rotation about the Fe—P and P—C bonds are estimated at 8.0 and 7.6 kcal respectively. The mechanism of interconversion of right and left handed helicies in the arylphosphine complexes is discussed and a number of possible pathways are proposed. A method of assigning resonances of diastereotopic nuclei to particular nuclei is presented.

Introduction

Preferred conformations about metal—ligand bonds have been reported in several organometallic systems [1-5]. In certain instances tertiary phosphines have been used as additional ligands which influence the population distribution of the conformers [4,5]. Concurrently, restricted rotation about the phosphorus—carbon bond was proposed in arylphosphines [5-7]. The series of compounds,

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* For part XVIII, see ref. 33.

η^5-C_5H_5FeCOCNL (L = PPh_3, PPh_2Me, $PPhMe_2$ and PMe_3), has allowed the determination of conformational preferences about the iron—phosphorus bond, in addition to the elucidation of certain aspects of the rotation about the phosphorus—carbon bonds. The study of such effects has been greatly facilitated by the use of a lanthanide shift reagent. The complex Eu(fod)$_3$* is one of a number of paramagnetic shift reagents which have been widely used in structural and conformational studies of organic molecules, but the value of which for studying organometallic conformational effects is relatively unexplored.

Results

Data from infrared spectra of the phosphine complexes are summarized in Table 1. Although all complexes were readily soluble in chloroform, the carbonyl stretching bands were too broad (~30 cm^{-1}) to detect asymmetry or to compare half-widths. Narrow symmetric bands were observed in cyclohexane solutions of all but the triphenyl derivatives, which were insoluble in the less polar solvent. Slightly broader half-widths were seen in the mixed phosphine complexes than in the trimethyl complex. Addition of an excess of Eu(fod)$_3$ to cyclohexane solutions of each complex resulted in a shift to higher frequency of about 10 cm^{-1} and an approximate doubling of bandwidths. In these solutions as well, only single symmetric bands were observed for each compound. Values for ν_{max} vary over a small range but are consistent with those observed by Tolman with the same series of phosphines in Ni(CO)$_3$L complexes [8].

Room temperature PMR spectra of all of the complexes gave sharp, well resolved signals with complex patterns arising only in the phenyl regions (Table 2). Phosphorus—proton couplings of approximately 10 Hz and 2 Hz were observed for methyl and cyclopentadienyl resonances, respectively, in each of the complexes. In the dimethylphenyl spectra the magnetically nonequivalent methyl groups, resulting from the asymmetry at the iron center, were observed as two distinct doublets. A similar observation for the diphenylmethyl analog was obscured by the complex phenyl pattern. The phenyl pattern in the nickel complex remained sharp upon lowering the temperature to −65°C. No coupling between the phosphorus and the cyclopentadienyl protons was observed in the nickel spectra.

Addition of the lanthanide shift reagent, Eu(fod)$_3$, resulted in downfield shifts of the proton resonances and provided first-order coupling patterns for the

TABLE 1

INFRARED DATA FOR THE CARBONYL COMPLEXES

Compound	ν_{max}(CO) (cm^{-1}, C_6H_{12} solution)	ν_{max}(CO) (cm^{-1}, $CHCl_3$ solution)
η^5-C_5H_5FeCOCNPMe$_3$	1964 ($\nu_{1/2}$ = 5.1 cm^{-1})	1962
η^5-C_5H_5FeCOCNPPhMe$_2$	1963 ($\nu_{1/2}$ = 7.1 cm^{-1})	1962
η^5-C_5H_5FeCOCNPPh$_2$Me	1967 ($\nu_{1/2}$ = 7.0 cm^{-1})	1968
η^5-C_5H_5FeCOCNPPh$_3$	insoluble	1969

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* fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethylheptandione.

TABLE 2

PROTON NMR DATA AT ROOM TEMPERATURE

Compound	δ [a]	Assignment	Multiplicity [b]	Rel. int.	J(P—H) (Hz)
η^5-$C_5H_5FeCOCNPMe_3$	1.57	Me	d	9	10.4
	4.62	Cp	d	5	1.4
η^5-$C_5H_5FeCOCNPPhMe_2$	1.82	Me	d	3	10.1
	1.98	Me	d	3	10.8
	4.64	Cp	d	5	1.6
	7.8	Ph	m	5	
η^5-$C_5H_5FeCOCNPPh_2Me$	2.07	Me	d	3	9.6
	4.52	Cp	d	5	1.8
	7.5	Ph	m	10	
η^5-$C_5H_5FeCOCNPPh_3$	4.48	Cp	d	5	1.4
	7.8	Ph	m	15	
η^5-$C_5H_5NiCNPPh_3$	5.32	Cp	s	5	<0.2
	7.7	Ph	m	15	

[a] ppm from TMS in $CDCl_3$ solution. [b] s = singlet, d = doublet, m = multiplet.

phenyl protons. The relative shifts vary considerably and are compared in Table 3 to the shift of the averaged cyclopentadienyl protons. Shifts of phenyl protons in the *ortho* position were much larger than those of *meta* or *para* positions. The triphenylphosphine nickel complex had slightly larger, though very similar, relative shifts than its iron analog. The magnetic nonequivalence of the two phenyl groups in η^5-$C_5H_5FeCOCNPPh_2Me$ was observed upon addition of $Eu(fod)_3$, as two distinct patterns for the *ortho* protons emerged. Phosphorus—proton couplings remained constant despite addition of the paramagnetic complex. Significant broadening of both methyl and cyclopentadienyl signals in η^5-$C_5H_5FeCOCNPMe_3$ was observed at −25°C in the presence of $Eu(fod)_3$. Broadening was also observed for the *ortho* signal of η^5-$C_5H_5FeCOCNPPh_3$ at −20°C under similar circumstances.

Room temperature, proton decoupled, ^{13}C NMR spectra of the complexes likewise gave sharp, resolved signals with the exception of the cyano carbon, which was broadened, as expected, by the quadrupole effects of the adjacent nitrogen atom. Carbon—phosphorus couplings were observed in all signals except the cyclopentadienyl carbon nuclei (Table 4). The largest value of J(P—C) was that of the carbon in the phenyl ring bonded to the phosphorus and was 40-45 Hz. Carbon nuclei in the 2 and 3 positions of the phenyl rings had smaller, al-

TABLE 3

RELATIVE SHIFTS OF PROTONS UPON ADDITION OF $Eu(fod)_3$ [a]

Compound	Cp	Me	*ortho*	*meta*	*para*
η^5-$C_5H_5FeCOCNPMe_3$	1.00	0.98			
η^5-$C_5H_5FeCOCNPPhMe_2$	1.00	1.16, 1.35	1.00	0.32	0.32
η^5-$C_5H_5FeCOCNPPh_2Me$	1.00	1.38	1.23, 0.87	0.12, 0.19	0.12, 0.19
η^5-$C_5H_5FeCOCNPPh_3$	1.00		1.34	0.24	0.16
η^5-$C_5H_5NiCNPPh_3$	1.00		1.49	0.31	0.20

[a] In room temperature solutions of $CDCl_3$.

TABLE 4

^{13}C NMR DATA AT ROOM TEMPERATURE

Compound	δ [a]	Assignment	Mulitplicity [b]	J(P—C) (Hz)
η^5-C_5H_5FeCOCNPMe$_3$	19.96	Me	d	31.8
	82.39	Cp	s	<0.2
	216.91	CO	d	29.4
η^5-C_5H_5FeCOCNPPhMe$_2$	18.03	Me	d	31.8
	18.72	Me	d	34.8
	82.95	Cp	s	<0.2
	128.79	C_3, C_5	d	9.4
	129.23	C_2, C_6	d	9.2
	130.10	C_4	s	2.0
	138.31	C_1	d	42.9
	217.31	CO	d	29.4
η^5-C_5H_5FeCOCNPPh$_2$Me	19.40	Me	d	34.5
	83.61	Cp	s	<0.2
	128.68	C_3, C_5 (2)	d	7.4
	130.82	C_4	s	2.0
	131.07	C_2, C_6	d	9.9
	131.32	C_4	s	2.0
	132.17	C_2, C_6	d	9.5
	135.61	C_1	d	44.0
	136.99	C_1	d	41.9
	217.00	CO	d	27.0
η^5-C_5H_5FeCOCNPPh$_3$	84.17	Cp	s	<0.2
	128.55	C_3, C_5	d	9.7
	130.54	C_4	s	2.0
	133.22	C_2, C_6	d	9.5
	134.95	C_1	d	44.0
	217.55	CO	d	27.2

[a] ppm from TMS in $CDCl_3$. [b] s = singlet, d = doublet.

most identical, couplings of slightly less than 10 Hz. The methyl nuclei were coupled by slighly more than 30 Hz and the carbonyl nuclei by slightly less than that amount. The magnetic nonequivalence of methyl and phenyl groups in η^5-C_5H_5FeCOCNPMe$_2$Ph and η^5-C_5H_5FeCOCNPPh$_2$Me, respectively, was evident by the presence of two sets of methyl and phenyl resonances in the appropriate spectra.

The effect of adding Eu(fod)$_3$ paralleled that observed in the PMR spectra. Relative shifts are summarized in Table 5. Couplings between the carbon and phosphorus nuclei did not change upon addition of the shift reagent.

TABLE 5

RELATIVE SHIFTS OF CARBON NUCLEI UPON ADDITION OF Eu(fod)$_3$

Compound	Cp	CO	C_1
η^5-C_5H_5FeCOCNPMe$_3$	1.00	1.69	0.71
η^5-C_5H_5FeCOCNPPhMe$_2$	1.00	1.79	0.83 (Me), 0.76 (Me), 0.69 (Ph)
η^5-C_5H_5FeCOCNPPh$_2$Me	1.00	1.73	0.96 (Me), 0.78 (Ph), 0.56 (Ph)
η^5-C_5H_5FeCOCNPPh$_3$	1.00	1.71	0.77
Calculated	1.00	1.61	1.04 (R_1), 0.83 (R_2), 0.58 (R_3)

Discussion

Consideration of the piano stool geometry of the iron complexes allows one to discern an orientation of the tertiary phosphine which would minimize steric interactions and most certainly represent an energy minimum in rotation about the Fe—P bond (Figure 1). The asymmetry of the iron center would require like groups in the 1, 2 and 3 positions to be nonequivalent. However, only one methyl signal is observed in η^5-$C_5H_5FeCOCNPMe_3$ at room temperature, indicating that rotation about the Fe—P bond is rapid in this complex. Similarly, addition of $Eu(fod)_3$ to η^5-$C_5H_5FeCOCNPPh_3$ separates the phenyl resonances until single multiplets are observed for *ortho*, *meta* and *para* protons of the three rings, again implying rapid rotation about the metal—phosphorus bond. Carbon-13 spectra of the trimethyl phosphine and triphenyl phosphine complexes also show single resonances for the phenyl and methyl groups.

The observation of rapid rotation about the metal—phosphorus bond in trimethyl and triphenyl phosphine complexes implies a similar situation in both η^5-$C_5H_5FeCOCNPPh_2Me$ and η^5-$C_5H_5FeCOCNPMe_2Ph$ compounds, for which the barriers resulting from steric interaction should be similar. However, the configuration indicated in Figure 1 would predict three possible conformations for each complex (Figure 2), which would result in a thermodynamically controlled population distribution in which conformations were rapidly exchanged by rotation. The paramagnetic shift reagent, which has been shown to coordinate to the cyanide [9], would be expected to cause different downfield shifts for nuclei in the three positions of Figure 1. A structural model of the compound, using X-ray data available for a number of similar complexes, was constructed in order to predict the effect of the shift reagent, assuming dipolar interactions and approximate geometries. The calculated values of shifts for the phosphorus-bound nuclei in the three positions of Figure 1 are given in Table 5; the details of the calculation are given in the Experimental section.

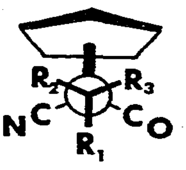
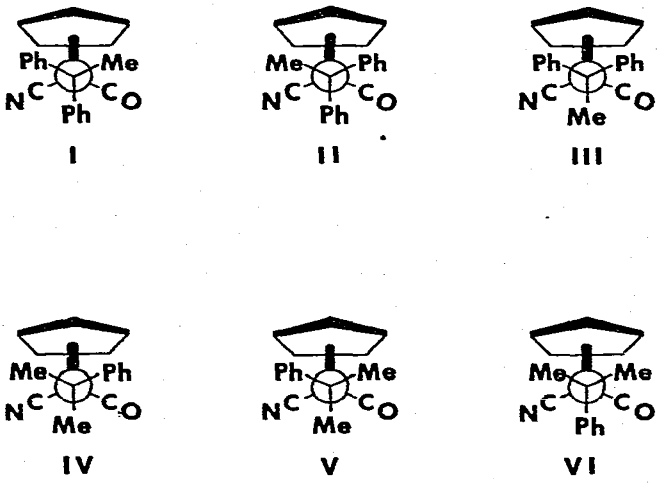


Fig. 1. Preferred conformation of a trisubstituted phosphine ligand.



I II III IV V VI

Fig. 2. Conformers of methyldiphenylphosphine and dimethylphenylphosphine ligands.

The trimethylphosphine and triphenylphosphine compounds, lacking conformational preferences, (as in I, II and III) have relative shifts representing an average of equal contributions from the shifts of the three positions. In contrast, carbon nuclei in the same positions are shifted differently in both η^5-C_5H_5Fe-COCNPPh$_2$Me and η^5-C_5H_5FeCOCNPPhMe$_2$, implying some degree of conformational preference. Also, PMR spectra indicate the nonequivalent *ortho* protons of the phenyl groups are shifted quite differently, relative to the cyclopentadiene. In the diphenyl complex, the observed ^{13}C shifts are strikingly similar to those predicted for conformation III and bear no resemblance to either II or I. The similarity of the carbonyl and cyanide ligands would most likely result in significant populations of both I and II, if III were not the most favored conformation. However, as an example, an average of the expected shifts for I and II would result in values of 0.94 (Ph), 0.81 (Ph), and 0.71 (Me), which do not correlate with the observed shifts.

The preference of the two phenyl groups for an orientation that places them closest to the cyclopentadienyl ring seems at first glance unlikely, assuming the latter to be bulkier than either the carbonyl or cyanide group. Indeed, Baird et al. [3] found evidence of greater steric requirements on the part of the cyclopentadienyl group than either a triphenylphosphine or carbonyl group, in a series of alkyl-nickel and -iron compounds [3]. There appear, however, to be significant differences between the phosphine and alkyl systems. For example, the geometrical positions of the phosphine substituents relative to the rest of the molecule are, by virtue of the increased length of phosphorus—metal and phosphorus—carbon bonds, at a greater distance than are the substituents on a metal-bonded carbon atom. Groups attached to a coordinated phosphorus are also bent away from the phosphorus metal axis to the extent that M—P—C angles average 116° instead of the tetrahedral angle of 109° [10]. The comparison here also involves the relative steric requirements of a methyl group relative to a phenyl group in the given geometry and is a tertiary system, in contrast to the primary and secondary alkyls studied by Baird. With respect to an orientation towards the cyclopentadienyl ring, molecular models indicate similar steric interactions of methyl and *ortho*-phenyl protons. However, the phenyl rings possess added flexibility as a result of rotation about the carbon—phosphorus bond and can minimize this interaction by twisting slightly. The methyl group is less able to minimize its interaction. On the other hand, when directed away from the cyclopentadienyl ring, the methyl group has no interaction with the remaining two ligands whereas the *ortho* protons of the phenyl rings are in close proximity to the carbonyl and cyanide groups over a relatively wide angle of rotation about the carbon—phosphorus bond. The preference of the complex for conformation III therefore does not seem unreasonable.

The paramagnetic ^{13}C shifts of the dimethylphenyl complex do not fit the predictions of any of the individual conformations IV-VI. The similarity of carbonyl and cyanide groups would imply that IV and V would have nearly equal energies. An average of these two conformations would predict shifts of 0.93 (Me), 0.81 (Me), and 0.70 (Ph), which are in reasonable agreement with the observed results and significantly different from those predicted for conformation VI. The choice of conformations is consistent with that of the diphenyl compound, in that each phenyl ring is oriented toward the cyclopentadienyl ring and not toward the carbonyl and cyanide groups.

A comparison of the observed and calculated paramagnetic shifts of the carbon nuclei bound to phosphorus allows the assignment of the unshifted resonances to particular diastereotopic nuclei. The phosphorus atom is a prochiral center permitting the use of the pro-*R* and pro-*S* nomenclature outlined by Hanson [11]. In the preferred conformation of the diphenylmethyl complex (III in Figure 2), the phenyl group in position 3 (Figure 1) is pro-*R* and the group in position 2 is pro-*S*. When extrapolated to zero shift reagent concentration, the relative shifts of the two carbon resonances listed in Table 4, when compared to those calculated for the two positions in Figure 1, indicate that the signal at 136.99 ppm can be assigned to the pro-*S* phenyl group and the signal at 135.61 ppm to the pro-*R* phenyl group.

A similar analysis of the dimethylphenyl complex indicates that the pro-*R* methyl group would occupy positions 1 and 2 with the pro-*S* group occupying positions 1 and 3 (IV and V in Figure 2). Therefore the resonance at 18.72 ppm would seem to correspond to the chemical shift resulting from the pro-*R* environments with the signal at 18.03 ppm corresponding to the pro-*S* group, although the assignment is not as secure as in the diphenylmethyl case.

This approach to assignments could be extended to other diastereotopic nuclei in a wide variety of compounds with the aid of calculated relative isotropic shifts for various orientations.

Use of a lanthanide shift reagent in a conformational analysis must eventually result in a consideration of the effect of coordination of the reagent to the system itself. Some change in the population of conformers might be expected in the system under study, resulting from the steric interaction of europium ligands with the phosphine substituents. However, any significant distortion of the geometry or change in conformational preference would most likely affect the ^{31}P—^{13}C and ^{31}P—^{1}H coupling constants, which would be expected to differ somewhat for each of the configurational positions 1, 2 and 3. Differences of this nature have been reported by Bushweller and Lourandos [11] for the *trans* and *gauche* positions of methyl groups in $M(CO)_5PPh_2$-t-butyl complexes.

All observed values of *J*(P—H) and *J*(P—C) remain virtually constant upon successive additions of $Eu(fod)_3$. Also, addition of the shift reagent does not change the infrared spectra of the complexes capable of rotational isomerism to a greater extent than those for which all conformations are equal.

Evidence for conformational isomerism is not readily apparent from the infrared spectra. Bands for the diphenylmethyl and dimethylphenyl complexes are only slightly broader than that of the trimethyl complex and this may result from rotational isomerism about the carbon—phosphorus bond, as will be discussed later. However, from the paramagnetic shift data, only the dimethylphenyl complex would be expected to have a significant population of more than one rotamer. Additionally, the carbonyl band seems to be relatively insensitive to changes in the phosphine ligand. Substitution of a phenyl group for one of the methyls in η^5-$C_5H_5FeCOCNPMe_3$ results in a barely perceptible shift of about 1 cm^{-1} for ν_{max}. Presumably, conformers IV and V could have nearly degenerate carbonyl bands, excluding any drastic change in population resulting from use of cyclohexane as the solvent instead of chloroform.

Determination of the rate of rotation about the phosphorus—iron bond was complicated by several factors. Without the use of lanthanide shift reagents, the phenyl portion of the PMR spectrum remained an unresolved multiplet. Maximum separation of the multiplet was achieved in the η^5-$C_5H_5NiCNPPh_3$ complex using $CDCl_3$ as solvent. The multiplet remained sharp to −65°C, the point at which the chloroform froze. Broadening and coalescence of this multiplet has been observed for the compounds η^5-$C_5H_5NiPPh_3R_F$ (R_F = $CF(CF_3)_2$, CF_2CF_3 and CF_3) at temperatures below −53°C, with the point of coalescence occurring at lower temperatures as the bulk of R_F is decreased [5]. Thus the cyanide analog, presumably less bulky than even the CF_3 compound, would be expected to exhibit broadening of phenyl protons only at low temperatures.

Use of the shift reagent $Eu(fod)_3$ had the effect of increasing the separation of averaged signals and should have increased the temperature at which broadening would be observed. However, the rapid exchange between free and complexed $Eu(fod)_3$ is slowed at lower temperatures, which broadens all shifted resonances. This phenomenon is illustrated in the low temperature PMR spectrum of η^5-$C_5H_5FeCOCNPMe_3$, where broadening of both methyl and cyclopentadienyl signals occurred at about −25°C. (Sufficient $Eu(fod)_3$ had been added to cause shifts of just over 500 Hz.) The decrease in the rate of exchange of free and bound shift reagent has been noted previously [13,14]. Although the exchange rate of $Eu(dpm)_3$* is slightly faster than $Eu(fod)_3$ [13], any advantage in using this shift reagent was negated by poor solubility and somewhat wider linewidths. $Pr(fod)_3$ was also investigated as a possible substitute but appeared to cause broadening in the same temperature range and resulted in even wider linewidths.

Despite our inability to study the low temperature spectra, an estimate of the maximum energy barrier for rotation about the iron—phosphorus bond could be obtained using the broadening data and fast exchange calculations for three equally populated sites. An estimate of the relative chemical shifts of the unaveraged *ortho* protons upon coordination of $Eu(fod)_3$ was made using the structural data and methods outlined in the Experimental section. The *ortho* protons within a ring were assumed to rotate about the P—C_1 vector and to exchange positions rapidly. The three orientations in Figure 1 have calculated shifts in the approximate ratio of 3.28/2.17/1.00. In the sample to which $Eu(fod)_3$ was added, this resulted in values of 6.10, 4.15 and 1.92 ppm downfield from the unshifted resonance. Broadening of the *ortho* multiplet was observed at −20°C. Assuming a minimum observable broadening of 0.5 Hz, a value of $k = 6.6 \times 10^5$ is obtained. This gives a value of $\Delta G^* = 8.0$ kcal/mol and represents an upper limit for the barrier to rotation.

Molecules containing aromatic rings bonded to a central atom sometimes demonstrate isomerism due to restricted internal motions. Crystal structure determinations of triphenylphosphine and a number of similar compounds [14-16] have shown that in all of these the aryl groups adopt a propeller-like conformation (Figure 3). This propeller-chirality may be that of a right- or a left-handed helix, with interconversion occurring by concerted rotation about the carbon—phosphorus bonds.

Room temperature ^{13}C and ^1H NMR spectra of all of the arylphosphine

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* dpm = di(2-piraloyl)methane.

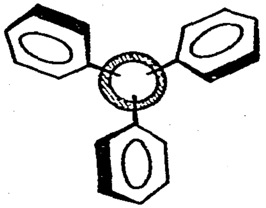

Fig. 3. The propeller chirality of the triphenylphosphine ligand.

compounds contain averaged signals for the *ortho* and *meta* nuclei, indicating rotation about the carbon—phosphorus bond must be rapid. Addition of sufficient Eu(fod)$_3$ to cause a large downfield shift of the *ortho* resonance should increase the chemical shift difference between the unaveraged signals and enhance the possibility of slowing the exchange. However, as previously indicated, exchange between free and bound shift reagent also causes broadening upon lowering the temperature. Again, an estimate for the maximum value of the barrier to rotation can be calculated at the temperature at which broadening was first observed. The limiting equation for fast exchange of two proton sites was used:

$$k = \frac{\pi(\delta\nu)^2}{2W}$$

where k is the rate of exchange, W is the minimum observable peak widening, and $\delta\nu$ is the separation between the unaveraged proton resonances. The value for $\delta\nu$ was estimated from a geometric model (Experimental) and assumes rapid rotation about the phosphorus—metal bond and a locked propeller conformation for the phenyl groups. The approximations indicate that the isotropic shifts of the nonequivalent *ortho* protons would be in a ratio of about 1 to 7.8 for both right- and left-handed conformations. In the sample to which Eu(fod)$_3$ was added this resulted in values of 718 and 92 Hz downfield shifts from the unperturbed resonance. The calculation assumes that one set of unaveraged resonances, representing equal populations of both diastereomers formed by the right- and left-handed helicies, represents the slow exchange situation. Since the existence of the diastereomers results from the asymmetry of the iron center and the carbonyl and cyanide groups are sterically similar, the approximation would seem to be a reasonable one. Using a value of 0.5 Hz for W, a value of 1.23×10^6 sec^{-1} was calculated for k, which at —20°C yields a free energy of activation of 7.6 kcal/mol.

Determinations of P—C rotational barriers providing direct comparison to this work have not been available in the literature, with the exception of the recent report by Bushweller [12] of a value of 8.3 kcal/mol for the rotation of a t-butyl group about the P—C bond in M(CO)$_5$(PPh$_2$-t-Bu) complexes. The lower estimate of the P—C barrier determined for the arylphosphines under study seems logical as the steric requirements of a t-butyl group appear to be considerably greater than those of another phenyl and, therefore, would be expected to increase rotational barriers.

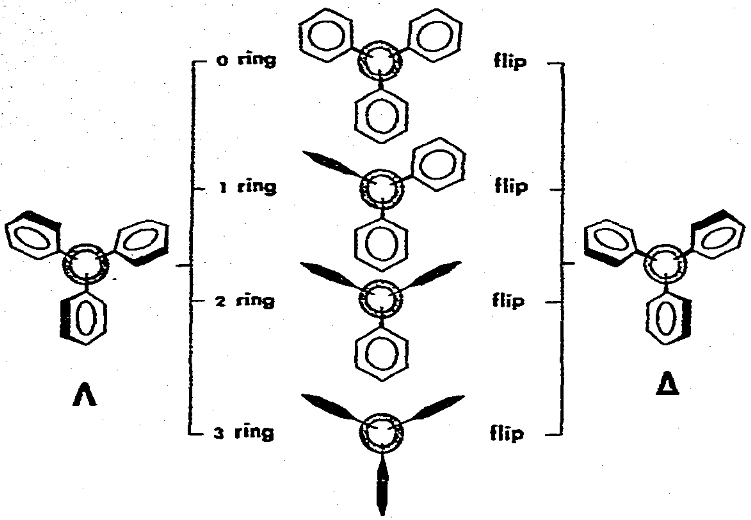

Fig. 4. The four rotational (flip) mechanisms for the Ar_3PM system adapted from the work of Gust and Mislow [6]. The shaded circle represents the metal atom behind the phosphorus atom. The central structures indicate the approximate geometry of the transition states.

Some comparison to measurements in the free ligand can be made, however. A value of 11.3 kcal/mol has been suggested for the barrier in trimesitylphosphine [18,19]. This value, though significantly larger than the barrier reported here, most likely reflects the increased steric interaction of the substituted aryl groups*.

Reasonable mechanisms by which the left- and right-handed helices might be interconverted have been discussed by Gust and Mislow [6]. Four rotational mechanisms involving interdependent rotations of the three rings have been postulated by Kurland [20]. Although a great number of mechanisms that reverse the helicity of the aryl rings may be envisioned, those suggested by Kurland appear to be quite reasonable and account for all experimental observations to date [6]. Our comments on the mechanistic implications in the system under study will therefore center on the pathways proposed by Kurland. These paths, as outlined by Gust and Mislow [6], are shown in Fig. 4. A "flip" is a rotation through a transition state where the ring is perpendicular to a reference plane formed by the three carbon atoms attached to the phosphorus. In the zero-ring flip, all three rings rotate through a transition state where the normal to each ring lies in a plane perpendicular to the reference plane.

The lack of substituents on the rings prevents the determination of a single mechanism as the means of interconversion but careful examination distinguishes two groups of mechanisms that would have different results**. A mechanism

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* Temperature dependence of the PMR spectrum of $PdCl_2(PH\text{-}t\text{-}Bu_2)_2$ has been attributed to hindered rotation about the metal—phosphorus bond [21]; however this effect may arise from hindered rotation about the P—C bond as well.

** There are two diastereoisomers present when one considers the helicity in the triphenylphosphine attached to a chiral metal center. The (*S*)-metal configuration shown in Figure 1 gives rise to two structures *S*-Λ and *S*-Δ. Then depending upon the orientation of the *ortho* position (*endo* near the metal; *exo* away from the metal) four environments are possible: Λ-*endo*, Λ-*exo*, Δ-*endo*, Δ-*exo*.

involving only three-ring or zero-ring flips would not interchange the *ortho* and *meta* positions on a given ring and should result in two signals for nuclei in those positions and become evident upon addition of Eu(fod)$_3$. A one-ring or two-ring flip mechanism would result in averaging of both positions and would result in a single resonance for *ortho* and *meta* positions, as is observed. A zero-ring flip followed by a three-ring flip, essentially rotating the ring a full 360°, would also produce the averaged resonances observed.

A conformational analysis study of triphenylphosphine by Brock and Ibers [22] suggest that the zero-ring flip is approximately 150 kcal/mol less favorable than the three-ring flip. Thus, it appears that the rearrangement most probably occurs via a series of one-ring and/or two-ring flips.

A reduction in the number of phenyl rings likewise decreases the number of possible concerted mechanisms. The diphenylmethyl complex in which the *ortho* positions are also averaged must interconvert its chirality by either a one ring flip or by rotation of both rings through zero followed by two ring flips.

In the case of the dimethylphenyl complex, the mechanisms can be limited to either a flip back and forth between right- and left-handed orientations, resulting in two *ortho* and *meta* signals, or complete rotation about the carbon—phosphorus bond, resulting in an averaged signal for both positions. The later possibility coincides with the spectroscopic observations and may suggest that a similar rotational mechanism accounts for the interconversion in the diphenyl- and triphenyl-phosphine complexes.

Experimental

Preparations, reactions, and purifications were carried our under a nitrogen atmosphere. Chromatographic separations utilized low activity alumina (Fisher A-540). NMR spectra were obtained using Varian HA-100 and CFT-20 spectrometers. Infrared spectra were obtained using a Perkin—Elmer 421 spectrometer calibrated with DCl. Chemical analyses were performed by the Baron Consulting Analytical Laboratory, Milford, Connecticut.

Syntheses

As a precurser to the iron cyanide complexes, the dark green iodine derivatives were prepared by the irradiation of η^5-$C_5H_5FeCO_2I$ with the appropriate

TABLE 6

PROPERTIES OF THE IODINE COMPOUNDS

Compound	CO$_{max}$ [a]	Yield (%)	M.p. (°C)	Found (calcd.) (%)	
				C	H
η^5-$C_5H_5FeCOIPMe_3$	1950	72	135-137 (dec.)	30.70 (30.71)	4.11 (4.01)
η^5-$C_5H_5FeCOIPPhMe_2$	1950	80	98	see ref. 23	
η^5-$C_5H_5FeCOIPPh_2Me$	1952	61	145-148 (dec.)	47.96 (47.93)	3.86 (3.81)
η^5-$C_5H_5FeCOIPPh_3$	1954	75	230-235 (dec.)	see ref. 24	

[a] Chloroform.

phosphine, following the procedure of Brunner et al. [23]. Although the triphenylphosphine [24] and dimethylphenylphosphine [23] iodine complexes have been mentioned in the literature, the properties of all of the iodine compounds which were prepared are summarized in Table 6.

The cyanide complexes were each prepared from the appropriate iodine complex according to the following procedure. An equimolar amount of silver tetrafluoroborate was added to a 200 ml methanol solution of η^5-C_5H_5FeCOI-PMe$_3$ (0.02 mol). Immediate precipitation of silver iodide was noted and a two molar excess of sodium cyanide was added to the solution of the η^5-C_5H_5FeCOI-PMe$_3$ cation. After four hours the reaction mixture was filtered and the solvent removed. The residue was dissolved in methylene chloride and loaded on a column of alumina in petroleum ether. A large green band* eluted slowly with 2/1 petroleum ether/methylene chloride, eventually separating from a smaller yellow band. The yellow band was eluted rapidly with methylene chloride and identified as the desired product, η^5-C_5H_5FeCOCNPMe$_3$. Crystallization from benzene/hexane gave products with the properties summarized in Table 7. The dimethylphenyl and diphenylmethyl complexes were prepared in exactly the same manner. The preparation of the triphenylphosphine complex differed in that dimethyl formamide was used instead of methanol as the solvent. The solids were air-stable but chloroform solutions decomposed upon standing.

The nickel complex was prepared by adding bis(triphenylphosphine)dichloronickel(II) (4.5 g), prepared by the method of Venanzi [25] to nickelocene (1.3 g) in THF and heating under reflux for six hours. The solvent was removed and the residue crystallized from benzene/hexane. The 4.9 g (85% yield) of bright red-purple needles of η^5-C_5H_5NiClPPh$_3$ were air dried and exhibited a melting point of 138-140°C. The freshly-prepared sample of η^5-C_5H_5NiClPPh$_3$ (1.0 g, 0.0023 mol) was dissolved in acetone and 0.46 g (0.0024 mol) of silver tetrafluoroborate added. The color changed immediately from red to dark green-brown, as AgCl precipitated. An excess of sodium cyanide (0.36 g) was added and the solution was left to stir overnight. The acetone was then removed and the residue dissolved in methylene chloride and loaded on an alumina column

TABLE 7

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF CYANIDE DERIVATIVES

Compound	Color	Yield (%)	M.p. (°C)	Found (calcd.) (%)		
				C	N	H
η^5-C_5H_5FeCOCNPMe$_3$	yellow	50	122-124	48.43 (47.84)	5.44 (5.58)	5.55 (5.62)
η^5-C_5H_5FeCOCNPMe$_2$Ph	amber	20	oil	[a]		
η^5-C_5H_5FeCOCNPMePh$_2$	yellow	20	132-135	63.87 (64.03)	3.47 (3.73)	4.72 (4.83)
η^5-C_5H_5FeCOCNPPh$_3$	yellow	60	225 (dec.)	68.50 (68.67)	3.10 (3.20)	4.69 (4.61)
η^5-C_5H_5NiCNPPh$_3$	green	85	125	70.09 (69.95)	3.27 (3.40)	5.06 (4.89)

[a] Although not subjected to elemental analysis, this compound was conclusively identified by ^{1}H and ^{13}C NMR spectra and infrared spectra, all of which showed no evidence of impurities.

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* A structure similar to the iodide is expected for this green product; however the infrared spectrum (1945 cm^{-1}) indicates that it is not the starting material.

in petroleum ether. Two bands appeared on the column. The first, a green band, was eluted with methylene chloride/acetone in a 4/1 ratio. The second band eluted at a slower rate with the same solvents. It was red and presumed to be η^5-$C_5H_5NiClPPh_3$. The green band was concentrated and crystallized from benzene/hexane. It was identified as the desired η^5-$C_5H_5NiCNPPh_3$.

Calculation of paramagnetic shifts

Utilization of lanthanide complexes in NMR studies has centered around the $(3 \cos^2\theta_i - 1/r_i^3)$ dependence of shifts arising from pseudocontact interaction [26-28] (where θ_i is the angle between the vector, r_i, from the lanthanide metal to nucleus i in the complexed substrate and the vector joining the metal atom to the donor atom.)

To calculate relative values of the shift expected for a particular geometry, a model of the appropriate complex was constructed using X-ray structure data available for a number of similar compounds. A summary of the angles and bond lengths employed is found in Table 8.

The calculation for the relative shift of the averaged carbon nuclei in the cyclopentadienyl group was made by averaging the values of 10 equidistant positions of the carbon nuclei obtained by rotation about the metal—ring axis. For the Fe—P rotational calculations, relative shifts for the *ortho*-substituted protons were determined by averaging the shifts of all *ortho* positions in the right- and left-handed conformation for each position in Figure 1. For the P—C calculation, the shifts of each set of nonequivalent protons were computed and averaged for the three configurations of Figure 1.

The isotropic shifts were considered to arise entirely from dipolar interactions. Previous studies have indicated that severe difficulties arise from contact effects predominantly at the first three atoms from the coordination site [32]. Since the carbon-1 of the phenyl groups are five atoms from the metal contact effects should be minimal.

TABLE 8

BOND LENGTHS AND ANGLES USED IN SHIFT CALCULATIONS

Bond	Angle	Value (Å)	Value (°)	Ref.
C—C(C_5H_5)		1.43		29
Fe—C(C_5H_5)		2.10		29
Fe—C(CO)		1.75		30
Fe—C(CN)		1.75		[a]
Fe—P		2.24		10
P—C(C_6H_5)		1.86		10
C—C(C_6H_5)		1.40		10
C—N		1.15		[a]
Eu—N		2.65		31
	C(CO)—Fe—C(CN)		90	10
	C(CO)—Fe—P		90	10
	C(CN)—Fe—P		90	10
	Fe—P—C(C_6H_5)		116	10
	C—P—C		103	10
	C—C—C(C_6H_5)		120	10

[a] Bond lengths for Fe—C(CN) and C—N were assumed to equal those of Fe—C(CO) and C—O.

Conclusion

The succesful application of a lanthanide shift reagent to the determination of conformational effects and rotational barriers in a series of organometallic complexes has been demonstrated. For both η^5-$C_5H_5FeCOCNPPh_2Me$ and η^5-$C_5H_5FeCOCNPPhMe_2$, conformations in which the phenyl rings are oriented toward the cyclopentadienyl ligand appear to be favored. Broadening of the *ortho* proton signal in low temperature spectra of η^5-$C_5H_5FeCOCNPPh_3$ in the presence of $Eu(fod)_3$ allowed the estimation of maximum barriers to rotation about the Fe—P and P—C bonds, with values of 7.6 and 8.0 kcal/mol respectively. The data suggest the mechanism of interconversion of right- and left-handed helices in the arylphosphine complexes involves complete rotation about the C—P bond, although in the diphenyl and triphenyl cases a combination of one and/or two ring flips cannot be excluded. In previous observations of chemical shift differences in diastereotopic nuclei it has been impractical to assign a given resonance to a particular nucleus or group. Particularly when one conformation is prevalent the assignments can be readily made by extrapolating isotropic shifts to zero shift reagent concentration.

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