Stereochemistry of 5-Substituted η^4-Cyclopentadiene Transition-metal Complexes

Stephen G. Davies,* Steven D. Moon, Stephen J. Simpson, and Susan E. Thomas
The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

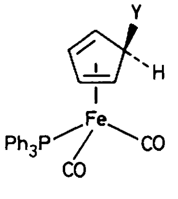
The use of long range ^1H–^{31}P spin-spin coupling constants as criteria for the assignment of the stereochemistry of 5-substituted η^4-cyclopentadiene transition-metal complexes is described.

Nucleophilic addition to cyclopentadienyl ligands bonded to 18-electron organotransition-metal cations is generally accepted to be stereospecific with the nucleophile approaching the unco-ordinated face of the cyclopentadienyl ligand to yield *exo* 5-substituted η^4-cyclopentadiene complexes.[1] This is consistent with these addition reactions involving S_N2 displacement of the metal–carbon bond by the nucleophile with the carbon atom being attacked undergoing inversion of configuration.[2] The most common criterion for assigning the stereochemistry of 5-substituted η^4-cyclopentadiene complexes has been the presence or absence of an i.r. absorption at *ca.* 2 750 cm^{-1} attributed to C–H_{exo}.[3] This absorption was however initially misassigned to C–H_{endo} and this has resulted in its subsequent history being rather confused.[4] Recently serious doubt about the validity of this criterion has been expressed.[5] We describe here the use of long range ^1H–^{31}P coupling constants to assign unambiguously the stereochemistry of such complexes.

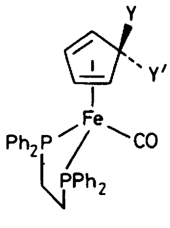
Long range spin-spin coupling between nuclei occurs over four bonds between atoms in a ' W ' arrangement.[6] This is a well established phenomenon in hydrocarbon molecules but has not been extensively exploited in organometallic complexes. In cyclopentadiene complexes H_{exo} but not H_{endo} is in the required geometric arrangement with any co-ordinated phosphorus atoms for such long range coupling to be expected, assuming rotation about the diene–metal bond. Examination of the 300-MHz n.m.r. spectra of a range of cyclopentadiene complexes containing phosphine ligands demonstrates that $^1H_{exo}$–^{31}P coupling can indeed be readily observed.

Results and Discussion

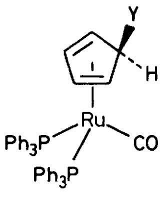
In the 300-MHz n.m.r. spectra of the η^4-cyclopentadiene complexes listed in the Table H_{endo} generally appears as an unresolved multiplet ($w_{\frac{1}{2}}$ *ca.* 15 Hz) showing coupling to H_{exo} and also to the olefinic protons. Selective decoupling experiments confirm this and demonstrate that there is no observable $^1H_{endo}$–^{31}P coupling. In contrast in each case H_{exo} appears as a well defined multiplet showing coupling to H_{endo} and also to each co-ordinated phosphorus. For example, for complex (1) H_{exo} appears as a triplet showing equal coupling to H_{endo} and the one phosphorus on the iron. In complexes (3) and (6), however, H_{exo} appears as a doublet of triplets consistent with coupling to H_{endo} and to two equivalent co-ordinated phosphorus atoms. Similarly H_{exo} for (8) appears as a doublet of quartets due to coupling to H_{endo} and three equivalent phosphorus atoms whereas for the same reasons H_{exo} for (10) is a double double triplet since in this case only two of the phosphorus atoms are equivalent. Selective decoupling of the phosphorus atoms resulted in the expected collapse of the H_{exo} multiplets.



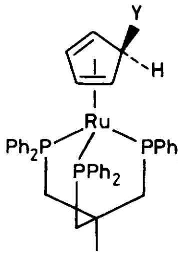
(1; Y = H)
(2; Y = D)



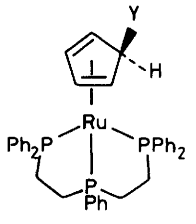
(3; Y = H Y' = H)
(4; Y = D Y' = H)
(5; Y = H Y' = D)



(6; Y = H)
(7; Y = D)



(8; Y = H)
(9; Y = D)



(10; Y = H)
(11; Y = D)

The coupling between the diene protons and H_{exo} cannot be resolved but is however much smaller (<2 Hz) than for H_{endo}. This is in agreement with the methylene carbon being out of the plane of the other four carbons[4] such that the dihedral angles between C^1–H and C^5–H_{exo} and C^5–H_{endo} approximate to 90 and 30° respectively with the geometry of C^1 and C^4 being closer to sp^3 rather than sp^2.

All of the diene complexes described above were prepared by the action of lithium aluminium hydride on the corresponding cyclopentadienyl cations, except (1) which was prepared using sodium tetrahydroborate. The corresponding monodeuterides were prepared under similar conditions with lithium aluminium deuteride or sodium tetradeuterioborate in the case of (2). In each case the signal assigned to H_{exo} was completely absent from the ^1H n.m.r. spectrum of the deuterides confirming that as anticipated stereospecific *exo* addition had occurred. Complex (5) with deuterium in the *endo* position was prepared by thermal rearrangement of $[FeD(\eta^5\text{-}C_5H_5)(CO)(Ph_2PCH_2CH_2PPh_2)]$[7,8] and in this case the signal assigned to H_{endo} in the spectrum of (3) was completely absent from the spectrum of (5).

In the i.r. spectra of each of the cyclopentadiene complexes we have studied, the absorption at *ca.* 2 750 cm^{-1}

Table. Characteristic spectroscopic data for cyclopentadiene-iron and -ruthenium complexes

Complex	$\nu(C{-}H_{exo})$/ cm^{-1}	δ/p.p.m.				J_{HH}/ Hz	J_{PH}/ Hz	Complex	$\nu(C{-}D_{exo})$/ cm^{-1}
		$H^{1,4}$	$H^{2,3}$	H_{endo}	H_{exo}				
(1) $[Fe(\eta^4\text{-}C_5H_6)(CO)_2(PPh_3)]$ [a]	2 730	2.27	5.13	2.78	2.24 (t)	10.5	10.5	(2)	2 080m, 2 060m, 2 015w
(3) $[Fe(\eta^4\text{-}C_5H_6)(CO)(Ph_2PCH_2CH_2PPh_2)]$ [b]	2 740	2.43	4.89	3.03	2.75 (dt)	10.0	9.3	(4)	2 060m, 2 040m
(6) $[Ru(\eta^4\text{-}C_5H_6)(CO)(PPh_3)_2]$ [c]	2 750	2.13	5.26	2.51	2.94 (dt)	10.4	19.7	(7)	2 075w, 2 065m
(8) $[Ru(\eta^4\text{-}C_5H_6)\{MeC(CH_2PPh_2)_3\}]$ [d]	2 715	2.59	5.85	3.54	4.01 (dq)	9.0	14.2	(9)	2 050m, 2 020m, 1 995w
(10) $[Ru(\eta^4\text{-}C_5H_6)\{PhP(CH_2CH_2PPh_2)_2\}]$ [d]	2 750	2.90	5.36	2.58	3.57 (ddt)	10.3	8.1 18.8	(11)	2 045m, 2 015m

[a] A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 1961, 3172. [b] Ref. 7. [c] S. G. Davies, S. D. Moon, and S. J. Simpson, unpublished work. [d] S. G. Davies, H. Felkin, T. Fillebeen-Khan, F. Tadj, and O. Watts, *J. Chem. Soc., Chem. Commun.*, 1981, 341.

ascribed to $C{-}H_{exo}$[3] was absent from the spectra of the corresponding *exo* deuterides. It had, however, been replaced by a $C{-}D_{exo}$ absorption at *ca.* 2 040 cm^{-1} (see Table). In the case of the *endo* deuterium complex (5), the $C{-}H_{exo}$ absorption was present at 2 730 cm^{-1} together with a $C{-}D_{endo}$ absorption at 2 165 cm^{-1}. The agreement between the H_{exo} and H_{endo} assignments on the basis of $^1H_{exo}{-}^{31}P$ coupling and the H_{exo} i.r. absorptions allows renewed confidence to be placed in the use of the latter for the determination of the stereochemistry of 5-substituted cyclopentadiene complexes. It should be noted, however, that two other criteria occasionally used to assign stereochemistry in these systems are not reliable: trityl tetrafluoroborate does not always selectively remove H_{exo} in preference to H_{endo}[9] and the chemical shift of H_{endo} is not always at a lower field to that of H_{exo} (see Table).

The use of the $^1H_{exo}{-}^{31}P$ spin-spin coupling criterion described here to determine the stereochemistry of cyclopentadiene systems should be applicable to other systems such as cyclohexadienyl, cyclohexadiene, cycloheptatriene, *etc.* We are presently exploring these possibilities.

Acknowledgements

We thank the British Petroleum Company Ltd. for a Fellowship (to S. J. S.) and Laporte Industries Ltd. for a studentship (to S. E. T.). Johnson Matthey are gratefully acknowledged for a generous loan of ruthenium.

References

1 S. G. Davies, M. L. H. Green, and D. M. P. Mingos, *Tetrahedron*, 1978, **34**, 3047.
2 S. G. Davies, ' Organotransition Metal Chemistry: Applications to Organic Synthesis,' Pergamon Press, Oxford, 1982.
3 M. R. Churchill and R. Mason, *Proc. R. Soc. London, Ser. A*, 1964, **279**, 191.
4 M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3753; G. Fachinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, 1974, 516.
5 J. W. Faller, *Inorg. Chem.*, 1980, **19**, 2857.
6 J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, 1963, **85**, 2514; S. D. Robinson and A. Sahajpal, *Inorg. Chem.*, 1977, **16**, 2718, 2722; Y. Wakatsuki, K. Aoki, and H. Yamazaki, *J. Am. Chem. Soc.*, 1979, **101**, 1123.
7 S. G. Davies, J. Hibberd, and S. J. Simpson, *J. Organomet. Chem.*, 1983, **246**, C16.
8 S. G. Davies, J. Hibberd, S. J. Simpson, and O. Watts, *J. Organomet. Chem.*, 1983, **241**, C13.
9 A. N. Nesmeyanov, N. A. Vol'Kenau, L. S. Shilovtieva, and V. A. Petrakova, *J. Organomet. Chem.*, 1975, **85**, 365.

Received 8*th November* 1982; *Paper* 2/1882