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Conformation–Reactivity Relationships for the Organotransition-Metal Complexes (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)R and (η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)R (R = Alkyl and Aryl)

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Abstract: A conformational analysis is described for pseudooctahedral complexes of the type (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)R (**1**) and (η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)R (**2**) (R = alkyl and aryl). The analysis is based upon extended Hückel calculations performed on the model iron complexes (η^5-C$_5$H$_5$)Fe(CO)(PPhH$_2$)R [R = CH$_3$, C$_2$H$_5$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$, Sn(CH$_3$)$_3$, and Ph] and rhenium complexes (η^5-C$_5$H$_5$)Re(NO)(PPhH$_2$)R [R = C$_2$H$_5$, CH$_2$Ph, and CH$_2$(2,6-C$_6$H$_3$Me$_2$)]. For R groups in **1** and **2** with a single C$_\alpha$ substituent (e.g., C$_2$H$_5$ and CH$_2$Ph), the most preferred conformation places the C$_\alpha$ substituent between the cyclopentadienyl and the CO(NO) ligands. For R groups in **1** and **2** with two C$_\alpha$ substituents [e.g., CH(CH$_3$)$_2$], the most stable conformation has the two substituents straddling the cyclopentadienyl ligand. These most stable conformations correlate well with known X-ray crystal structures for **1** and **2**. The conformational analysis elaborated herein is used to explain the high stereospecificities that have been observed in the reactions of **1** and **2**.

I. Introduction

Organotransition-metal complexes form a class of very important molecules, not only because of their inherently interesting physical and chemical properties but also because of the significant impact they are having on synthetic organic chemistry.[1-5] Many novel synthetic applications of organotransition-metal complexes have been reported in the recent literature which provide methods for synthetic transformations which are difficult or impossible to achieve by more conventional routes. Of crucial note is the observation that reactions at organic ligands bound to the (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$) fragment are highly stereoselective.[6-25] Similar observations have been noted in extensive studies on the corresponding (η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)R[26-33] and other systems.[15,18,30-34] Despite these advances, little has been reported concerning the detailed conformational analysis of such transition-metal complexes and how this relates to the stereoselectivities of subsequent reactions.[7,35]

The primary focus of the study reported here is the development of a conformational model for organotransition-metal complexes of the type (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)R (**1**) and (η^5-C$_5$H$_5$)Re-(NO)(PPh$_3$)R (**2**) (R = alkyl, substituted alkyl, and aryl). The
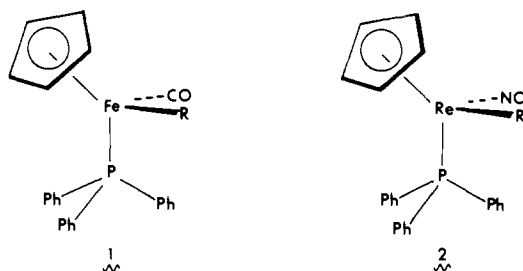
application of this conformational model to a rationalization of the chemical reactivity of complexes **1** and **2** is then described. Complexes of general type **1** and **2** are particularly suited to conformational analysis for several reasons; they are the most abundant general class of organotransition-metal complex for which a very large body of spectroscopic data and chemical reactivity information is available, a number of stereospecific reactions have been reported for several complexes of type **2**, and no general theory has been advanced which correctly predicts all the stereochemical properties of these complexes. However, a generally accepted[36] and frequently used but approximate conformational model[37-42] for these systems has been in the literature for more than 10 years.

Our new conformational model for complexes of type **1** and **2** is based on consideration of their structural features and on

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Table I. Pseudooctahedral Character of **1** and **2** as Determined by X-ray Crystallographic Analysis (Cp = η^5-C$_5$H$_5$)

iron complexes	bond angle, deg			
	P–Fe–C$_\alpha$	P–Fe–CO	C$_\alpha$–Fe–CO	ref
CpFe(PPh$_3$)(CO)CH$_2$O-menthyl	92.0	91.7	89.3	a
CpFe(PPh$_3$)(CO)CH$_2$CO$_2$-menthyl	90.9	92.7	95.9	a
(*RR,SS*)-CpFe(PPh$_3$)(CO){COCH(Me)Et}	89.3	92.1	94.8	b
CpFe(PPh$_3$)(CO)C$_6$H$_5$	88	87	88	c
CpFe(f$_6$fos)(CO)Sn(CH$_3$)$_3$^{d}	97.1	96.1	83.5	e
CpFe(PPh$_3$)(CO)COPh	88	86	93	f
(*SS*)-Cp′Fe(PPh$_3$)(CO)COCH$_3$^{g}	90.6	94.6	92.4	h
(*SR*)-Cp′Fe(PPh$_3$)(CO)I^g	94.3	91.2	91.7	h
CpFe(PPh$_3$)(CO)SO$_2$-*i*-Pr	93.0	95.8	92.3	i
CpFe(PPh$_3$)(CO)CO$_2$-menthyl	89.9	91.7	90.9	j
CpFe(PPh$_3$)(CO)C$_4$H$_3$S	91	92	92	k
(*Z*)-CpFe(PPh$_3$)(CO)C(OMe)=CHCH$_3$	92.0	91.7	93.7	l

rhenium complexes^m	bond angle, deg			
	P–Re–C$_\alpha$	P–Re–NO	C$_\alpha$–Re–NO	ref
CpRe(PPh$_3$)(NO)CH$_2$Ph	87.4	93.9	93.8	n
CpRe(PPh$_3$)(NO)(η^2-CH$_2$=O)$^+$		88.4	95.9	o
CpRe(PPh$_3$)(NO)(η^2-CH$_2$=S)$^+$		88.5	90.6	o
CpRe(PPh$_3$)(NO){CH(CH$_2$Ph)Ph}	93.6	90.0	90.6	p
CpRe(PPh$_3$)(NO)(=CHPh)$^+$	93.2	91.0	99.8	p
CpRe(PPh$_3$)(NO)CHO	85.0	92.8	92.7	q

^{a} Reference 46. ^{b} Reference 11. ^{c} Reference 47. ^{d} f$_6$fos = (1,2-PPh$_2$)$_2$C$_5$F$_6$. ^{e} Reference 48. ^{f} Reference 49. ^{g} Cp′ = 1-methyl-3-phenylcyclopentadienyl. ^{h} Reference 50. ^{i} Reference 51. ^{j} Reference 52. ^{k} Reference 53. ^{l} Reference 9. ^{m} (η^5-C$_5$Me$_5$)Re(NO)(PPh$_3$)(=CH$_2$)$^+$ is not included in this table due to disorder in the crystal. See ref 29. ^{n} Reference 44. ^{o} Reference 54. ^{p} Reference 32. ^{q} Reference 55.

molecular orbital calculations of the extended Hückel type[43] with parameters detailed in the Appendix section. Support for this model will be presented in terms of X-ray crystallographic results and ^{1}H NMR spectroscopic data. The ability of the model to evaluate the stereoselectivities observed will be described with particular attention being focused on aspects of chemical reactivities which were difficult to rationalize in terms of the previous model. A series of generalizations which describe the conformational properties of **1** and **2** and which predict reactivities and stereoselectivities of these complexes will be formulated.

II. Conformational Model for (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)R (1) and (η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)R (2)

Although complexes of type **1** and **2** are frequently described as pseudotetrahedral,[13,15,19,41,44,45] both in discussions of these molecules and in their two-dimensional representations, an examination of available X-ray crystallographic data[9,11,32,44-55] for

complexes generalized by structures **1** and **2** clearly demonstrates that they are octahedral (Table I).[7] While these comlexes are not perfectly symmetrical, the bond angle between any two of the directly bonded atoms of the ligands R, CO(NO), and PPh$_3$ and the metal is close to 90°. In addition, the bond angle between the centroid of the cyclopentadienyl ligand, the metal, and any other ligand is ca. 125°. This structural feature is illustrated by the Newman projection **3** (looking from C$_\alpha$ of R to metal) which emphasizes the pseudooctahedral structure of complexes **1** and **2** and is the appropriate representation for the analysis which follows. Note that the bite angle between the CO(NO) ligand

3
pseudo–octahedral

4
pseudotetrahedral
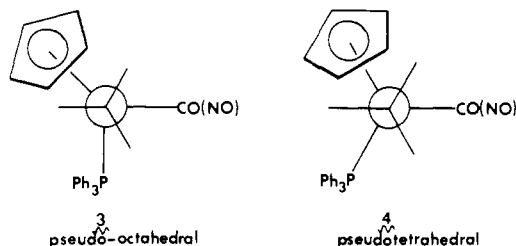
and the PPh$_3$ ligand is 90° while that between either of these ligands and the Cp group is 135°. In addition, when one considers the Newman projection **3**, one must remember that the P, M, and CO(NO) atoms are in the same plane while the centroid of the Cp ligand is substantially behind the plane (c.f., **1–2**). In contrast, the previous description of the structures for complexes **1** and **2** as pseudotetrahedral implies a 109.5° bond angle between any

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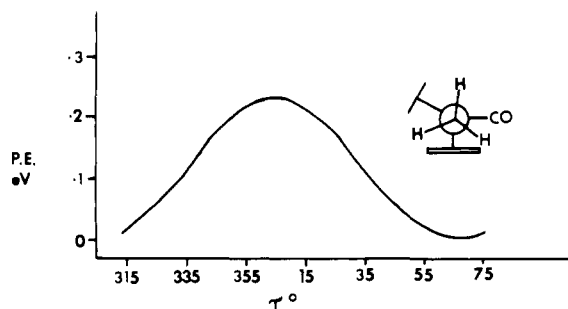
Figure 1. Calculated potential energy (electronvolts) vs. torsional angle $\tau(H_\alpha - C_\alpha - Fe - P)$ for $(\eta^5-C_5H_5)Fe(CO)(PPhH_2)C_\alpha H_3$ (7).

two ligands and the metal atoms, as illustrated by **4**.

A complete conformational analysis of complexes generalized by **3** is an unrealistic challenge given the size of the molecule and the many degrees of freedom available to it. Consequently, some simplifying assumptions have to be made. For the evaluation and prediction of the stereochemical consequences of reactions on the ligand R, the conformation of the groups attached to the α carbon of R (C_α) relative to the ligands around the metal is of most interest. The extended Hückel molecular orbital algorithm, a procedure well documented in the literature for these types of organotransition-metal complexes,[43,56-62] was employed for the conformational analysis of complexes **1** and **2**. Both electronic and steric effects on rotational energy profiles in organo-transition-metal complexes related to **1** and **2** have been recently published by Hoffmann et al.[58-61] For calculations of this nature, it has been standard practice to examine the structure–energy relationships by using abridged analogues of **1** and **2**, i.e., where the PPh₃ ligand has been replaced by PH₃.[32,58] This approach simplifies the calculations and reduces the required computer time since the inclusion of three phenyl rings considerably adds to the computational complexity. In our preliminary studies, we also made this simplifying assumption but rapidly concluded that PPh₃ was not well modeled by PH₃ for these complexes. Examination of all available X-ray structural data for complexes of this type shows that one phenyl group consistently lies close under the ligand R in a plane approximately parallel to the plane formed by Fe (or Re), C_α, and CO (or NO), and chemical evidence shows that the P–phenyl rings exert a considerable influence of the properties of R.[6-13] We turned our attention therefore to the analogous complexes **5** where one phenyl substituent on the phosphorus was retained, i.e., PPh₃ was modeled with PPhH₂. Furthermore, in
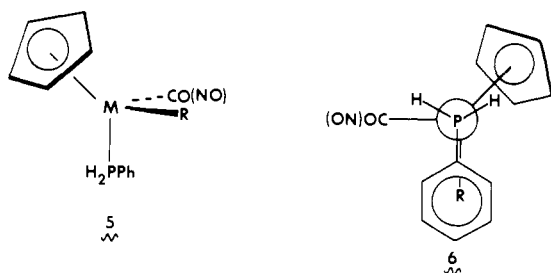
order to treat the possible interactions between the R substituent and the PPh₃ ligand in **1**, we restricted rotation about the metal phosphorus bond such that the metal–C_α bond essentially eclipsed the P–C_{ipso} bond as shown in **6**.

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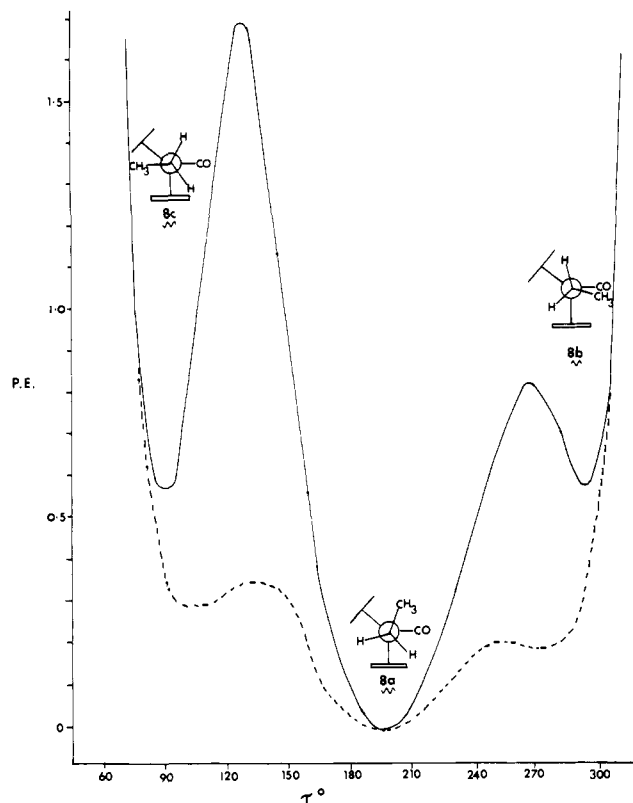(62) Kubáček, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

To characterize the nature of the potential energy function for rotation about the metal–C_α bond, extended Hückel calculations were performed on the series of compounds **7–15**.

	R = CH₃			R = CH₂CH₃
7	R = CH₃		**13**	R = CH₂CH₃
8	R = CH₂CH₃		**14**	R = CH₂Ph
9	R = CH(CH₃)₂		**15**	R = CH₂(2,6-C₆H₃Me₂)
10	R = C(CH₃)₃			
11	R = Sn(CH₃)₃			
12	R = Ph			

As the starting point in all the calculations, available X-ray crystallographic data for the required structural parameters (bond lengths, bond angles, and torsional angles) were used for which the leading references can be found in Table I. It was further assumed that the two ortho carbons of the phenyl ring were essentially equidistant from the plane containing the CO(NO), Fe(Re), and C_α of the R substituent, as illustrated in **6**. Furthermore, since the iron system is of particular interest to us, most of the calculations were performed on iron rather than on the rhenium complexes.

In the figures which follow, the abscissa refers to the torsional angle $\tau \equiv \tau(X-C_\alpha-M-P)$ where X is the specified C_α substituent. A positive value refers to a clockwise rotation of X from the eclipsed position, as indicated in the Newman projection **16**. In
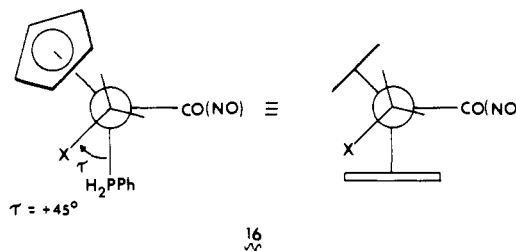
each case, the ordinate gives the potential energy in the electronvolts (1 eV = 23 kcal).

A. $(\eta^5-C_5H_5)Fe(CO)(PPhH_2)CH_3$ **(7).** The variation of potential energy for rotation of the methyl group about the C_α–Fe bond for $(\eta^5-C_5H_5)Fe(CO)(PPhH_2)CH_3$ (7) is shown in Figure 1. The energy minima for rotation of the symmetrical methyl group (3-fold barrier to rotation) are at ca. $\tau = 65°, 185°$, and $305°$. In these equivalent conformations, one hydrogen is essentially antiperiplanar to the Fe–P bond, i.e., between the cyclopentadienyl and the CO ligands, a second hydrogen is between CO and PPhH₂ ligands but closer to the CO ligand, and the third hydrogen atom is between the cyclopentadienyl and the PPhH₂ ligands. The energy maxima are found where one hydrogen eclipses the Fe–P bond. The calculated barrier for **7** (ca. 0.25 eV; 6 kcal/mol) is in line with previous studies [$(\eta^5-C_5H_5)$·Fe(CO)₂CH₃: 5.4 kcal/mol (experimental);[63] 2.9 kcal/mol (theoretical)[58]].

No effort has been made to optimize geometry although this would undoubtedly lower this calculated barrier. Nevertheless, as in previous studies, the trends obtained should be clear indications of preferred conformations.

From these results, a major difference between a tetrahedral geometry about the metal (old model)[36-42] and a pseudooctahedral geometry (this work) is apparent. For the pseudooctahedral geometry, it is impossible to perfectly stagger or eclipse simultaneously all three methyl hydrogens with the other three metal

(63) Value quoted in ref 58 and attributed to J. W. Norton.

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Figure 2. Calculated potential energy (electronvolts) vs. torsional angle $\tau(C_\beta-C_\alpha-Fe-P)$ for $(\eta^5-C_5H_5)Fe(CO)(PPhH_2)C_\alpha H_2CH_3$ (8) (solid line) and $(\eta-C_5H_5)Re(NO)(PPhH_2)C_\alpha H_2C_\beta H_3$ (13) (dashed line).

ligands. The results in Figure 1 also indicate that the $PPhH_2$ ligand is the largest ligand on iron and that orientation of any substituent on C_α toward this ligand will be destabilizing.

As indicated previously, a wide variety of X-ray crystallographic results indicate that complexes of type **7** are pseudooctahedral.[7] To determine whether the extended Hückel algorithm was capable of reproducing this experimental observation, the relationship between the PE function and two variables, namely the iron-to-methyl carbon distance and the angle between any two of the ligands CO, $PPhH_2$, or CH_3 and the metal for the symmetrical complex **7** was investigated. A PE minimum is found at $d_{Fe-CH_3} \cong 2.15$ Å and for bond angles of 94.5°. The former value correlates well with measured $Fe-C_\alpha$ bond lengths, and the bond angle of 94.5° is consistent with pseudooctahedral (90°) but not pseudotetrahedral (109.5°) geometry.

B. $(\eta^5-C_5H_5)Fe(CO)(PPhH_2)CH_2CH_3$ (8) and $(\eta^5-C_5H_5)Re-(NO)(PPhH_2)CH_2CH_3$ (13). The potential energy curve for rotation of the ethyl group about the $Fe-C_\alpha$ bond in $(\eta^5-C_5H_5)-Fe(CO)(PPhH_2)CH_2CH_3$ (8) is shown in Figure 2. The most stable conformation **8a** is at $\tau \cong 195°$ where the methyl group is located between the two smallest ligands on iron, the cyclopentadienyl, and the CO. In this and most of the figures which follow, the portions of the energy curve relating to the energy maxima are not drawn. These regions have been omitted because complete energy minimization, which has not been performed, undoutedly would decrease substantially the energy at these torsional angles. The positions of the energy minima and the lowest barriers between them are of primary interest in this study. We have, in many cases, however, iteratively examined the effect of varying a number of structural parameters on the total energy and find only slight to moderate variations in the regions of the energy minima but substantial energy variations in the regions of the energy maxima.

Two other, less stable, conformations, **8b** and **8c**, are also apparent. Conformation **8b** occurs at $\tau \cong 295°$ and corresponds to the conformation in which the methyl group has just passed the CO ligand, approaching the $PPhH_2$ ligand. Conformation **8c** has the methyl group between the cyclopentadienyl and the

$PPhH_2$ ligands at $\tau \cong 90°$, i.e., closer to the cyclopentadienyl than to the $PPhH_2$. Both of the latter two energy wells are clearly unsymmetrical as rotation of the methyl group toward the $PPhH_2$ ligand between $\tau \cong \pm 80°$ causes a very significant destabilization and is indicative of the powerful steric hindrance resulting when any α substituent (in this case, CH_3) comes in close proximity to the phenyl ring of the $PPhH_2$ ligand. Although not included in Figure 2, the PE maximum was found at ca. $\tau = 0°$.

Gradually distorting the molecule **8** by increasing the bond angles $\angle PFeC_\alpha$, $\angle PFe(CO)$, and $\angle C_\alpha Fe(CO)$ from 90° → 99° gave calculated PE curves of essentially the same form with conformations **8a** and **8c** remaining unchanged in energy but with conformation **8b** becoming relatively more stabilized.

Although it is known from X-ray crystallographic studies that the three phenyl rings in complexes **1** and **2** are splayed in a distorted propeller fashion with the phenyl ring below the R substituent being approximately coplanar with the plane containing CO, Fe, and C_α but tilted slightly away from R,[64] the above calculations assume that the ortho (and meta) pair of carbon atoms are equidistant from this plane. In order to evaluate this assumption, the phenyl ring in **8** was rotated about the $P-C_{ipso}$ bond by $\pm 20°$ and $\pm 40°$ and the conformational PE curve for rotation about $Fe-C_\alpha$ recalculated. In all cases examined, rotation about $P-C_{ipso}$ led to overall destabilization but the general features of the PE curve remained essentially unchanged. Overall, these calculations demonstrate that the initial assumption is valid.

Similar calculations were performed on the analogous rhenium complex $(\eta^5-C_5H_5)Re(NO)(PPhH_2)CH_2CH_3$ (13), the results of which are also shown in Figure 2. The conformation PE curve is essentially the same for the iron complexes, with the slight difference that for the iron complex the minima are defined better. This may reflect the relatively shorter metal-C_α bond length for the iron complexes. In a manner analogous to that performed on the methyl complex **7**, the pseudooctahedral character of the iron ethyl complex **8** was investigated. An energy minimum at $d_{Fe-C_\alpha} \cong 2.20$ Å and bond angles $\cong 92.0°$ was found.

C. $(\eta^5-C_5H_5)Re(NO)(PPhH_2)(CH_2Ph)$ (14) and $(\eta^5-C_5H_5)-Re(NO)(PPhH_2)[CH_2(2,6-C_6H_3Me_2)]$ (15). The conformational analysis for the benzyl complex **14** is based on X-ray crystal structures reported by Gladysz et al. for $(\eta^5-C_5H_5)Re(NO)-(PPh_3)CH_2Ph$ (17) and $(\eta^5-C_6H_5)Re(NO)(PPh_3)CH(CH_2Ph)Ph$ (18).[32,44] Figure 3 shows the PE curve for rotation about the $Re-C_\alpha$ bond for **14** and **15** with the orientation of the plane of the benzyl phenyl fixed perpendicular to the planes containing the atoms C_{ipso}, C_α, and Re. One predominant minimum at $\tau \cong 205°$ is observed which corresponds to a conformation in which the benzyl phenyl is approximately halfway between the cyclopentadienyl and NO ligands (**14a**). This corresponds excellently with the observed X-ray structural results where $\tau = 203°$.[44] A second minimum, essentially a shoulder, is also found at $\tau = 115°-135°$. Any conformation between $\tau = \pm 110°$ is energetically highly unfavorable due to steric interactions between the benzyl phenyl group and the P–phenyl group(s).

The validity of restricting the orientation of the plane of the benzyl phenyl ring as described above was examined for several τ values (i.e., at fixed τ values, the PE function for rotation of the benzyl phenyl about the $C'_{ipso}-C_\alpha$ bond was calculated). At the minimum ($\tau = 205°$), the plane of the benzyl phenyl ring does indeed prefer to be approximately perpendicular to the plane containing C'_{ipso}, C_α, and Re. This is fully consistent with the X-ray crystallographic findings and observations of Gladysz where the angle between these planes is 84.5°.[32,44] The above orientation of the phenyl ring is however obviously not the most favorable for all τ values. Detailed calculations reveal that among other possible distortions (c.f. above), rotational motion about the $Re-C_\alpha$ bond will be coupled to rotation about the $C_\alpha-C_{ipso}$ bond. This is however only important when the two phenyl groups (i.e., the benzyl phenyl and the P–Ph) are close together. At the extremes **14c** and **14d**, the calculated PE minima are where the two phenyl

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(64) We have made this observation following detailed examination of numerous X-ray crystallographic structures.
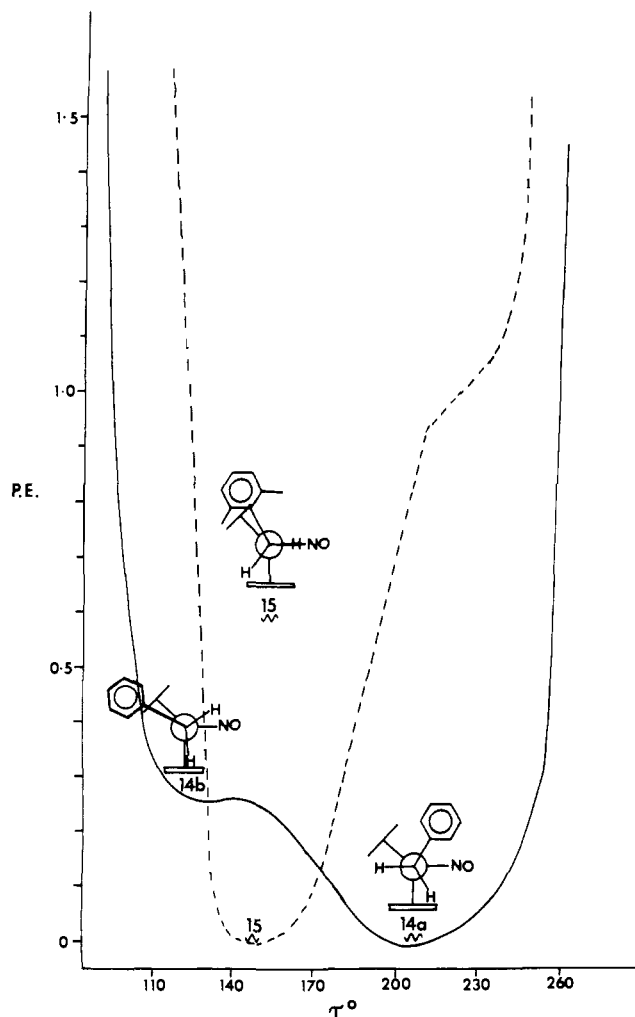
Figure 3. Calculated potential energy (electronvolts) vs. torsional angle $\tau(C_{ipso}-C_\alpha-Fe-P)$ for $(\eta^5\text{-}C_5H_5)Re(NO)(PPhH_2)CH_2Ph$ (**14**) (solid line) and $(\eta^5\text{-}C_5H_5)Re(NO)(PPhH_2)C_\alpha H_2(2,6\text{-}C_6H_3Me_2)$ (**15**) (dashed line). In both calculations, the plane of the benzyl phenyl was kept essentially perpendicular to the plane containing C_{ipso}, Re, and C_α (see text for discussion).

rings are essentially coplanar for **14c** and twisted 60° for **14d**. Conformations **14c** and **14d** are however still less stable than **14a**.
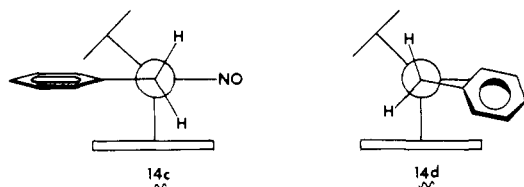
The extended Hückel algorithm again predicted the pseudooctahedral character of this complex, giving an average value of 93° for the angles between the Re atom and any two of the atoms N, P, or C_α (experimental value 91.7°).

The crucial difference between the ethyl complexes **8** and **13** and the benzyl complexes **14** is that the conformation that would place the C_α substituent between the CO and PPhH$_2$ ligands is energetically extremely unfavorable for the larger phenyl group in **14** (Figure 3) although it corresponds to a PE well for the smaller methyl group (**8b**) in **8** and **13** (see Figure 2). Distortion of the molecule **14** away from pseudooctahedral geometry, as described above for the ethyl complex **8**, only broadened somewhat the overall energy well for **14**, but no new minima (e.g., one that would correspond to **8b** in Figure 2) were apparent.

Because it plays an important role in the varied chemistry of these complexes, the more substituted $(\eta^5\text{-}C_5H_5)Re(NO)$-$(PPh_3)[CH_2(2,4,6\text{-}C_6H_2(CH_3)_3]^{26}$ was examined by using the
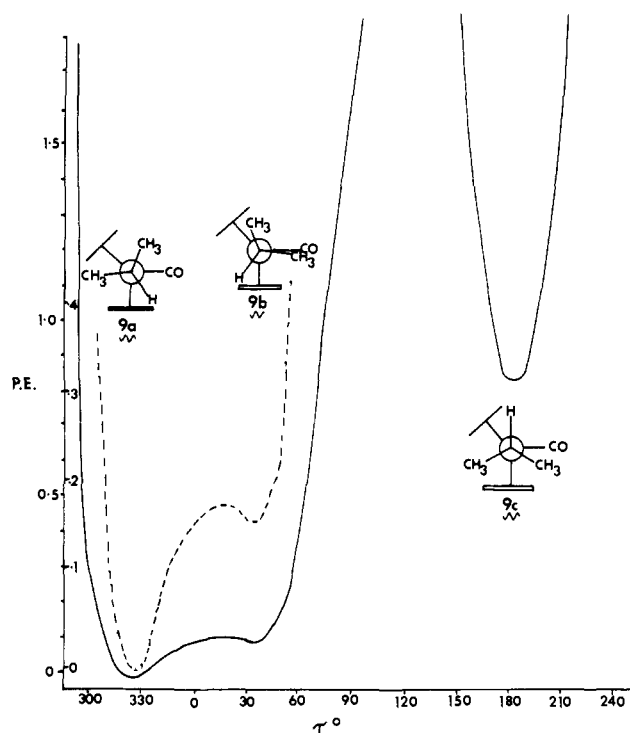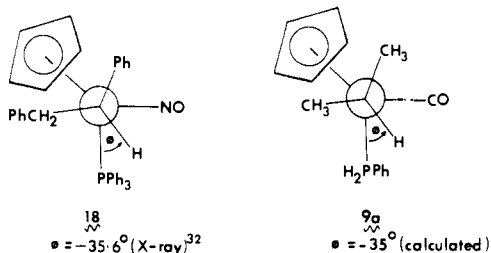

Figure 4. Calculated potential energy (electronvolts) vs. torsional angle $\tau(H_\alpha-C_\alpha-Fe-P)$ for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPhH_2)C_\alpha H_\alpha(CH_3)_2$ (**9**). The dashed curve illustrates the expanded scale indicated on the ordinate.

model $(\eta^5\text{-}C_5H_5)Re(NO)(PPhH_2)[CH_2(2,6\text{-}C_6H_3(CH_3)_2]$ **15**. In a manner analogous to that performed on the benzyl complex **14**, a wide variety of orientations and tilts of the dimethylphenyl group were examined by using the extended Hückel algorithm. By far, the most stable conformations available to this species position the substituted phenyl ring between the cyclopentadienyl and NO ligands, with the plane of the ring perpendicular to the plane containing Re, C_{ipso}, and C_α. As shown in Figure 3 (dotted line), only a very restricted region of the potential torsional motion is available for **15**. Rotation either about the Re–C_α bond or about the C_α–C_{ipso} bond brings at least one methyl substituent into close proximity with either the P–phenyl group, the NO ligand, or the cyclopentadienyl ligand.

D. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPhH_2)CH(CH_3)_2$ (**9**). Figure 4 illustrates the conformational PE curve for rotation about the Fe–C_α bond in the isopropyl complex **9**. The preferred conformation **9a** has two methyl groups straddling the cyclopentadienyl. A second less-stable conformation **9b** is also suggested. These conformations correlate well with those found for the ethyl complex **8** (Figure 2). Once again, any rotation that places a methyl group close to the phenyl ring is significantly destabilizing. There is also a third metastable minimum **9c** at a much higher energy where the two methyl groups straddle the Fe–P bond. This is obviously highly unstable with both methyl groups close to the phenyl but rotation in either direction will introduce even more severe interactions (see below).

Although the isopropyl iron complex $(\eta^5\text{-}C_5H_5)Fe(CO)$-$(PPh_3)CH(CH_3)_2$ and the analogous rhenium complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)CH(CH_3)_2$ (**19**) are known, their X-ray crystallographic analyses have not been reported. Such a study has been performed, however, on the structurally related rhenium complex **18**.[32] The observed conformation for **18** matches very closely that calculated as being most stable (**9a**) for the iron isopropyl complex **9**.

E. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPhH_2)C(CH_3)_3$ (**10**) and $(\eta^5\text{-}C_5H_5)$-$Fe(CO)(PPhH_2)Sn(CH_3)_3$ (**11**). Figure 5 (solid line) illustrates the conformational PE curve for rotation about the Fe–C_α bond for the *tert*-butyl complex **10**. The energy minima occur when two of the methyl groups straddle the Fe–P bond and are analogous to the metastable minimum **9c** described above for the isopropyl complex **9** (Figure 4). The unavoidable severe inter-

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18
● = −35·6°(X-ray)[32]

9a
● = −35°(calculated)

actions between the *tert*-butyl and phenyl groups makes some optimization of structural parameters desirable in this case. When a symmetrical arrangement is maintained at the metal center, increasing the bond angles between the iron atom and any two of the ligands CO, P, or C_α initially decreases the total energy of the complex as does increasing the $Fe-C_\alpha$ bond length from 2.15 Å, the most stable arrangement for the optimum conformation being found at $d_{Fe-C_\alpha} \cong 2.20$ Å with the above angles being 99.8°.

Although the *tert*-butyl complex $(\eta^5-C_5H_5)Fe(CO)(PPh_3)C-(CH_3)_3$ is unknown, X-ray crystallographic data have been obtained for the related trimethyltin complex $(\eta^5-C_5H_5)Fe(CO)-(1,2-(PPh_2)_2C_5F_6)Sn(CH_3)_3$ (20).[48] The PE curve calculated for the model $Sn(CH_3)_3$ complex 11 is also shown in Figure 5 (dashed line) and correlates extremely well with the *tert*-butyl derivative 10. The same geometry optimization for 11 as described above for 10 gave a minimum energy geometry for the preferred conformation at $d_{Fe-Sn} = 2.65$ Å for a P-Fe-Sn angle of 99.75°. These values compare favorably with the experimentally determined values for 20 of 2.57 Å and 97.1°, respectively.[48] In addition, the experimentally observed torsional angle $\tau(C-Sn-Fe-P) = -47.2°$[48] is consistent with the calculated value of −55°.

F. $(\eta^5-C_5H_5)Fe(CO)(PPhH_2)Ph$ (12). The final complex examined in this study is the phenyl compound 12. The PE function for rotation about the $Fe-C_\alpha$ bond is shown in Figure 6. The rather broad energy well corresponds to the two phenyl rings being approximately parallel, consistent with the X-ray crystallographic data reported for $(\eta^5-C_5H_5)Fe(CO)(PPh_3)Ph$.[47] The PE maximum occurs when the planes of the two phenyl groups are perpendicular to each other.

III. Structural and Conformational Generalizations for Complexes 1 and 2

The extended Hückel calculations described above for complexes 7–15 and X-ray crystal structural data allow a number of structural and conformational generalizations to be made concerning complexes of types 1 and 2.

(1) *For R groups with at least one C_α hydrogen, the energetically accessible conformations all prefer a pseudooctahedral geometry at the metal center*, that is, with the three bonds M-PPh_3, M-CO(NO), and M-R approximately mutually perpendicular and all subtending an angle of approximately 125° with the metal-cyclopentadienyl centroid line. Available X-ray crystallographic data are consistent with this generalization and are given in Table I. For complexes with no α-hydrogen, e.g., 1 and 2 where R = *t*-Bu or $SnMe_3$, all conformations with a pseudooctahedral metal geometry are energetically unfavorable and severe geometric distortions occur.

(2) *One phenyl group of the PPh_3 ligand lies in a plane close to (3–4 Å) and roughly parallel to the plane containing the metal, CO(NO) and C_α.*[7] *Consequently, no C_α substituent can dip more than ca. 10° below the plane containing the metal, CO(NO), and C_α without severe distortion of the overall structure.* The energetically unfavorable zone for C_α substituents is indicated in 21.
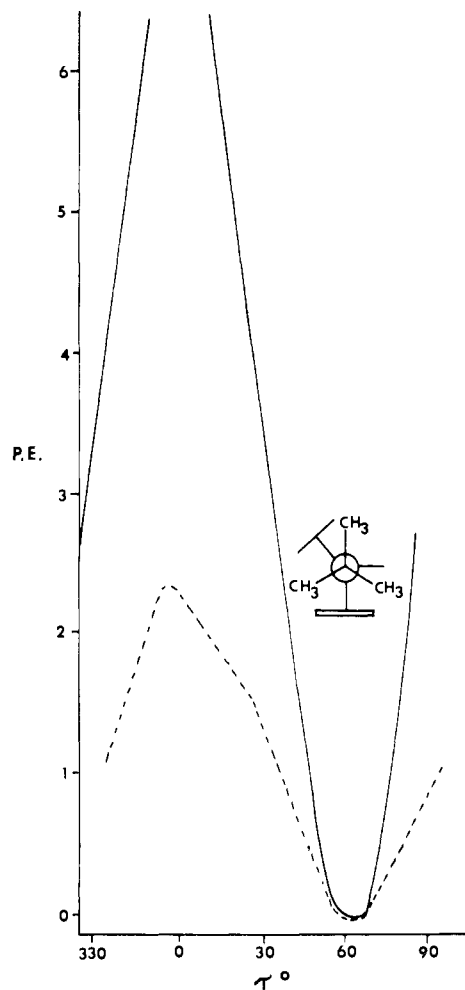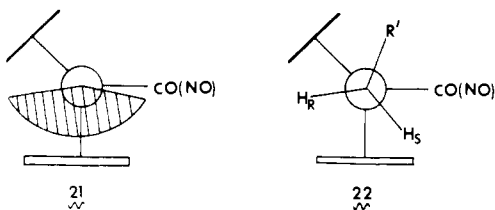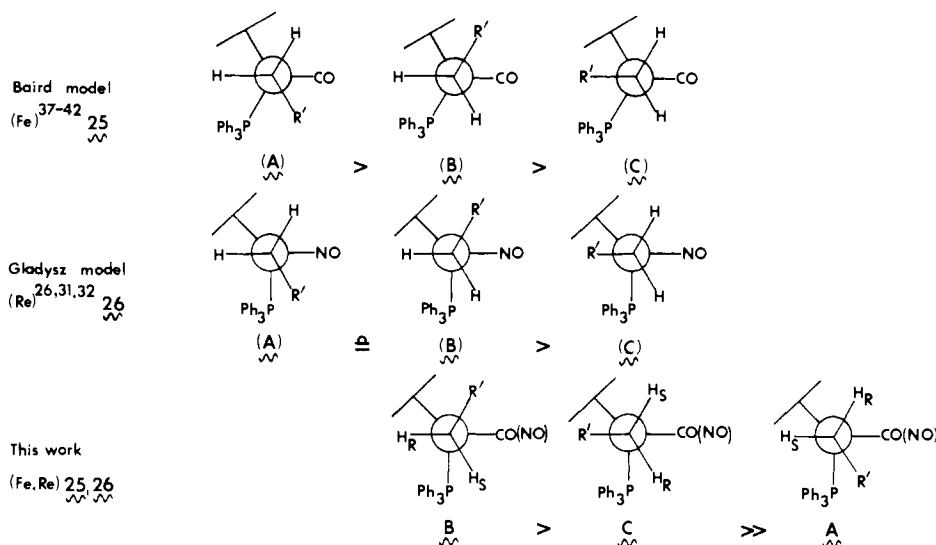

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Figure 5. Calculated potential energy (electronvolts) vs. torsional angle $\tau(C_\beta-atom_\alpha-Fe-P)$ for $(\eta^5-C_5H_5)Fe(CO)(PPhH_2)C_\alpha(C_\beta H_3)_3$ (10) (solid line) and $(\eta^5-C_5H_5)Fe(CO)(PPhH_2)Sn_\alpha(C_\beta H_3)_3$ (11) (dashed line).

Table II. Three-Bond Proton-Phosphorus Coupling Constants for $(\eta^5-C_5H_5)Fe(CO)(PPh_3)CH_2R'$ and $(\eta^5-C_5H_5)Re(NO)(PPh_3)CH_2R'$

complex	$^3J_{PH_S}$	$^3J_{PH_R}$	ref
$(\eta^5-C_5H_5)Fe(CO)(PPh_3)CH_2R'$			
R' = Me	12	2	a, b
R' = SiMe_3	14	2	a, c
R' = SiMe_2Ph	13	2	a, d
R' = Ph	10.6	4.1	a
R' = SO_2O(l-menthyl)	11	1	a
$(\eta^5-C_5H_5)Re(NO)(PPh_3)CH_2R'$			
R' = Ph	8.0	3.0	f
R' = 2,4,6-C_6H_2Me_3	1.5	8.9	g
R' = Bu'	12.8	0	h

a For a summary of data from different primary sources, see ref 36, Table 18, pp 177–185. *b* Reference 22. *c* References 39 and 41. *d* Pannell, K. H. *Transition Met. Chem.* (*Weinheim Ger.*) 1975/1976, *1*, 36. *e* Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* 1976, *15*, 1910. *f* References 32 and 44. *g* Reference 26. *h* Reference 31.

(3) *For R groups with a single C_α substituent (e.g., CH_2CH_3 and CH_2Ph), the most preferred conformation places the C_α substituent between the cyclopentadienyl and CO(NO) ligands* 22. For sterically undemanding C_α substituents (e.g., Me), less stable but accessible conformations with the C_α substituent between the PPh_3 and the cyclopentadienyl or the CO(NO) ligands also exist. The latter appears however to be highly unfavorable for larger C_α substituents (e.g., phenyl). For extremely large C_α substituents (CMe_3 and $SnMe_3$), the distinctly lowest energy conformation is 22. In order to facilitate the calculations, it was assumed that the $Fe-C_\alpha$ and the $P-C_{ipso}$ bonds were eclipsed and that the two ortho carbons of the shielding phenyl group were
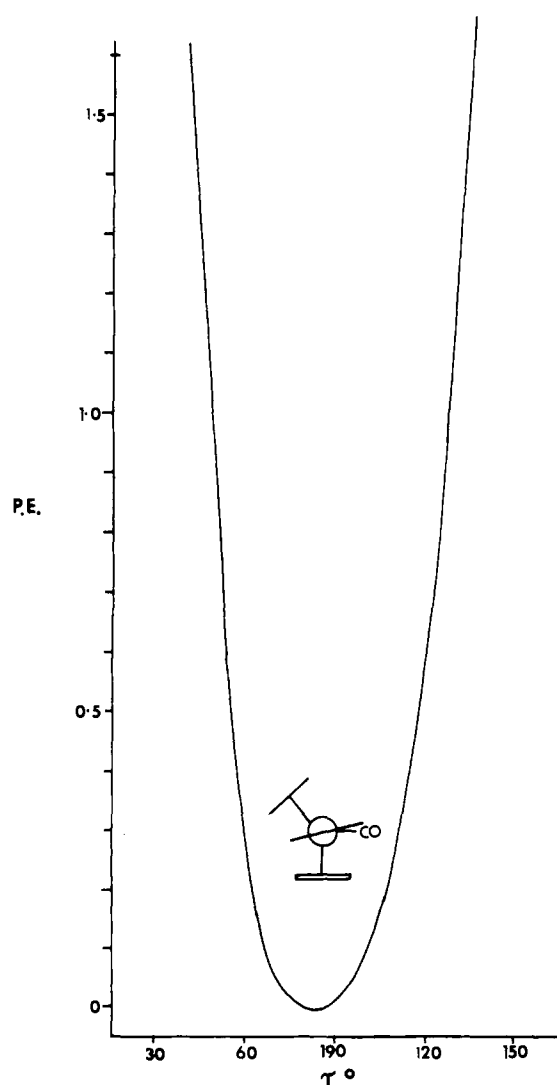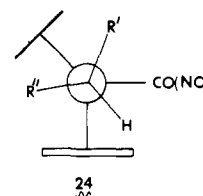
Chart I. Comparison of Conformational Stabilities Deduced from the Previous and Current Models for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2R'$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)CH_2R'$ [66]

Figure 6. Calculated potential energy (electronvolts) vs. torsional angle $\tau(C_{ortho}\text{-}C_{ipso}\text{-}Fe\text{-}P)$ for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPhH_2)Ph$ (12).

eoever is tilted to bring the ortho carbon nearest to CO(NO) closer to the $M\text{-}C_\alpha\text{-}CO(NO)$ plane, i.e., **23**.[65] Both these phenomena

23

will have the effect of destabilizing, still further, conformations with C_α substituents between CO and PPh_3 but relatively stabilizing conformations with C_α substituents between cyclopentadienyl and PPh_3.

(4) *For R groups with two C_α substituents* [*e.g., $CH(CH_3)_2$*], *the stable conformation has the two substituents straddling the cyclopentadienyl ligand, e.g.,* **24** *with only the C_α hydrogen being below the plane containing the metal, CO(NO), and C_α.*

24

IV. Discussion

An earlier conformational analysis for $(\eta^5\text{-}C_5H_5)Fe(CO)\text{-}(PPh_3)CH_2R'$ proposed by Baird et al. was based on a tetrahedral model with the size of $\eta^5\text{-}C_5H_5 > PPh_3 > CO$ and resulted in the conclusion that the conformer stabilities (populations) were A > B > C (Chart I).[37–42] This model was later extended and adapted by Gladysz et al., with $PPh_3 > \eta^5\text{-}C_5H_5$, to the corresponding pseudooctahedral rhenium complexes **26** with the conclusion that the conformer stabilities were A ≅ B > C (Chart I).[26,31,32] Chart I compares the stable conformations from the earlier models with those described here. Of paramount importance is the fact that the postulated "most stable" conformation A in the previous studies is highly disfavored in the present one for all but very small R' groups (e.g., H and Me). The present analysis indicates that the

essentially equidistant from the plane containing M, C_α, and CO(NO). From the available X-ray data, however, it is evident that for both the iron and rhenium complexes, the $P\text{-}C_{ipso}$ bond is orientated somewhat toward the $M\text{-}CO(NO)$ bond and mor-

(65) We have examined this structural feature for a number of complexes, including CpRe(NO)(PPh₃)=CHPh⁺,[32] CpRe(NO)(PPh₃)CH(CH₂Ph)Ph,[32] CpRe(NO)(PPh₃)(η²-H₂C=S),[54] CpRe(NO)(PPh₃)CHO,[55] CpFe(CO)-(PPh₃){COCH(Me)Et}, and (Z)-CpFe(CO)(PPh₃)C(OMe)=CHCH₃.[9]

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Table III. Parameters Used in Extended Hückel Calculations[a]

orbital	H_{ij}, eV	ζ_1	ζ_2	C_1[b]	C_2[b]
Fe 3d	−12.7	5.35	1.80	0.5366	0.6678
Fe 4s	−9.17	1.90			
Fe 4p	−5.35	1.90			
C 2s	−21.40	1.625			
C 2p	−11.40	1.625			
H 1s	−13.6	1.30			
P 3s	−18.6	1.66			
P 3p	−14.0	1.60			
Sn 5s	−13.04	2.129			
Sn 5p	−6.76	1.674			
Re 5d	−12.66	5.343	2.277	0.6359	0.5677
Re 6s	−9.36	2.398			
Re 6p	−5.96	2.372			
O 2s	−32.3	2.275			
O 2p	−14.8	2.275			
N 2s	−26.0	1.950			
N 2p	−13.40	1.950			

[a] Parameters taken from ref 32 and 58–62. [b] Contraction coefficients used in the double-ζ expansion.

interaction of the R group with the PPh$_3$ ligand can be much greater than with the cyclopentadienyl ligand. This is reasonable since the PPh$_3$ is restricted to one of the octahedral sites whereas the cyclopentadienyl is spread over three sites. Thus, the orientation of the R substituent is controlled by the PPh$_3$ ligand–R interaction.

Interpretations of some very elegant ^{1}H NMR$^{37-42}$ and stereochemical studies^{26,31} have relied on the high-energy conformation A and merit reexamination. The $^3J_{PH}$ coupling constants between phosphorus and the diastereotopic α-hydrogens for several complexes of the types **25** and **26** have been found to be temperature-dependent, and this has been explained in terms of an equilibrium between stable conformers.^{26,31,41} This may be reasonable when R' in **25** and **26** is small (e.g., CH$_3$) but not when R' is large (e.g., Ph t-Bu, and SiMe$_3$). The present model would predict that in general at low temperatures, R' groups in **25** and **26** would adopt conformation B and therefore, from application to the Karplus equation J_{PH_R}, would be close to zero whereas J_{PH_S} would be large. High temperatures will alter the conformer populations within the same potential energy well and increased population of conformation D, for example, where J_{PH_R} would be large but J_{PH_S} small, would also account for the observed J_{PH} temperature dependence. Furthermore the above analysis allows assignment of the chemical shifts of the α-protons from **25** and **26** (Table II).
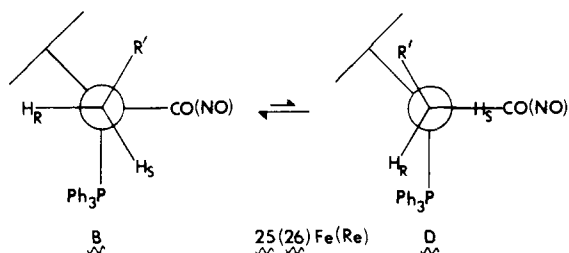
It is important to note that in the complex **26** where R' = mesityl, the present model (Figure 3) would predict that the equilibrium B ⇌ D would favor conformer D and, hence, consistent with experimental observations,^{26} the assignment of the chemical shifts and coupling constants for the α-hydrogens is reversed in this case (Table II).

Hydride abstractions by the trityl cation from the rhenium complexes **26** (R' = aryl) exhibit stereoselectivities which vary with the aryl substituent.^{26,32} Consistent with the current conformational analysis, the trityl cation could approach an α-hydrogen only between the cyclopentadienyl and either the PPh$_3$ or the NO ligands, although due to its large bulk it would much prefer the latter less-encumbered trajectory. It would prefer therefore to abstract H$_S^-$ from conformation **17C** (**26C**). For all but the largest R' groups (e.g., Me or Ph), not only will both conformations B and C be populated but the energy barrier to

interconversion will be relatively small and their interconversion rate therefore fast. Consequently, the trityl cation is able to abstract H$_S^-$. For very large R' groups (e.g., mesityl), only conformations in which R' lies between the cyclpentadienyl and CO(NO) will be populated; therefore the trityl cation can only abstract H$_R^-$ (cf. **27**). The reported stereoselectivities for H$_S^-$ over H$_R^-$ removal are 99:1, 50:50, and 1:99 for **26** with R' = phenyl **17**, 2-methylphenyl, and mesityl **27**, respectively. These results
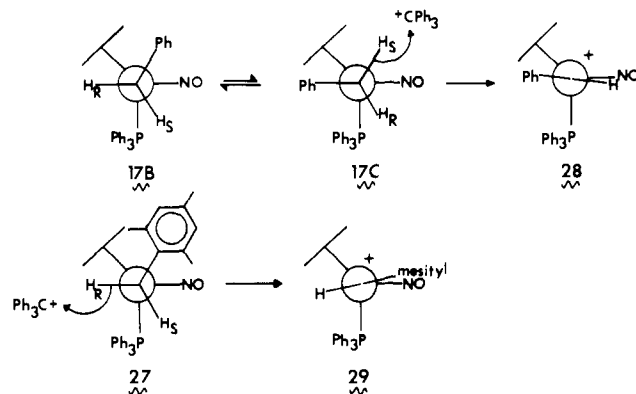
are entirely consistent with the above analysis and the Curtin–Hammett principle.^{67} Furthermore α-hydride abstraction from complexes **17** and **27** produces the synclinal **28** and anticlinal **29** carbene cations, respectively.^{26,31,32}

The rhenium ethyl complex **30**^{31} behaves in an identical manner with the benzyl complex **17** in that it undergoes exclusive α-hydride abstraction to give only the synclinal complex **31**, consistent with trityl cation abstracting hydride from conformation **30C**. For
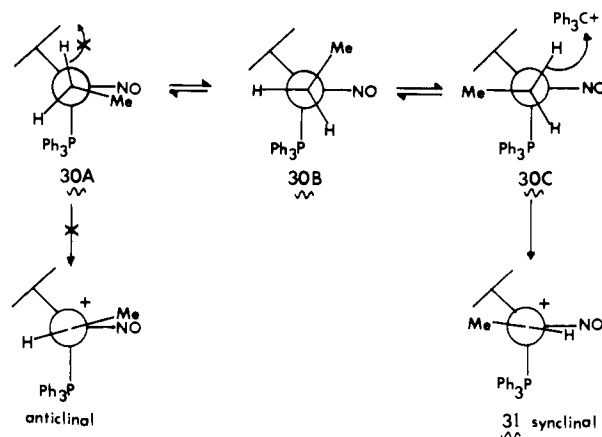
complex **30**, conformation **30A** is also available but it is unreactive toward trityl cation presumably because hydride removal would

(66) A pairwise comparison of the postulated stable conformations of the model proposed herein (Chart I, line 3) and the conformations of the generally accepted model of Baird proposed many years ago (Chart I, line 1) is rendered difficult because our model is based on the pseudooctahedral nature about the metal while the literature model is based on a pseudotetrahedral-metal geometry. For molecules generalized by (η^5-C$_5$H$_5$)M(CO)(PPh$_3$)CH$_2$R, the literature model$^{37-42}$ asserts three energy minima symmetrically located 120° apart; our alternative model suggests three minima, ca. 90° apart (and 180° apart at the extremes) when R is small in size, two minima ca. 100° (and 260°) apart for moderately sized R, and one minimum for very bulky R. (Of course, other local but significantly destabilized minima are possible on the conformational PE surface.) A pairwise comparison of the PE curves for the literature model vs. the current model is further complicated by the necessity of arbitrarily referencing one curve to the other. In our preliminary paper, we displayed such a comparison, with the two curves referenced to initial eclipsing of the cyclopentadienyl ligand with a R group at τ(R–C$_\alpha$–M–Cp) = 0°. Alternative arbitrary references could have been chosen, e.g., τ(R–C$_\alpha$–M–P) = 0°, thereby leading to a different overlapping of the literature PE curve$^{37-42}$ with the current model's PE curve(s). We do not include a figure illutrating these comparisons, due to the implicit arbitrary nature of such a comparison. In our preliminary communication, we depicted (incorrectly) the mirror image of the literature curve, further complicating this comparison.

(67) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

involve severe interactions between the trityl cation and the cyclopentadienyl ligand.

For complexes with two C_α substituents, all conformations that would make the sole α-hydrogen accessible to trityl cation are energetically extremely unfavorable. It is not surprising therefore that in complete contrast to the ethyl complex **30**, which undergoes exclusive α-hydride abstraction, the isopropyl complex **32** undergoes β-hydride abstraction to give the propene complex **33**.[31]
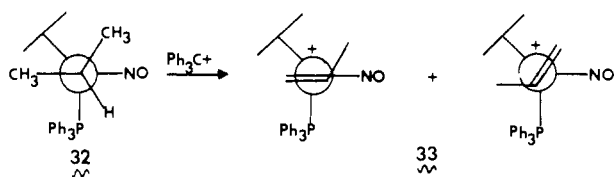
The C_α-methoxy complexes **34** and **35** behave similarly. On treatment with trityl cation, **34** loses hydride,[68] as an α-hydrogen is sterically available, whereas **35** loses methoxide,[69] since the α-hydrogen is not available to trityl abstraction.

$(C_5H_5)Fe(CO)(PPh_3)CH(OMe)Ph \xrightarrow{Ph_3C+} (C_5H_5)Fe(CO)(PPh_3)=CHPh$

35
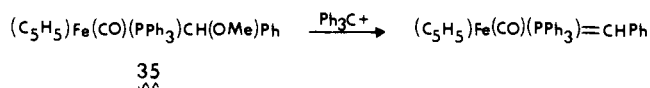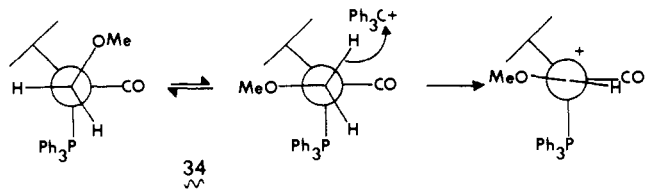
For the more highly substituted complexes $(\eta^5$-$C_5H_5)Fe(CO)(PPh_3)CHR'R''$, the literature model[37-42] predicts that conformations in which the larger of the R',R'' substituents (arbitrarily chosen to be R') lies anti to the cyclopentadienyl moiety (e.g., **36** and **37**) while the current model, based on the
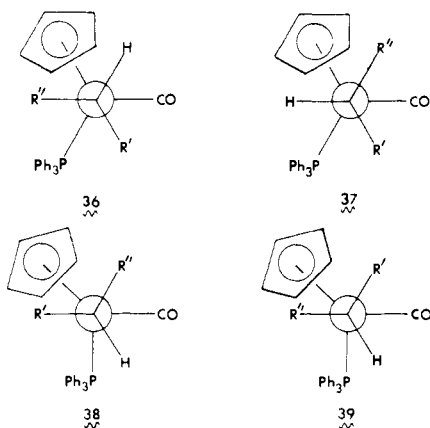
conformational analyses of $(\eta^5$-$C_5H_5)Fe(CO)(PPh_3)CH_2R'$ and $(\eta^5$-$C_5H_5)Fe(CO)(PPh_3)CHR_2'$, predicts conformations **38** and **39** and related conformations in which neither R' nor R'' dips much below the plane defined by CO, Fe, and C_α.

V. Concluding Remarks

A conformational analysis model has been presented in this study for organotransition-metal complexes of the general types $(\eta^5$-$C_5H_5)Fe(CO)(PPh_3)R$ (**1**) and $(\eta^5$-$C_5H_5)Re(NO)(PPh_3)R$ (**2**) (R = alkyl and aryl). The model is based on detailed extended Hückel calculations, the most stable conformations from which correlate well with known X-ray crystal structures. Furthermore

the conformational analysis model developed herein can explain the stereochemical outcome of the stereospecific reactions observed for complexes **1** and **2**.

The extended Hückel calculations accurately mirrored the known structural characteristics of a wide set of different complexes **1** and **2** where R = benzyl, phenyl, trimethylstannyl, and 1,2-diphenylethyl. This success not only supports the conformational analysis model presented herein but validates the use of the extended Hückel algorithm for predicting structural characteristics of organotransition-metal complexes, especially those in which steric factors are dominating.

This initial analysis has been restricted to complexes **1** and **2** where R = alkyl or aryl. However, we are presently expanding this conformational analysis model to other classes of complexes generalized by **1** and **2** (e.g., R = acyl, carbene, etc.).

It is clear from the results and discussions above that conformational analysis of these highly substituted organotransition-metal complexes is in its formative stages. The models presented herein were designed to provide the initial basis for understanding and evaluating the stereochemical intricacies of these compounds. However, before we can be definitive about such topics as potential energy barriers for rotations, geometries, and detailed structural features of sterically hindered complexes or of higher energy but stable conformations, additional experimental and theoretical results must become available. In combination with X-ray crystallographic analyses, very detailed theoretical calculations including complete geometry optimization will be an asset in these studies.

It is clear from the recent work of many laboratories including those of Brunner,[14,15,19] Brookhart,[19,20] Flood,[16-18] Gladysz,[26-33] Liebeskind,[13] Reger,[23-25] and ourselves[6-12] that these types of complexes will make increasing contributions to asymmetric organic synthesis. Unified experimental, structural, and theoretical studies will undoubtedly accelerate the success in this relatively new but already promising field.[70-72]

Appendix

The calculations were of the extended Hückel type, with "weighted" H_{ij}'s. The parameters used are listed in Table III and were taken from the recent literature.[32,58-62] Additional calculations using other parameters, both with "weighted" and "unweighted" H_{ij}'s, were also performed: the results were qualitatively very similar.

The structures, for which calculations were performed, were input by using the standard internal coordinate system. Two different formulations were used. In the first, the initial atom

(68) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604.

(69) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. For the analogous reaction with $(\eta^5$-$C_5H_5)Fe(CO)(PPh_3)CHMeOMe$, see: Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31-C36.

(70) Hunter and Baird[71] have recently reported a ^1H NMR NOE difference study of $(\eta^5$-$C_5H_5)Fe(CO)(PPh_3)CH_2Si(CH_3)_3$ (**40**). One result is particularly impressive. Irradiation of the cyclopentadienyl proton resonance results in a positive enhancement of one of the α-hydrogen atom resonances and a negative enhancement of the other α-hydrogen atom resonance. Based on this study, Hunter and Baird[71] and Cameron and Baird[72] concluded that the preferred conformation of **40** to **25B**, where the $Si(CH_3)$ group lies within the Cp–(CO) bite angle (c.f. Chart I, bottom line) as opposed to the previously published Baird model[37-42] in which the $Si(CH_3)_3$ group would have been within the (PPh_3)–(CO) bite angle (c.f. Chart I, top line, structure A). Thus, Prof. Baird's latest experiment results and conclusions support and indicate the effectiveness of our new conformational model.

(71) Hunter, B. K.; Baird, M. C. unpublished results. We thank Prof. Baird for making these results available to us prior to publication.

(72) Cameron, A. D.; Baird, M. C. *J. Chem. Soc., Dalton Trans.*, in press.

was the transition metal, and a typical "piano-stool" arrangement was constructed around this atom. In the second, the initial atom was the phosphorus of the PPhH$_2$ ligand, the second atom was the transition metal, and the octahedral character of the complex was constructed by specifying the bond angles each ligand made with the phosphorus atom. That the two input approaches were identical was checked by comparison of the external coordinates of a complex whose structure was input in both modes. For calculations on **7**, **8**, **9**, **10**, **12**, **13**, and **14**, the symmetrical "piano-stool" arrangement was used with structural parameters either from related X-ray determinations or by assuming a pseudooctahedral complex of bond angles of 90°. For **11** and **15**, the second input mode was utilized and again the structural parameters were obtained from X-ray determinations. When experimental structural data was lacking, standard bond lengths (c.f.: Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley, New York, 1975; Tables 2-3 and 2-4) and bond angles (109.5° for tetrahedral, 120° for the phenyl ring bond

angles) were used. All calculations were performed on the Oxford University Computer Service's ICL 2988 computer running under VME.

Stereoselective Oxidative Addition of Silanes and Hydrogen Halides to the Iridium(I) Cis Phosphine Complexes IrX(CO)(dppe) (X = Br, CN; dppe = 1,2-Bis(diphenylphosphino)ethane)

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Abstract: The oxidative addition of silanes, R$_n$Cl$_{3-n}$SiH (n = 3, R = Et, Ph, OEt; n = 2, R = Me; n = 1, R = Me), to the Ir(I) cis phosphine complexes IrX(CO)(dppe) (X = Br, CN; dppe = 1,2-bis(diphenylphosphino)ethane) has been found to proceed stereoselectively under kinetic control. Of the four possible diastereomers that can form by concerted cis addition of the Si–H bond to the iridium(I) center, the one having hydride trans to CO and Si trans to P(dppe) is formed initially with >98% stereoselectivity. For X = Br, this diastereomer is not the thermodynamically favored product. Isomerization of the initially formed silyl hydride product to the equilibrium mixture of diastereomers follows first-order kinetics for the triphenylsilyl derivative with k_1 = 0.015 min^{-1}. The rate of isomerization for the kinetic silyl hydride adducts decreases in the order Et$_3$SiH > Ph$_3$SiH > (OEt)$_3$SiH > Me$_2$ClSiH with the MeCl$_2$SiH derivative not isomerizing even after prolonged heating. The most stable diastereomer for X = Br has hydride trans to Br and silyl trans to P(dppe). For X = CN, the kinetic isomer with H trans to CO and Si trans to P(dppe) is also the most stable isomer, although other isomers are observed to form after initial reaction. Secondary chemistry of the triethylsilyl hydride products for X = Br and CN is observed over longer reaction times leading to the formation of IrHX$_2$(CO)(dppe) (X = Br), IrH$_2$(SiEt$_3$)(CO)(dppe), and Et$_3$SiSiEt$_3$. This secondary chemistry is consistent with reductive elimination/oxidative addition sequences. The oxidative addition of HX to IrX'(CO)(dppe) also proceeds stereoselectively, giving the isomer with H trans to X' and X trans to P(dppe). This diastereomer results from cis addition in which H–X approaches the square-planar Ir(I) complex with its axis parallel to X'–Ir–P. Thus, while R$_3$SiH and HX both add to IrX(CO)(dppe) by a cis concerted mechanism, the diastereoselection for HX is opposite to that for R$_3$SiH. It is proposed that this difference arises because the silane approach to the Ir(I) complex is nucleophilic while that of HX is electrophilic.

In previous reports we have described the kinetic stereoselectivity of H$_2$ oxidative addition to IrX(CO)(dppe) complexes, (dppe = 1,2-bis(diphenylphosphino)ethane), which are cis-phosphine analogues of Vaska's complex, *trans*-IrCl(CO)(PPh$_3$)$_2$.[1,2] This oxidative addition can proceed along two possible pathways, i and ii, as shown in eq 1, leading to different diastereomers for the concerted cis addition of H$_2$. Pathway i corresponds to H$_2$ approach to the square-planar complex with the molecular axis of H$_2$ parallel to P–Ir–CO as shown in A. The concerted oxidative
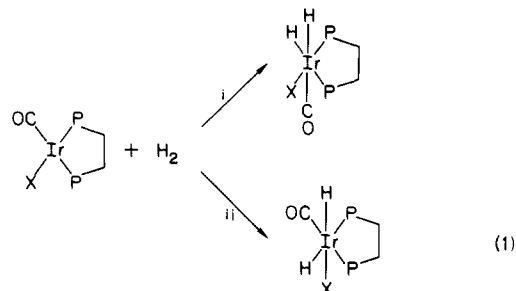
(1)

addition along i takes place with a bending of the trans P–Ir–CO axis so that one hydride of the product becomes trans to CO and

(1) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148–3160.

(2) Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772–7774.