Conformational Analysis for the Alkyl Ligands (R) in Complexes of the Type $(\eta^5\text{-}C_5H_5]Fe(CO)(PPh_3)R$

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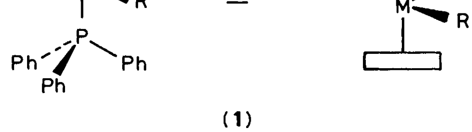
Conformational analysis of organotransition metal complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R$ demonstrates that the previously assumed most stable conformation is energetically extremely unfavourable, and the predominant conformations are herein established.

A wide variety of stereospecific chemical reactions have been observed on the alkyl ligand of the pseudo-octahedral complexes generalized by (**1**).[1,2] Unfortunately no general theory has been advanced which predicts the stereochemical properties of these complexes. Although conformational models for (**1**) have appeared in the literature,[2–5] they have been based on erroneous assumptions which have either led to incorrect conformational energy profiles[3,4] (see below) or have induced investigators to conclude that their experimental results were inexplicable.[2,6] We now present a conformational analysis for (**1**) which is supported by extended Hückel (EH) calculations and by n.m.r. spectroscopic data.

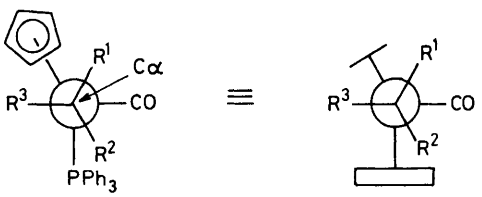
Complexes of the type (**1**) are pseudo-octahedral and not pseudotetrahedral, in that the bond angles between any two of the ligands CO, PPh_3, or R and the metal atom are *ca.* 90° while the bond angles between the cyclopentadienyl ligand–metal atom–any other ligand are *ca.* 125°.[7] This geometry places the alkyl group R of (**1**) in a rather unique molecular environment. The Newman projection of (**1**) emphasises the compounds pseudo-octahedral structure and is the appropriate representation for the analysis which follows.



(**1**)

R = alkyl or substituted alkyl.

Figure 1 (solid line) illustrates the results of our extended Hückel calculations† on $CpFe(CO)(PPhH_2)CH_2Me$ (Cp =



Newman projection of (**1**).

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† All calculations were of the extended Hückel type with an unweighted H_{ij} formula. (*c.f.* R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397; J. H. Ammeter, H. B. Bürgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 3686). The ligand geometry about iron was assumed to be a symmetrical, pseudo-octahedral 'piano stool' in which $<$P–Fe–Cp = $<C_\alpha$–Fe–Cp = $<$C(O)–Fe–Cp = 128° (Cp = centroid of the $\eta^5\text{-}C_5H_5$ group). The orientation of the phenyl ring was adjusted such that (a) it was essentially bisected by the Fe–C_α bond; and (b) $|\tau(C_{ortho}\text{–}C_{ipso}\text{–P–Fe})| = |\tau(C_{ortho'}\text{–}C_{ipso}\text{–P–Fe})| = 90°$. Bond distances, bond angles, and torsional angles used were based on available *X*-ray data for related iron complexes. Standard parameters were employed for carbon, hydrogen, and oxygen. Those utilised for the other atoms were as follows: Fe 4s, $H_{ii} = -7.079$ eV, $\zeta = 1.388$; Fe 4p, $H_{ii} = -4.183$ eV, $\zeta = 1.145$; Fe 3d, $H_{ii} = -16.54$ eV, $\zeta_1 = 5.35$ (coefficient = 0.5366), $\zeta_2 = 1.80$ (coefficient = 0.6678); P 3s, $H_{ii} = -18.6$ eV, $\zeta = 1.66$; P 3p, $H_{ii} = -14.0$ eV, $\zeta = 1.6$. Calculations using a weighted H_{ij} formula lead to essentially the same results. Full details will appear in the complete paper.

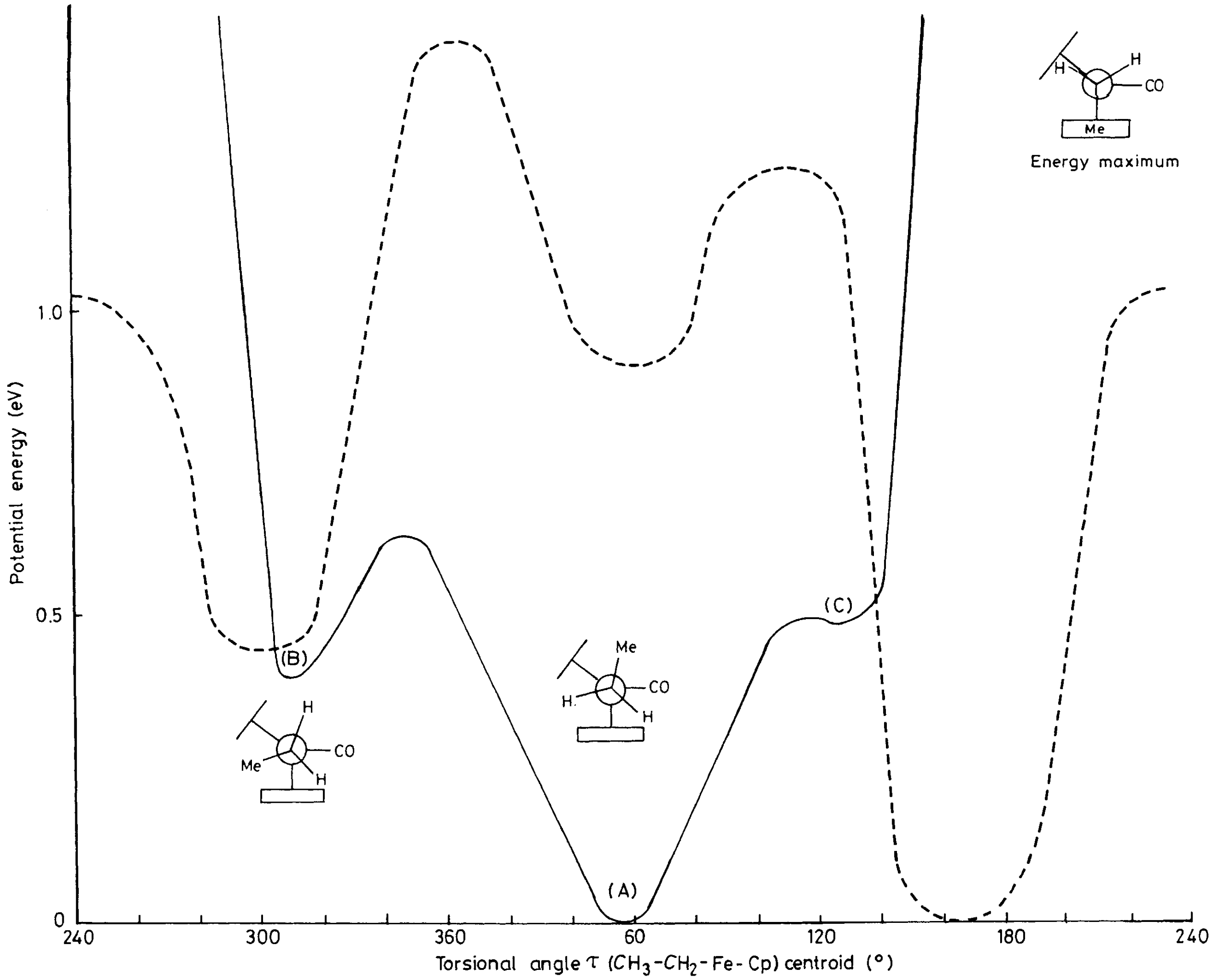
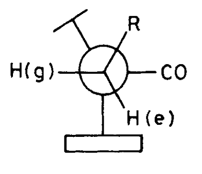
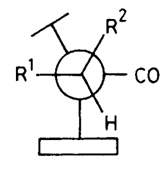


Figure 1. Solid line: Extended Hückel calculated rotational energy profile for CpFe(CO)(PPhH_2)CH_2Me. Dashed line: Literature model (ref. 3) for CpFe(CO)(PPh_3)CH_2R. The ordinate scale for the two curves is referenced to initial eclipsing of the Cp ligand with the R(Me) group at τ(R–C_α–Fe–Cp centroid) = 0°.



(A)



(D)

η^5-C_5H_5). The most critical feature is the potential energy function for rotation about the C_α–C_β bond, *i.e.*, the disposition of the methyl group. Three minima are observed. In the two most stable conformations (A) and (B), the methyl group positions itself between the ligands which form a 125° bond angle with the metal. The third minima (C) is essentially a shoulder on the steep portion of the PE curve. The most striking feature of these results is the severe steric interactions which occur when the methyl group is in the vicinity of the PPhH_2 ligand. Similar EH calculations for other complexes such as CpFe(CO)(PPhH_2)R (R = Ph and CH_2OMe) provide further support for the important generalisation that it is energetically extremely unfavourable for an alkyl or aryl group to dip much below the plane containing the CO, Fe, and C_α(R) atoms.

Table 1. Coupling constants for CpFe(CO)(PPh_3)$C_\alpha H_2$R (**2**) and CpFe(CO)(PPh_3)$C_\alpha HR^1R^2$ (**3**).[a]

Complex type	C_α-Substituent(s)	$^3J_{P-H(e)}$ (Hz)	$^3J_{P-H(g)}$ (Hz)
(**2**)[b]	Me	12	2
	Ph	10.7	3.9
	$SiMe_3$	14	2
	$SiMe_2$Ph	13	2
	SO_2-O-menthyl	11	1
(**3**)[c]	Ph, $SiMe_3$	7.7	—
	Ph, OMe	9	—
	OEt, Me	7.5	—

[a] For a summary of the available data, see: 'Gmelin Handbuch der Anorganischen Chemie,' Berlin, 1983; Vol. B11, 1983. [b] Conformation (A). [c] Conformation (D).

Table 1 lists the three bond H_α–C_α–Fe–P coupling constants ($^3J_{P-H}$) for a series of CpFe(CO)(PPh_3)CH_2R complexes (**2**). Invariably, one $^3J_{P-H}$ is large (*ca.* 11—14 Hz) and the other is small (*ca.* 1—4 Hz). Inspection of the PE curve in Figure 1 and application of the Karplus relationship[8] allows the larger ^3J to be assigned to the coupling of the phosphorus atom with the

$CpFe(CO)(PPh_3)CH_2R$

(2)

$CpFe(CO)(PPh_3)CHR^1R^2$

(3)

nearly eclipsed α-proton and the smaller ^3J to be assigned to the P coupling with the *gauche* α-proton of the most stable rotamer (A).

EH calculations predict that more highly substituted complexes (**3**) [*e.g.* $CpFe(CO)(PPh_3)CHMe_2$] exist primarily in the conformation illustrated as (D). Rotation about the metal–C_α–bond in either direction is destabilising, in that an alkyl group would be forced towards the bulky PPh_3 ligand. Support for this conclusion is again obtained from the large coupling constant observed (Table 1) between the single H_α and the P for (**3**).

The PE curve shown by the dotted line in Figure 1 represents the previous[3] and generally accepted conformational model for these systems. The previous analysis was based on the unsubstantiated assumption[3] that a tetrahedral model is sufficient to describe these systems and that the ligand steric requirements are in the order η^5-$C_5H_5 > PPh_3 >$ CO. *X*-Ray crystallographic data clearly shows that these complexes are nearly octahedral[7] and, together with our EH calculations and the coupling constant relationships, indicate that the ligand steric requirements are $PPh_3 \gg \eta^5$-C_5H_5. The previously[3] 'most stable' conformation is shown now by our work to be an energy maximum, while the then 'least stable' conformation is now assigned to that of greatest stability. The literature analysis[3—5] for (D) would have predicted $^3J_{P-H}$ to be small, as H_α would have been *gauche*, also contrary to the experimental observations.

In our full paper, we will demonstrate that this conformational analysis will serve as the cornerstone in evaluating the chemical reactivities of these valuable synthetic intermediates. In addition, this new conformational model will allow the understanding of previously unrationalised[2,6] chemical reactivities of these and related complexes *e.g.*, (η^5-C_5H_5)Re(NO)(PPh_3)R.

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