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MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

IX*. PHOSPHAFERROCENES AND THEIR PROTONATED DERIVATIVES

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Summary

A number of mono- and di-phosphaferrocenes have been synthesised and their NMR (^1H, ^{31}P) and Mössbauer spectra measured. The presence of a phosphorus atom in the cyclopentadienyl (Cp) moiety causes a reduction of about 0.3 mm s^{-1} in the quadrupole splitting (QS) compared with that of ferrocene. The effect appears to be additive, as does the effect of Cp ring substituents. Thus 2,5-diphenylphosphaferrocene (I), 3,3′,4,4′-tetramethyldiphosphaferrocene (II) and 2,2′,5,5′-tetraphenyldiphosphaferrocene (III) have QS values of 2.03, 1.82 and 1.52 mm s^{-1}, respectively.

III dissolves readily and reversibly in triflic acid (CF_3SO_3H) to give a phenyl ring protonated species. The Mössbauer spectrum of the frozen solution shows a significant increase in QS to 1.77 mm s^{-1} which is interpreted in terms of iron participation in the stabilisation of the σ complex. H/D exchange reactions and oxidation of phosphaferrocenes are briefly reported together with an improved synthesis of the important precursor, 1,2,5-triphenylphosphole.

Introduction

In contrast to the extensive investigations of the chemistry of ferrocene, the heterocyclopentadienyl analogues, such as aza- and phospha-ferrocene, have received little attention. The former was first prepared in 1964 [2,3], whereas the latter has only been synthesised fairly recently by Mathey and co-workers [4]. Both mono- [5] and di-phosphaferrocenes [6] have now been characterised, and some reports on their structure and reactivity [6–9] have appeared, largely due to the pioneering work of Mathey. Since the heterocyclopentadiene precursors containing other elements are readily accessible [10,11], it is clear that the synthesis of a wide range of heteroferro-

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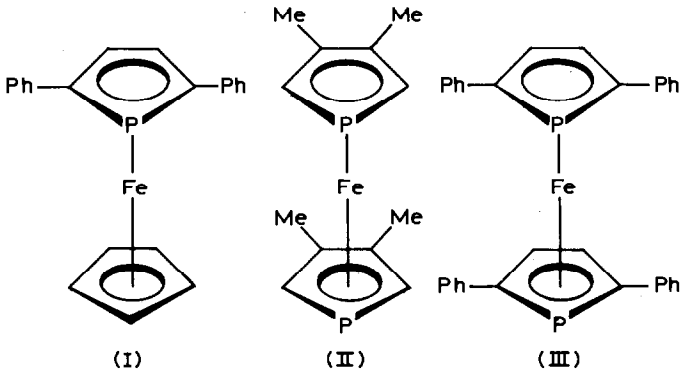
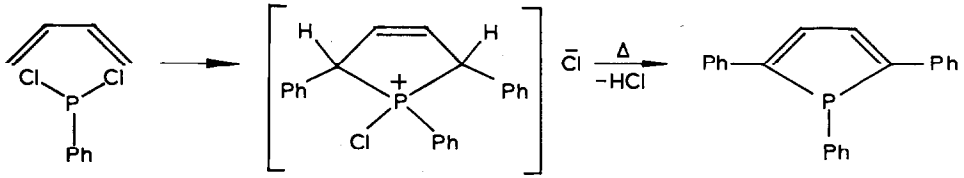
cenes is now feasible. Both arsa- [12–14] and stiba-ferrocenes [15] have been recently reported, a prelude, no doubt, to a widening of interest in these novel ferrocene analogues. We report in this paper a Mössbauer study of mono- and diphosphaferrocenes in strongly acidic media as part of a continuing programme devoted to Mössbauer investigations of ferrocene complexes.

Results and discussion

The three principal phosphaferrocenes used in this study are I–III. These were



prepared according to literature methods [4,6,16]. An improved synthesis of 1,2,5-triphenylphosphole (precursor to both I and III) was found. The original method [17], which involved cycloaddition of 1,4-diphenylbutadiene to dichlorophenylphosphine at elevated temperature (10 h at 220°C), suffered from temperature control problems such that little reaction occurred below 210°C and substantial decomposition took place above 225°C. We found that refluxing a solution of diphenylbutadiene in



$PhPCl_2$ (b.p. 222°C) yielded the desired phosphole in 70% yield after only 3 h.

All attempts to prepare 2,3,4,5-tetraphenylphosphaferrocene, and 2,2′,3,3′,4,4′,5,5′-octaphenyldiphosphaferrocene failed [4].

Phosphaferrocenes in strongly acidic media

III dissolved readily in 98% sulphuric acid to give a deep red solution which gradually turned orange. The ^1H NMR spectrum of freshly prepared solutions showed no iron protonation, as deduced from the absence of a signal at −2.0 ppm which is highly characteristic of such species [18]. The β hydrogen signal (δ 7.10 ppm) appeared downfield from that of III itself and the aromatic signal appeared as a quartet (δ 7.55 ppm, J 8 Hz). Sulphonation in ferrocene systems occurs very readily on the cyclopentadienyl (Cp) rings. Here, attack at the phenyl rather than the

Cp ring is apparently favoured, indicating that the presence of the phosphorus atom deactivates the latter towards electrophilic attack. Further evidence to support this comes from studies in trifluoromethanesulphonic acid (CF_3SO_3H, triflic acid) which is the strongest protic acid known, and is non oxidising and non-sulphonating [19]. III dissolved in CF_3SO_3H to give a stable deep red solution whose ^1H NMR spectrum showed no Fe-H resonances. III was recovered unchanged on quenching in water. III was dissolved in CF_3SO_3D and quenched in D_2O. The recovered III was dissolved in $CDCl_3$ and the ^1H NMR run. A 55% reduction in the aromatic signal was observed compared with undeuteriated material at the same concentration, whereas the intensity of the β hydrogen signals remained unchanged. These findings are commensurate with hydrogen–deuterium exchange in the *ortho* and *para* positions of the phenyl ring, with no exchange of the Cp hydrogens.

^{31}P NMR were run on CF_3SO_3H solutions of III, 1,2,5-triphenylphosphole and triphenylphosphine. The results appear in Table 1. The ^{31}P signal of III was reported previously [6] as 63.6 ppm but the reference and chemical shift convention were not specified. 3,3′,4,4′-tetramethyldiphosphaferrocene showed a ^{31}P shift of +184.6 relative to P_4O_6 [20] where the positive value in this case indicates an upfield shift. P_4O_6 is 112 ppm downfield from H_3PO_4, which gives δ for II as −72 ppm. In this work a positive sign indicates a downfield shift from the reference (85% H_3PO_4).

The most striking feature of the data in Table 1 is that whereas both triphenylphosphine and 1,2,5-triphenylphosphole are protonated at phosphorus in CF_3SO_3H, as shown by the typically large $J(^{31}P-^1H)$ of ~500 Hz, both diphosphaferrocenes are not phosphorus protonated. However, the δ values of both II and III indicate pronounced deshielding with normal line-widths. The absence of Fe-H signals in the ^1H NMR, together with the H/D exchange described above, clearly identify the site of protonation as being on the phenyl rings in III. Further substantiation comes from Mössbauer spectra of frozen CF_3SO_3H solutions (vide infra). The considerable difference in ^{31}P chemical shift of the tetramethyl (−72 ppm) relative to the tetraphenyl (+62 ppm) reflects the electron-releasing and electron-withdrawing effects of the methyl and phenyl groups, respectively. It seems likely that for II, protonation occurs on the Cp ring which would account for the very large downfield shift (166 ppm) observed on changing from solvent benzene to CF_3SO_3H. The comparable shift for III is only 76 ppm where the charge is more remote from the phosphorus atom.

TABLE 1

^{31}P NMR DATA FOR DIPHOSPHAFERROCENES (II, III), TRIPHENYLPHOSPHOLE AND Ph_3P IN SOLVENTS BENZENE (B) AND TRIFLIC ACID (TFMSA)

Compound	Solvent	δ (ppm) [a]	$J(^{31}P-^1H)$ (Hz)
Ph_3P	B	+5.82	–
Ph_3P	TFMSA	+7.03	505
1,2,5-Triphenylphosphole	B	−2.86	–
1,2,5-Triphenylphosphole	TFMSA	−6.04	502
III	B	+62.64	–
III	TFMSA	+139.46	–
II	TFMSA	+93.85	–

[a] δ in ppm from 85% H_3PO_4 as reference.

In view of the lack of H/D exchange of the Cp protons in III, it is likely that the phenyl and Cp rings are not coplanar.

Mössbauer results

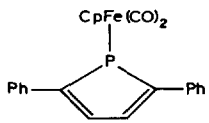
From the data in Table 2, it is clear that both mono- and di-phosphaferrocenes have markedly lower QS values than that of ferrocene.

We have recently analysed Mössbauer data for ferrocene derivatives as a function of substituent groups from which it is established that conjugate electron-withdrawing groups systematically lower QS values. The effect was also noted by Good et al. [22]. The substituent causes electron delocalisation from the metal and the contribution to the electric field gradient from the d electron is reduced as deduced molecular orbital arguments [23,24]. The effect on IS is small, being a secondary effect caused by decreased electron shielding.

In the analysis of our data, the effect of the hetero atom and the effect of the ring substituents on QS have to be separated. Methyl substituents increase QS values [25], (viz. 0.03 mm s^{-1} for diethylferrocene, 0.05 mm s^{-1} for tetramethylferrocene) whereas phenyl substitution causes a lowering of about 0.06 mm s^{-1} [26]. Thus in terms of the methyl substituent effect alone, the QS of II should be 2.45 mm s^{-1}, taking a QS value of 2.40 mm s^{-1} for ferrocene itself [22]. The observed value is 1.82 mm s^{-1} which implies a reduction in QS of about 0.3 mm s^{-1} for each phosphocyclopentadiene ring, assuming additivity. Thus the unsubstituted mono- and di-phosphaferrocenes should have QS values of 2.1 (cf. azaferrocene [21]) and 1.8 mm s^{-1}, respectively. Taking into account the effect of the two phenyl groups in I, the calculated QS should be ~ 2.0 mm s^{-1} which is in good agreement with the observed value of 2.03 mm s^{-1}. For III the calculated value is 1.56 mm s^{-1} which again is quite close to the observed value of 1.52 mm s^{-1}. Thus it seems that the different effects on QS are additive, though one must expect deviations from such additivity for the more sterically crowded derivatives [25]. The probable reason for

TABLE 2

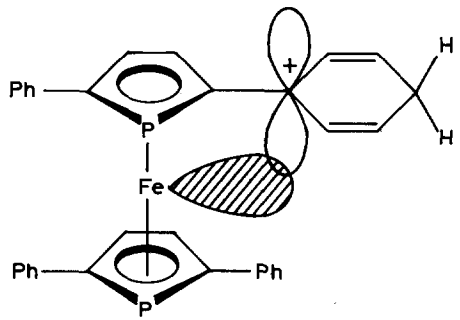
^{57}Fe MÖSSBAUER DATA (isomer shift, IS, mm s^{-1}, quadrupole splitting, QS, mm s^{-1}) FOR PHOSPHAFERROCENES AND RELATED SPECIES AT 80 K IN SOLID STATE (S) AND FROZEN CF_3SO_3H SOLID SOLUTION (FSS)

Compound	Phase	QS	IS
I	S	2.03(1)	0.56(2)
2-phenyl-3,4-dimethylphosphaferrocene	S	2.22(4)	0.55(2)
II	S	1.82(1)	0.51(1)
III	S	1.52(2)	0.57(2)
III	FSS	1.77(2)	0.55(2)
	S	1.58(1)	0.73(1)
Azaferrocene [a]	S	2.14	0.57

[a] See ref. 21 (at 25°C).

the marked lowering of QS by the phosphorus atom is that the P atom attracts electronic charge from the ring based orbitals. Evidence that this is so is the marked preference for electrophilic reactions to occur at the P atom [8,9] and that H/D exchange reactions in tetraphenylphosphaferrocene prefer phenyl ring to Cp ring sites.

The other notable feature of the results in Table 2 is the marked increase in QS of 0.25 mm s^{-1}, when III is dissolved in CF_3SO_3H. This result is very much in keeping with previous work on ferrocenyl carbenium ions recently undertaken in these laboratories [27–29], where increases in QS were found due to iron participation by e_{2g} orbitals in the stabilisation of these ions. Such would be the case for III since all the evidence points to phenyl ring protonation. It is probable that III on protonation yields a σ complex where the positive charge is stabilised by analogous overlaps of e_{2g} with empty p orbitals on the α carbon.



Other reactions

Oxidation of III by $FeCl_3$, H_2O_2 and CCl_3CO_2H did not give the corresponding ferrocinium ions but resulted in extensive decomposition and liberation of Fe^{3+} ions. This behaviour is probably the result of oxidation of the P atom which weakens the Fe–ligand bonding. The monophosphaferrocenes were noticably more prone to aerial oxidation than their diphosphaferrocene counterparts. Attempts to scramble ligands by treating III with ferrocene in refluxing cyclohexane using $AlCl_3$/Al [30] failed.

Experimental

^1H NMR spectra were run on a Varian EM 360 spectrometer. All chemical shift (δ, ppm) are reported relative to an external TMS standard. ^{31}P spectra were obtained using a Bruker WP 80 spectrometer using 85% H_3PO_4 as reference and adopting the "downfield-positive" convention for chemical shifts. Mössbauer spectra were run either on solids or on frozen solid solutions (CF_3SO_3H) as previously described [31]. Trifluoromethanesulphonic acid was obtained from 3M Chemical Co. and purified by distillation under N_2 (b.p. 163°C). CF_3SO_3D was prepared by careful addition of D_2O to a 10% excess of $(CF_3SO_2)_2O$ and allowing to stand at room temperature overnight. The product (98.5 at %D) was distilled from the reaction mixture.

Preparation of phospholes

3,4-Dimethyl-1-phenylphosphole was prepared according to Mathey's recently published improved one-pot synthesis [32].

1,2,5-Triphenylphosphole

1,4-Diphenylbutadiene (20 g, 0.097 mol) was refluxed for 3 h in dichlorophenylphosphine (70 ml) (b.p. 222°C) under nitrogen. After cooling, the mixture set to a yellow crystalline mass. This was broken up and added portionwise to ice cold KOH solution (15%) to hydrolyse the excess phosphine. The yellow solid remaining was filtered off, washed with water and dried. It was recrystallised from $CHCl_3$ to give 21.2 g (70%) of 1,2,5-triphenylphosphole IV (m.p. 188°C) (187–189°C ref. 17). Pentaphenylphosphole was prepared by standard methods [10,33].

Preparation of mono- and di-phosphaferrocenes

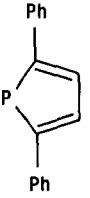
3,3′,4,4′-Tetramethyldiphosphaferrocene and 2,2′,5,5′-tetraphenyldiphosphaferrocene were prepared according to literature procedures [6,20] modified by using $AlCl_3$ as catalyst. Attempts to synthesise octaphenyldiphosphaferrocene by the above methods failed.

3,4-Dimethylphosphaferrocene (V) was prepared by refluxing a solution of 3,4-dimethylphenylphosphole and $[CpFe(CO)_2]_2$ in xylene [5]. A small quantity of the 2 phenyl derivative of V was also obtained.

Preparation of 2,5-diphenylphosphaferrocene

IV (2 g, 6.4 mmol) and $[CpFe(CO)_2]_2$ (2.28 g, 6.4 mmol) were refluxed in xylene (50 ml) for 18 h. The mixture was cooled, filtered and the volume reduced to ~ 5 ml. The extract was chromatographed on a neutral alumina column eluting with benzene. Unreacted IV eluted first, followed by an orange-red band which yielded after removal of solvent and trituration with cold EtOH an orange-red solid (1.5 g, 66%) NMR (δ ppm $CDCl_3$) 7.0 m, 10H 5.64d ($J(^{31}P-^{1}H)$ 5 Hz) 2H, 4.10s 5H.

As with the other monophosphaferrocenes, the product appeared to undergo facile air oxidation with the result that no elemental analysis was attempted. A more stable form was obtained by dissolving the product in CF_3SO_3H and reprecipitating by careful dropwise addition to water. This yielded an orange solid which melted sharply at 55–56°C. The mass spectrum showed a parent ion at m/e 356. Other major peaks were observed at m/e 291 ($M - C_5H_5$) and 121 ($M - C_4H_4P$).

Preparation of  [16]

IV (2 g, 6.4 mmol) was refluxed in dry THF (50 ml) under argon with sodium (0.6 g, 0.026 g atom). The progress of the reaction was monitored by TLC and was judged complete after 5 h. The cooled solution was filtered and t-butyl chloride (0.58 g, 6.4 mmol) in THF (5 ml) added to destroy the PhNa produced. The solution was stirred for 30 min then $CpFe(CO)_2I$ (1.94 g, 6.4 mmol) added to produce a blood-red colouration. The solution was stirred under argon for 15 h (small portions

of solution rapidly turned yellow on exposure to air due to oxidation to the phosphine oxide). The solvent was blown dry using a stream of dry argon. The resulting purple residue was taken up in CH_2Cl_2, filtered and washed with water. After drying ($MgSO_4$) and removing the solvent a violet-red powder was obtained. Yield 1.8 g (70%, NMR: 7.3m, (12H), 4.20 ppm (5H). The product was air sensitive.

Thermal decomposition of the σ complex in refluxing xylene (12 h) yielded the corresponding diphenylphosphaferrocene (10%).

Exchange reactions

III (0.05 g, 0.1 mmol) was dissolved in CF_3SO_3D (1 ml) and allowed to stand at room temperature for 10 min. The deep red solution was added dropwise to D_2O (2 ml) at 0°C. The resulting orange-red precipitate was filtered and dried. Yield 0.045 g. This was dissolved in $CDCl_3$ (2 ml) and the ^1H NMR run. The results were compared with an undeuteriated sample of III under the same conditions. No appreciable change occurred in the β hydrogen signal, but 55% reduction in the aromatic signal occurred. This corresponds to the reduction expected if all the *ortho* and *para* hydrogens had exchanged. Account was taken of the statistical scrambling of label between these sites and CF_3SO_3D.

Acknowledgement

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References

1 Part VIII. M.C. Clemance, R.M.G. Roberts and J. Silver, J. Organometal. Chem., 247 (1983) 219.
2 K.K. Joshi, P.L. Pauson, A.R. Qazi and W.H. Stables, J. Organometal. Chem., 1 (1964) 471.
3 R.B. King and M.B. Bisnette, Inorg. Chem., 3 (1964) 796.
4 F. Mathey, A. Mitschler and R. Weiss, J. Amer. Chem. Soc., 99 (1977) 3537.
5 F. Mathey, J. Organometal. Chem., 139 (1977) 77.
6 G. de Lauzon, B. Deschamps, J. Fischer, F. Mathey and A. Mitschler, J. Amer. Chem. Soc., 102 (1980) 994.
7 B. Deschamps, J. Fischer, F. Mathey and A. Mitschler, Inorg. Chem., 20 (1981) 3252.
8 B. Deschamps, J. Fischer, F. Mathey, A. Mitschler and L. Ricard, Organometallics, 1 (1982) 312.
9 G. de Lauzon, B. Deschamps and F. Mathey, Nouv. J. de Chem., 4 (1980) 683.
10 F.C. Leavitt, T.A. Manuel, F. Johnson, L.U. Matternas and D.S. Lehman, J. Amer. Chem. Soc., 82 (1960) 5099.
11 E.H. Braye, W. Hubel and I. Caplier, J. Amer. Chem. Soc., 83 (1961) 4406.
12 E.W. Abel, I.W. Nowell, A.G.J. Modinos and C. Towers, J. Chem. Soc., Chem. Commun., (1973) 258.
13 G. Thiollet, R. Poilblanc, D. Voigt and F. Mathey, Inorg. Chim. Acta, 30 (1978) L294.
14 F. Mathey, R. Poilblanc and G. Thiollet, Inorg. Chim. Acta, 32 (1979) L67.
15 A.J. Ashe and T.R. Diephouse, J. Organometal. Chem., 202 (1980) C95.
16 E.H. Braye and K.K. Joshi, Bull. Soc. Chem. Belges, 80 (1971) 651.
17 I.G.M. Campbell, R.C. Cookson, M.B. Hocking and A.N. Hughes, J. Chem. Soc., (1965) 2184.
18 R.M.G. Roberts, J. Silver, R.J. Ranson and I.E.G. Morrison, J. Organometal. Chem., 219 (1981) 233.
19 R.D. Howells and J.D. McCown, Chem. Rev., 77 (1977) 69.
20 G. de Lauzon, F. Mathey and M. Simalty, J. Organometal. Chem., 156 (1978) C33.
21 R.B. King, L.M. Epstein and E.W. Gowling, J. Inorg. Nucl. Chem., 32 (1970) 441.
22 M.L. Good, J. Buttone and D. Foyt, Ann. N.Y. Acad. Sci., 239 (1974) 193.
23 R.L. Collins, J. Chem. Phys., 42 (1965) 1072.
24 C.B. Harris, Inorg. Chem., 7 (1968) 1517.
25 S. Iijima, I. Motoyama and H. Sano. Bull. Chem. Soc. Jap., 53 (1980) 3180.

26 R.A. Stukan, S.P. Gubin, A.N. Nesmeyanov, V.I. Goldonskü and E.F. Makarov, Teor. Exper. Khim. Akad. Nauk. SSSR, 2 (1966) 805.
27 G. Neshvad, R.M.G. Roberts and J. Silver, J. Organometal. Chem., 221 (1981) 85.
28 G. Neshvad, R.M.G. Roberts and J. Silver, J. Organometal. Chem., 236 (1982) 237.
29 G. Neshvad, R.M.G. Roberts and J. Silver, J. Organometal. Chem., 240 (1982) 265.
30 R.G. Sutherland, W.J. Pannekoek and C.C. Lee, Ann. N.Y. Acad. Sci., 295 (1977) 192.
31 J. Peterson, J. Silver, M.T. Wilson and I.E.G. Morrison, J. Inorg. Biochem., 13 (1980) 75.
32 A. Breque, F. Mathey and P. Savignac, Synthesis, (1981) 983.
33 E.H. Braye, I. Caplier and R. Saussez, Tetrahedron, 27 (1971) 5523.