Conformational Analysis of [(η^5-C_5H_5)Fe(CO)(PPh_3)CH_2OMe]: Solvent Dependence of Conformer Populations

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In polar solvents the complex [(η^5-C_5H_5)Fe(CO)(PPh_3)CH_2OMe] adopts, for steric and dipolar reasons, a conformation which places the methoxy group between the cyclopentadienyl and CO ligands, whereas in a non-polar solvent at low temperature dipolar effects dominate over steric effects and the preferred conformation places the methoxy group antiperiplanar to the CO ligand between the cyclopentadienyl and PPh_3 ligands.

The preferred conformations for alkyl groups attached to the chiral auxiliary [(η^5-C_5H_5)Fe(CO)(PPh_3)] are determined by steric factors.[1—3] The PPh_3 group is very much larger than the cyclopentadienyl ligand, which in turn is much bigger than the CO ligand. Thus site *A* (Figure 1) is sterically the least encumbered space between the medium and small ligands, followed by site *B*, whereas site *C* is inaccessible to all but the smallest groups (*e.g.* H). Thus even for the ethyl complex (**1**) only the conformation which places the relatively small methyl group in site *A* is populated.[3]

In order to probe the possible contributions of polar effects to conformational preferences in this system we have carried out a conformational analysis, described here, for the complex [(η^5-C_5H_5)Fe(CO)(PPh_3)CH_2OMe] (**2**),[4] where we have introduced a small polar substituent on C_α.

The major polar contribution to the overall dipole of the moiety [(η^5-C_5H_5)Fe(CO)(PPh_3)] will be due to the iron–phosphorus bond being substantially polarised (Fe^-–P^+), since there is essentially no back-bonding to the phosphorus. The iron–carbon monoxide bond is not expected to be significantly polarised, whereas any small polarisation that exists in the cyclopentadienyl–Fe bond is expected to align in part with the Fe–P dipole. Therefore for the CH_2OMe ligand in the complex (**2**), if steric effects dominate, conformation (**2A**) will be favoured, whereas if polar effects are important conformations close to (**2D**) will maximise the overall dipole and those close to (**2B**) will minimise it (steric effects will always operate to exclude conformations where the OMe dips much below the plane C_α–Fe–CO).

In the 300 MHz ^1H n.m.r. spectrum of (**2**) in the polar solvent CD_2Cl_2 the diastereotopic protons H(1) and H(2) appear at δ 4.07 ($^3J_{PH}$ 6.34 Hz) and 4.37 ($^3J_{PH}$ 4.91 Hz), respectively. Monitoring $^3J_{PH}$ over the temperature range 233—293 K showed no variation within experimental error. The spectroscopic data obtained for (**2**) in CD_2Cl_2 are entirely consistent with a single conformation close to (**2A**) being populated. Conformation (**2A**) would be both sterically and electrostatically favoured and would account for H(1) being shielded relative to H(2) by the proximate phenyl group[5] and, according to the Karplus equation, having the larger $^3J_{PH}$ value.[6] That $^3J_{PH}$ for H(1) in the complex (2) is not as large as that for the complex (1) ($^3J_{PH}$ 12.1 Hz) may be attributed to the effect of the *trans* electronegative oxygen.[7] Additional support for (**2A**) being the favoured conformation in CD_2Cl_2 was provided by nuclear Overhauser (n.O.e) difference spectroscopy. Irradiation at the frequency of the *ortho*-phenyl protons gave large enhancements to both H(1) (13.8%) and H(2) (15.4%) signals, whereas irradiation at the frequency of H(1) enhanced the H(2) signal (26%), and that of the *ortho*-protons (3%), but not that of the cyclopentadienyl protons.

In the 300 MHz ^1H n.m.r. spectrum of (**2**) at 297 K in the non-polar solvent C_6D_6 the signals due to the diastereotopic protons H(1) and H(2) appear at δ 4.68 ($^3J_{PH}$ 4.81 Hz) and 4.32 ($^3J_{PH}$ 6.94 Hz), respectively. This is consistent with conformation (**2B**) being preferred in C_6D_6 with H(1) exhibiting the smaller $^3J_{PH}$ and appearing downfield of H(2) which is shielded by a proximate phenyl group. Confirmation of this assignment was provided by n.O.e difference spectroscopy: irradiation at the frequency of the *ortho*-phenyl protons showed enhancement of the H(2) signal (7.6%) but *not* that of H(1). The $^3J_{PH}$ values of H(1) and H(2) for (**2**) in [$^2H_8$]toluene

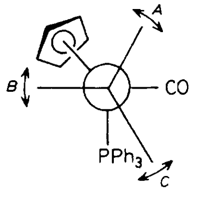
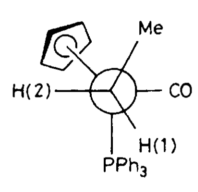
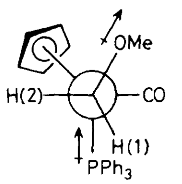


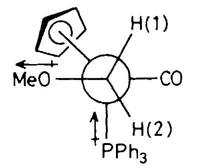
Figure 1



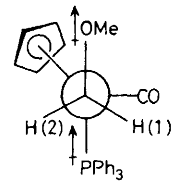
(**1**)



(**2A**)
sterically favoured



(**2B**)
minimum dipole



(**2D**)
maximum dipole

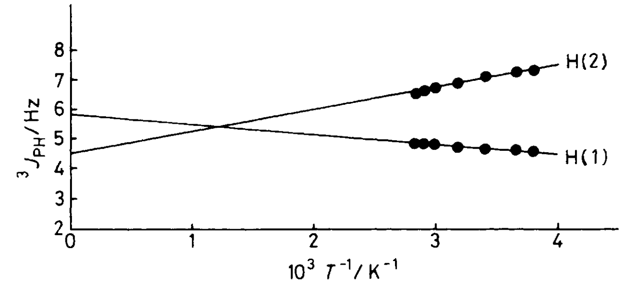


Figure 2. $^3J_{PH}$ *vs.* (temperature)$^{-1}$ for [(η^5-C_5H_5)Fe(CO)(PPh_3)-CH_2OMe] (**2**).

varied over the temperature range 263—363 K; this is in contrast with (**2**) in CD_2Cl_2 and with the complex (**1**) in CD_2Cl_2 and in [$^2H_8$]toluene, which showed no variation. Such a variation with temperature indicates the population of more than one conformation. Extrapolation of the variable temperature data to infinite temperature (Figure 2) indicates that $^3J_{PH}$ tends towards values observed for (**2**) in CD_2Cl_2, indicating that at infinite temperature only conformation (**2A**) would be populated. This situation may arise when for two conformations ΔH° is small but ΔS° is large, so that at high temperature the $T\Delta S^\circ$ term becomes dominant. In conformation (**2B**) the *O*-methyl group is constrained to lie antiperiplanar to the C_α–Fe axis whereas in conformation (**2A**) many more orientations of the *O*-methyl group are accessible. At higher temperatures the *O*-methyl group is effectively larger, as a result of rotation about the C_α–O bond; steric considerations, which favour (**2A**), then become dominant.

The foregoing data indicate that the complex (**2**) exists in conformation (**2A**) in CD_2Cl_2 but in conformation (**2B**) in C_6D_6. Entirely consistent with this are the smooth changes in $^3J_{PH}$ and chemical shifts that are observed in a range of mixed solvent systems (CD_2Cl_2/C_6D_6); cross-over is observed for both chemical shifts and $^3J_{PH}$.

An *X*-ray crystal structure of (**2**) reveals that conformation (**2B**), in which the overall dipole is minimised, is adopted in the solid state.[8] Significantly, the *X*-ray crystal structure, reported by Flood *et al.*,[9] of the corresponding menthyl-complex (+)-(*S*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)CH_2O(−) menthyl] showed that conformation (**2A**), in which the steric interactions with the bulky menthyl group are minimised, is preferred.

In summary, the conformation adopted by the complex [(η^5-C_5H_5)Fe(CO)(PPh_3)CH_2OMe] is governed by steric and electrostatic factors. In a polar solvent both steric and dipolar effects favour conformation (**2A**). In a non-polar solvent at low temperature conformation (**2B**) is favoured for electrostatic reasons but at high temperature steric and entropy factors dominate and conformation (**2A**) again predominates.

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References

1 J. I. Seeman and S. G. Davies, *J. Am. Chem. Soc.*, 1985, **107**, 6522.
2 A. P. Ayscough and S. G. Davies, *J. Chem. Soc., Chem. Commun.*, 1986, 1648.
3 S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton, and M. Whittaker, *J. Organomet. Chem.*, 1987, **320**, C19; *Chem. Ind. (London)*, 1987, 338; *J. Am. Chem. Soc.*, 1987, in the press.
4 T. C. Flood, F. J. D. DiStanti, and D. L. Miles, *Inorg. Chem.*, 1976, **15**, 1910.
5 J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, 1957, **79**, 846.
6 M. Karplus, *J. Am. Chem. Soc.*, 1963, **85**, 2870.
7 C. A. G. Haasnoot, F. A. A. M. De Leeuw, and C. Altona, *Tetrahedron*, 1980, **36**, 2783.
8 S. G. Davies, R. H. Jones, T. R. Maberly, and K. H. Sutton, in preparation.
9 C.-K. Chou, D. L. Miles, R. Bau, and T. C. Flood, *J. Am. Chem. Soc.*, 1978, **100**, 7271.