Solution Structure and Dynamic Behaviour of two Isomers of $[Fe_3(CO)_9\{P(OR_3)\}_3]$ (R = Me, Et, or Ph) Derivatives

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The reaction between $[Fe_3(CO)_{12}]$ and $P(OR)_3$ (R = Me, Et, or Ph) in the presence of the bimetallic catalyst $[\{Fe(CO)_2(PPh_3)(SEt)\}_2]$ affords two 1,2,3-trisubstituted isomers which rapidly interconvert at room temperature on the n.m.r. time-scale. The solution structures and dynamics have been elucidated for both isomers by means of variable-temperature ^{31}P and ^{13}C n.m.r. studies. In polar solvents the major isomer shows a $[Fe_3(CO)_{12}]$-like structure whereas the minor one contains only terminally bonded CO groups. The observation of three equally intense carbonyl resonances in the low-temperature-limiting spectra (R = Me or Et) supports a D_3 structure for this isomer. The equilibration of axial CO ligands occurs readily as the temperature is increased; this rearrangement may be ascribed to the motion of the Fe_3 triangle inside the polyhedral cloud of ligands or alternatively to an interconversion between a left-hand screw with a right-hand screw.

A large number of *X*-ray,[1–6] i.r.,[7] n.m.r.,[8] and theoretical investigations[9,10] of iron group cluster carbonyl derivatives has been devoted to rationalizing the structural changes and the dynamic behaviour in solution and in the solid state of M_3L_{12} species. The possibility of different bonding modes of the CO ligand to one or more metal atoms and the similar energies obtained from theoretical calculations[10] for the C_{2v}, D_3, and D_{3h} symmetry of $M_3(CO)_{12}$ molecules justify the noticeable structural changes as well as the widespread stereochemical non-rigidity found in this class of derivatives.

In order to get more insight into the parameters affecting the solution structures and dynamic behaviour of these systems we have undertaken an n.m.r. study of related phosphine and phosphite substituted derivatives of $M_3(CO)_{12}$. The reaction of $[Fe_3(CO)_{12}]$ with Group 15 ligands has been extensively studied in the last two decades.[11–16] Trisubstituted trinuclear derivatives of formula $[Fe_3(CO)_9L_3]$ have been synthesized with phosphites, tertiary phosphines, arsines, and stibines (except the bulky PPh_3, $AsPh_3$, and $SbPh_3$ which form only the monosubstituted derivatives).[13]

The structure of $[Fe_3(CO)_9(PMe_2Ph)_3]$, as elucidated by single-crystal *X*-ray diffraction analysis,[15] shows two bridging carbonyls and three phosphorus donor atoms lying at equatorial sites slightly above the plane of the metal triangle. On the basis of i.r. data both in solution and in the solid state, Grant and Manning[11] suggested that the trisubstituted derivatives with Group 15 ligands exist as an inseparable mixture of bridged and non-bridged forms and the relative ratio between such isomers is strictly dependent on the solvent and the encumbrance of the phosphite ligand. For bulky substituents such as cyclo-C_6H_{11} or Pr^i, they showed that only the non-bridged form is present in solution as well as in the solid state. In this paper we deal with the characterization of the solution structures and dynamics of the two isomeric forms by means of variable-temperature (v.t.) ^{31}P and ^{13}C n.m.r. spectroscopy.

Results and Discussion

The thermal reaction of $[Fe_3(CO)_{12}]$ with $P(OR)_3$ affords the 1,2,3-trisubstituted derivatives, namely $[Fe_3(CO)_9\{P(OR)_3\}_3]$ [R = Me (**1a**), Et (**1b**), or Ph (**1c**)] in addition to the corresponding mono- and di-substituted trinuclear products and the monometallic complexes $[Fe(CO)_4\{P(OR)_3\}]$ and *trans*-$[Fe(CO)_3\{P(OR)_3\}_2]$.[13] When the reaction is carried out at room temperature in the presence of the bimetallic catalyst $[\{Fe(CO)_2(PPh_3)(SEt)\}_2]$[17] the yield of the desired trisubstituted products is markedly improved, since the mild experimental conditions prevent cluster breakdown, which leads to monometallic derivatives.

V.t. ^{31}P n.m.r. spectra suggest the presence of two 1,2,3-trisubstituted isomers, which interconvert at room temperature and above. At −60 °C ($CDCl_3$) their ratio is about 9/1, 3/1, and 1/1 for (**1a**), (**1b**), and (**1c**) respectively. In each case the major isomer (**1′**) exhibits three distinct ^{31}P resonances whereas the minor one (**1″**) shows a single peak at any temperature and thus bears three equivalent phosphorus ligands.

The ratio between the two isomers is markedly solvent and temperature dependent. For $P(OEt)_3$ derivatives we note that in polar solvents isomer (**1′**) dominates and its concentration increases as the temperature decreases; on the other hand, isomer (**1″**) becomes predominant when the solvent is n-pentane. Solvent effects seem then responsible for minor differences observed in the isomer ratio[18] as well as in chemical shift values[19] reported for one of these derivatives from different laboratories. The behaviour is reminiscent of the earlier observations made by Cotton and Hunter[20] on the i.r. spectra of $[Fe_3(CO)_{12}]$ in solvents with different polarities which were interpreted on the basis of the simultaneous presence of 'a whole range of structures with varying degree of establishment of bridging.'

The ^{13}C n.m.r. spectra are fully consistent with the presence of two isomers: the observation (in the low-temperature limiting spectra in polar solvent) of a more intense pattern made up of one set of μ-bridging CO groups and three sets of terminally bonded CO groups in a relative intensity ratio of 2:2:4:1 clearly indicates for the major isomer (**1′**) a $[Fe_3(CO)_{12}]$-like structure as found for $[Fe_3(CO)_9(PMe_2Ph)_3]$[15] (Figure 1).

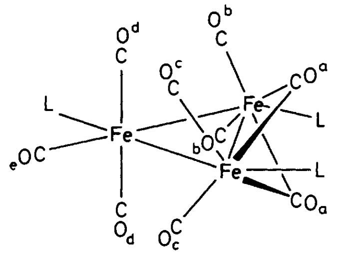
The single ^{31}P resonance supports a symmetrically substituted structure for (**1″**) as found for the analogous $[Ru_3(CO)_9(PMe_3)_3]$[21] and $[Os_3(CO)_9L_3]$ (L = PEt_3[22] or PMe_2Ph[23]) derivatives, but the observation of three sets of terminally bonded CO groups in an integrated intensity ratio of 1:1:1 in the low-temperature-limiting spectrum of (**1″a**) and (**1″b**) makes this assignment less straightforward and deserves further discussion (see below).

In the Table the ^{13}C and ^{31}P n.m.r. data of the three

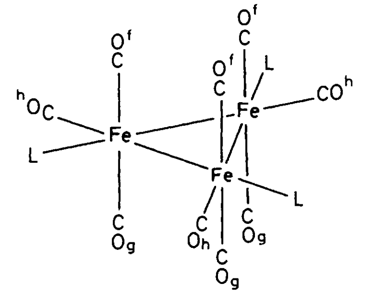
Table. N.m.r. low-temperature-limiting spectral data (J in Hz)

Compound	Isomer	^{13}C, δ^{a}/p.p.m.	^{31}P, δ^{b}/p.p.m.
(1a)	**(1′a)**	253.4 (s, 2), 221.4 (d, 2, J_{CP} = 29.5), 215.7 (d, 4, J_{CP} = 19), 211.3 (s, 1)	170.2 (d, 1, J_{PP} = 6.3), 163.5 (d, 1, J_{PP} = 6.3), 161.6 (s, 1)
	(1a″)	231.6 (s, 3), 229.0 (s, 3), 210.6 (s, 3)	167.4
(1b)	**(1′b)**	253.4 (s, 2), 222.2 (d, 2, J_{CP} = 28.9), 216.1 (d, 4, J_{CP} = 20), 211.7 (s, 1)	168.1 (d, 1, J_{PP} = 6.2), 161.4 (d, 1, J_{PP} = 6.2), 159.6 (s, 1)
	(1″b)	232.4 (s, 3), 229.1 (s, 3), 210.9 (s, 3)	165.4
(1c)	**(1′c)**	248.2 (s, 2), 221.5 (d, 2, J_{CP} = 24.1), 215.5 (d, 2, J_{CP} = 15.2), 214.3 (d, 2, J_{CP} = 15.2), 209.9 (s, 1)	160.0 (d, 1, J_{PP} = 25.4), 159.7 (d, 1, J_{PP} = 25.4), 145.7 (s, 1)
	(1″c)	227.1 (d, 6, J_{CP} = 21.0), 209.4 (s, 3)	156.7

[a] Phosphorus coupling to axial but not to equatorial carbonyls in variously substituted trimetallic clusters has been previously observed (ref. 22; R. F. Alex and R. K. Pomeroy, *J. Organomet. Chem.*, 1985, **284**, 379). Solvent CD_2Cl_2, −92 °C. [b] Solvent $CDCl_3$, −60 °C.



(1′)



(1″)

Figure 1. Proposed structures for the two isomers of $[Fe_3(CO)_9\{P(OR)_3\}_3]$ (R = Me, Et, or Ph)

derivatives considered in this work are reported for the low-temperature-limiting spectra and assigned to each isomer (**1′**) and (**1″**). Figures 2 and 3 show the v.t. ^{13}C and ^{31}P n.m.r. spectra of $[Fe_3(CO)_9\{P(OEt)_3\}_3]$ (**1b**).

The exchange process (see spectrum at −15 °C in Figure 2) occurring between the bridging CO groups and the doubly intense set of terminal groups can be accounted for in terms of a 'merry-go-round' mechanism involving carbonyls a—c of isomer (**1′b**) lying in a plane orthogonal to the Fe_3 triangle. This kind of carbonyl exchange involving six CO ligands in a plane perpendicular to the metal triangle is rather common and has already been reported by Lewis and co-workers[22] for $[Os_3(CO)_{11}(PEt_3)]$ and $[Os_3(CO)_{10}(PEt_3)_2]$ derivatives. The remaining resonances at 222.2 and 211.7 p.p.m. are assigned to carbonyls d and e of the same isomer (**1′b**) according to their relative intensities and on the basis of the commonly accepted rule that axial CO groups fall at lower field than the corresponding equatorial ones.[24]

A slight increase in temperature causes a marked broadening of the remaining resonances (0 °C) indicating that a scrambling process is taking place between carbonyl d and e in (**1′b**) as well as among axial (f, g) and equatorial (h) carbonyls in (**1″b**). Likely these processes occur through a turnstile rotation at the substituted metal unit, $Fe(CO)_3L$, as shown by Deeming *et al.*[23] for $[Os_3(CO)_9(PMe_2Ph)_3]$. The incipient decomposition of the sample observed as the temperature is further increased prevented the achievement of good-quality ^{13}C n.m.r. spectra and this does not allow us to forward any explanation for the isomerization process, which certainly occurs as shown by v.t. ^{31}P spectra.

An interesting process is observed for the minor isomer (**1″b**) at low temperature. The less intense pattern (see spectrum at −47 °C) is made up of two sets of terminally bonded CO groups in the integrated ratio 2:1 assigned respectively to axial (f, g) and equatorial (h) carbonyls. On lowering the temperature from −47 to −92 °C (solvent CD_2Cl_2), the axial CO ligands (f, g) are no longer equivalent in the low-temperature-limiting spectrum ($\Delta G^{\ddagger}$ = 38.6 kJ mol^{-1}). The remarkably low values of their chemical shifts support a significant semibridging character of these carbons. This observation is consistent with a considerable distortion towards D_3 symmetry achieved by a twisting of the $Fe(CO)_3L$ moieties about the Fe–Fe vectors.

If we assume that the arrangement of the outer ligand atoms [O of CO and P of $P(OEt)_3$] gives rise to an icosahedron very distorted toward a cubo-octahedron as found by Bruce *et al.*[21] in the analogous non-bridged $[Ru_3(CO)_9(PMe_3)_3]$ derivative, where the D_{3h} symmetry is lowered by a concerted twisting of the $M(CO)_3L$ units in order to relieve ligand–ligand interactions, it is straightforward to note that such a 'frozen' structure exhibits the axial CO groups split into two sets. In the above derivative this causes the presence of crystallographic disorder since two molecules are present per unit cell with opposite orientation of the metal triangle within the distorted icosahedron.[6] The equivalence of the axial CO groups can be therefore reached by means of rotation of the metal triangle within the polyhedron as originally proposed by Johnson and co-worker[9,25,26] to explain the dynamics found in metal carbonyl clusters (Scheme 1). These findings represent, to our knowledge, the first direct observation of a motion of a metallic moiety inside the ligand polyhedron detected *in solution*, while this behaviour has been unambiguously shown in the solid state for $[Fe_3(CO)_{12}]$[27] and $[Co_4(CO)_{12}]$,[28] where the ligand envelope is certainly more rigid because of packing constraints.

An alternative way of looking at the exchange of CO(f) and CO(g) is to assume the occurrence of a 'screwing' mechanism,* *i.e.* a left-hand screw interconverts with a right-hand screw (Scheme 2). Such a process is detected also for (**1″a**) with a very similar $\Delta G^{\ddagger}$ value (37.4 kJ mol^{-1}) but is not observed at all for

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* We thank a referee for bringing this point to our attention.

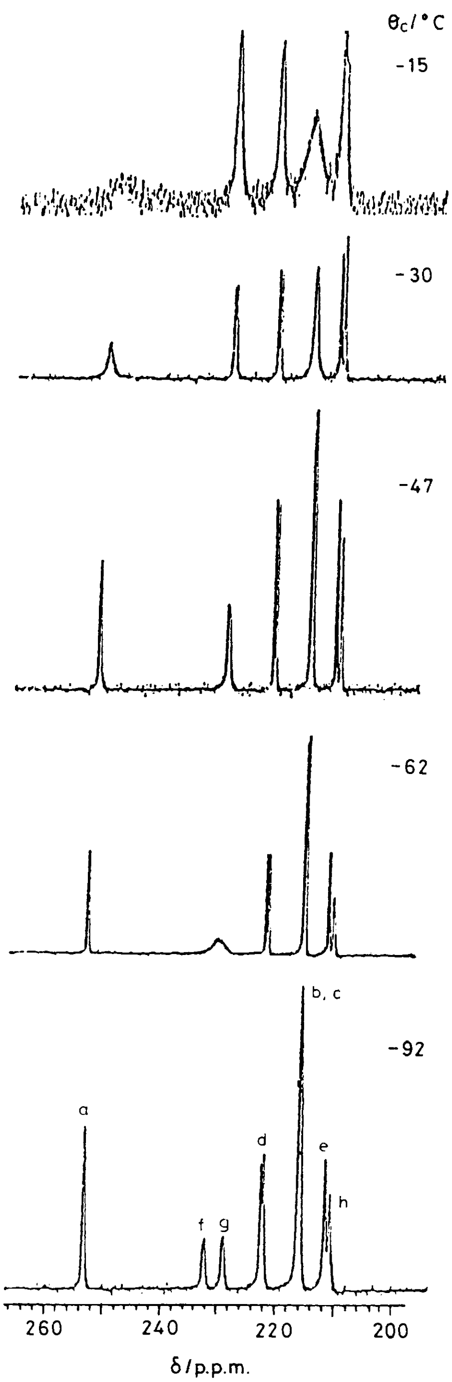


Figure 2. V.t. ^{13}C n.m.r. spectra of $[Fe_3(CO)_9\{P(OEt)_3\}_3]$ in CD_2Cl_2

(1″c). The reason lies in the subtle balance of steric properties of the different phosphites which are in turn responsible for the increase in the energy barrier involved in the motion of the metal triangle.

In the general context of solid-state and solution structures of trimetallic clusters, the formation of isomer type (1″) (non-bridged structure) as a consequence of replacement of three CO groups by phosphites in $[Fe_3(CO)_{12}]$ is of some interest. It is important to recall that the corresponding mono- and di-substituted[19] derivatives exhibit $[Fe_3(CO)_{12}]$-like structures only. Two structural archetypes are known for $[M_3(CO)_{12}]$ clusters and their various Group 15 ligand derivatives: these are exemplified by $[Fe_3(CO)_{12}]$ (C_{2v} symmetry, two bridging CO) and $[M_3(CO)_{12}]$ (M = Ru or Os) (D_{3h} symmetry, all terminal CO). Johnson and Benfield[9,25,26] have investigated the polyhedron formed by the oxygen atoms of the carbonyls in several binary clusters and pointed out that in $[Fe_3(CO)_{12}]$ the ligand envelope defines an icosahedron while in $[M_3(CO)_{12}]$ (M = Ru or Os) an anticubo-octahedron. In this model the size of the metal triangle is of crucial importance: $[Fe_3(CO)_{12}]$ takes up the sterically favoured icosahedral structure while $[M_3(CO)_{12}]$ (M = Ru or Os) assumes the anticubo-octahedral geometry in order to accommodate the larger metal frameworks. Now it is well established, especially on the basis of the structural determinations carried out by Bruce[29] on trimetallic derivatives, that the average metal–metal distance within a triangular cluster increases with the degree of substitution of CO by phosphine or phosphite ligands. The peripheral atom polyhedron smoothly changes from an icosahedron to a cubo-octahedron in order to accommodate metal triangles gradually increasing in size. This nicely explains the occurrence of 1,2,3-trisubstituted $[Fe_3(CO)_9\{P(OR)_3\}_3]$ isomers (1″)

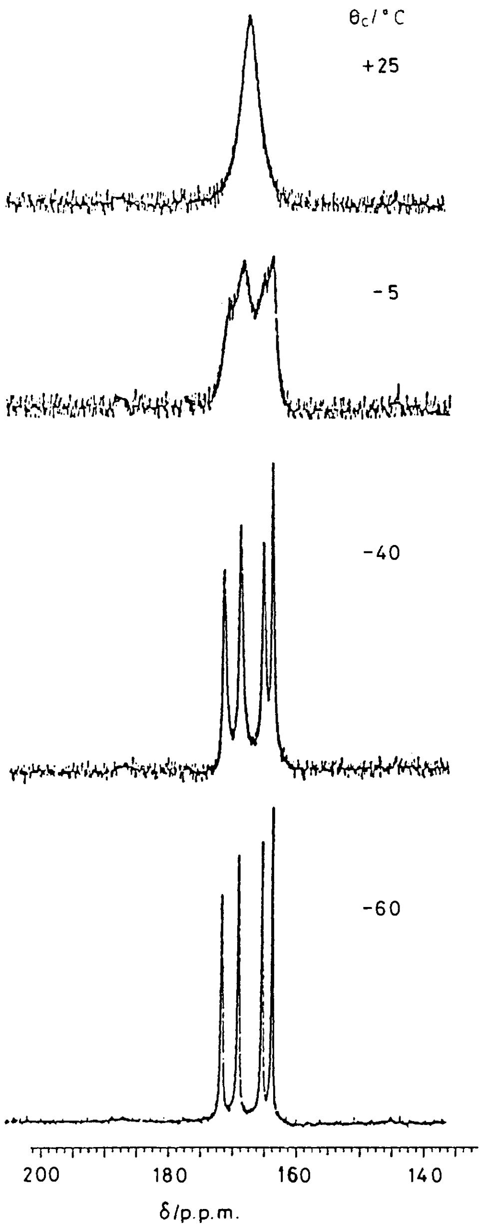
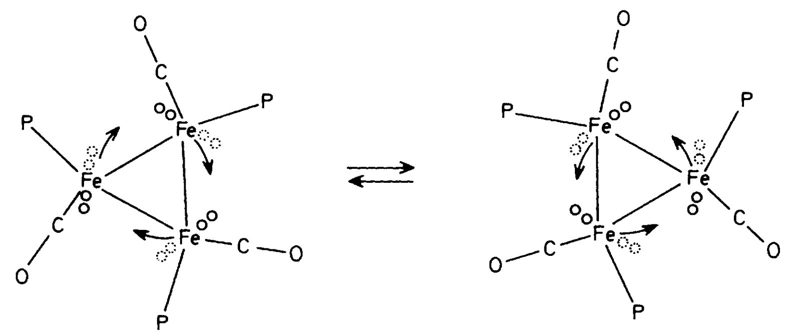
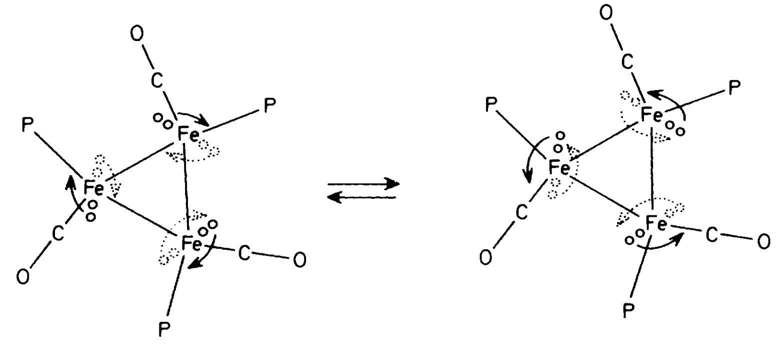


Figure 3. V.t. ^{31}P n.m.r. spectra of $[Fe_3(CO)_9\{P(OEt)_3\}_3]$ in $CDCl_3$



Scheme 1.



Scheme 2.

having an all terminal CO structure. The fact that the relative abundance of isomer (**1''**) *vs.* (**1'**) follows the *same* order of steric encumbrance of the phosphito ligands [$P(OPh)_3 >$ $P(OEt)_3 > P(OMe)_3$] and *not* that of their basicity suggests that steric factors are more responsible for the metal-core expansion than electronic effects (*i.e.* the increase in electron density on the metal atoms, perhaps in antibonding orbitals, would cause the cluster to expand[30]).

It is clear that the alternative considerations[31] which argued that ligands more basic then CO increase the electron density on the cluster and then increase the metal-to-carbonyl π^* bonding, so stabilizing a structure with bridging carbonyl groups, do not fit with these experimental results.

Experimental

The compound $[Fe_3(CO)_{12}]$ was obtained from Strem Chem. Inc. and used without further purification. $[\{Fe(CO)_2(PPh_3)(SEt)\}_2]$ was synthesized according to the published procedure.[32] Dry, deoxygenated solvents were employed in all preparations.

All the reactions were carried out in double-necked flasks under nitrogen; the $[Fe_3(CO)_{12}]$ catalyst mol ratio was always 10:1. In a typical run, $[Fe_3(CO)_{12}]$ (500 mg), $P(OR)_3$ (0.2 cm^3), and $[\{Fe(CO)_2(PPh_3)(SEt)\}_2]$ (85 mg) were stirred in n-hexane (150 cm^3) at +30 °C for 2 h. The reaction mixture was filtered, concentrated at reduced pressure, and separated by t.l.c. [adsorbent SiO_2, eluant light petroleum (b.p. 40—60 °C) and diethyl ether (10%, v/v)] to give $[Fe_3(CO)_9\{P(OR)_3\}_3]$ derivatives (*ca.* 70%) along with small amounts of mono- and di-substituted derivatives and traces of $[Fe(CO)_4\{P(OR)_3\}]$ and $[Fe(CO)_3\{P(OR)_3\}_2]$.

N.m.r. spectra were recorded on a JEOL GX270/89 spectrometer at 67.9 (^{13}C) and 109.6 (^{31}P) MHz respectively; chemical shifts are reported in p.p.m. positive downfield with respect to tetramethylsilane (^{13}C) and 85% H_3PO_4 (^{31}P).

Acknowledgements

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