

Measurement of the Coupling Constants $^1J(^{57}\text{Fe}-^{13}\text{C})$ and $^1J(^{57}\text{Fe}-^{31}\text{P})$ in Phosphine and Carbonyl Complexes of Iron

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Summary $^1J(^{57}\text{Fe}-^{13}\text{C})$ for $[\text{Fe}(\text{CO})_5]$ and $^1J(^{57}\text{Fe}-^{31}\text{P})$ for $[\text{Fe}(\text{CO})_4(\text{PEt}_n\text{Ph}_{3-n})]$ ($n = 1-3$) are reported; it is concluded that these complexes probably undergo intramolecular carbonyl exchange at room temperature. ALTHOUGH there are many diamagnetic complexes containing iron directly bonded to a magnetically active nucleus, *e.g.*, ^1H , ^{13}C , or ^{31}P , and iron contains 2.19% of ^{57}Fe ($I = \frac{1}{2}$), there have been no reports of the observation

of satellites due to coupling of other nuclei to ^{57}Fe . This is rather surprising as the existence of ^{57}Fe is well known from the extensive use of Mossbauer spectroscopy to examine this isotope.

The complexes $[\text{Fe}(\text{CO})_4(\text{PEt}_n\text{Ph}_{3-n})]$ ($n = 1-3$) have been examined by ^{31}P n m r spectroscopy with complete decoupling of the protons. In each case several pairs of weak satellites due to $^1J(^{57}\text{Fe}-^{31}\text{P})$ and $J(^{13}\text{C}-^{31}\text{P})$ were observed. The coupling constants due to $J(^{13}\text{C}-^{31}\text{P})$ were assigned by measuring such couplings in the ^{13}C n m r spectra (see Table). $^1J(^{57}\text{Fe}-^{31}\text{P})$ increases as n decreases

TABLE

^{31}P Chemical shifts (w r t 85% H_3PO_4 , increasing frequency taken as being negative) and $^1J(^{57}\text{Fe}-^{31}\text{P})$ for the complexes $[\text{Fe}(\text{CO})_4(\text{PEt}_n\text{Ph}_{3-n})]$ ($n = 1-3$), in CH_2Cl_2 solution containing ca 10% C_6F_6 (^{19}F field/frequency lock) and the ^{13}C chemical shift (w r t Me_4Si , increasing frequency taken as being positive) and $^1J(^{57}\text{Fe}-^{13}\text{C})$ for neat $[\text{Fe}(\text{CO})_5]$ containing ca 10% C_6F_6 and ca 5% Me_4Si

	$\delta(^{31}\text{P})$ (± 0.2 p p m)	$^1J(^{57}\text{Fe}-^{31}\text{P})$ (± 0.4 Hz)
$[\text{Fe}(\text{CO})_4(\text{PEt}_3)]$	-62.7	25.9
$[\text{Fe}(\text{CO})_4(\text{PEt}_2\text{Ph})]$	-65.2	26.5
$[\text{Fe}(\text{CO})_4(\text{PEtPh}_2)]$	-67.3	27.4
	$\delta(^{13}\text{C})$ (± 0.2 p p m)	$^1J(^{57}\text{Fe}-^{13}\text{C})$ (± 0.4 Hz)
$[\text{Fe}(\text{CO})_5]$	211.9	23.4

The same behaviour has been found previously for the analogous complexes¹ $[\text{W}(\text{CO})_5(\text{PBu}_n\text{Ph}_{3-n})]$ ($n = 0-3$).

It is also possible to detect weak satellites due to $^1J(^{57}\text{Fe}-$

$^{13}\text{C})$ in the ^{13}C n m r spectra of $[\text{Fe}(\text{CO})_5]$ (see Table also). The measurement of $^1J(^{57}\text{Fe}-^{13}\text{C})$ is of particular interest as $^1K(^{57}\text{Fe}-^{13}\text{C})$ may then be compared with related reduced coupling constants.² As might be expected from the Fermi contact equation, $^1K(^{57}\text{Fe}-^{13}\text{C})$ for $[\text{Fe}(\text{CO})_5]$ ($238 \times 10^{20} \text{ cm}^{-3}$) lies intermediate between $^1K(^{51}\text{V}-^{13}\text{C})$ ³ for $[\text{V}(\text{CO})_6]^-$ ($146 \times 10^{20} \text{ cm}^{-3}$) and $^1K(^{59}\text{Co}-^{13}\text{C})$ ⁴ for $[\text{Co}(\text{CO})_4]^-$ ($402 \times 10^{20} \text{ cm}^{-3}$).

This work also adds weight to conclusions reached by previous workers.⁵ They found that although there are two environments for the carbonyl groups in the trigonal bipyramidal structure of $[\text{Fe}(\text{CO})_5]$ only one ^{13}C n m r signal was found, even at -63° . They concluded that intramolecular exchange was probably occurring but accidental coincidence of the two resonances could not be eliminated. The observation of $^1J(^{57}\text{Fe}-^{13}\text{C})$ excludes the possibility of intermolecular exchange. For the complexes, $[\text{Fe}(\text{CO})_4(\text{PEt}_n\text{Ph}_{3-n})]$ ($n = 1-3$), only one ^{13}C CO resonance is observed, and in each case the coupling $^2J(^{31}\text{P}-^{13}\text{C})$ (19 Hz) is clearly resolved. It is very unlikely that there will be accidental coincidence of two resonances for four different complexes, and intermolecular exchange is not occurring, as $^2J(^{31}\text{P}-^{13}\text{C})$ is observed. It is therefore concluded that intramolecular exchange is probably occurring.

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¹ R. L. Keiter and J. G. Verkade, *Inorg Chem*, 1969, **8**, 2115.

² $K(A-B) = J(A-B)h / 2\pi \gamma_A \gamma_B$, see for example W. McFarlane, *Quart Rev.*, 1969, **23**, 187.

³ P. C. Lauterbur and R. B. King, *J. Amer. Chem. Soc.*, 1965, **87**, 3266.

⁴ E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc. (A)*, 1967, 148.

⁵ R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, 1962, **58**, 1893, and references therein.