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Preparation and characterization by ^{31}P-NMR spectroscopy of mixed disubstituted [Fe(CO)$_3$LL′] complexes

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Abstract

The disubstituted complexes [Fe(CO)$_3$LL′], where L and L′ are different phosphine ligands have been prepared by reaction of the hydrosilyl derivatives [Fe(CO)$_3$L(H)SiPh$_3$] with L′. Good results were obtained for L = PMe$_3$ and L′ = PPh$_3$, P(OPh)$_3$, P(OEt)$_3$ or P(O-i-Pr)$_3$ but with L′ = PMe$_2$Ph, PMePh$_2$, PEt$_3$, a mixture of homo and mixed disubstituted derivatives were obtained. The results can be interpreted in terms of exchange of the L ligand in [Fe(CO)$_3$L(H)SiPh]$_3$ with L′. The variations in the ^{31}P{^{1}H} NMR chemical shifts and $^2J_{PP}$ coupling constants are discussed in the light of the properties of the ligands, and good correlations are revealed with the cone angle and the pK_a, respectively.

Introduction

Carbonyl complexes of iron ([Fe(CO)$_5$], [Fe$_2$(CO)$_9$], [Fe$_3$(CO)$_{12}$]) react with phosphine ligands L to give mixtures of the mono- and di-substituted derivatives [Fe(CO)$_4$L] and [Fe(CO)$_3$L$_2$] [1]. This behavior is due to the reactivity of the intermediate [Fe(CO)$_4$], which is obtained whatever carbonyl complex of iron is used [2]. For a long time [Fe(CO)$_4$L] and [Fe(CO)$_3$L$_2$] derivatives were obtained by a difficult process of separation of the product mixtures.

Shriver [3] and Coville [4] obtained pure [Fe(CO)$_4$L] compounds from a reaction of [Fe(CO)$_5$] and L in the presence of catalysts. Pure [Fe(CO)$_3$L$_2$] compounds were recently obtained by irradiation of cyclohexane solutions of [Fe(CO)$_5$] in the presence of L, from which [Fe(CO)$_3$L$_2$] separates [5] or by reaction of [Fe(CO)$_5$] with L in the presence of NaBH$_4$[6]. We also obtained the complex [Fe(CO)$_3$(PPh$_3$)$_2$] by reaction of [Fe(CO)$_4$(H)(SiPh$_3$)] with PPh$_3$ [7]; [Fe(CO)$_4$(H)(SiPh$_3$)] is readily prepared by irradiation of [Fe(CO)$_5$] in the presence of HSiPh$_3$ [8].

Having observed this last reaction we decided to prepare the mixed disubstituted derivatives [Fe(CO)$_3$LL′] by reaction of L′ with [Fe(CO)$_3$L(H)(SiPh$_3$)], which is

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readily prepared by irradiation of [Fe(CO)$_4$L] and HSiPh$_3$ [7,9]. These disubstituted complexes had been never described in the literature, since it is difficult to carry out the disubstitution reaction in two steps and because the reaction of Fe(CO)$_4$L with L occurs only at a very high temperature [10].

Experimental section

The solvents (benzene, CH$_2$Cl$_2$, ethyl ether, n-hexane, CH$_3$CN) were purified and dried by standard procedure [11], and deaerated with nitrogen because of the high reactivity of the hydrosilane complexes towards oxygen. The complexes [Fe(CO)$_3$(PMe$_3$)(H)(SiPh$_3$)] (**1**) and [Fe(CO)$_3$(PPh$_3$)(H)(SiPh$_3$)] (**2**) were prepared as described in ref. 7 and [Fe(CO)$_3$(PMe$_3$)$_2$I$_2$] was prepared as described in ref. 12.

Authentic specimens of [Fe(CO)$_3$L$_2$] and [Fe(CO)$_4$L] were prepared as described in ref. 13. PMe$_3$ was prepared as described in ref. 14. The other phosphine ligands were commercial materials (Strem) and used without further purification.

IR spectra were recorded on a Perkin–Elmer 983 spectrometer and ^{1}H NMR and ^{31}P NMR spectra on a Bruker AC 200 spectrometer. Details of the IR and NMR spectra of the complexes described in this paper are given in Table 1. The ^{1}H NMR shifts are relative to tetramethylsilane as internal reference, and the ^{31}P NMR shifts relative to 85% H$_3$PO$_4$ in D$_2$O, with a positive sign indicating a shift to lower field.

Preparation of [Fe(CO)$_3$(PMe$_3$)(PPh$_3$)] (3). To a solution of **1** (0.560 g) in benzene kept at 60 ° C was added a five-fold excess of PPh$_3$. After 4 h the reaction was complete and the solvent was removed under vacuum. The solid residue was washed with n-hexane, which dissolved out traces of [Fe(CO)$_3$(PMe$_3$)$_2$], **1**, [Fe(CO)$_4$(PMe$_3$)] and the excess of PPh$_3$ and HSiPh$_3$. The residue was crystallized from ethyl ether as a yellow solid. Yield: 35% (m.p. 209–210 ° C). Anal. as C$_{24}$H$_{24}$O$_3$P$_2$Fe: calcd.: C, 60.3; H, 5.1; found: C, 61.3; H, 5.1%.

Preparation of [Fe(CO)$_3$(PMe$_3$)L′] [L′ = P(OPh)$_3$ (4), P(OEt)$_3$ (5), P(O-i-Pr)$_3$ (6)]. A procedure similar to that used for **3** was employed in the preparation of **4**, but the purification was a little different. When the dried solid was washed with n-hexane all the solid residue dissolved, but when the solution was cooled to −18 ° C the mixed disubstituted **4** separated as white crystals. Traces of the ligand P(OPh)$_3$ were removed by pumping. Yield: 45% (m.p. 136–137 ° C). Anal. as C$_{24}$H$_{24}$O$_6$P$_2$Fe: calcd.: C, 54.8; H, 4.6; found: C, 54.9; H, 4.7%.

A similar procedure was used for the reactions with P(OEt)$_3$ and P(O-i-Pr)$_3$ except that complex **5** was not purified; for complex **6**: yield 32% (m.p. 139–140 ° C); anal. as C$_{15}$H$_{30}$O$_6$P$_2$Fe: calcd: C, 42.4; H, 7.1; found: C, 43.3; H, 7.3%.

Reaction of 1 with L′ = PEt$_3$, PMe$_2$Ph, PMePh$_2$ and P(C$_6$H$_{11}$)$_3$. The reactions were carried out in benzene at 60 ° C with a 3–5-fold excess of L′, and were complete in 3–4 hours. Attempts to separate the products were unsuccesful. The composition of the reaction mixture was determined by ^{31}P NMR spectroscopy.

When L′ = PEt$_3$, PMe$_2$Ph, PMePh$_2$ were used, all the possible disubstituted derivatives were observed: [Fe(CO)$_3$L$_2$], [Fe(CO)$_3$L′$_2$] and [Fe(CO)$_3$LL′]. The spectroscopic data for these complexes are given in Table 1.

With L′ = P(C$_6$H$_{11}$)$_3$ [Fe(CO)$_4$L], [Fe(CO)$_4$L′] and [Fe(CO)$_3$L$_2$] were formed, along with traces only of [Fe(CO)$_3$LL′].

Exchange reaction of 1 with PMePh$_2$. The reaction was carried out in an NMR tube at room temperature. Complex (**1**) was dissolved under nitrogen in C$_6$D$_6$

Table 1

Relevant ^1H and $^{31}P\{^1H\}$ (CD_2Cl_2) NMR and IR (n-hexane) spectra

Complex	^{31}P NMR, δ (ppm) [J (Hz)]	^1H NMR, δ (ppm) [J (Hz)]	$\nu(CO)$ (cm^{-1})
$Fe(CO)_4(PMe_3)$	35.10 s [a]	0.91 d ($^2J_{PH} = 10.5$)	2051, 1977 1935
$Fe(CO)_4(PPh_3)$	73.88 s [a]		2051, 1979 1945
$Fe(CO)_4(P(C_6H_{11})_3)$			2045, 1971 1929
$Fe(CO)_3(PMe_3)_2$	42.05 s	1.45 ($^2J_{PP} = 23.5$, $^2J_{PH} = 10.3$; $^4J_{PH} = -1.8$) [b]	1879
$Fe(CO)_3(PPh_3)_2$	85.53 s		1886
$Fe(CO)_3(PPh_2Me)_2$	67.68 s		1884
$Fe(CO)_3(PPhMe_2)_2$	52.80 s		1882
$Fe(CO)_3(PEt_3)_2$	73.07 s		1877
$Fe(CO)_3(PMe_3)(PPh_3)$	L: 45.74 d L′: 84.52 d ($^2J_{PP} = 28.4$)	1.70 d ($\lvert ^2J_{PH} + {}^4J_{P'H} = 9.9 \rvert$)	1937.5(vw) 1886
$Fe(CO)_3(PMe_3)(PPh_2Me)$	L: 44.21 d L′: 67.00 d ($^2J_{PP} = 26.8$)		1883
$Fe(CO)_3(PMe_3)(PPhMe_2)$	L: 43.20 d L′: 52.12 d ($^2J_{PP} = 24.5$)		1881
$Fe(CO)_3(PMe_3)(PEt_3)$	L: 43.89 d L′: 72.09 d ($^2J_{PP} = 22.9$)		
$Fe(CO)_3(PMe_3)(P(OPh)_3)$	L: 39.10 d L′: 184.16 d ($^2J_{PP} = 77.3$)	1.49 dd ($^2J_{PH} = 10.3$; $^4J_{PH} = 1.6$)	1890.0(vw) 1902.5
$Fe(CO)_3(PMe_3)(P(OEt)_3)$	L: 41.63 L′: 189.89 ($^2J_{PP} = 67.0$)		1887.5
$Fe(CO)_3(PMe_3)(P(OiPr)_3)$	L: 41.62 L′: 186.91 ($^2J_{PP} = 65.8$ ($^2J_{PH} = 10.2$; $^3J_{P'H} = 10.3$)	1.63 d $^2J_{PH} = 10.0$ $^4J_{PH} = 1.6$	1884.0, 1890(sh), 1898.5
$Fe(CO)_3(PMe_3)(H)(SiPh_3)$	14.07 s [a]	-9.59 d ($^2J_{H-Fe-P} = 30.0$)	1969, 2035 [a]
$Fe(CO)_3(PPh_2Me)(H)(SiPh_3)$	42.31 s [a]	-8.82 d ($^2J_{H-Fe-P} = 28.0$)	
$Fe(CO)_2(PPh_2Me)(PMe_3)$	L: 34.77 s L′: 49.78 s		1876, 1813

[a] Benzene. [b] Calculated value [20].

containing a 2–3-fold excess of $PMePh_2$. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. After 24 h $[Fe(CO)_3(PMePh_2)(H)(SiPh_3)]$ (**7**) had been formed, along with traces of $[Fe(CO)_3(PMe_3)_2]$, $[Fe(CO)_3(PMePh_2)_2]$ and $[Fe(CO)_3(PMe_3)(PPh_3)]$. After two days the ratio of **1** to **7** reached a constant value, and the proportion of the disubstituted derivatives increased. The reaction was complete after 12 days.

Reaction of 2 with PMe_3. To a solution of **2** (0.38 g) in 35 ml of benzene, thermostated at 60 °C, was added an excess of PMe_3 in ethyl ether. The solid formed was dissolved in n-hexane and $[Fe(CO)_3(PMe_3)_2]$ was recovered as yellow crystals. Only traces of $[Fe(CO)_3(PPh_3)_2]$ and $[Fe(CO)_3(PMe_3)(PPh_3)]$ were observed in solution.

Stability of complex 1. A solution of **1** in benzene was thermostated at 60 °C. The formation of $[Fe(CO)_4(PMe_3)]$ and $[Fe(CO)_3(PMe_3)_2]$ (ratio: 0.91) and a decomposition product was observed. A solution of the decomposition product in 85% aqueous HNO_3 showed no ^{31}P NMR signal.

Reduction of $[Fe(CO)_3(PMe_3)I_2]$. A solution of $[Fe(CO)_3(PMe_3)I_2]$ (0.220 g) in CH_3CN was thermostated at −18 °C. An excess of sodium amalgam (1.2%) was added to the stirred solution. After 1 h the reduction was complete and $[Fe(CO)_4(PMe_3)]$ and $[Fe(CO)_3(PMe_3)_2]$ were present in a 2.97/1 ratio.

Photochemical reaction of $[Fe(CO)_4(PMe_3)]$ in the presence of L′. Under a flow of argon, a solution of $[Fe(CO)_4(PMe_3)]$ (1 g) in n-hexane (300 ml) containing a 2-fold excess of PPh_3 was irradiated at room temperature with a medium-pressure Hg lamp. The intensities of CO stretching bands decreased and a yellow precipitate appeared. After 8 h the $[Fe(CO)_4(PMe_3)]$ had disappeared and the precipitate was filtered off and was identified from its IR and ^{31}P NMR spectra as a mixture of $[Fe(CO)_3(PMe_3)(PPh_3)]$ and $[Fe(CO)_3(PPh_3)_2]$.

With $L' = PMePh_2$ the reaction proceeded in a similar manner but a mixture of $[Fe(CO)_3(PMePh_2)_2]$ and $[Fe(CO)_2(PMe_3)(PMePh_2)_2]$ was obtained as an orange precipitate.

Discussion

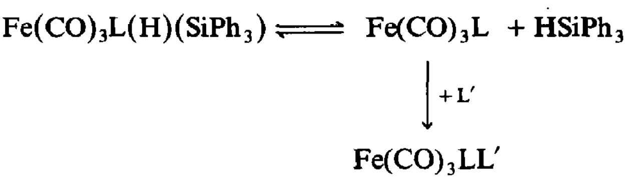
Reaction mechanism

The simultaneous formation of $[Fe(CO)_4L]$ and $[Fe(CO)_3L_2]$ in the reaction of various iron carbonyl complexes ($[Fe(CO)_5]$, $[Fe_2(CO)_9]$, $[Fe(CO)_4(\eta^2\text{-olefin})]$) with phosphine ligands is attributable to the reactivity of the intermediate $[Fe(CO)_4]$ [2]. It can give the dimer $[Fe_2(CO)_8]$ [15], which reacts quickly with L to give $[Fe(CO)_4L]$ and $[Fe(CO)_3L_2]$ in various ratios depending on basicity of the ligand but not on its concentration [2].

The intermediate $[Fe(CO)_3L]$, obtained either by reduction with sodium amalgam of $[Fe(CO)_3LI_2]$ or by elimination of $HSiPh_3$ from the $[Fe(CO)_3L(H)(SiPh_3)]$ complexes, also reacts in a similar manner to give a mixture of $[Fe(CO)_4L]$ and $[Fe(CO)_3L_2]$. In this case, however, the ratio depends on the ligand concentration, and in the presence of an excess of L only the disubstituted complex is formed [7]. This behaviour suggested to us a method of making disubstituted derivatives of iron $[Fe(CO)_3L_2]$ by a photochemical reaction of $[Fe(CO)_4L]$ in the presence of an excess of L. As described in the Experimental Section, this procedure gave good yields of the disubstituted complexes, but trisubstituted derivatives were also formed.

The reactivity of $[Fe(CO)_3L]$, obtained by thermal elimination of $HSiPh_3$ from the $[Fe(CO)_3L(H)(SiPh_3)]$ complexes, offers a route to the mixed disubstituted complexes $[Fe(CO)_3LL']$. Photochemical activation of $[Fe(CO)_4L]$ in the presence of L′ does not give only [$Fe(CO)_3LL'$], but rather all the possible disubstituted derivatives since the UV light activates both the Fe–CO and Fe–L bond in [$Fe(CO)_4L$] [16].

The route to [$Fe(CO)_3LL'$] is depicted in Scheme 1:



Scheme 1

In the absence of L′ the intermediate $Fe(CO)_3L$ reacts to give [$Fe(CO)_4L$] and [$Fe(CO)_3L_2$]. In the presence of L′ the reaction might give [$Fe(CO)_3LL'$]. With L = PMe_3 and L′ = PPh_3, $P(OPh)_3$, $P(OEt)_3$ and $P(O\text{-}i\text{-}Pr)_3$ the reaction proceeds in this way and good yields of [$Fe(CO)_3LL'$] are obtained (see Experimental Section). With L′ = PMe_2Ph, $PMePh_2$, PEt_3 mixtures of [$Fe(CO)_3L_2$], [$Fe(CO)_3L'_2$] and [$Fe(CO)_3LL'$] are formed, and these are difficult to separate owing to their similar solubilities in various solvents. With L = PPh_3 and L′ = PMe_3, only [$Fe(CO)_3L'_2$] is obtained. With L = PMe_3 and L′ = $P(C_6H_{11})_3$, [$Fe(CO)_4L$], [$Fe(CO)_4L'$], [$Fe(CO)_3L_2$], and [$Fe(CO)_3L'_2$] are formed. This behaviour cannot be explained in terms of Scheme 1, since an increase in basicity and a decrease in steric hindrance should increase the ease of formation of the mixed complexes.

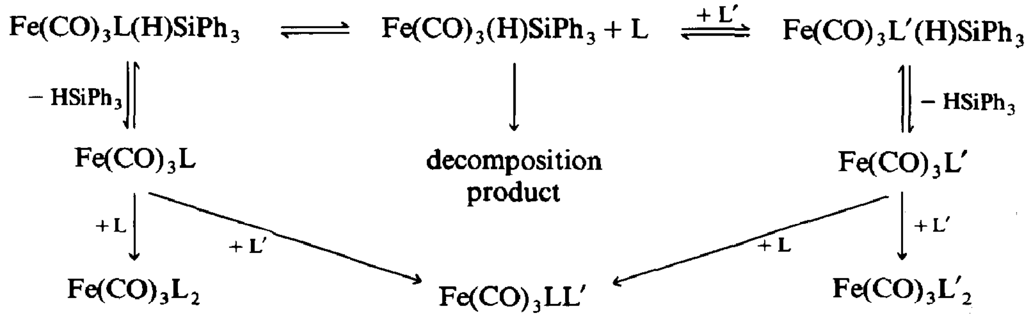
The experimental results can be interpreted in terms of exchange between the L′ and L ligand in the hydrosilane, as shown in Scheme 2:

$$Fe(CO)_3L(H)SiPh_3 + L' \rightleftarrows Fe(CO)_3L'(H)SiPh_3 + L$$

Scheme 2

This reaction was observed at room temperature.

The overall mechanism is thus that depicted in Scheme 3:



Scheme 3

With more basic ligands (L′ = PMe_2Ph, $PMePh_2$, PEt_3) the extent of exchange increases and formation of mixtures of [$Fe(CO)_3L_2$], [$Fe(CO)_3L'_2$] and [$Fe(CO)_3LL'$] is favoured. The formation of the intermediate [$Fe(CO)_3(H)SiPh_3$] is supported by the observation of the decomposition product that does not contain phosphorus. When L′ is $P(C_6H_{11})_3$ the high steric hindrance lowers the rate of reaction of $[Fe(CO)_3L]$ and $[Fe(CO)_3L']$ with L′, and reactions occurs via dimer to give $[Fe(CO)_4L]$, $[Fe(CO)_3L_2]$, and $[Fe(CO)_4L']$.

With the less basic ligands ($L' = PPh_3$, $P(OPh)_3$, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$) the exchange process is inhibited and formation of $[Fe(CO)_3LL']$ is favored.

In the reaction of $[Fe(CO)_3(PPh_3)(H)SiPh_3]$ with PMe_3 the high basicity of PMe_3 shifts equilibrium (2) to the right, and the formation of $[Fe(CO)_3(PMe_3)_2]$ is observed.

The lability of the ligand L in $[Fe(CO)_3L(H)SiPh_3]$ is surprising; in fact, when there is only one Fe–L bond in the complex it is very strong, and the strength decreases with increase in the number of Fe–L bonds. The lability of the Fe–L bond can be attributed to the strong *trans* effect of the $SiPh_3$ group [17]. A high lability of the group *trans* to the substituted silyl has been observed in various complexes of iron and ruthenium [18].

Discussion of IR and NMR spectra

Details of the CO stretching frequencies and a few relevant ^1H- and ^{31}P-NMR signals are given in Table 1.

Complexes $Fe(CO)_3L_2$ show a very intense CO stretching band, which can be accounted for on the basis of the D_{3h} symmetry. With this symmetry only E' is IR active, A_1' being infrared inactive. Mixed complexes $Fe(CO)_3(PMe_3)L'$ show two CO stretching bands for the most hindered L′ ligands, one very strong and the other very weak. With the less hindered ligands only one strong CO stretching band is observed. This behaviour can be accounted for in terms of a C_{3v} symmetry. With this symmetry two CO stretching bands of A_1 and E symmetry should be observed in the intensity ratio $I(A_1)/I(E) = [3\cot^2(\theta/2) - 1]/4$, where θ is the angle between the CO ligands [19]. With the three ligands in a plane $\theta = 120°$ and $I(A_1)/I(E) = 0$. When the ligand L′ is very bulky the three CO ligands are not in a plane and the A_1 band is observed. For $L' = P(O\text{-}i\text{-}Pr)_3$ three CO stretching bands are observed, probably because of various conformers.

$^{31}P\{^1H\}$ NMR spectra of the mixed disubstituted complexes $Fe(CO)_3(PMe_3)L'$ show two doublets interpretable as an AX system. In a few cases the proton spectrum allows measurement of the coupling constants for coupling of the methyl proton with the phosphorus atoms of PMe_3 and L′ ligand. The coupling constant between the two phosphorus atoms of the complex $Fe(CO)_3(PMe_3)_2$ was determined by considering the spin system as $X_9AA'X_9'$ as described by Harris [20]. The value obtained is in agreement with that observed for the mixed disubstituted complexes. The derived coupling constants $^2J_{PH} = 10.3$ Hz and $^4J_{PH} = -1.8$ Hz are in agreement with those observed for similar systems that deceptively show triplets [21] ($J \simeq 4$–5 Hz) for which the triplet coupling constants are equal to $\frac{1}{2}(^2J_{PH} + {}^4J_{PH})$ [22].

The values of the chemical shifts of the phosphorus atom of the ligand L′ of the series $Fe(CO)_3(PMe_3)L'$ ($L' = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3, PEt_3, $P(OPh)_3$, $P(O\text{-}i\text{-}Pr)_3$, $P(OEt)_3$) ($\delta L'(Fe)$) are related to the chemical shifts of the phosphorus [23] in the ligands L′ ($\delta L'$) as shown in the following equation (see Fig. 1):

$$\delta L'(Fe) = 87.31 + 0.742\delta L', \qquad r = 0.9998$$

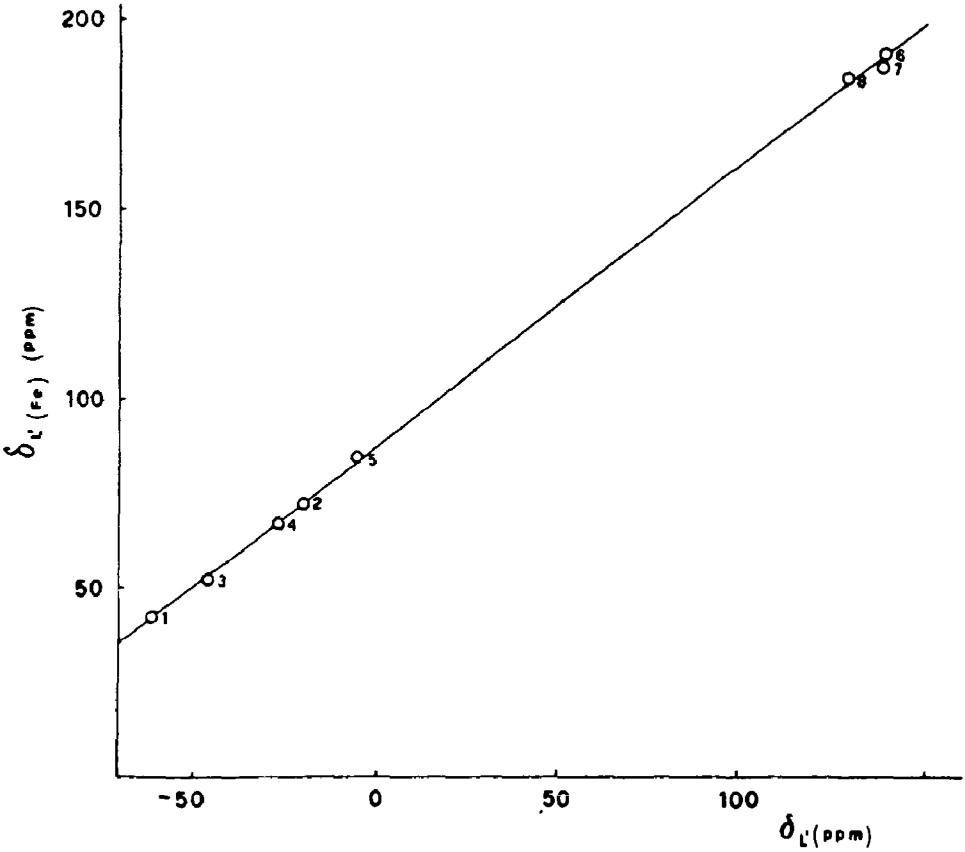


Fig. 1. Plot of the chemical shift of the phosphorus atom of the ligand L′ in the complexes [$Fe(CO)_3(PMe_3)L'$] [δL′(Fe)] against the chemical shift of the phosphorus atom of the free ligand L′ (δL′). L′ = PMe_3 (1), PEt_3 (2), PMe_2Ph (3), $PMePh_2$ (4), PPh_3 (5), $P(OPh)_3$ (6), $P(OEt)_3$ (7), $P(O\text{-}i\text{-}Pr)_3$ (8).

The excellent correlation indicates that the coordination to the metal involves a linear deshielding of the phosphorus atom along the series.

In order to correlate the chemical shifts δL′(Fe) with the properties of the ligand L′, use of several types of parameters was attempted [24], such as the Brønsted basicity (pK_a) [25], the cone angle (θ) [26], and the parameter χ [27]. The best correlation, for the phosphine complexes, was obtained by using the θ parameter (Fig. 2):

$$\delta L'(Fe) = -130.94 + 1.4893\theta \qquad r = 0.9671$$

The three factors that appear to dominate ^{31}P chemical shift δ are the difference in electronegativity in the bond P–X (ΔE), the change in the π-electron overlap (Δn_π), and the change in the σ-bond angle ($\Delta\theta$) [28]. For our phosphine compounds E and n_π remain constant, allowing a linear dependence on the θ angle. The chemical shifts of the phosphite compounds do not seem to vary with the parameters considered above, remaining nearly constant at 184–190 ppm as θ, pK_a and χ are varied.

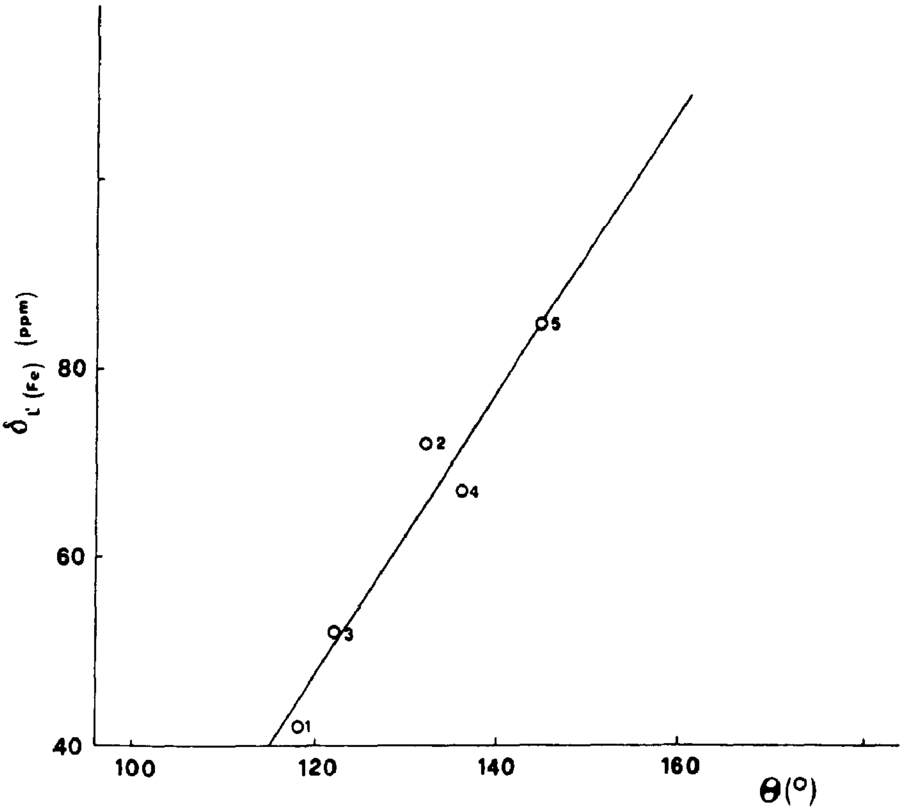


Fig. 2. Plot of the chemical shift of the phosphorus atom of the ligand L′ in the complexes $Fe(CO)_3(PMe_3)L'$ [δL′(Fe)] against cone angle θ of the L′ ligand. L′ = PMe_3 (1), PEt_3 (2), PMe_2Ph (3), $PMePh_2$ (4), PPh_3 (5).

The values of the coupling constants ${}^2J_{PP}$ for the complexes $Fe(CO)_3(PMe_3)L'$ are linearly related to the pK_a, an increase in the basicity of L′ resulting in a decrease in ${}^2J_{PP}$. For $L' = PR_3$, the following correlation was obtained (see Fig. 3):

$$ {}^2J_{PP} = 31.1 - 0.94pK_a \qquad r = -0.9895 $$

and for $L' = P(OR)_3$:

$$ {}^2J_{PP} = 73.4 - 1.96pK_a \qquad r = -0.9999 $$

If only the Fermi contact interaction is considered, ${}^2J_{PP}$ depends mainly on the effective nuclear charges of the two coupling nuclei ($Z_p{}^3$) and on the degree of *s* character in the bonds between the nuclei [29]. The higher electronegativity of oxygen than carbon makes the phosphorus atom of the phosphite less screened, so that there is an increase in the effective nuclear charge and thus in the coupling constant ${}^2J_{PP}$. In the two series of ligands the contributions due to Z_p and hybridization of the phosphorus atom cannot be separated, but a good correlation with the pK_a is obtained because this takes account of both the different electro-

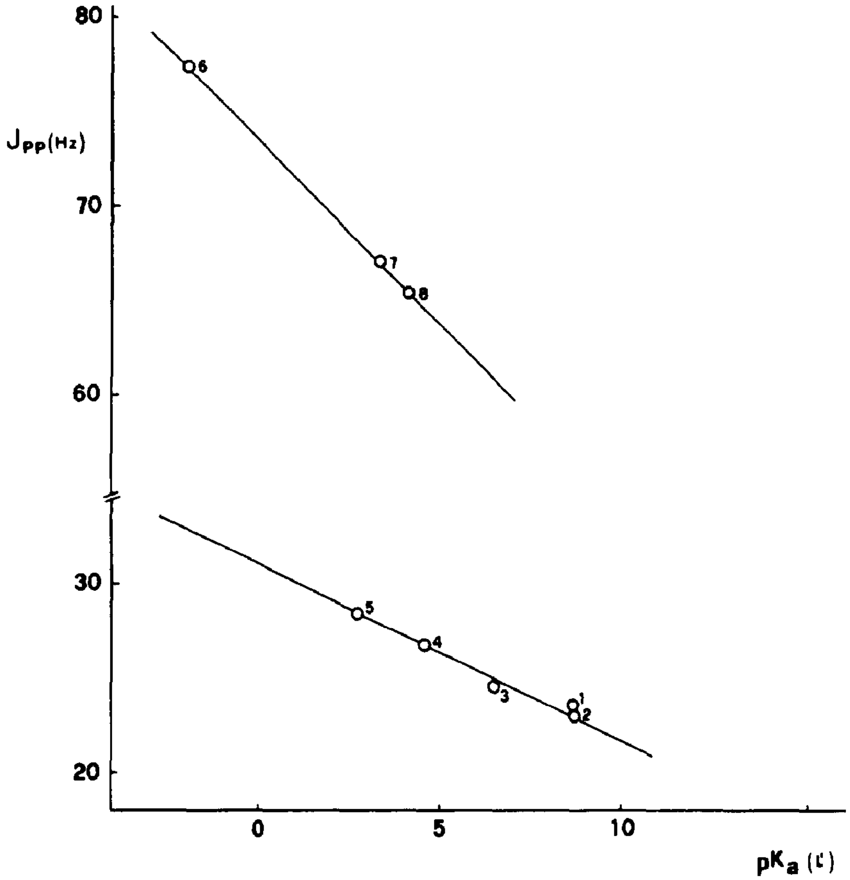


Fig. 3. Plot of PP coupling constant ($^2J_{PP}$) in the complex Fe(CO)$_3$(PMe$_3$)L′ against the pK_a of the L ligand. L′ = PMe$_3$ (1), PEt$_3$ (2), PMe$_2$Ph (3), PMePh$_2$ (4), PPh$_3$ (5), P(OPh)$_3$ (6), P(OEt)$_3$ (7), P(O-i-Pr)$_3$ (8).

negativity of the substituents and the change of hybridization of the phosphorus atom [24].

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