Notes

Carbon-13 and Phosphorus-31 Nuclear Magnetic Resonance Studies of the Fluxional Behaviour of the Complexes $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$ and $[Fe_3(CO)_{10}\{P(OMe)_3\}\{P(OPh)_3\}]$

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Variable-temperature ^{31}P and ^{13}C n.m.r. studies on the fluxional behaviour of the disubstituted derivatives $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$ and $[Fe_3(CO)_{10}\{P(OMe)_3\}\{P(OPh)_3\}]$ have uncovered the existence of several 1,2 isomers. Evidence is presented to suggest that phosphite ligand mobility plays a role in the isomerization processes at higher temperatures.

Carbon-13 and ^{1}H n.m.r. spectroscopy have proven to be indispensable tools for both the determination of solution-state structures and the study of cluster fluxionality. There are instances, however, in which even these techniques provide only a minimal amount of structural information. A classic example is the ^{13}C n.m.r. spectrum of $[Fe_3(CO)_{12}]$.[1] At temperatures as low as −160 °C the spectrum consists of a single sharp resonance, revealing the existence of a low-energy fluxional process (estimated to be <20.9 kJ mol^{-1}) that equilibrates all twelve carbonyl ligands. Evidence of $^{57}Fe-^{13}C$ coupling was observed in a subsequent ^{13}C n.m.r. study,[2] this being indicative of an intramolecular mechanism in which all carbonyls have equal access to all three iron atoms.

Several proposals have been advanced to explain the fluxional behaviour of $[Fe_3(CO)_{12}]$ based on the above evidence. Cotton and Troup[3] suggested the now familiar 'merry-go-round' or 'bridge-walking' mechanism. An alternative view, put forth by Johnson,[4] suggested that the icosahedral arrangement of the carbonyl ligands remained intact during the fluxional process and the equilibration resulted from the reorientation of the iron triangle within this icosahedron. More recently, Benfield and Johnson[5] have described ligand mobility in $[Fe_3(CO)_{12}]$ and other clusters in terms of polytopal rearrangements involving the interconversion of different ligand polyhedra of very nearly equal energies.

Some insight into the enigmatic behaviour of the carbonyl ligands may be gained by investigation of the fluxionality of substituted derivatives of $[Fe_3(CO)_{12}]$ containing 'non-mobile' ligands. This prompted Johnson and co-workers[6] to attempt to extend the polytopal rearrangement mechanism to the monosubstituted phosphine and phosphite clusters, $[Fe_3(CO)_{11}L]$ [L = $P(OEt)_3$, $P(OPh)_3$, $P(OPr^i)_3$, or PMe_2Ph], which they studied by ^{13}C and ^{31}P n.m.r. spectroscopy. Using the polytopal rearrangement mechanism they were able to obtain the same patterns of carbonyl equivalence as those observed in the high- and low-temperature ^{13}C n.m.r. spectra (relative intensity ratios of 10:1 and 6:4:1 respectively).

We had prepared several disubstituted derivatives of $[Fe_3(CO)_{12}]$ as part of a study on the synthesis of mixed-metal cluster compounds, and now report their fluxional behaviour which is not consistent with the above mechanisms.

Results and Discussion

Dynamic ^{31}P *and* ^{13}C *N.M.R. Studies of* $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$.—The variable-temperature ^{31}P and ^{13}C n.m.r. spectra have been recorded for $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$. The relevant data are presented in Table 1.

Table 1. Phosphorus-31 and ^{13}C n.m.r. data for $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$[a]

T/°C	δ/p.p.m.		
(a) ^{31}P[b]			
−80	166.6 (5.5) [1]	161.5 [1.4]	155.6 [1]
−60	166.8 [1]	161.8 [1.4]	156.2 [1]
20		161.8	
(b) ^{13}C[c]			
−80	251.2, 214.3, 212.3 [1.4] [2.8] [2.8]	221.5, 220.9, [2] (d, 6.8) [6]	209.5, 202.4 (d, 6.9) [1] [1]
−60	Very broad	221.7, 220.9, [2] (d, 6.3) [6]	209.7, 202.7 (d, 4.9) [1] [1]
−40	*ca.* 224 [7]	221.4 (t, 6.8) [8]	210.1, 203.6, [1] [1]
−20	224.8 [7]	221.3 (t, 6.8) [9]	206.7 [1]
0	224.9 [7]	221.1 [9]	207.1 [1]
20	224.1 [7]	221.2 [9]	207.7 [1]
30	222.3		

[a] Relative integration given in square brackets. [b] $^{3}J(^{31}P-^{31}P)$/Hz given in parentheses. [c] $^{2}J(^{13}C-^{31}P)$/Hz given in parentheses.

At −80 °C three resonances were observed in the ^{31}P n.m.r. spectrum: a resolved doublet at 166.6 [$J(^{31}P-^{31}P) = 5.5$ Hz], a sharp singlet at 161.5, and a broadened resonance at 155.6 p.p.m. with a relative intensity ratio of 1:1.4:1 respectively. The outer two resonances, which grew in simultaneously and integrate as 1:1, are assigned to two phosphorus nuclei within the same molecule but in chemically non-equivalent environments. The most reasonable structure is one in which one phosphite ligand is located on a six-co-ordinated iron atom and the other on a seven-co-ordinate iron atom [Figure, (**I**) or (**III**), where $P_a = P_b = P(OMe)_3$]. The solid-state structure of $[Fe_3(CO)_9(PMe_2Ph)_3]$ is known to have two phosphine ligands bonded to seven-co-ordinate iron atoms, both *trans* to the unbridged Fe–Fe bonds, and the third in an equatorial position on the six-co-ordinate atom.[7] The low-temperature ^{31}P n.m.r. spectrum of $[Fe_3(CO)_9\{P(OMe)_3\}_3]$ shows two close resonances at 160.9 and 162.9 p.p.m., upfield from a third resonance at

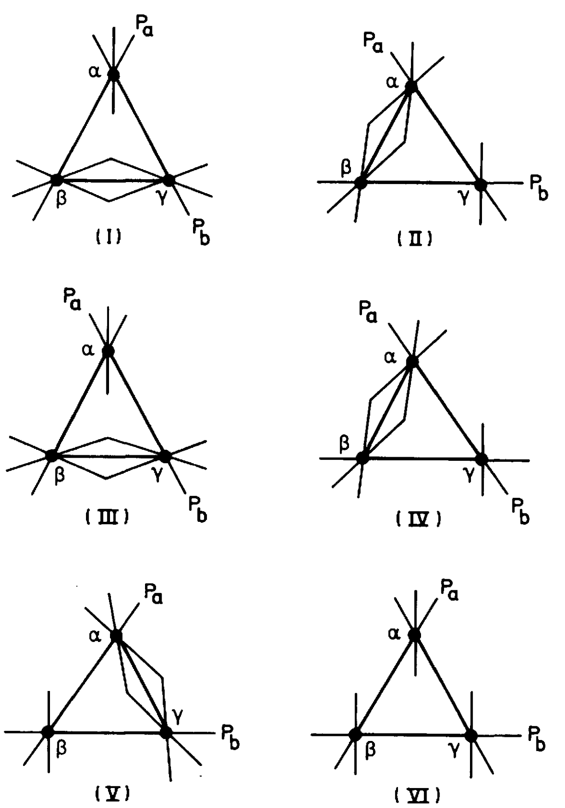

Figure. Isomeric forms of $[Fe_3(CO)_{10}L_2]$. The CO ligands are represented by lines. In isomer (**I**) the phosphite ligand labelled P_a is in an equatorial position *trans* to Fe(β) while P_b is *cis* to the doubly CO bridged Fe(γ)–Fe(β) edge and *trans* to Fe(α)

170.9 p.p.m.[8] This would seem to indicate that the downfield and upfield resonances observed for $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$ are due to the six-co-ordinate [Figure, (**I**) (P_a) or (**III**) (P_a)] and seven-co-ordinate [Figure, (**I**) (P_b) or (**III**) (P_b)] environments respectively. The low-field resonance exhibits the *cis* coupling expected for either isomer (**I**) or (**III**) [$J(^{31}P-^{31}P) = 5.5$ Hz], however, the high-field peak is too broad to observe coupling of this magnitude. (The linewidth is *ca.* 3 times the coupling observed for the downfield resonance. This broadening appears to be a consequence of a relaxation effect.) The resolved central singlet represents two phosphorus nuclei in chemically equivalent environments. There are two possible structures which conform to this information [Figure, (**V**) and (**VI**)].

The ^{13}C n.m.r. spectrum at −80 °C consists of seven resonances which have been assigned to isomers (**I**) or (**III**) and (**V**); the relative abundance of these isomers agrees with that observed in the ^{31}P n.m.r. spectrum. The downfield peak in the bridging carbonyl region at 251.2 p.p.m. and the two resonances at 214.3 and 212.3 p.p.m. are all fairly broad, integrating as 1:2:2 respectively. This is consistent with the presence of isomer (**V**) (Figure), in which the two phosphite ligands are in equivalent environments. The four carbonyl ligands on Fe(β) must undergo axial–equatorial exchange which ultimately renders them equivalent. By symmetry, the four carbonyl ligands on Fe(α) and Fe(γ) occupy equivalent environments. The remaining four resonances at 221.5, 220.9, 209.5, and 202.4 p.p.m. have a relative intensity ratio of 2:6:1:1 and are attributed to either isomer (**I**) or (**III**). The two unique carbonyl ligands at 209.5 [d, $J(^{13}C-^{31}P) = 6.9$ Hz] and 202.4 p.p.m. are assigned to the equatorial positions on Fe(α) and Fe(β) respectively. This implies that neither axial–equatorial exchange on Fe(α) nor triangular face rotation on Fe(β) is occurring. If the resonance at 221.5 p.p.m. is due to the axial carbonyl ligands on Fe(α), then the doublet observed at 220.9 p.p.m. is associated with the 'walking' of the six carbonyl ligands along Fe(β)–Fe(γ) with an average coupling of $J(^{13}C-^{31}P) = 6.8$ Hz. However, if the peak at 221.5 p.p.m. is due to the two remaining carbonyl ligands bound to Fe(β), which is consistent with the absence of ^{31}P coupling, then a fluxional process exists which interchanges the two bridging carbonyl ligands, the carbonyl ligands on Fe(γ), and the axial positions on Fe(α). This is inconsistent with both the bridge-walking mechanism and the polytopal rearrangement as developed for monosubstituted complexes. The relative abundance of isomer (**V**) to that of (**I**) or (**III**) is 0.7:1 in both the ^{13}C and ^{31}P n.m.r. spectra.

Upon raising the probe temperature to −60 °C, the ^{13}C resonances due to isomer (**V**) have broadened considerably, making them barely discernible from the baseline, whereas those assigned to isomer (**I**) or (**III**) remain essentially unchanged. The fact that the ^{31}P n.m.r. spectrum still exhibits a sharp singlet for isomer (**V**), and there is yet no interconversion of isomer (**V**) and (**I**) or (**III**), strongly suggests that the equilibration of the ten carbonyls in isomer (**V**) does not occur by a simple bridge-walking mechanism.

At −20 °C the two outer resonances in the ^{31}P n.m.r. spectrum have coalesced, resulting in a broadening of the base of the sharp central singlet. It appears that an exchange process is starting to occur which renders P_a and P_b equivalent [*i.e.* (**I**) $\rightleftharpoons$ (**II**) or (**III**) $\rightleftharpoons$ (**IV**)]. Of the two possibilities, both of which involve the bridging carbonyl ligands moving to different edges of the iron triangle, we favour (**III**) $\rightleftharpoons$ (**IV**) on the following grounds: (*i*) *trans*-disposed phosphine ligands have been observed for $[Os_3(CO)_{10}(PMe_2Ph)_2]$,[9] and (*ii*) besides the 'walking' of the bridging carbonyl ligands, the process which exchanges the non-equivalent $P(OMe)_3$ ligands in (**I**) $\rightleftharpoons$ (**II**) must also allow P_a and P_b to 'swing' back and forth between the two equatorial sites available to them. This type of process has been proposed for a similar compound, $[Os_3(CO)_{10}(PMe_2Ph)_2]$, but only at very high temperatures (>60 °C).[9] More consistent with the low-energy process is (**III**) $\rightleftharpoons$ (**IV**), which also involves bridge-walking, but unlike (**I**) $\rightleftharpoons$ (**II**), does not require phosphite ligand mobility.

The ^{13}C n.m.r. spectrum at this temperature is consistent with the above proposals. The sharp triplet at 221.3 [$J(^{13}C-^{31}P) = 6.8$ Hz] and the broad resonance at 206.7 p.p.m. integrate as 9:1. (A triplet is observed at 221.3 p.p.m. where two overlapping doublets are predicted.) This suggests that the three carbonyl ligands on Fe(α) are now becoming involved in bridge formation along both Fe(α)–Fe(β) and Fe(β)–Fe(γ), the effect of which is to achieve chemical exchange of the two phosphite ligand environments [Figure, (**III**) $\rightleftharpoons$ (**IV**)]. This must be a concerted operation, the unique carbonyl ligands on Fe(β) occupying a pivotal position. The resonance that has appeared at 224.8 p.p.m. corresponds to the process which equilibrates all ten carbonyl ligands in isomer (**V**).

As the temperature was raised to 20 °C, a single, broad resonance at 161.8 p.p.m. is observed in the ^{31}P n.m.r. spectrum. Similarly the resonances in the ^{13}C n.m.r. spectrum have broadened and begun to merge, indicating that two exchange processes are occurring, namely (**III**) $\rightleftharpoons$ (**IV**) and more slowly, (**III**) or (**IV**) $\rightleftharpoons$ (**V**). Thus the carbonyl ligands appear to be moving along the third edge, Fe(α)–Fe(γ), but this also implies the occurrence of another process involving phosphite ligand mobility. The mechanism involved must achieve axial–equatorial exchange of the three carbonyl ligands on Fe(α) and Fe(γ) as well as movement of the phosphite ligand from one equatorial site to another. Although phosphite ligands are conventionally thought of as being non-mobile, a recent investigation of the fluxional behaviour of $[Os_3(CO)_7\{P(O-$

Table 2. Phosphorus-31 and ^{13}C n.m.r. data for $[Fe_3(CO)_{10}\{P(OMe)_3\}\{P(OPh)_3\}]^a$

T/°C	δ/p.p.m.					
(*a*) $^{31}P^b$						
−60	163.9, [1]	159.8, (12.2) [4]	159.2, [1.8]	155.1, [1.8]	153.6, (12.2) [4]	146.9 [1]
−20		159.9 (13.2) [1]			152.1 (12.4) [1]	
22		160.0 [1]			152.1 [1]	
(*b*) $^{13}C^c$						
−80	220.1 (br), [4]	219.4 (br), [12]	210.2, [1]	209.9, [1]	201.3, [1]	201.0 [1]
	250.0, [2]	213.5, [2]	211.2 (br), [4]	208.5, [1]	207.1 [1]	

[a] Relative integration given in square brackets. [b] $^3J(^{31}P-^{31}P)$/Hz given in parentheses. [c] Recorded using nuclear Overhaüser enhancement.

$Me)_3\}_5]$ strongly supports the existence of a process, dubbed the trigonal-twist mechanism, which effects this type of chemical exchange.[10]

Finally, at 30 °C the ^{13}C n.m.r. resonances due to isomers (**III**) or (**IV**) and (**V**) have almost completely coalesced. The signal at 207.7 p.p.m. corresponding to the equatorial carbonyl ligand on Fe(β) [isomer (**III**)/(**IV**)] disappears as the interconversion of the two isomers destroys the integrity of this unique site.

Dynamic ^{31}P *and* ^{13}C *N.M.R. Studies of* $[Fe_3(CO)_{10}\{P(OMe)_3\}\{P(OPh)_3\}]$.—In order to test the validity of our interpretation of the ^{13}C and ^{31}P n.m.r. spectra of $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$, we chose to study the disubstituted derivative, $[Fe_3(CO)_{10}\{P(OMe)_3\}\{P(OPh)_3\}]$. The large chemical shift differences observed in the ^{31}P n.m.r. spectra of the monosubstituted clusters, $[Fe_3(CO)_{11}L]$ [L = $P(OMe)_3$, δ = 159.6; L = $P(OPh)_3$, δ = 149.6 p.p.m.], allowed assignment of the observed resonances in $[Fe_3(CO)_{10}\{P(OMe)_3\}\{P(OPh)_3\}]$ to a particular phosphite ligand.

The ^{31}P n.m.r. spectra for $[Fe_3(CO)_{10}\{P(OMe)_3\}\{P(OPh)_3\}]$ were recorded from 22 to −60 °C. The salient data are presented in Table 2. On the basis of our interpretation of the n.m.r. spectra for $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$, we would expect to see evidence of three isomers [Figure, (**III**)—(**V**), where $P_a = P(OMe)_3$ and $P_b = P(OPh)_3$].

At −60 °C a similar pattern to that obtained in the low-temperature ^{31}P n.m.r. spectrum of $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$ is observed. Based on the chemical shift differences of the monosubstituted $P(OMe)_3$ and $P(OPh)_3$ derivatives, we can tentatively assign the downfield resonances at 163.9, 159.8, and 159.2 and the upfield resonances at 155.1, 153.6, and 146.9 p.p.m. to the $P(OMe)_3$ and $P(OPh)_3$ ligands respectively. Thus there are three isomers present in a 1:4:1.8 ratio. The two doublets at 159.8 and 153.6 p.p.m. (integrating as 1:1) result from an isomer in which both phosphite ligands are in equivalent positions and are coupled to one another [$J(^{13}P-^{31}P)$ = 12.2 Hz] [Figure, (**V**)]. As the resonances upfield from the central doublets are assigned as phosphite ligands bonded to seven-co-ordinate iron atoms and those downfield to phosphite ligands bonded to six-co-ordinate iron atoms, the remaining four broad signals in this spectrum are assigned as follows: the downfield $P(OMe)_3$ peak and the upfield $P(OPh)_3$ peak integrate as 1:1 and hence represent isomer (**III**), while the two 'inner' resonances integrating as 1.8:1.8 represent isomer (**IV**).

As the probe temperature was raised to −20 °C the four resonances due to isomers (**III**) and (**IV**) broadened and collapsed, indicating that the two isomers are interconverting. The two central doublets were still distinguishable as such but significantly broadened. Upon reaching 22 °C these signals are extremely broad and no coupling is detected, as isomers (**III**)—(**V**) begin to interconvert.

In a final experiment, the ^{13}C n.m.r. spectrum of $[Fe_3(CO)_{10}\{P(OMe)_3\}\{P(OPh)_3\}]$ at −80 °C was recorded using nuclear Overhaüser enhancement (Table 2). The interpretation of this spectrum is consistent with our previous assignments of the ^{13}C n.m.r. spectra of $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$ and the low-temperature ^{31}P n.m.r. spectrum of $[Fe_3(CO)_{10}\{P(OMe)_3\}\{P(OPh)_3\}]$. The exchange of the six carbonyl ligands in isomers (**III**) and (**IV**) gives rise to a broad signal at 219.4 p.p.m. The resonance at 220.1 p.p.m. is associated with either the axial carbonyl ligands on Fe(α) or Fe(β), while the two unique equatorial positions on Fe(α) and Fe(β) are assigned to the signals at 210.2, 209.9 p.p.m. and 201.3, 201.0 p.p.m. respectively. The downfield resonance at 250.0 and the broad unsymmetrical peak at 211.2 p.p.m. respectively are attributed to the bridging and axial carbonyl ligands on Fe(α) and Fe(γ) [Figure, isomer (**V**)]. However, isomer (**V**), unlike the corresponding isomer for $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$, does not exhibit any evidence of the axial–equatorial exchange of carbonyls on Fe(β) at low temperatures. The reason for the higher activation energy required for such a process in $[Fe_3(CO)_{10}\{P(OMe)_3\}\{P(OPh)_3\}]$ is unknown.

In conclusion, variable-temperature ^{31}P and ^{13}C n.m.r. spectroscopy have shown that the disubstituted clusters $[Fe_3(CO)_{10}LL']$ [L = L′ = $P(OMe)_3$; L = $P(OMe)_3$, L′ = $P(OPh)_3$] exist as a mixture of 1,2 isomers which interconvert as the temperature is raised. Although a detailed mechanism is not proposed on the basis of the n.m.r. data, the observed exchange processes do not support a mechanism which involves simple 'walking' of the carbonyl ligands along an iron–iron bond, followed by movement of the bridging ligands about the three iron–iron bonds. The data also are not consistent with Johnson's mechanism[6] as proposed for monosubstituted complexes with 'non-mobile' ligands.

Experimental

General.—All reactions were carried out under argon using conventional vacuum-line techniques. All compounds were purified by column chromatography using silica gel (80—100 mesh) and hexane–benzene mixtures as eluants. Phosphorus and ^{13}C n.m.r. spectra were recorded on either a Varian XL 200 MHz or Brüker 400 MHz spectrometer. Phosphorus-31 n.m.r. samples were run as CH_2Cl_2 solutions using $P(OMe)_3$ as an external reference while ^{13}C n.m.r. spectra were run as CH_2Cl_2–CD_2Cl_2 (1:1) solutions. Chemical shifts for ^{31}P n.m.r. spectra are reported relative to H_3PO_4 and ^{13}C n.m.r. spectra relative to $SiMe_4$.

Synthesis of ^{13}CO-*enriched* $[Fe_3(CO)_{12}]$ *and Derivatives.*—The compound $[Fe_3(CO)_{12}]$ (500 mg, 1 mmol) was dissolved in dichloromethane with *ca.* 1 cm^3 NCMe added. After cooling to −60 °C, a solution of Me_3NO (75 mg, 1 mmol) was added over 2 h. The system was then evacuated and placed under an atmosphere of ^{13}CO. The solution was left to stir, keeping the temperature below −20 °C. After 44 h the i.r. spectrum revealed that the $[Fe_3(CO)_{12}]$ was sufficiently enriched.

The compound $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$ was prepared using ^{13}CO-enriched $[Fe_3(CO)_{12}]$ (200 mg, 0.4 mmol) by slow addition of an Me_3NO solution (2 equivalents) at −60 °C, in the presence of a stoicheiometric amount of $P(OMe)_3$; $[Fe_3$-

$(CO)_{10}\{P(OMe)_3\}\{P(OPh)_3\}]$ was obtained by a similar method by treating $[Fe_3(CO)_{11}\{P(OMe)_3\}]$ with 1 equivalent of Me_3NO in the presence of $P(OPh)_3$.

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