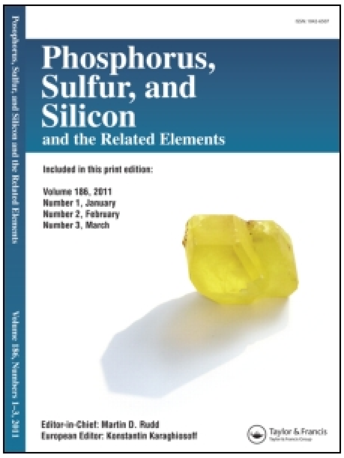


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

^{1}H AND ^{13}C NMR SPECTRAL STUDIES OF SOME CYCLOPENTADIENYL IRON PHOSPHITE COMPLEXES. COMMENTS UPON THE EXTRACTION OF J_{HP} AND J_{CP} COUPLING CONSTANTS

Philip Duncanson[a]; Alan G. Osborne[a]
[a] Department of Chemistry and Biological Chemistry, University of Essex, Colchester, England

To cite this Article Duncanson, Philip and Osborne, Alan G.(1995) ''H AND ^{13}C NMR SPECTRAL STUDIES OF SOME CYCLOPENTADIENYL IRON PHOSPHITE COMPLEXES. COMMENTS UPON THE EXTRACTION OF J_{HP} AND J_{CP} COUPLING CONSTANTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 107: 1, 235 — 244

To link to this Article: DOI: 10.1080/10426509508027939

URL: http://dx.doi.org/10.1080/10426509508027939

Phosphorus, Sulfur, and Silicon, 1995, Vol. 107, pp. 235–244
Reprints available directly from the publisher
Photocopying permitted by license only

^{1}H AND ^{13}C NMR SPECTRAL STUDIES OF SOME CYCLOPENTADIENYL IRON PHOSPHITE COMPLEXES. COMMENTS UPON THE EXTRACTION OF J_{HP} AND J_{CP} COUPLING CONSTANTS

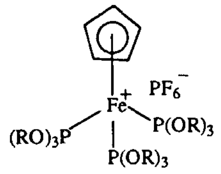
PHILIP DUNCANSON and ALAN G. OSBORNE*
Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, England

(Received July 27, 1995; in final form August 15, 1995)

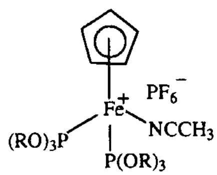
An AA'_nX sub spectral analysis approach is proposed for the extraction of J_{HP} and J_{CP} coupling constants from the NMR spectra of cyclopentadienyliron phosphite complexes. Correlations with earlier corrected splitting values are presented.

Key words: J_{HP} and J_{CP} coupling constants, cyclopentadienyliron phosphite complexes, AA'_nX sub spectra system, "virtual" coupling.

Ligand exchange reactions of η^6-arene-η^5-cyclopentadienyliron cations with phosphite esters under either thermal or photochemical conditions have recently attracted some interest.[1–3] The resultant complexes (e.g. **1**–**3**) have subsequently become versatile reagents for the synthesis[4–6] of a range of Fe^{II} piano-stool complexes which have a useful role as electron transfer catalysts for the control of reactivity pathways.[7,8]



1 R=CH$_3$, **2** R=CH$_2$CH$_3$, **3** R=C$_6$H$_5$



4 R=CH$_3$

Harris[9] has commented that the analysis of the ^{1}H NMR spectra of inorganic compounds that contain two or more phosphorus nuclei and which do not exhibit first order character have appeared to cause some mystification, especially when the spin systems are symmetric. Treatment of such spectra as $AA'A'' \ldots X_nX'_nX''_n \ldots$ systems was suggested and a procedure for the extraction of $J_{AX} + J_{AX'} + J_{AX''} \ldots$ was given. However, despite the availability of this excellent monograph,[9] examples of inappropriate spectral analysis still continue to appear[6,10,11] which have also been perpetuated in some more recent ^{13}C NMR studies.[6,12]

In view of the continuing difficulties that the extraction of the appropriate J_{HP} and J_{CP} couplings still appears to present we now wish to report a simpler and more convenient approach for the analysis and presentation of these spin systems. This approach has been applied to the ^1H and ^{13}C NMR spectra of the aforementioned *tris* phosphite complexes **1–3** and also to the acetonitrile complex **4**.[10]

DISCUSSION

The underlying principles behind the simplified spectral analysis techniques for the complexes **1–3** presented in this paper may best be understood by reference to the more basic "model" ABX spin system,[13a] where X = ^1H and the A & B heteronuclei are ^{31}P. Using the "X approximation approach" the X portion of such a second order system will comprise 6 lines symmetrically distributed about δ_x. The two strongest lines have a separation equal to $J_{AX} + J_{BX}$. A special example of the ABX system must now be considered in which $J_{BX} = 0$.[13b] In such cases the X portion still comprises 6 lines, however, the outermost two are often quite weak and distant, and are frequently undetected, such that they have been described as "wings". It is the resultant multiplicity of the remaining 4 stronger lines in the central X portion which, if analysed by a first order approximation, will produce erroneous results. This is because the observed multiplicity does *not* result from direct interactions with *both* nuclei A and B. Because of this unexpected additional multiplicity this effect has been termed[14] a "virtual coupling."

The possible appearances for the central portion of the X signal have been shown diagrammatically in Figure 1.

In case a the outer lines have merged to give the appearance of a broadened simple doublet.

In case b, the 4-line pattern has the appearance of a doublet of doublets, however, the "roofing" effects are clearly inconsistent.

In case c, the appearance could again be taken as a doublet of doublets, or possibly of a 1:1:1:1 quartet. However, the latter description would only be strictly applicable for coupling to a single I = 3/2 nucleus.

In case d, the inner lines have merged to give the appearance of an apparent triplet. First order analysis, such that $J_{AX} = J_{BX}$ would, however, be inappropriate due to the broadened central band and considerable deviation from the expected 1:2:1 peak heights. For this case the outermost "wings" have also been illustrated.

However, for all of cases a–d, the separation between lines 2 and 5 gives J_{AX} + J_{BX} (which with $J_{BX} = 0$ actually represents J_{AX}). This sum is the only accessible spectral parameter which may be readily extracted in all cases.

The above general principles may now be applied to the phosphite ester complexes **1–3**. As suggested by Harris[9] such spectra should ideally be analysed as the full 30-spin $AA'A''X_9X'_9X''_9$ (retaining X = ^1H) system for the methyl protons of **1** and **2**, or as the full $AA'A''X_6X'_6X''_6$ system for the methylene protons of **2** to assess the required heteronuclear coupling. However, since any $^8J_{HH}$ coupling between CH_3 or CH_2 groups bonded to the magnetically non-equivalent ^{31}P nuclei may be taken as zero, then these alkyl protons may therefore be considered as effectively magnetically equivalent with respect to heteronuclear effects. The spin system may accordingly be simplified to a more manageable sub system. Such a procedure has merit since many spectral simulation programmes do not allow treatment of 21- or 30-spin sys-

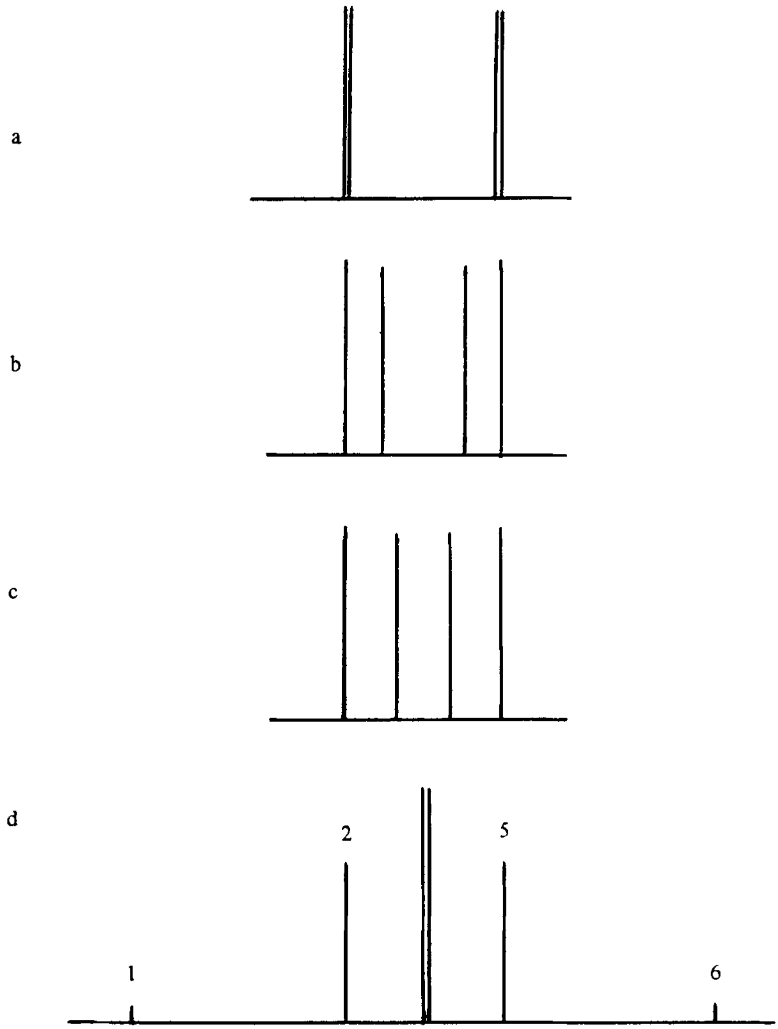
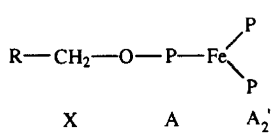


FIGURE 1 Appearance of X portion of ABX "virtual" coupled system (after Reference 13b): a–c) central portion only, d) complete X pattern, 1 & 6 = "wings." In all cases (2–5) = $J_{AX} + J_{BX}$.

tems. However, the necessary constraints recommended by Harris[9] must be heeded. We therefore propose that the sub system be designated as $AA_2'X$, *viz*:

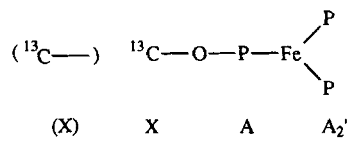


R = H or Alkyl

Such a designation has been proposed so as to retain a considerable degree of similarity between this sub system, $AA_2'X(J_{A'X} = 0)$ and the "model" ABX system ($J_{BX} = 0$) discussed earlier.

The X protons exhibit a ^3J coupling to the nearer ^{31}P nucleus (J_{AX}) and also two potential ^5J long range couplings to the chemically equivalent, but magnetically different more distant ^{31}P nuclei ($J_{A'X}$). For this simplified approach to be applicable it is necessary that $^5J_{A'X}$ be zero, which we have assumed to be the case.

It must be borne in mind that this simplified approach is only applicable if the subsequent spectral analysis is limited to the extraction of the value of (J_{AX} + $J_{A'X}$) from lines 2 and 5 of the central portion of the X signal (compare Figure 1). Moreover, the approach may also be extended to the ^{13}C-{^1H} spectrum. In this case proton X is replaced by carbon X, *viz*:



For each carbon nucleus the spectrum may be treated as an $AA_2'X$ sub system with the following coupling interactions applicable:

Complex	X Nucleus	J_{AX}	$J_{A'X}$
1	$^{13}CH_3$	$^2J_{CP}$	$^4J_{CP}$
2	$^{13}CH_2$	$^2J_{CP}$	$^4J_{CP}$
	$^{13}CH_3$	$^3J_{CP}$	$^5J_{CP}$
3	^{13}C-Ph$_{ipso}$	$^2J_{CP}$	$^4J_{CP}$
	^{13}C-Ph$_{ortho}$	$^3J_{CP^*}$	$^5J_{CP^*}$

* Not observed.

A discussion of the J_{HP} and J_{CP} couplings in the phosphite complexes **1**–**4** is now presented. Our 300 MHz ^1H spectral results are shown in Table I.

For the simple trimethylphosphite complex **1** the earlier literature assignments[3,6] are generally satisfactory. Thus Gill and Mann[3] utilized the full spectral analysis suggested by Harris[9] to obtain a value of 10.8 Hz for J_{HP} (J_{HP} + $J_{HP'}$ + $J_{HP''}$). That their value at 80 MHz, and that obtained (10.7 Hz) in the present work at 300 MHz (see Table I) are consistent clearly confirms that the use of the major line separation to provide the required coupling constant sum is a valid approach. Although Schumann[6] also obtained a value of 10.8 Hz for J_{HP}, the signal multiplicity was described as a 1:1:1:1 quartet, which is not appropriate. Such a pattern is merely a special case of the $AA_2'X$ sub system, which resembles that noted earlier for the "model" ABX system, see Figure 1c. For the triethylphosphite complex **2**, the earlier studies[3,6] also require comment. Gill and Mann[3] extracted a value of J_{HP} of 4.1Hz from the methylene signals whilst irradiating the CH_3 resonance, since the former signal was insufficiently resolved at low field. A diminished splitting value was reported, which is now considered to result from the incorrect line separation being used since the deviation appears to be too significant to be attributable to a Bloch-Siegert effect.[15] In the present work, the methylene resonance appeared as a clearly defined quartet of 4-line $AA_2'X$ multiplets (see Figure 2a) from which a value of J_{HP} of 6.4 Hz was obtained. This is consistent with the later work of Schumann,[6] the inappropriate 1:1:1:1 quartet description again being given.

For the triphenylphosphite complex **3**, although the aromatic region was better

TABLE I
300 MHz ^{1}H NMR spectra of Phosphite complexes (δ p.p.m, J in Hz)

Complex	Cp		Ligand		
	δ	J_{HP}	δ	J_{HP}	J_{HH}
1	4.88 (q)	1.1	CH_3 : 3.83 (m)^a	10.7^c	----
2	4.78 (q)	1.2	CH_3 : 1.35 (t)	----	7.0
			CH_2 : 4.22 (q of m)^a	6.4^c	7.0
3	5.09 (q)	1.5	*o*-Ph : 7.05-7.11 (m)	----	----
			m/*p*-Ph : 7.20-7.32 (m)	----	----
4	4.71 (t)	1.3	CH_3 : 3.84 (m)^b	10.9^c	----
			CH_3CN : 2.46 (t)	1.2	----

a - X portion of $AA_2'X$ sub system (4 - lines)

b - X portion of $AA_2'X$ sub system (80 MHz : 3 lines,[10] 300 MHz : 4 lines)

c - J_{HP} + ($J_{HP'}$ = 0)

resolved at high field (see Table I) the definitive identification of any $^4J_{HP}$ coupling at the *ortho*-protons did not prove possible.

We have further extended our study (see Table I) to include the acetonitrile complex **4**, since the spectral interpretation of this compound has also presented some problems.[10,11] In accordance with one of the earlier investigations,[10] both the Cp and CH_3CN protons interact with the two ^{31}P nuclei which are equidistant from these sites to give simple triplets as expected for the appropriate A_5X_2 or A_3X_2 (X = ^{31}P) heteronuclear systems. However, in the later study made by Schumann *et al.*[11] these fine couplings were not resolved.

The coupling effects at the phosphite methyl protons are quite different, since the two ^{31}P nuclei are then not equidistant and hence must be treated as being magnet-

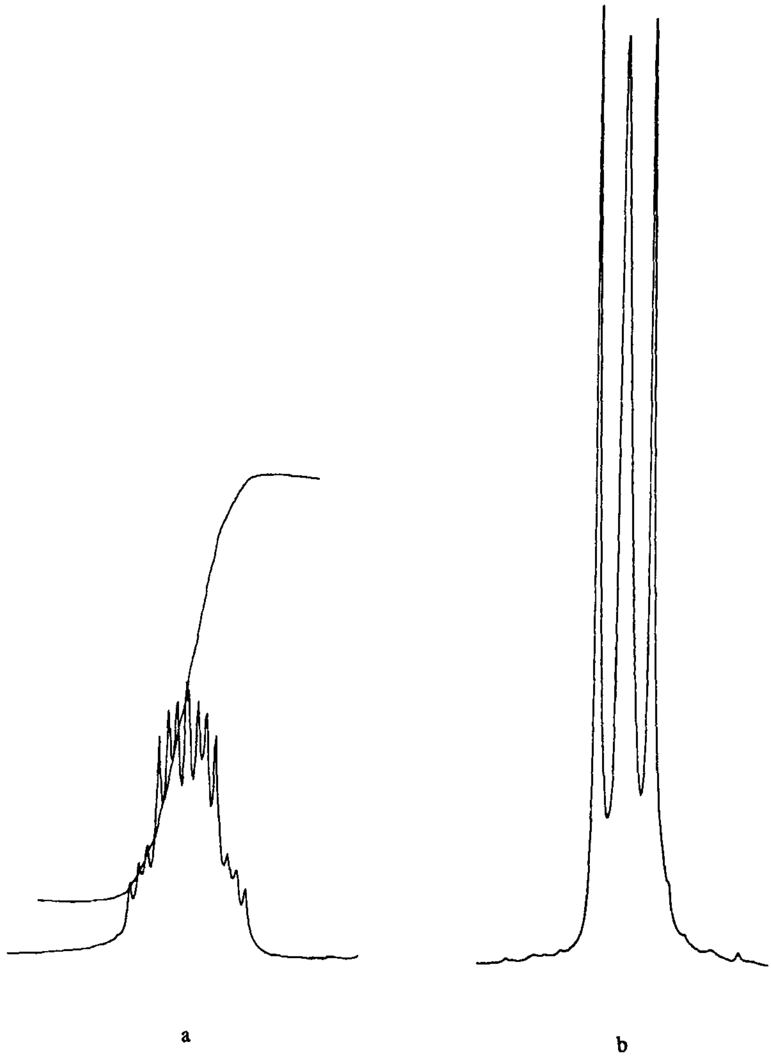


FIGURE 2 300 MHz ^{1}H NMR Spectra: a) phosphite CH_2 of complex **2** and b) phosphite CH_3 of complex **4**.

ically non-equivalent. The sub system applicable in this case is therefore AA′X, which may be treated as for $AA_2'X$. Gill and Mann[10] observed an "apparent" triplet at 80 MHz from which J_{HP} = 10.8 Hz was extracted by the procedure of Harris.[9] Such an analysis is entirely appropriate since the signal observed is just a special case for this sub system and is similar to that experienced for the "model" ABX case, see Figure 1d. In the present work at 300 MHz, a 4-line pattern was observed, see Figure 2b, from which J_{HP} = 10.9 Hz was obtained. However, in the later study by Schumann *et al.*[11] the phosphite methyl protons were regarded as a true triplet arising from equal couplings to the phosphorus nuclei with J_{PH} = 5.0 Hz. This analysis, and also those for the other nitrile complexes included in their study, is

TABLE II
75 MHz ^{13}C NMR spectra of phosphite complexes (δ p.p.m, J in Hz)

Complex	Cp		Ligand		
	δ	J_{CP}	δ	J_{CP}	J_{CP}^{lit}
1	82.47 (s)		CH_3 : 54.70 (m) [a]	8.6 [b,d]	5.7
2	82.68 (q)	0.8	CH_3 : 16.83 (m) [a]	6.3 [c,d]	2.1
			CH_2 : 63.37 (m) [a]	8.9 [b,d]	3.0
3	83.21 (s)		*i*-Ph : 153.09 (m) [a]	15.3 [b]	5.2
			o-Ph : 122.33		
			m-Ph : 131.24		
			p-Ph : 126.73		

a - X portion of $AA_2'X$ sub system (4 - lines)

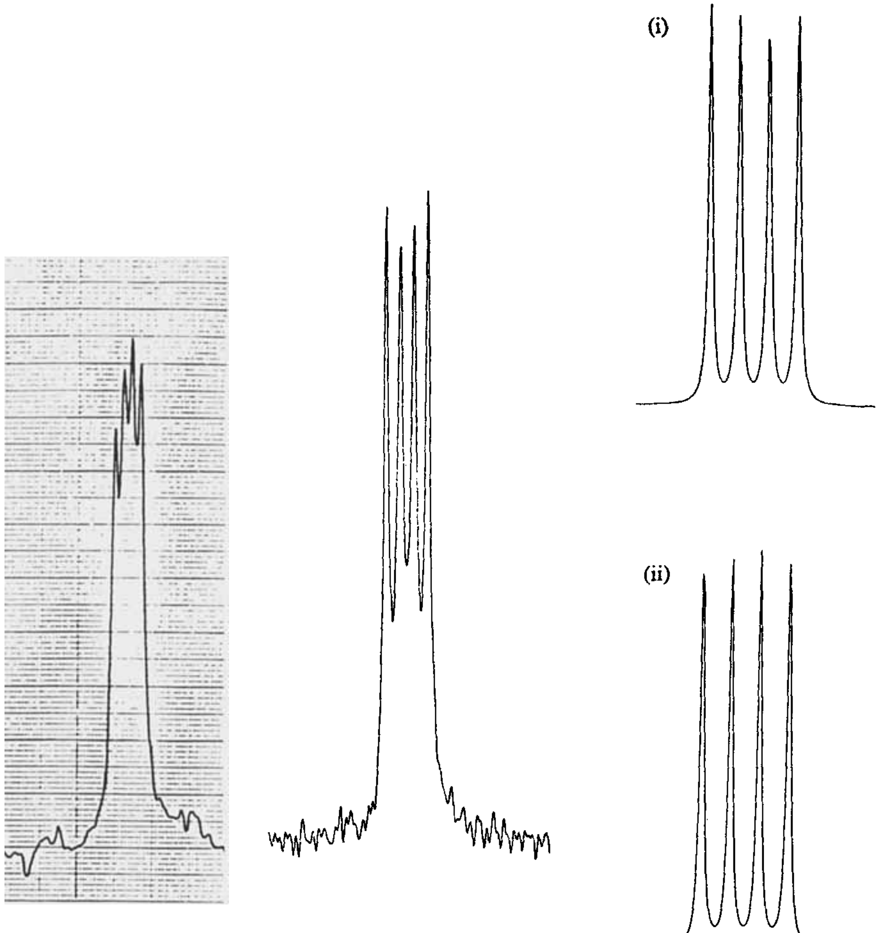
b - $^2J_{CP} + {}^4J_{CP'}$

c - $^3J_{CP} + {}^5J_{CP'}$

d - values obtained at 15 MHz were : **1**, 8.6 Hz; **2** CH_3- 6.3 Hz ; CH_2- 9.0 Hz.

inappropriate and accordingly the values need to be multiplied by a factor of 2 to provide the required values.

Some preliminary ^{13}C NMR studies of cyclopentadienyliron phosphite complexes have already been reported, however, their analysis for J_{CP} coupling constants has been fraught with difficulty.[6,12] Our results are presented in Table II.

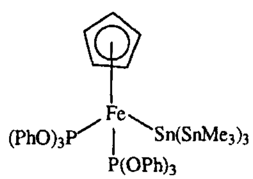


a b

c

FIGURE 3 ^{13}C NMR spectra of phosphite CH_3 of complex 1: a) at 15 MHz; b) at 75 MHz and c) LAOCOON 5 simulation, (i) $J_{AA'}$ = 20 Hz, (ii) $J_{AA'}$ = 30 Hz.

In an early 25 MHz investigation, Kläui and Werner[12] studied the related *bis* (triphenylphosphite) nonamethyltetrastannane complex **5**.



5

The ^{13}C spectra of the complex and of the triphenylphosphite ligand were illustrated in the paper. Whereas the *ipso*-phenyl signal of the ligand was a singlet, that of the complex was a triplet due to "splitting by the ^{31}P" for which $J_{CP} = 8$ Hz was reported.

The only study of the *tris* phosphite complexes **1–3** is that by Schumann,[6] in which the multiplicity of those carbon signals coupled to ^{31}P was again reported as a 1:1:1:1 quartet and it was supposed that the individual line separations represented the appropriate $^{2}J_{CP}$ or $^{3}J_{CP}$ couplings. Such an analysis is clearly inappropriate.

For our work, the ^{13}C NMR studies were conducted at two different frequencies, 15 MHz and 75 MHz. In all of the spectra, at both frequencies, the coupled nuclei appeared as 4-line patterns. (see Figures 3a and 3b) which resembled those noted earlier for the "model" ABX system, see Figure 1c. Analysis of these signals may again be satisfactorily undertaken as an AA'_2X sub system ($X = {}^{13}C$). Two simulations of the system using $J_{AX} = 9$ Hz, $J_{A'X} = 0$ Hz with (i) $J_{PP} = 20$ Hz and (ii) $J_{PP} = 30$ MHz have been performed. The results are also shown in Figure 3, an excellent correlation may be seen. The values used for $^{2}J_{P\text{-}Fe\text{-}P}$ ($J_{AA'}$) were estimates since suitable literature values do not appear to be readily available.[16,17]

Some correlations with the earlier coupling studies are now presented. For the trimethylphosphite complex **1**, the earlier J_{CP} value[6] of 5.7 Hz was obtained from a 1:1:1:1 quartet, however, it would appear that this represents the separation between only 3 lines, since multiplication by a factor of 1.5 gives $J = 8.55$ Hz, close to the value obtained in the present work (see Table II). In the case of the triethylphosphite complex **2**, the earlier values obtained from individual line separations require multiplication by a factor of 3 to give $^{2}J_{CP} = 9.0$ Hz, and $^{3}J_{CP} = 6.3$ Hz, consistent with our values (see Table II). Similar re-assessments of the earlier values for $^{2}J_{CP}$ of **3** ($5.2 \times 3 = 15.6$ Hz) and of **5** ($8 \times 2 = 16$ Hz) also produce consistent results for the *ipso*-phenyl carbons. Although the Cp carbon signals for **1** and **3** both appeared as singlets at 75 MHz (with some broadening apparent) that for **2** was split into a very fine quartet, $J_{CP} = 0.8$ Hz.

We recommend that for the extraction of J_{HP} and J_{CP} coupling constants the AA'_nX sub spectrum approach be used to obtain values of $J_{HP}(+J_{H'P})$ and $J_{CP}(+J_{C'P})$, and the signals be described as the appropriate multiplets. Moreover, any literature coupling constants obtained from simple "triplet" or "quartet" line separations will require multiplication by the appropriate factor to provide suitable corrected values.

EXPERIMENTAL

300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra were measured on a Bruker AC 300 spectrometer as previously described.[18] 15 MHz ^{13}C NMR spectra were obtained using a Jeol FX 60 instrument as previously described.[19] Spectral simulations were performed using a LAOCOON 5 program supplied by NMRI Ltd.

The complexes were synthesised by the established procedure indicated; **1** and **2** (Reference 3), **3** (Reference 2) and **4** (Reference 8).

ACKNOWLEDGEMENTS

Thanks are due to Dr. I. R. Herbert, Courtaulds Research Ltd, Coventry for measuring the 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra and for the AA'_2X spectral simulations.

REFERENCES

1. M. L. H. Green and R. N. Whitely, *J. Chem. Soc. A*, 1943 (1971).
2. T. P. Gill and K. R. Mann, *Inorg. Chem.*, **19**, 3007 (1980).
3. T. P. Gill and K. R. Mann, *J. Organomet. Chem.*, **216**, 65 (1981).
4. J. Ruiz, M. Lacoste and D. Astruc, *J. Amer. Chem. Soc.*, **112**, 5471 (1990).
5. C. C. Lee, M. Iqbal, U. S. Gill and R. G. Sutherland, *J. Organomet. Chem.*, **288**, 89 (1985).
6. H. Schumann, *J. Organomet. Chem.*, **293**, 75 (1985).
7. D. Astruc, M.-H. Desbois, M. Lacoste, F. Moulines, J.-R. Harmon and F. Varret, *Polyhedron*, **22**, 2727 (1990).
8. D. Astruc, *Acc. Chem. Res.*, **24**, 36 (1991).
9. R. K. Harris, *Inorg. Chem.*, **5**, 701 (1966).
10. T. P. Gill and K. R. Mann, *Inorg. Chem.*, **22**, 1986 (1983).
11. H. Schumann, L. Eguren and J. W. Ziller, *J. Organomet. Chem.*, **408**, 361 (1991).
12. W. Kläui and H. Werner, *J. Organomet. Chem.*, **54**, 331 (1973).
13. H. Günther, NMR Spectroscopy, An Introduction (Wiley, Chichester, 1970), (a) pp. 160–8, (b) pp. 168–70.
14. J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).
15. A. E. Derome, Modern NMR Techniques for Chemistry Research (Pergamon, Oxford, 1987), pp. 156–9.
16. J. C. Tebby, Ed., CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data (CRC Press, Boca Raton, 1991).
17. D. G. Gorenstein, Ed., Phosphorus 31 NMR, Principles and Applications (Acad. Press, London, 1984).
18. A. G. Osborne and I. R. Herbert, *Spectrosc. Letters*, **24**, 733 (1991).
19. A. G. Osborne and J. J. Hastings, *Spectrochim. Acta*, **47A**, 1583 (1991).