Letters

Conformation analysis of compounds of the type [Fe(η^5-C_5H_5)(CO)(PPh_3)(CH_2R)] (R = alkyl or aryl)

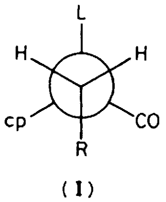
One of us reported several years ago[1] that, for compounds of the type [Fe(η^5-C_5H_5)(CO)(PPh_3)(CH_2R)] (**1**) (R = alkyl or aryl), the values and temperature dependencies of the vicinal P–H_α spin–spin coupling constants, ^3J(P–H), can be interpreted (assuming staggered energy minima and using the Karplus relationship[2]) in terms of both restricted rotation about the iron–carbon bonds and unequal population of three staggered rotamers, (**I**)—(**III**) (cp = η^5-C_5H_5, L = PPh_3). Using well established procedures for the analysis of time-averaged n.m.r. spectra, we showed quite unequivocally that the lowest energy rotamer has very unequal ^3J(P–H), as would be expected for (**II**) or (**III**), and it was argued on steric grounds that (**III**) would be less crowded than (**II**), and therefore more stable. The individual values for *gauche* and antiperiplanar ^3J(P–H) were also derived for (**1**), and shown to predict fairly accurately the averaged ^3J(P–H) of the methyl compound, [Fe(η^5-C_5H_5)(CO)(PPh_3)Me].

In order to relate the more familiar principles of organic stereochemistry to what was at the time a novel approach to organometallic stereochemistry, we referred to the iron compounds topologically as being pseudotetrahedral. We drew attention to the fact that the bond angles at iron are not in fact *ca.* 109°, but found that using more correct angles was much less convenient and gave essentially the same results.[3]

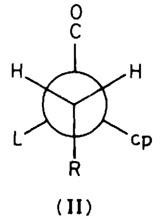
Recently, however, Seeman and Davies[4] have presented criticisms of our approach. Although they have not suggested an alternative interpretation of our experimental results, Seeman and Davies claim that our conclusions lead to incorrect conformational energy profiles and that theoretical calculations can provide better estimations of conformational energies. In fact Seeman and Davies have considerably misquoted and misrepresented our results and conclusions and, in our opinion, some of their claims do not stand close examination.

Seeman and Davies begin with the semantic argument that the type of compound in question is better considered as being pseudo-octahedral, with non-tetrahedral bond angles, and that considering the bond angles in this light would lead to reinterpretation of our data. In fact the Karplus relationship is applicable to compounds with non-tetrahedral bond angles,[5] and Seeman and Davies ignore our evidence, mentioned above, that changing the bond angles does not alter the interpretations to be drawn from the experimental results. Indeed, rather than re-examine the experimental data in the light of the perceived failings in our approach, Seeman and Davies carry out extended-Hückel calculations of the conformational energy profile for rotation about the Fe–C bond and present a calculated potential energy diagram, superimposing it on what they imply is our literature model and suggesting that our very different conclusions about the structural features of the energy minima were quite incorrect. However, they not only misquote our conformational energy differences by more than an order of magnitude, but they attribute incorrect energy minima to the various conformations suggested by us.

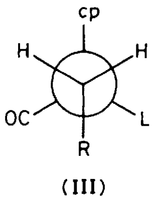
While insufficient information was given to check the calculations† we note that the geometries were not optimised. The resulting energies must therefore be regarded as being very approximate, and the very small calculated differences in the energy minima (<0.5 eV; eV $\approx 1.60 \times 10^{-19}$ J) may not even be significant. We have found, for instance, using extended-Hückel calculations, that the barrier to rotation of the ethylene in [Fe(η^5-C_5H_5)$(CO)_2$(C_2H_4)]$^+$ is reduced from *ca.* 0.9 to *ca.* 0.2 eV on geometry optimisation,[6] as has been anticipated.[7]



(I)



(II)



(III)

Seeman and Davies do attempt to relate the published room-temperature ^3J(P–H) data for compounds such as (**1**) to R–CH_α–Fe–P torsional (dihedral) angles, but fail to consider the full implications of the temperature dependencies of the n.m.r. parameters. They clearly accept the validity of the Karplus relationship to the system under consideration, and recognise that small (*ca.* 1 Hz) and large (>14 Hz) P–H couplings are to be attributed to mutually *gauche* and eclipsed (or antiperiplanar) orientations, respectively, of the C–H_α and Fe–P bonds. They then assign the larger ^3J(P–H) to the 'nearly eclipsed α-proton' of their low-energy conformation, ignoring the facts that the 'eclipsed' hydrogen atom in their diagram actually has a torsional angle of *ca.* 50° rather than 0°, and that the energy barriers to interconversion of the rotamers are sufficiently low that the reported n.m.r. parameters are actually temperature-dependent, weighted averages of the parameters of all three rotamers. Thus if their energy profile were correct, extrapolation of the averaged observed values of ^3J(P–H) of (**1**) to 0 K would result in two very small ^3J(P–H) values being anticipated for the most stable rotamer, as the two torsional angles are essentially *gauche* angles. This prediction is quite contrary to the experimental results, which strongly suggest that the low-energy rotamer has ^3J(P–H) of *ca.* 1 and *ca.* 17 Hz.[1] Seeman and Davies' interpretation of the intermediate values (8–10 Hz) of the single ^3J(P–H) of secondary alkyl compounds of the type [Fe(η^5-C_5H_5)(CO)(PPh_3)(CHRR′)] must also be incorrect. Rather than implying a single rotamer, the data suggest time-averaged populations of at least two rotamers, as has been demonstrated in one case.[8]

Having made the above points, we wish also to describe very preliminary attempts[9] to utilise nuclear Overhauser enhancement (n.O.e.) difference spectroscopy[10] (this technique was not available when our earlier work[1] was done) in an effort to determine directly the preferred geometries in solution of compounds such as (**1**). Our initial experiments are concerned with the sterically very crowded, relatively rigid [Fe(η-C_5H_5)(CO)(PPh_3)(CH_2SiMe_3)],[1] coupled with the previously reported temperature dependencies of the vicinal coupling constants[1] and considerations of space-filling models. Our results strongly suggest that the trimethylsilyl group pre-

---

† Non-standard atomic parameters were also used. While the source(s) of the H_{ii} and ζ parameters used for Fe and P is not stated, the values quoted are not those normally used by, for instance, R. Hoffmann (T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801).

ferentially oscillates between the bulky C_5H_5 and PPh_3 ligands, the bottom of the potential well being a rotamer which appears to have dihedral angles somewhere between those of rotamers (**A**) and (**C**) of Seeman and Davies,[4] *i.e.* with the $SiMe_3$ group almost eclipsing the CO and an α-hydrogen atom almost eclipsing the Fe–P bond [and hence exhibiting both a large ^3J(P–H) and, because of the shielding effects of the aryl ring currents,[11] a relatively high-field chemical shift]. A second rotamer must also be thermally accessible and significantly populated, but its structure cannot yet be deduced. This interpretation, if general, could constitute the first indication that our earlier assumption of staggered energy minima is unwarranted. It also suggests that the calculations of Seeman and Davies do define approximately the structure of the low-energy rotamer, but not the relative energies of the various rotamers.

The impetus for the work of Seeman and Davies lies in the need for a rationale for their observations that, for instance, the α-carbon atoms of compounds of the type $[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)L]$ (L = alkyl, acyl, or carbene) are shielded from external attack on one side by the PPh_3 group.[12] We would argue, however, that the elegant experimental results of Davies and co-workers[12] may not be inconsistent with our general conclusions, as steric restraints to attack by an external reactant need not correlate exactly with steric restraints to internal rotation. Furthermore, many of the reactions of interest may proceed under electronic as well as steric control.[13]

Alan D. Cameron
Michael C. Baird*

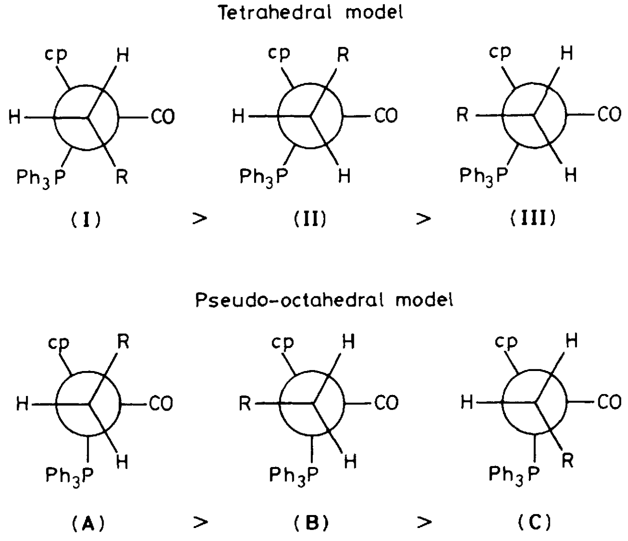
Department of Chemistry
Queen's University
Kingston
Canada K7L 3N6

Seeman and Davies reply. In a series of papers published from 1972 to 1977, Baird and co-workers[1,8,14–16] developed a conformational analysis model for organotransition metal complexes of the type $[M(\eta^5\text{-}C_5H_5)(CO)(PR_3)(CH_2R)]$.

Baird's model predicted 'that primary alkyl compounds of the type $[Fe(\eta^5\text{-}C_5H_5)(CO)(L)(CH_2R)]$ can exist as three staggered rotamers, (**I**), (**II**), (**III**), and that, of these, (**I**) should be the most stable.[1] Since the development of the Baird conformational model, rapid advancements in organotransition metal chemistry have occurred. The major developments include[17] the synthesis of a wide variety of complexes possessing novel structural features, the accumulation of *X*-ray and spectroscopic data for these complexes, and the discovery that many reactions involving these complexes are highly stereo-controlled leading frequently to stereoselective transformation. Importantly, no further advancement in conformational analysis has been proposed for these complexes, even though the generally accepted Baird model is not fully capable of explaining some of the more recent chemical results.[13,17–19]

Recently we presented, in the form of a communication,[4] a new conformational analysis for complexes of the type $[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(CH_2R)]$. Our conformational analysis was at variance with the previous model and because the initial proponent of the first model continues to advocate the Baird model we highlight here the major differences between the two.

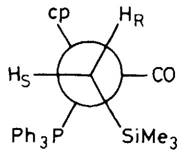
Baird's model was based on three assumptions:[1,14] that the geometry around iron could be considered as tetrahedral, that the most stable conformation would be one of the three possible staggered conformations (**I**), (**II**), or (**III**), and that the CO was the least bulky ligand. Based on these assumptions logic dictated that conformation (**I**) was the most stable and that the cyclopentadienyl ligand exerted greater steric hindrance than the triphenylphosphine ligand.[14,15] The conclusion was drawn that '$[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(CH_2R)]$ exists almost exclusively in conformations in which the groups R are as far as possible from the cyclopentadienyl group'.[14] These assumptions and conclusions formed the basis of later discussions of the conformational properties of related complexes.[1,16] The only subsequent comment concerning the original assumptions was: 'It is convenient to consider all gauche angles as being very similar, *i.e.* about 60°, although it is realised that the P–Fe–C_{alkyl}, P–Fe–CO, and OC–Fe–C_{alkyl} bond angles are likely to be considerably less than tetrahedral angles'.[17] The implication of this statement and the comments made by Baird in his Letter are that it is unimportant as far as conformational analysis is concerned whether these complexes are considered as tetrahedral or pseudo-octahedral.



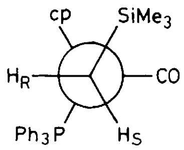
Scheme. Conformation stabilities

In contrast to Baird's model, in our opinion it is crucial to base any conformational analysis on a pseudo-octahedral model.[4,17] The pseudo-octahedral nature of these complexes is demonstrated by *X*-ray structure analyses performed on these types of complexes.[4,18] It is important to emphasise the geometric consequences of pseudo-octahedral geometry. A pseudo-octahedral model would have the cyclopentadienyl ligand occupying three of the octahedral sites while the triphenylphosphine would be restricted to one, thus reducing the effective size as seen by CH_2R of the cyclopentadienyl with respect to the triphenylphosphine. Furthermore in a pseudo-octahedral model three completely staggered conformations equivalent to Baird's (**I**), (**II**), and (**III**) are not possible. The preliminary communication[4] outlined our conformational analysis based on the pseudo-octahedral model. Due to an error in our draftsmanship Baird's qualitative energy profile was inverted about the 60° line but this is no way affected the overall conclusion, namely that the most stable conformation according to Baird's (tetrahedral) analysis was the least stable according to our (pseudo-octahedral) analysis. The Scheme compares the conformational stabilities deduced from the two models (cp = cyclopentadienyl). According to our model, when R is large then only the conformation where R resides between the cyclopentadienyl and the CO is permitted whereas according to Baird the conformation where R resides between the CO and the PPh_3 is the most stable.

For the complex $[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(CH_2SiMe_3)]$ (**1**; R = $SiMe_3$) our analysis predicts conformation (**1A**) with $J(PH_S)$ large and $J(PH_R)$ small as being the most stable. In



(1I)



(1A)

contrast, Baird's analysis predicted conformation (**1I**) with $J(PH_R)$ large and $J(PH_S)$ small. By analogy with the corresponding acyl complexes $[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(COR)]$,[20] for conformation (**1A**) we would expect H_S (large J) to be shifted upfield because it lies over a phenyl group of the PPh_3 whereas in conformation (**1I**), H_S (small J) would be shifted upfield. The coupling constants and chemical shifts [δ −0.2, J(PH) = 2 Hz; δ −1.2, J(PH) = 13 Hz][21] for the diastereotopic protons H_R and H_S are consistent with (**1A**) but not with (**1I**). The n.O.e. difference results reported by Baird in his Letter and more fully elsewhere[22] add further support to our model.

As we pointed out in our full paper[18] the conformational analysis of these complexes is in a formative stage. The new models presented are designed to provide the initial basis for understanding and evaluating the stereochemical intricacies of these compounds. Obviously before we can be definitive about such topics as energy barriers for rotations and detailed structural features and absolute energy differences between stable conformations considerable additional experimental and theoretical results are required. In combination with *X*-ray crystallographic analyses, very detailed theoretical calculations including complete geometry optimisation will be an asset in these studies. Our preliminary communication[4] and the corresponding full paper[18] are intended to provide a workable conformational model useful for the prediction and explanation in qualitative terms of the stereochemical results in this area. Baird's latest experimental results indicate the effectiveness of the new conformational analysis.[22]

Jeffrey I. Seeman

Philip Morris Research
P.O. Box 26583
Richmond
Va. 23261
U.S.A.

Stephen G. Davies

The Dyson Perrins Laboratory
South Parks Road
Oxford OX1 3QY

References

1 K. Stanley and M. C. Baird, *J. Am. Chem. Soc.*, 1975, **97**, 4292.
2 D. G. Gorenstein, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1983, **16**, 1.
3 Ref. 39 of ref. 1.
4 J. I. Seeman and S. G. Davies, *J. Chem. Soc., Chem. Commun.*, 1984, 1019.
5 M. Karplus, *J. Am. Chem. Soc.*, 1963, **85**, 2870.
6 S. C. Wright, A. D. Cameron, and M. C. Baird, unpublished work.
7 B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585.
8 K. Stanley and M. C. Baird, *J. Am. Chem. Soc.*, 1977, **99**, 1808.
9 B. K. Hunter and M. C. Baird, unpublished work.
10 J. K. M. Sanders and J. D. Mersh, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1983, **15**, 353.
11 F. A. Bovey, 'Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1969, p. 64.
12 See, for instance, G. J. Baird, S. G. Davies, R. H. Jones, K. Prout, and P. Warner, *J. Chem. Soc., Chem. Commun.*, 1984, 745; P. J. Curtis and S. G. Davies, *ibid.*, p. 747; S. G. Davies, I. M. Dordor and P. Warner, *ibid.*, p. 956.
13 See, for instance, W. A. Kiel, G-Y. Lin, A. B. Constable, F. B. McCormick, C. E. Strouse, O. Eisenstein, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1982, **104**, 4865.
14 J. Thomson, W. Keeney, M. C. Baird, and W. F. Reynolds, *J. Organomet. Chem.*, 1972, **40**, 205.
15 K. Stanley and M. C. Baird, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 1111.
16 K. Stanley and M. C. Baird, *J. Am. Chem. Soc.*, 1975, **97**, 6598.
17 S. G. Davies and J. I. Seeman, *Tetrahedron Lett.*, 1984, 1845.
18 J. I. Seeman and S. G. Davies, *J. Am. Chem. Soc.*, 1985, **107**, in the press.
19 W. A. Kiel, G-Y. Lin, G. S. Bodner, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1983, **105**, 4958.
20 S. G. Davies, I. M. Dordor, J. C. Walker, and P. Warner, *Tetrahedron Lett.*, 1984, 2709.
21 K. H. Parnell, *Chem. Commun.*, 1969, 1346.
22 B. K. Hunter and M. C. Baird, *Organometallics*, 1985, **4**, 1481.

Received 23rd *November* 1984; *Paper* 4/1996