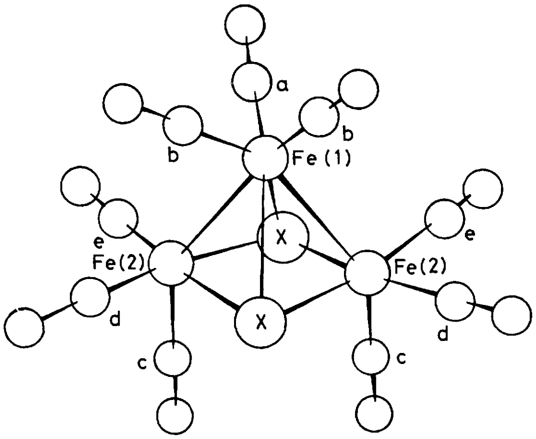
Dynamic Properties and Solution Structures of the Clusters $[Fe_3(CO)_9X_2]$ (X = S, Se, Te, or NMe) and their Derivatives

By **Silvio Aime, Luciano Milone,* Rosanna Rossetti,** and **Pier L. Stanghellini,** Istituto di Chimica Generale ed Inorganica, Corso Massimo d'Azeglio 48, 10125 Torino, Italy

Variable-temperature ^{13}C n.m.r. spectra of the title species have shown that two distinguishable steps occur in the exchange of the carbonyl groups: in the first step the carbonyls at the apical iron atom become equivalent and in the second those at the basal Fe. The replacement of one carbonyl group with a Group 5 ligand yields one isomer, whereas in the case of the disubstituted derivatives two positional isomers have been obtained. The substitution with Group 5 ligands occurs more easily at the basal iron atoms: at the axial position in the monosubstituted derivative and at the axial and an equatorial position at each basal Fe in the most abundant disubstituted isomer. The structure of the adduct $[Fe_3(CO)_9(PBu^n{}_3)Te_2]$, an intermediate in the formation of the monosubstituted derivatives, is discussed. The dynamic properties of the phosphorus derivatives have also been determined.

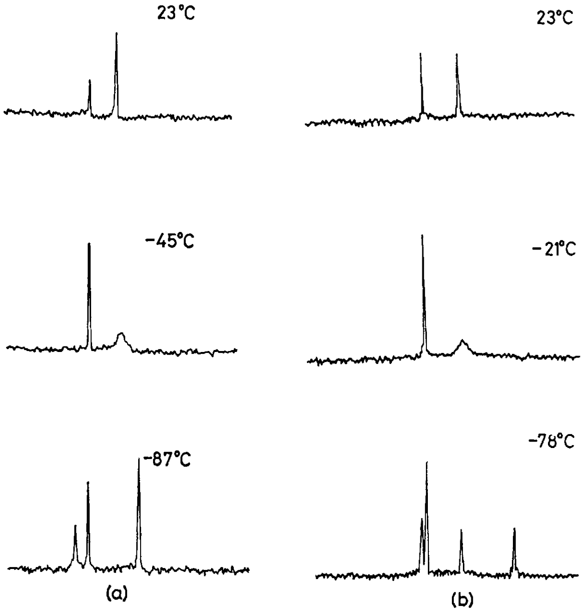
STRUCTURAL data of a variety of $[Fe_3(CO)_9X_2]$ (X = Se,[1] S,[2] NMe,[3] or $NNCPh_2$[4]) species have shown that they have the same framework geometry. Two Fe atoms and the two X atoms are located at alternate corners of the base of a distorted tetragonal pyramid, whose apex is occupied by the third iron atom; three terminal carbonyls are bonded to each iron atom. A similar structure has been inferred for the derivatives $[Fe_3(CO)_9X(Y)]$ (X,Y = S, Se, or Te).[5] By treating $[Fe_3(CO)_9X_2]$ species with Group 5 ligands (L), the derivatives $[Fe_3(CO)_{9-n}L_nX_2]$ (n = 1—3) have been obtained.[6-8] In the case of X = Te, quite stable $[Fe_3(CO)_9LX_2]$ adducts have also been obtained.[6] However, it is not known whether the substitution of carbonyls is easier at the apical seven-co-ordinated iron atom or at the basal iron atoms. Similarly the binding site of the ligand in the adducts is undetermined. We report the results of a ^{13}C n.m.r. investigation of the parent clusters, of the adduct $[Fe_3(CO)_9(PBu^n{}_3)Te_2]$, and of some derivatives with $PBu^n{}_3$ and $P(OPh)_3$. This study allowed us to determine the dynamic properties and the solution structures of these species.



(1), (2)

RESULTS AND DISCUSSION

The Species $[Fe_3(CO)_9X_2]$ (X = NMe, S, Se, *or* Te) (1) *and* $[Fe_3(CO)_9Se(Te)]$ (2).—The ^{13}C n.m.r. chemical shifts measured for (1) and (2) are reported in Table 1. According to the solid-state structures,[1-4] five resonances are expected for the carbonyls of (1). However, in the spectra obtained at the lowest temperatures we have observed in each case two or three resonances only with relative intensities from low to high field of 3 : 2 : 4 for (1a) and (1b), 5 : 4 for (1c), and 2 : 3 : 4 for (1d) (Figure 1).



(a) (b)

FIGURE 1 Variable-temperature ^{13}C n.m.r. spectra of (a) $[Fe_3(CO)_9Te_2]$ (1d) and (b) $[Fe_3(CO)_9Se(Te)]$ (2)

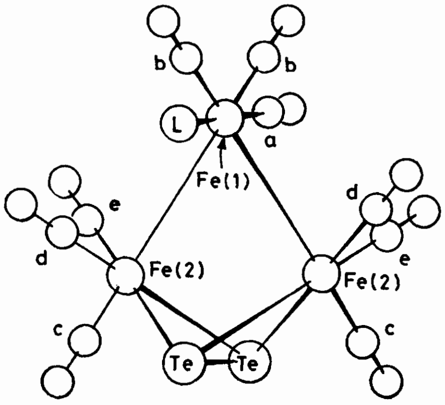
TABLE 1

Carbon-13 n.m.r. chemical shifts of $[Fe_3(CO)_9X_2]$ (1),(2) in the carbonyl region (relative intensities in parentheses) [a]

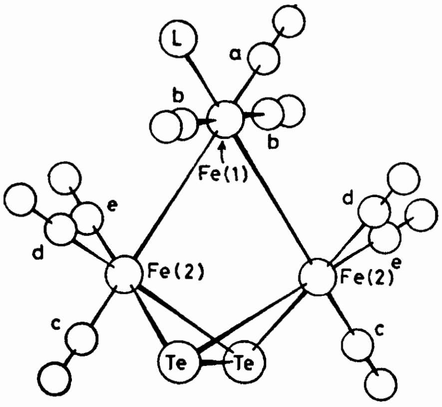
Compound	X	Fe(1)(CO)	$Fe(2)(CO)_{ax}$	Average $Fe(2)(CO)_{ax}$	$Fe(2)(CO)_{eq}$
(1a)	(NMe)	215.1(3)	211.2(2)	207.3 [b]	205.0(4)
(1b)	S	210.3(3)	209.5(2)	204.8 [b]	201.9(4)
(1c)	Se	211.5(3)	211.5(2)	206.1 [b]	203.2(4)
(1d)	Te	213.3(3)	214.9(2)	209.6 [b]	207.2(4)
(2)	Se,Te	212.5(3)	213.2(2)	207.9 [b]	208.2(2) 201.7(2)

[a] At −85 °C if not otherwise stated. [b] At 26 °C.

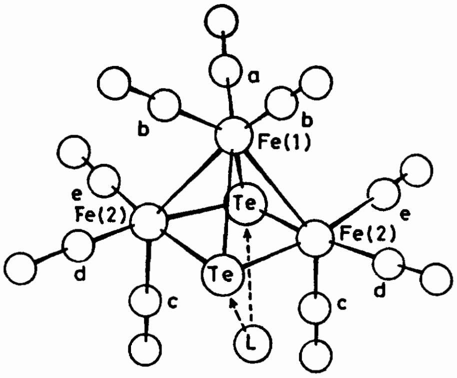
The resonance of intensity 3 is assigned to the carbonyls bonded to the apical iron (CO_a and CO_b), that of intensity 2 to the apical carbonyls bound to the basal iron atoms (CO_c), and that of intensity 4 to the remaining carbonyls (CO_d and CO_e).* Thus if considerations of overlapping are ignored, the unique resonance observed for CO_a and CO_b suggests that the scrambling of these carbonyls is still fast on the n.m.r. time scale which also makes equivalent CO_d and CO_e.† This is not surprising in view of the observed decrease of the energy barrier for localised scrambling of the carbonyls upon increase of the co-ordination number of the metal atom.[9] As the temperature is raised the resonances of intensity 2 and 4 broaden, collapse, and merge in a new peak, whereas the resonance of intensity 3 remains sharp. Increasing the temperature to 90 °C does not cause further changes in the spectra. The exchange of the carbonyls is then localised at Fe(1) in the first step, and localised at each Fe(2) in the second stage; ‡ delocalised exchange between the CO groups of Fe(1) and Fe(2) does not occur.



(A)



(A)



(B)

(3)

The dynamic behaviour of (2) is similar to that of (1); however the spectral features are different (Figure 1). Three resonances of equal intensity are observed in the low-temperature limiting spectrum for the CO groups bound to Fe(2) as the result of there being two different chalcogen atoms in the molecule.

For both sets of the average chemical shifts of the CO groups bonded to Fe(1) and those of the CO groups bound to Fe(2) of (1*b*)—(1*d*) and of (2) there is a shift towards low field as the electronegativity of X_2 decreases; this is more sizeable for the CO groups bound at Fe(2). This trend has been explained in terms of an increase in the electron density at the metal which causes an increase in the metal–carbon π bonding and hence a decrease in the carbon–oxygen π-bond order.[10] The same effect is

---

* In (1*c*) there is overlapping of the signals of CO_a, CO_b, and CO_c.

† The ^{13}C n.m.r. spectrum of (1*a*) recorded at −120 °C on a Bruker HW-360 spectrometer still shows the same features, further evidence that CO_a and CO_b are rapidly exchanging.

‡ The symmetry of the molecule does not allow us to rule out, on the experimental evidence, delocalised exchange of the CO groups between the basal iron atoms; however, we feel this cannot be the case since it is difficult to envisage a mechanism for such delocalised exchange, which would require in a bridged carbonyl intermediate either chalcogen–carbon bonding or carbonyl bridges between the basal non-bonded iron atoms.

responsible for the frequency change of the CO stretching modes, whose frequencies [11] are linearly correlated with the chemical-shift values. For X = NMe, δ(CO) for the carbonyls bound to Fe(1) is greater than the value determined for X = Te, whereas the δ(CO) for the carbonyls bound to Fe(2) is between the values observed for X = Se and X_2 = SeTe. Thus a simple relationship between the chalcogen series and the N complex does not seem to exist. Such discrepancy was also noticed in the kinetic behaviour of these complexes.[12]

The Compound $[Fe_3(CO)_9(PBu^n_3)Te_2]$ (3).—These adducts are the intermediates in the reaction leading to formation of the monosubstituted derivatives $[Fe_3(CO)_8LX_2]$. They have only been observed for X_2 = Se, Te and X = Te, but only for X = Te are they stable enough to be characterized.[6] The ^{13}C n.m.r. chemical shifts measured for (3) are shown in Table 2. Four resonances are observed at 218.2, 207.8, 206.6, and 205.9 p.p.m. (−90 °C) (Figure 2). As the temperature is raised, the peaks at 218.2 and 206.6 p.p.m. broaden, collapse, and merge into a singlet, whereas the two doublets remain unchanged. The relative intensities in the room-temperature spectrum are approximately 6 : 2 : 1 from low to high field. Comparing the spectral features and the dynamic behaviour of (3) with that of (1*d*) it follows that: (*a*) the same pattern of resonances and analogous dynamic behaviour is observed for the six CO groups in both derivatives, thus, suggesting that two symmetry-equivalent $Fe(CO)_3$ groups are also present in (3); (*b*) the CO groups bound to the unique iron in (3) are the only ones showing sizeable phosphorus–carbon coupling constants; (*c*) whereas the CO groups at the unique iron in (1*d*) are non-rigid, the corresponding ones in (3) are rigid in the range of temperature examined; (*d*) the chemical shifts of the carbonyls of the two equivalent $Fe(CO)_3$ groups are at slightly lower field in (3) than in (1*d*) (Δ = 1.4 p.p.m.), whereas those of the unique iron are at substantially higher field (Δ = 5.9 p.p.m.).

On this basis alone it is difficult to postulate only one structure for (3). One possibility (A) is shown in the two isomeric forms with respect to the position of L at the octahedral iron: this structure accounts satisfactorily for the observed rigidity of the CO groups at Fe(1), and allows ready exchange of the CO groups at Fe(2). Additionally, the values of the ^2J(C–P) are in the range usually observed for cases in which the phosphorus and the carbon atoms are on the same metal atom.[13] However, in both isomers of structure (A) the multiplicity of the CO groups at the basal iron should be more than that observed: the relative intensities ought to be 2 : 2 : 2 for P–Fe–CO parallel to the two chalcogen atoms and 2 : 1 : 2 : 1 for CO–Fe–CO perpendicular to the two chalcogens. An alternative structure is (B), which is closely related to the parent $[Fe_3(CO)_9Te_2]$. The interaction of the phosphine with the cluster is suggested as being effected *via* an empty molecular orbital, probably the lowest unoccupied molecular orbital (l.u.m.o.), which has predominantly chalcogen character. Since no precedent is known for the postulated bonding of a Group 5 ligand to a cluster, ^{13}C n.m.r. data are not available for a comparison. Nevertheless, structure (B) could, in principle, fit the experimental results. It is favoured by the following chemical evidence: (*i*) the adducts are intermediates in the preparation of the monosubstituted derivatives of (1) with Group 5 ligands; [6] the substitution of one CO only occurs at one of the basal iron atoms (see below); (*ii*) the stability of the adducts increases as the electronegativity of the chalcogen atoms decreases which can only be explained by co-ordination of L through the chalcogen atoms.[11,14] It then follows that the observations (*i*) and (*ii*) favour structure (B) since too much reorganization of the cluster is needed to go from (A) to the monosubstituted derivatives, it would be unlikely that no monosubstituted derivatives with L at the unique iron were obtained from (A), and, finally, since in (A) there is no interaction of the entering ligand with the chalcogen atoms.

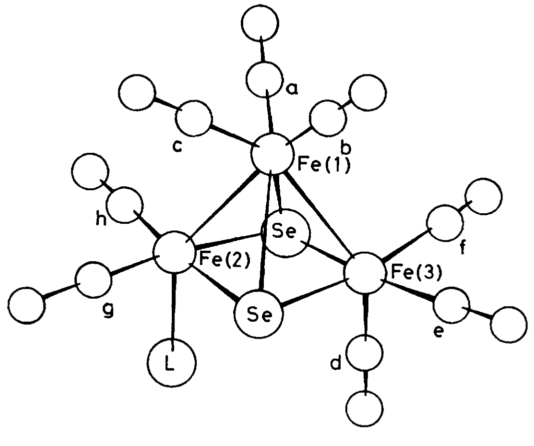
TABLE 2

Low-temperature ^{13}C n.m.r. chemical shifts of the CO groups of $[Fe_3(CO)_9LTe_2]$ (3), $[Fe_3(CO)_8LSe_2]$ (4), and $[Fe_3(CO)_7L_2Se_2]$ (5) (relative intensities in parentheses)

Compound	L	
(3)	PBu^n_3	CO_a 205.9(1),[a] CO_b 207.7(2),[b] CO_c 218.2(2), $CO_{d,e}$ 206.6(4)
(4*a*)	PBu^n_3	$CO_{a,b,c}$ 213.4(3), CO_d 213.8(1), $CO_{e,f}$ 204.1(2), $CO_{g,h}$ 205.9(2) [c]
(4*b*)	$P(OPh)_3$	$CO_{a,b,c}$ 212.7(3), CO_d 213.1(1), $CO_{e,f}$ 203.8(2), $CO_{g,h}$ 204.1(2) [d]
(5*a*)	PBu^n_3	$CO_{a,b,c}$ 217.0(3), CO_d 222.6(1),[e] CO_f 208.7(1),[f] $CO_{g,h}$ 211.0(2) [g]
(5*b*)	PBu^n_3	$CO_{b',c'}$ 219.3(2),[h] $CO_{d'}$ 215.9(1), $CO_{e',f'}$ 207.0(2), $CO_{g',h'}$ 210.1(2) [i]
(5*c*)	$P(OPh)_3$	$CO_{a,b,c}$ 214.2(3), CO_d 218.3(1),[j] CO_f 207.7(1),[k] $CO_{g,h}$ 206.7(2) [l]
(5*d*)	$P(OPh)_3$	$CO_{b',c'}$ 215.2(2),[m] $CO_{d'}$ 213.4(1), $CO_{e',f'}$ 204.8(2), $CO_{g',h'}$ 206.4(2) [n]

[a-n] $^2J(^{13}C-^{31}P)$ (Hz): 4.5, 20.2, 17.0, 20.0, 13.2, 12.2, 20.0, 22.5, 14.2, 18.0, 17.6, 22.4, 28.9, and 17.7, respectively.

The Species $[Fe_3(CO)_8LSe_2]$ (4) [L = PBu^n_3 *or* $P(OPh)_3$].—The chemical shifts are reported in Table 2.



(4)

At −80 °C four resonances (three singlets and one doublet) are observed for (4*a*) with relative intensity

1 : 3 : 2 : 2 from low to high field. The same features are present in the low-temperature spectrum of (*4b*), except for partial superposition of the resonances of intensity 2. Upon raising the temperature, the singlets of intensity 1 and 2 merge into a new peak, the resonance of intensity 3 remains unchanged and the doublet of intensity 2 shifts progressively to low field. Thus, the substitution of CO occurs at one of the Fe(CO)$_3$ units in the base of the pyramid. The substituting ligand goes in the axial position since only one signal of intensity 2 shows carbon–

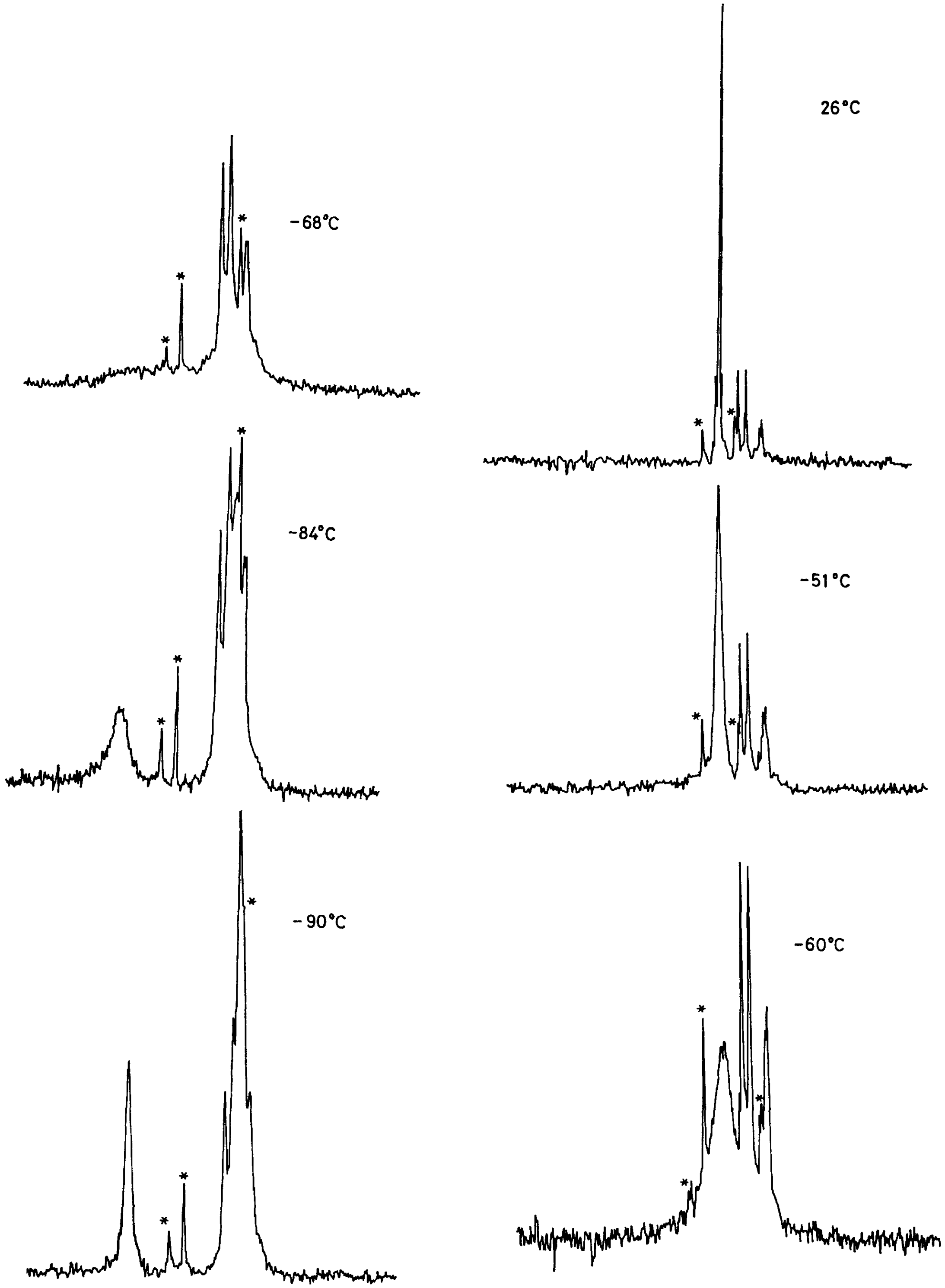
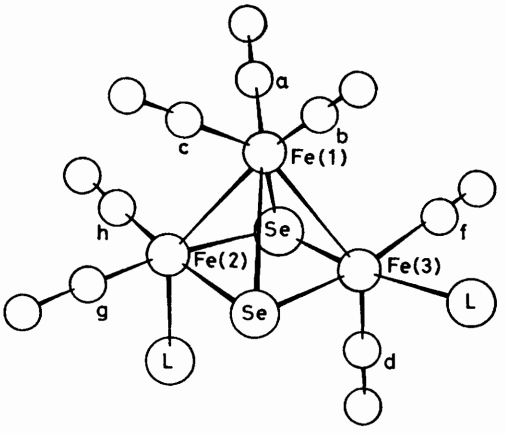


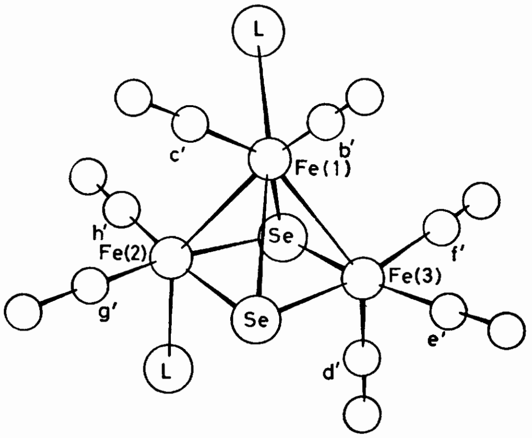
FIGURE 2 Variable-temperature ^{13}C n.m.r. spectra in the carbonyl region of [Fe$_3$(CO)$_9$(PBu$^n_3$)Te$_2$] (3) {the peaks marked with an asterisk are of [Fe$_3$(CO)$_9$Te$_2$] (1*d*)}; at 26 °C the major peak shows $^2J(^{13}\text{C}-^{125}\text{Te})$ 16.1 Hz

phosphorus coupling. Substitution of CO has been erroneously suggested to occur at the apical iron atom.[7] As expected, all the resonances are shifted downfield, the size of the shift being larger for the carbonyls attached to the iron atom at which substitution occurs and when the ligand is the phosphine.[15] As in (1) and (2) the exchange of the CO groups at Fe(1) is fast on the n.m.r. time scale but can be frozen at Fe(3). The downfield shift of the resonance of $CO_{g,h}$ as the temperature is raised is significant, being from 205.9 to 208.4 p.p.m. for (*4a*) and from 204.1 to 206.2 p.p.m. for (*4b*) in the temperature range -80 to 26 °C. This trend is opposite to that observed for the CO resonances of the spectra described earlier in this study where the upfield shift with temperature, observed over the same range, is always <1.0 p.p.m. A possible explanation is that, raising the temperature, the $Fe(2)(CO)_2L$ unit is no longer rigid. Because in these derivatives the shift of the CO in the axial position is downfield from those in the equatorial position for the basal $Fe(CO)_3$ moieties, the trend observed, rather than being just a temperature effect, can be interpreted as evidence of localised scrambling of the CO groups at Fe(2). Inspection of the values of ^2J(C–P) at various temperatures shows that it is invariant. Unfortunately the values of ^2J(C–P) are so close in the $Fe(CO)_2L$ units with the ligand in the equatorial position [(*5a*) and (*5c*), see below], that the invariance of ^2J(C–P) over the temperature range for the $Fe(2)(CO)_2L$ unit of (4) does not strengthen either hypothesis.

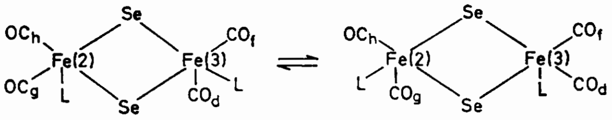
The Species $[Fe_3(CO)_7L_2Se_2]$ (5) [L = PBu^n_3 *or* $P(OPh)_3$].—As observed for (4) there are no significant differences between the spectra of the disubstituted derivatives $[Fe_3(CO)_7(PBu^n_3)_2Se_2]$ [(*5a*) and (*5c*)] and $[Fe_3(CO)_7\{P(OPh)_3\}_2Se_2]$ [(*5b*) and (*5d*)], thus the discussion is limited to the phosphine case. At -73 °C eight resonances appear in the spectrum of $[Fe_3(CO)_7(PBu^n_3)_2Se_2]$ (Figure 3), too many for just one species. Their behaviour with temperature and their spectral parameters suggest that two positional isomers are present.* Four resonances are then assigned to each isomer. In the most abundant isomer (*5a*) the second molecule of phosphine replaces a carbonyl in an equatorial position at the $Fe(3)(CO)_3$ unit of (4), whereas in the less abundant isomer (*5c*) the substitution occurs at the $Fe(1)(CO)_3$ unit of (4). Isomer (*5a*) is twice as abundant as (*5c*) and this ratio is maintained throughout the range of temperature examined. The signal of intensity 3 within the set of the peaks of (*5a*) (Table 2) indicates that at low temperature the localised scrambling of the CO groups at Fe(1) cannot be frozen in this case. On raising the temperature, all the resonances of (*5a*), except that of intensity 3, broaden, collapse, and merge into a doublet whose chemical shift is in excellent agreement with the calculated average (214.1 p.p.m.; $\Delta = 0.1$ p.p.m.). The experimental value of the two-bond carbon–phosphorus coupling constant of the doublet is 15.1 Hz which is exactly the value calculated for the average of the coupling constants of CO_d, CO_f, and $CO_{g,h}$ in the frozen structure. Such observations indicate that localised exchange of the CO groups occurs at each basal iron atom. This exchange may occur independently or as in the concerted process shown below.



(*5a*), (*5c*)



(*5b*), (*5d*)



On raising the temperature, changes in the spectral features of (*5b*) are observed: a progressive low-field shift of the signal assigned to $CO_{g',h'}$ and the appearance of the average peak for $CO_{d'}$ and $CO_{e',f'}$. Localised exchange then occurs at Fe(3) as in the monosubstituted derivatives; the occurrence of localised exchange at Fe(2) is debatable, as discussed for (4). The doublet assigned to $CO_{b',c'}$ remains unchanged throughout the temperature range showing that replacement of one CO with the phosphine prevents localised exchange at the $Fe(1)(CO)_3$ unit. The second molecule of a Group 5 ligand in the derivatives (5) induces a downfield shift

---

* Efforts to separate this mixture by t.l.c. gave no satisfactory results.

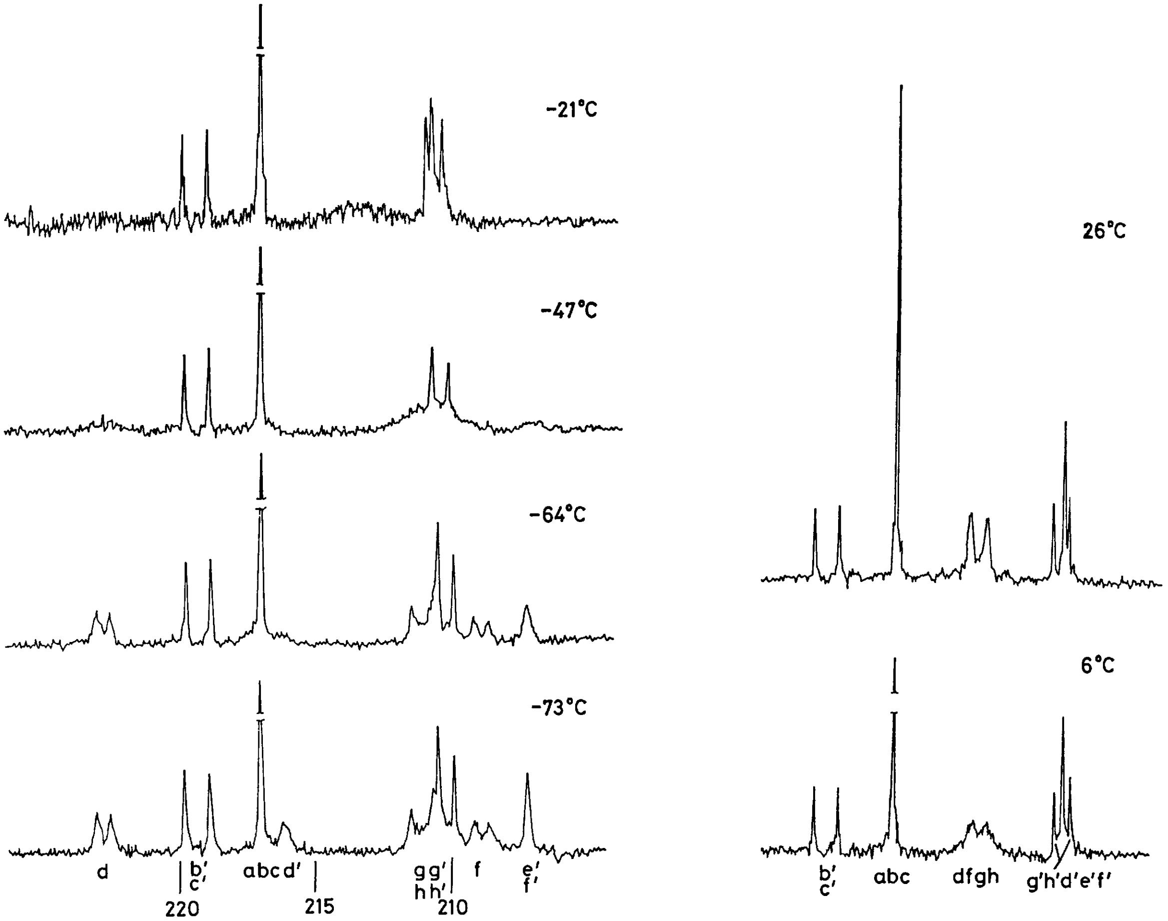


FIGURE 3 Variable-temperature ^{13}C n.m.r. spectra in the carbonyl region of $[Fe_3(CO)_7(PBu^n_3)_2Se_2]$ (*5a*) and (*5b*); at 26 °C the major peak shows $^2J(^{13}C-^{77}Se)$ 5.8 Hz

of all the resonances. This is larger in the phosphine case, whereas the $^2J(^{13}C-^{31}P)$ values are always larger in the phosphite case.

EXPERIMENTAL

Literature methods were used to prepare $[Fe_3(CO)_9X_2]$ (X = S, Se, Te,[16] or NMe [17]) and $[Fe_3(CO)_9Se(Te)]$ [5] complexes. The synthesis of the derivatives and the adduct has also been reported.[6] The ligands (Strem Chemical) were distilled under vacuum before use.

The $[Fe_3(CO)_9X_2]$ species were enriched by stirring, for anything from a few hours to several days, in a sealed ampoule at 70 °C in the presence of <1 atm * of 90% enriched ^{13}CO (Monsanto Research Corporation).

Carbon-13 n.m.r. spectra were recorded on a JEOL PFT 100 and on a Bruker HW-360 spectrometer operating in the Fourier-transform mode at 25.1 and at 90.5 MHz respectively. The chemical shifts are downfield positive with respect to tetramethylsilane as internal reference. Accumulations of 500—2 000 transients were made at a spectral width of 500—5 000 Hz. Solutions were sealed *in vacuo* in 10 mm tubes together with $SiMe_4$ as internal standard and with $Cr(acac)_3$ (acac = acetylacetonate) as inert relaxation agent. The solvents were $CDCl_3$, $CDCl_3$–CD_2Cl_2, and CF_2Cl_2–CD_2Cl_2. Deuteriated solvents were purchased from Commissariat a l'Energie Atomique and used immediately after drying over molecular sieves.

We thank Mr. W. Schittenhelm of Spectrospin AG (Zurich-Fallanden) for recording the spectra of $[Fe_3(CO)_9(NMe)_2]$ at high field.

[8/2105 *Received, 6th December*, 1978]

REFERENCES

[1] L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, 1963, **2**, 1067.
[2] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 493.
[3] P. J. Doedens, *Inorg. Chem.*, 1969, **8**, 570.
[4] P. R. Baikie and O. S. Mills, *Chem. Comm.*, 1967, 1228.
[5] R. Rossetti, G. Cetini, O. Gambino, and P. L. Stanghellini, *Atti Accad. Sci. Torino*, 1969—1970, **104**, 127.
[6] G. Cetini, P. L. Stanghellini, R. Rossetti, and O. Gambino, *J. Organometallic Chem.*, 1968, **15**, 373.
[7] M. K. Chaudhuri, A. Haas, and N. Welcman, *J. Organometallic Chem.*, 1975, **91**, 81.
[8] P. M. Treichel, W. K. Dean, and W. M. Douglas, *Inorg. Chem.*, 1972, **11**, 1609.
[9] S. Aime and L. Milone, *Progr. N.M.R. Spectroscopy*, 1977, **11**, 183.
[10] P. S. Braterman, D. W. Milne, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1973, 1027; G. M. Bodner and L. J. Todd, *Inorg. Chem.*, 1974, **13**, 1335.
[11] R. Rossetti, P. L. Stanghellini, O. Gambino, and G. Cetini, *Inorg. Chim. Acta*, 1972, **6**, 205.
[12] R. Rossetti and P. L. Stenghellini, *J. Co-ordination Chem.*, 1974, **3**, 217.
[13] M. H. Chisholm and S. Godleski, *Progr. Inorg. Chem.*, 1975, **20**, 299.
[14] G. Cetini, P. L. Stanghellini, R. Rossetti, and O. Gambino, *Inorg. Chim. Acta*, 1968, **2**, 433.
[15] S. Aime, L. Milone, R. Rossetti, and P. L. Stanghellini, *Inorg. Chim. Acta*, 1977, **25**, 103, and refs. therein.
[16] W. Hieber and J. Gruber, *Z. anorg. Chem.*, 1958, **91**, 296.
[17] M. Dekker and G. R. Knox, *Chem. Comm.*, 1967, 1243.

---

* Throughout this paper: 1 atm = 101 325 Pa.