Preparation and Spectroscopic Characterization of *trans*-$Fe(CO)_3L^1L^2$ (L^1, L^2 = Phosphine or Phosphite)

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The ^{57}Fe Mößbauer spectra of mixed ligand complexes of the type *trans*-$Fe(CO)_3L^1L^2$ (L^1 = triphenylphosphine or triphenylphosphite and L^2 = phosphine or phosphite) show a quadrupole-splitting doublet typical of the disubstituted iron carbonyls in trigonal bipyramidal symmetry. The inverse linear dependence of the isomer shifts on the CO stretching frequencies is interpreted on the basis of the strengthening triple-bond nature of the carbonyl ligands with increasing iron-to-phosphorus π-back donation. A linear correlation, with a positive slope, between the isomer shifts and the quadrupole splittings has revealed that the phosphorus-to-iron σ-donation is offset by the iron-to-phosphorus π-back donation. A correlation between the coordination shifts and the isomer shifts demonstrates that the iron-to-phosphorus π-back donation plays an important role in the Fe–P bond. The relatively large coupling constant of $^2J(P,P)$ reflects a strong interaction between *trans*-phosphorus ligands through the P–Fe–P bond.

Introduction

A variety of iron carbonyl complexes of the types $Fe(CO)_4L$ and $Fe(CO)_3L_2$ (L = phosphines, phosphites, arsines and stibines) were synthesized and characterized by infrared, ^{57}Fe Mößbauer, and ^{31}P NMR spectra. There is continuing interest in these mono- and disubstituted iron carbonyls because they provide an excellent opportunity to study the Fe–P bond by Mößbauer and NMR spectroscopy. In previous work we have prepared a wide range of trigonal bipyramidal $Fe(CO)_4L$ complexes to study their electronic properties on the basis of correlations between their spectroscopic parameters [1]. Only a limited number of mixed ligand complexes of the type $Fe(CO)_3L^1L^2$ (L^1, L^2 = phosphine or phosphite) has been synthesized although they should be a series of good model complexes to obtain some insight into the Fe–P or P–Fe–P bond by spectroscopy. Exceptionally, Allison *et al.* [2] synthesized a mixed ligand complex of iron carbonyl with 6,6,7-trioxa-1,4-diphosphabicyclo[2,2,2]octane, *i. e.* *trans*-$(CO)_3Fe(P(OCH_2)_3P)P(CH_2O)_3P$, and fully characterized the structure by both ^{31}P NMR and X-ray diffraction analysis. In the present paper we describe the preparation of *trans*-$Fe(CO)_3L^1L^2$, where L^1 is triphenylphosphine or triphenylphosphite and L^2 phosphine or phosphite. These model complexes with their wide range of electronic and steric characteristics can be used to elucidate the *trans*-effect of one phosphorus ligand on the electronic structure of another phosphorus ligand through the P–Fe–P bond. The nature of the Fe–P bond in *trans*-$Fe(CO)_3L^1L^2$ will here be discussed in the light of correlations among spectroscopic parameters such as νCO stretching frequencies, Mößbauer isomer shifts and quadrupole splittings, and ^{31}P NMR chemical shifts and coupling constants. Our particular interest is to learn how the axial coordination of two different kinds of phosphine and phosphite ligands to a central iron atom influences the electronic structure of *trans*-$Fe(CO)_3L^1L^2$ complexes.

Experimental

Dodecacarbonyltriiron, phosphines and phosphites were purchased from Strem Chemicals Inc. and Kanto Chemical Co., Inc. and used without further purification. All of the solvents were of reagent grade and dried prior to use or used as received. All manipulations were carried out under an argon atmosphere to prevent oxidation of compounds. The monosubstituted ironcarbonyls of the type $Fe(CO)_4L^1$ were prepared by variations on previously published syntheses [3]. The preparative procedure for $Fe(CO)_3L^1L^2$ is exemplified by that of $Fe(CO)_3(P(OPh)_3)(PPh_3)$, *i. e.* $L^1 = P(OPh)_3$ and $L^2 = PPh_3$. To a solution of $Fe_3(CO)_{12}$ (2.0 g:4.0 mmol) in 120 cm^3 of benzene was added 4.0 cm^3 (15 mmol)

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of $P(OC_6H_5)_3$ and refluxed under an argon atmosphere for 6 h. After filtration the reaction mixture was evaporated to dryness in a rotary evaporator. The addition of 100 cm^3 of hexane to the residue gave a colorless product, *i.e.* $Fe(CO)_3(P(OC_6H_5)_3)_2$. The hexane extract after removing the solid was chromatographed on an alumina column (30×1.8 cm i.d.) using hexane as an eluent. The yellow fraction was collected and brought to dryness to obtain $Fe(CO)_4P(OC_6H_5)_3$. The purity of the yellow crystalline product was checked by its IR spectrum. A mixture of $Fe(CO)_4P(OC_6H_5)_3$ (0.5 g:1.0 mmol) and $P(C_6H_5)_3$ (2.6 g:2.0 mmol) dissolved in benzene (0.5 cm^3) was irradiated under an argon atmosphere for 15 h with a 24 watt UV lamp of Wako Electric Co. The reaction mixture was cooled, filtered, and then evaporated to dryness. The residue was redissolved into a small amount of hexane and cooled in a refrigerator to obtain $Fe(CO)_3P(OC_6H_5)_3P(C_6H_5)_3$. The complexes of the type $Fe(CO)_3L^1L^2$ were either recrystallized from dichloromethane-hexane solution or purified by chromatography on an alumina column using hexane as an eluent. The complexes obtained were identified by their infrared spectra.

The infrared spectra were recorded in chloroform solution on a JASCO A-3 infrared spectrophotometer. The calibration of wavenumbers was carried out using polystyrene film. The ^{57}Fe Mößbauer spectra were measured with a Wissel constant-acceleration spectrometer equipped with a 10 mCi ^{57}Co source in a Pd matrix (The Radiochemical Centre, Amersham, England). The absorber was cooled to 77 K and the source maintained at room temperature. The spectra obtained were fitted to Lorentzian curves using an iterative least-square computer program. The isomer shifts were referred to iron foil at room temperature. The proton-decoupled ^{31}P NMR spectra were taken in a solution of deuterated chloroform with a Bruker-physik WP-80 instrument at room temperature. The chemical shifts are given relative to an external standard of 85% H_3PO_4.

Results

Three CO stretching bands became a broad band with a small splitting on going from monosubstituted $Fe(CO)_4L^1$ to disubstituted *trans*-$Fe(CO)_3L^1L^2$. This observation agrees with the group theoretical prediction that *trans*-$Fe(CO)_3L^1L^2$ is approximated to D_{3h} symmetry when neglecting the local symmetry of the functional groups directly attached to the phosphine or phosphite ligands. The ^{57}Fe Mößbauer spectra of *trans*-$Fe(CO)_3L^1L^2$ complexes showed a quadrupole-splitting doublet characteristic of disubstituted iron carbonyls in trigonal bipyramidal symmetry. The Mößbauer parameters observed for *trans*-$Fe(CO)_3L^1L^2$ are listed in Table I along with ligand

Table I. CO stretching frequencies and Mößbauer parameters observed for *trans*-$Fe(CO)_3L^1L^2$.

No.	L^2	νCO (cm^{-1})	Sum of Tolman's χ_i[a] $\Sigma\chi_{iL^1}+\Sigma\chi_{iL^2}$	δ (mms^{-1})	ΔEq (mms^{-1})	Cone angle[b] (deg)
	$L^1 = P(OC_6H_5)_3$					
1	$P(t\text{-}C_4H_9)_3$	1893, 1878	29.1	−0.080	2.84	182
2	$P(cyclo\text{-}C_6H_{11})_3$	1895, 1883	29.4	−0.105	2.55	170
3	$P(n\text{-}C_4H_9)_3$	1895, 1873	33.3	−0.126	2.43	132
4	$P(p\text{-}C_6H_4OCH_3)_3$	1908, 1895	39.3	−0.103	2.53	–
5	$P(p\text{-}C_6H_4CH_3)_3$	1902, 1892	39.6	−0.103	2.61	145
6	$P(m\text{-}C_6H_4CH_3)_3$	1912, 1898	40.2	−0.115	2.56	–
7	$P(C_6H_5)_3$	1908, 1894	42.0	−0.111	2.59	145
8	$P(OCH(CH_3)_2)_3$	1930, 1913	48.0	−0.128	2.30	130
9	$P(OC_4H_9)_3$	1930, 1913	48.6	−0.133	2.32	–
	$L^1 = P(C_6H_5)_3$					
10	$P(t\text{-}C_4H_9)_3$	1880, 1865	12.9	−0.080	2.86	182
11	$P(cyclo\text{-}C_6H_{11})_3$	1873, 1859	13.2	−0.114	2.58	170
12	$P(n\text{-}C_4H_9)_3$	1875, 1862	17.1	−0.100	2.40	132
13	$P(p\text{-}C_6H_4OCH_3)_3$	1878, 1869	23.1	−0.098	2.54	–
14	$P(p\text{-}C_6H_4CH_3)_3$	1880, 1853	23.4	−0.087	2.61	145
15	$P(m\text{-}C_6H_4CH_3)_3$	1892, 1879	24.0	−0.093	2.63	–
16	$P(C_6H_5)_3$	1891, 1878	25.8	−0.100	2.62	145
17	$P(OCH(CH_3)_2)_3$	1902, 1885	31.8	−0.130	2.17	130
18	$P(OC_4H_9)_3$	1902, 1867	32.4	−0.127	2.23	–

[a] Taken from Ref. [8]; [b] taken from Ref. [4].

cone angles taken from the literature [4]. The isomer shifts fall into the range from -0.133 to -0.080 mm $\mathrm{s^{-1}}$, which is typical of disubstituted iron carbonyls of the types $\mathrm{Fe(CO)_3L^1{}_2}$ and $\mathrm{Fe(CO)_3L^2{}_2}$ [5]. The quadrupole splittings range from 2.17 to 2.86 mm $\mathrm{s^{-1}}$ and are characteristic of those observed for trigonal bipyramidal iron carbonyls. Most of the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ spectra of *trans*-$\mathrm{Fe(CO)_3L^1L^2}$ gave two doublets, although it was impossible to identify the spectral peaks in some phosphite-phosphite complexes because of their rapid decomposition in the chloroform solution. The doublet of the coordinated phosphite was always observed downfield compared with that of the coordinated phosphine. Unexpectedly the complex *trans*-$\mathrm{Fe(CO)_3P(\textit{m}-C_6H_4CH_3)_3P(C_6H_5)_3}$ (No. 15) did not show any coupling between the phosphorus nuclei. The chemical shifts ($\delta_{^{31}\mathrm{P,L^2}}$) and the coupling constants $J(\mathrm{P-P})$ observed for *trans*-$\mathrm{Fe(CO)_3L^1L^2}$ are summarized together with the chemical shifts of the corresponding free ligands in Table II. The chemical shifts range from 61.3 to 124.8 ppm relative to 85% $\mathrm{H_3PO_4}$, while the coupling constants range from 5.5 to 86.1 Hz. The coordination shifts $\Delta\delta_{^{31}\mathrm{P,L^2}}$ which are defined as $\delta_{^{31}\mathrm{P,L^2}}$ (complex) $-$ $\delta_{^{31}\mathrm{P,L^2}}$ (free ligand), are also listed in Table II. The chemical shifts of the phosphite-coordinated site did not change within the present experimental errors upon the substitution of the axial carbonyl ligand for the second phosphine ligand $\mathrm{L^2}$. It was about 181.2 ppm for $\mathrm{Fe(CO)_3P(OC_6H_5)_3L^2}$ and about 81.7 ppm for $\mathrm{Fe(CO)_3P(C_6H_5)_3L^2}$, regardless of the nature of the ligand $\mathrm{L^2}$.

Discussion

A wide range of phosphine and phosphite ligands with strong σ-donor and virtually no π-acceptor properties was investigated with a view to elucidating some of the electronic and steric factors that influence the spectroscopic parameters. Firstly, a strong π-accepting triphenylphosphite was chosen as a ligand of the monosubstituted complex $\mathrm{Fe(CO)_4L^1}$ in order to prevent its ligand exchange reaction, which might occur in complexes of the type $\mathrm{Fe(CO)_3L^1L^2}$. Secondly, an intermediate π-accepting triphenylphosphine was selected as a ligand of monosubstituted $\mathrm{Fe(CO)_4L^1}$ to prepare a series of disubstituted *trans*-$\mathrm{Fe(CO)_3L^1L^2}$. The symmetry group of the *trans*-$\mathrm{Fe(CO)_3P_2}$ moiety is approximately $\mathrm{D_{3h}}$, when neglecting the local symmetry of the groups attached to the phosphorus atoms. Although there might be a potential barrier with respect to the rotation around the $\mathrm{C_3}$ axis of $\mathrm{D_{3h}}$ symmetry, the absolute position of the groups attached to the phosphorus atoms is not defined in the absence of any X-ray crystallographic data. The latter are determined by the following two requirements [2, 7]. One is the maximal overlap of atomic orbitals between the iron and the phosphorus atoms. The other is the steric hindrance exerted by the bulky ligands. Probably the groups attached to

Table II. $^{31}\mathrm{P}$ NMR parameters observed for *trans*-$\mathrm{Fe(CO)_3L^1L^2}$.

No.	$\mathrm{L^2}$	$\delta_{^{31}\mathrm{P,L^2}}$ (complex) (ppm)	$\delta_{^{31}\mathrm{P,L^2}}$ (ligand)[a] (ppm)	$\Delta\delta_{^{31}\mathrm{P,L^2}}$ (ppm)	$^2J(\mathrm{P-P})$ (Hz)
	$\mathrm{L^1 = P(OC_6H_5)_3}$				
1	$\mathrm{P(\textit{t}-C_4H_9)_3}$	124.8	62.2	62.6	73.2
2	$\mathrm{P(\textit{cyclo}-C_6H_{11})_3}$	83.7	11.0	72.7	73.2
3	$\mathrm{P(\textit{n}-C_4H_9)_3}$	61.3	−31.3	92.4	75.1
4	$\mathrm{P(\textit{p}-C_6H_4OCH_3)_3}$	72.5	−10.0	82.5	84.2
5	$\mathrm{P(\textit{p}-C_6H_4CH_3)_3}$	75.4	− 7.8	83.2	86.1
6	$\mathrm{P(\textit{m}-C_6H_4CH_3)_3}$	77.2	− 5.2	82.4	85.1
7	$\mathrm{P(C_6H_5)_3}$	78.0	− 6.6	84.6	84.6
	$\mathrm{L^1 = P(C_6H_5)_3}$				
10	$\mathrm{P(\textit{t}-C_4H_9)_3}$	65.3	62.2	3.2	14.3
11	$\mathrm{P(\textit{cyclo}-C_6H_{11})_3}$	87.3	11.0	76.3	27.5
12	$\mathrm{P(\textit{n}-C_4H_9)_3}$	62.5	−31.1	93.6	11.0
13	$\mathrm{P(\textit{p}-C_6H_4OCH_3)_3}$	76.6	−10.0	86.6	7.3
14	$\mathrm{P(\textit{p}-C_6H_4CH_3)_3}$	79.2	− 7.8	87.0	5.5
15	$\mathrm{P(\textit{m}-C_6H_4CH_3)_3}$	81.9	− 5.2	87.1	–
16	$\mathrm{P(C_6H_5)_3}$	81.6	− 6.6	88.5	–

[a] Taken from Ref. [6].

the phosphorus atoms are around the direction bisecting the C−Fe−C angles of the equatorial triangular $Fe(CO)_3$ moiety, but the superposition of the R groups is avoided. The parent complex $Fe(CO)_4L^1$ (L^1 = phosphine or phosphite) belongs to the symmetry group C_{3v} when neglecting the groups attached to the phosphorus atoms. On the other hand, the symmetry group of *trans*-$Fe(CO)_3L^1L^2$ is approximately D_{3h} or C_{3v}. Thus only one species, *i. e.* E′ for D_{3h} or E for C_{3v}, is expected to be infrared-active in the CO stretching region. The CO stretching mode of E′ in C_{3v} symmetry splits into two peaks due to the lowering of the site symmetry of the $Fe(CO)_3P_2$-moiety on going from mono-substituted trigonal bipyramidal $Fe(CO)_4Li^1$ to disubstituted *trans*-$Fe(CO)_3L^1L^2$.

The average CO stretching frequencies of the equatorial carbonyls are plotted against the sum of Tolman's χ_i values, *i. e.* $\Sigma\chi_i$ in Fig. 1, where the arithmetic mean of the split νCO frequencies is used as an average. Tolman's χ_i values are a measure of the electronic property of the groups directly attached to the phosphorus atoms [8]. Of course, the sum of Tolman's χ_i values, $\Sigma\chi_i$ is also a measure of the electron donor-acceptor property of the phosphorus ligand because of a substituent additivity rule. A linear correlation between the CO stretching frequencies and the sum of Tolman's χ_i values strongly suggests that the strength of the C−O bond is associated with the electron donor-acceptor property of the phosphine or phosphite ligand. In fact, the bonding property of the equatorial carbonyls is closely related to that of the Fe−P and Fe−C bonds. The C−O bond of the equatorial carbonyls is more influenced by changes in the π-back bonding than by those in the σ-bonding between Fe−C. Consequently, the CO stretching frequency is a measure of the strength of the iron-to-phosphorus π-back donation.

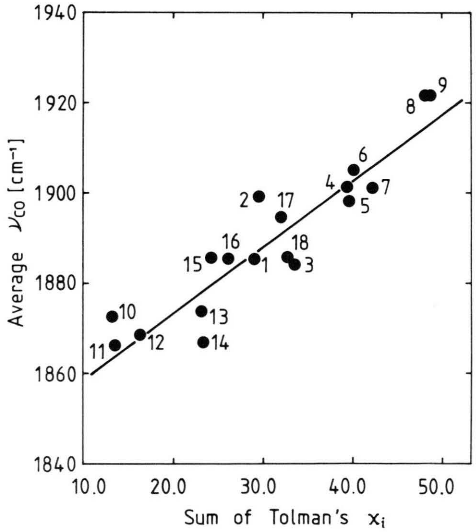

Fig. 1. Correlation between CO stretching frequencies and Tolman's χ_i in *trans*-$Fe(CO)_3L^1L^2$.

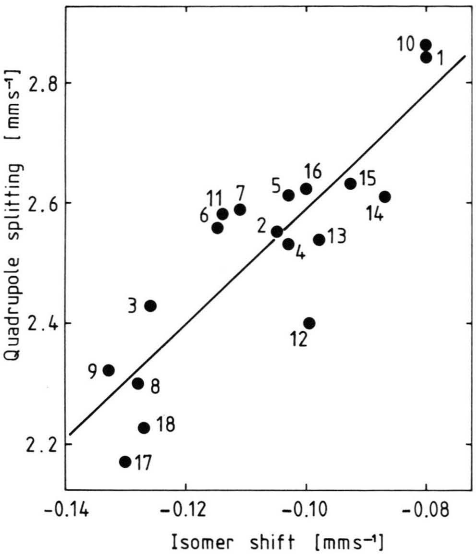

Fig. 2. Correlation between quadrupole splittings and isomer shifts in *trans*-$Fe(CO)_3L^1L^2$.

The isomer shifts are plotted against the quadrupole splittings in Fig. 2. In general, the isomer shift reflects the total electron density at the iron nucleus. It decreases either with increasing s-electron density through phosphorus-to-iron σ-donation or with the decrease in the shielding of s-electrons by decreasing 3d-electron density through iron-to-phosphorus π-back donation. The basicity of the axial phosphine or phosphite ligands is correlated to the isomer shifts. Thus, triphenylphosphite $P(OC_6H_5)_3$ competes more effectively for π-bonding when *trans* to $P(OC_6H_5)_3$ itself than when *trans* to a better π-acceptor such as a CO group. On the other hand, the quadrupole splitting is affected mainly by the asymmetry of 3d-electrons which increases with decreasing π-acceptor capability of the phosphorus ligands. The quadrupole splitting is decreased with the increasing π-acceptor power of the axial phosphorus ligands. The 3d-electrons taking part in the iron-to-phosphorus π-back donation make major contributions to the electric field gradient at the iron nucleus. The phosphite ligand with a larger π-acceptor power tends to give a smaller quadrupole splitting. A linear correlation with a positive slope indicates that the iron-to-phosphorus σ-donation is offset by the phosphorus-to-iron π-back donation. The quadrupole splitting is influenced not only by the asymmetry of 3d-electrons but also by the steric factor of the phosphorus ligand. The quadrupole splittings of *trans*-Fe(CO)$_3$L^{1}L^2 increase with the ligand cone angles (*cf.* Table I). The fact that the quadrupole splitting is affected by the bulkiness of the phosphine or phosphite ligand as well as by the π-acceptor power should be taken into consideration in discussing the linear correlation between the quadrupole splitting and the isomer shift.

The average CO stretching frequencies of the equatorial carbonyls are plotted against the isomer shifts in Fig. 3. As observed for the monosubstituted iron carbonyls of the type Fe(CO)$_4$L (L = phosphine and phosphite) [1], the νCO frequencies decrease with increasing isomer shifts. Consequently, the property of the Fe−P bond affects the C−O bond through the P−Fe−C bond.

The ^{31}P NMR chemical shift reflects the degree of the shielding at the phosphorus nucleus. The shielding at the phosphorus nucleus decreases with increasing σ-donation. The decrease in the shielding is also caused by the drift of d-electrons from the iron to the phosphorus atom because the drifted d-electrons shield the s-electrons at the phosphorus nucleus. The influence of the steric factor on the Fe−P bond is understood by the parallelism of the trends for $\delta_{^{31}P}$ and Tolman's cone angles in Fe(CO)$_3$L^{1}L^2 complexes (*cf.* Table I and II). In fact, steric crowding as encountered with bulky phosphines and phosphites leads to a decrease of Fe−P interaction.

The ^{31}P-coordination shifts are plotted against the isomer shifts in Fig. 4. The coordination shifts of *trans*-Fe(CO)$_3$L^{1}L^2, except for No. 1 and 3, tend to increase with the increasing isomer shifts. Insofar as *trans*-Fe(CO)$_3$P(OC$_6$H$_5$)$_3$L^2 complexes are concerned, the coordination shifts seem to decrease with increasing isomer shifts. The coordination shift is mainly associated with the amount of electron drift resulting from the coordination of the phosphorus ligand to the central iron, if the change in the stereochemistry of the groups attached to the phosphorus atom is neglected. Both the OPO and CPC angles of phosphite and phospine ligands are known to increase by about 3° upon coordination to iron [7]. The trends of the coordination shifts are correlated to the σ-donor and π-acceptor power as quantified by Graham's σ and π parameters [9] and reflect the elec-

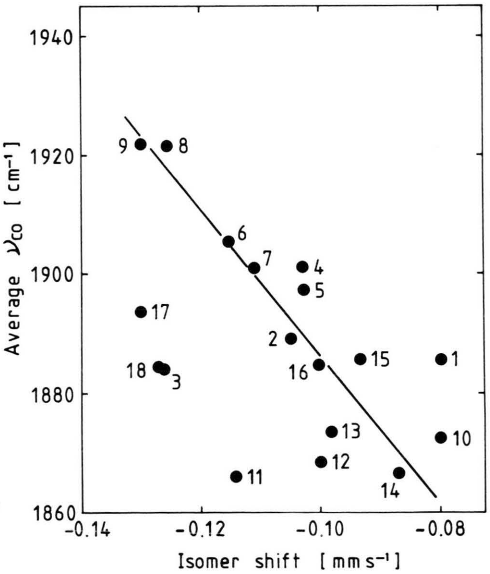

Fig. 3. Correlation between CO stretching frequencies and isomer shifts in *trans*-Fe(CO)$_3$L^{1}L^2.

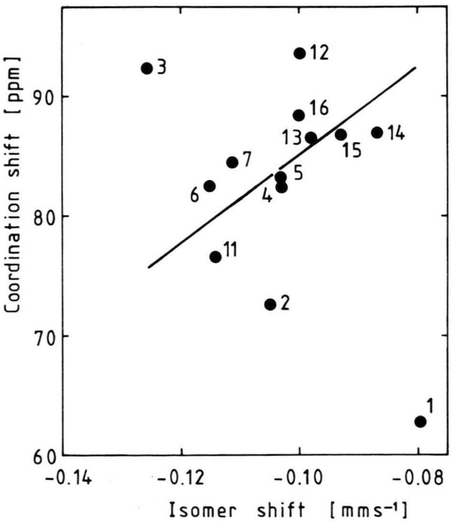

Fig. 4. Correlation between coordination shifts Δ^{31}P and isomer shifts in *trans*-Fe(COP)$_3$L^{1}L^2.

tronic and steric effects imposed by the substituents attached to the phosphorus atom. In *trans*-Fe(CO)$_3$L^{1}L^2, the σ-donor and π-acceptor powers of an Fe−P bond are in competition with those of another Fe−P bond in the *trans* position through the P−Fe−P bond. The balance of these effects makes the correlation between the coordination shifts and the isomer shifts complicated. As a result, a straightforward correlation could not be found for a series of *trans*-Fe(CO)$_3$L^{1}L^2.

The magnitude of the phosphorus-phosphorus (P−P) coupling through the iron atom is of significance in discussing the Fe−P bond, because an increase of ^2J(P−P) coupling constants is rationalized in terms of increasing Fermi contact contributions. The P−P coupling is affected by the σ-bonding rather than the π-back bonding. On the other hand, the π-back donation through the P−Fe−P bond can contribute indirectly to the P−P coupling, since the phosphorus-to-iron σ-donation is synergetically strengthened by the iron-to-phosphorus π-back donation. In view of this synergetic mechanism of the σ-bonding and π-back bonding properties, attempts were made to correlate the P−P coupling constants to the Mößbauer parameters. However, no linear correlation could be found between them, suggesting again a complicated mechanism.

The coupling constants would be expected to increase with the π-back donation from the central iron to the ligand L^2, and the CO stretching frequencies are a measure of this iron-to-phosporus π-back donation. Thus, the ^2J(P−P) coupling constants of *trans*-Fe(CO)$_3$L^{1}L^2 are plotted against the CO stretching frequencies in Fig. 5. Apparently the ^2J(P−P) coupling constants of *trans*-Fe(CO)$_3$L^{1}L^2, where L^1 is triphenylphosphite and L^2 is a variety of phosphines, are linearly correlated to the CO stretching frequencies. Any significant correlation between the coupling constants and the CO stretching frequencies could not be obtained for *trans*-Fe(CO)$_3$L^{1}L^2 complexes in which L^1 is triphenylphosphine and L^2 is a variety of phosphines. This is probably because not only the electronic factor but also the steric effect is important in the P−P coupling through the P−Fe−P bond.

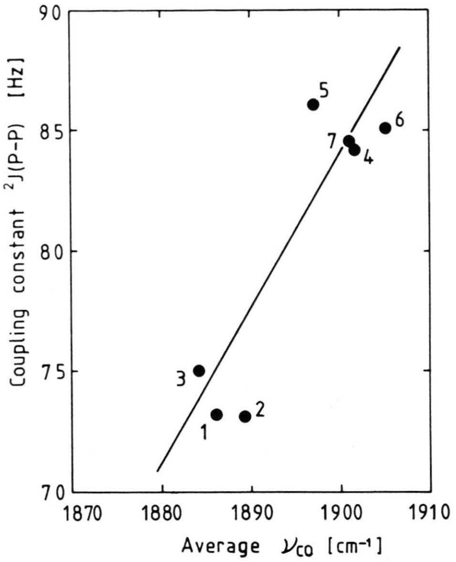

Fig. 5. Correlation between coupling constants ^2J(P−P) and CO stretching frequencies in *trans*-Fe(CO)$_3$L^{1}L^2.

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