Monocarbonyl Complexes of Iron(II): Preparation and Properties

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Iron(II) monocarbonyl complexes of the type $[FeX(CO)L_4]BPh_4$ [X = Cl or Br; L = $P(OMe)_3$, $P(OEt)_3$, or $PPh(OEt)_2$] and the dicarbonyl compound $[FeBr(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ have been prepared and characterized by i.r., ^1H and $^{31}P-\{^1H\}$ n.m.r. spectroscopy. Reactivity with some π-acceptor ligands has been investigated and synthesis of the new derivatives $[FeBr(4-Me-C_6H_4NC)_3L_2]^+$ [L = $P(OMe)_3$, $P(OEt)_3$, or $PPh(OEt)_2$] achieved.

A number of iron(II) carbonyl complexes have been reported[1] both with tertiary and secondary phosphines and with chelating diphosphine and diarsine ligands. Relatively less attention has been devoted to the phosphite ligands, although their appreciably stronger π-acceptor properties and decreased steric requirements[2] should make their study of considerable interest. Except for Bancroft's paper[3] on the reaction of $[FeI_2(CO)_4]$ with $P(OMe)_3$, no other carbonyl iron(II) derivatives have been reported with phosphite ligands. We have previously reported[4] on the chemistry of cobalt(I) carbonyl and nitrosyl compounds and now, as an extension of our studies, have investigated the reactivity of phosphite-containing iron(II) solutions toward carbon monoxide, giving new monocarbonyl complexes.

Experimental

Materials.—Diethoxyphenylphosphine was prepared following the method of Rabinowitz and Pellon.[5] Trimethyl and triethyl phosphite (Baker) were purified by distillation under nitrogen. *p*-Tolyl isocyanide was obtained by the phosgene method of Ugi *et al.*[6] Other reagents were purchased commercially in the highest available purity and used as received. Organic solvents were purified and dried by standard methods and distilled under a stream of nitrogen just prior to use.

Synthesis of the Complexes.—All preparations and reactions were carried out under an inert atmosphere using standard Schlenk techniques. Once isolated, the complexes were air-stable for 1—2 d. Physical and analytical data are given in Table 1.

cis- and *trans-*$[FeX(CO)L_4]BPh_4$ [X = Cl or Br; L = $P(OMe)_3$ or $P(OEt)_3$]. The appropriate phosphite was added to a solution of anhydrous $FeCl_2$ (1.27 g, 10 mmol) in 60 cm^3 of methanol or ethanol. The reaction mixture was stirred for 3 h and then allowed to stand under carbon monoxide for 2 h. After filtration, the addition of $NaBPh_4$ (3.4 g, 10 mmol) afforded a yellow precipitate which was washed with alcohol and dried under vacuum. The product was a mixture of the *cis* and *trans* isomers (an excess of the *cis* compound is often present) and their separation could be achieved by fractional crystallization. In a typical separation, the crude product (3 g) was mixed with 50 cm^3 of methanol or ethanol and enough acetone (5—10 cm^3) to produce a homogeneous solution at room temperature. By slow cooling at $-20\,^\circ C$ yellow crystals of *cis-*$[FeX(CO)L_4]$-BPh_4 separated out, which were washed and dried under vacuum (yield $\geqslant 40\%$). The solution was concentrated to *ca.* 50% and then warmed to 50 °C to transform the remaining *cis* complex to the *trans* isomer. The solution was then cooled to $-30\,^\circ C$ to give yellow crystals of *trans-*$[FeX(CO)L_4]BPh_4$, which were washed with alcohol and dried under vacuum (yield $\geqslant 20\%$).

trans-$[FeCl(CO)\{P(OEt)_3\}_4][FeCl_4]$. Triethyl phosphite was added to a concentrated solution of $FeCl_2$ (1.27 g, 10 mmol) in ethanol (30 cm^3). The reaction mixture was stirred for 3 h and carbon monoxide added. A yellow precipitate separated out after 1—2 h, which was filtered off and crystallized from dichloromethane–ethanol (yield $\geqslant 10\%$). It was subsequently discovered that the $[FeCl_4]^-$ counter ion originated from impure (oxidized) $FeCl_2$. Furthermore, addition of $NaBPh_4$ to the mother-liquor caused the precipitation of a mixture of *cis-* and *trans-*$[FeCl(CO)\{P(OEt)_3\}_4]BPh_4$.

trans-$[FeCl(CO)\{PPh(OEt)_2\}_4]BPh_4$. This compound was prepared following the method reported above starting from $FeCl_2$ in ethanol. In this case only the *trans* derivative was obtained as a yellow product which was crystallized from ethanol (yield $\geqslant 60\%$).

$[FeBr(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ and *trans-*$[FeBr(CO)-\{PPh(OEt)_2\}_4]BPh_4$. To a solution of $FeBr_2$ (1.08 g, 5 mmol) in ethanol (30 cm^3) was added diethoxyphenylphosphine (5 cm^3, 25 mmol) and the reaction mixture stirred for 3 h. Carbon monoxide (1 atm) was added and, after 3 h, the solution filtered. Addition of $NaBPh_4$ (1.7 g, 5 mmol) caused the precipitation of an orange product which was collected, washed with ethanol, and dried under vacuum. The more soluble $[FeBr(CO)_2\{PPh-(OEt)_2\}_3]BPh_4$ was extracted from the crude product with three 5-cm^3 portions of acetone. Addition of ethanol to this solution afforded a precipitate containing the two products which were removed by filtration. Orange crystals of $[FeBr-(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ separated by slow cooling of the remaining solution to $-30\,^\circ C$ and were collected, washed with ethanol, and dried under vacuum (yield $\geqslant 10\%$). Crystals of *trans-*$[FeBr(CO)\{PPh(OEt)_2\}_4]BPh_4$ were obtained by dissolving the orange residue in a mixture of ethanol–dichloromethane (30:5) at room temperature and cooling to $-30\,^\circ C$ (yield $\geqslant 50\%$).

$[FeBr(4-MeC_6H_4NC)_3L_2]BPh_4$ [L = $P(OMe)_3$, $P(OEt)_3$, or $PPh(OEt)_2$]. A warm solution of *cis-*$[FeBr(CO)L_4]BPh_4$ (2 mmol) in methanol or ethanol containing *p*-tolyl isocyanide (0.7 g, 6 mmol) was refluxed for 3 h. After the warm solution had been filtered, slow cooling to 4 °C caused the separation of red-orange crystals which were recrystallized from ethanol (yield $\geqslant 70\%$).

Physical Measurements.—Solution ^1H n.m.r. spectra were obtained with a Varian EM 390 spectrometer. Fourier-mode, proton-noise-decoupled ^{31}P n.m.r. spectra were collected on a Varian FT 80-A spectrometer operating at 32.203 MHz. All chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer. Solid-state spectra were obtained from KBr pellets; solution spectra were obtained using KBr cells. Electronic spectra were recorded on a Cary 219 spectrophotometer. Conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in nitromethane at 25 °C were measured with a 'Halosis' bridge. Magnetic susceptibility measurements were performed on powdered samples at

Table 1. Physical and analytical data

| | Analysis[a] (%) | | | |
Complex	C	H	M.p./°C	Λ_M/S cm² mol⁻¹
cis-[FeCl(CO){P(OMe)₃}₄]BPh₄	47.30 (47.55)	6.00 (6.05)	163	56.9
cis-[FeBr(CO){P(OMe)₃}₄]BPh₄	46.00 (45.40)	5.65 (5.75)	164	53.6
trans-[FeBr(CO){P(OMe)₃}₄]BPh₄	45.30 (45.40)	5.70 (5.75)	169	54.5
cis-[FeCl(CO){P(OEt)₃}₄]BPh₄	52.70 (53.35)	6.95 (7.30)	127	54.0
trans-[FeCl(CO){P(OEt)₃}₄]BPh₄	53.40 (53.35)	7.25 (7.30)	140	52.5
cis-[FeBr(CO){P(OEt)₃}₄]BPh₄	51.30 (51.30)	6.85 (7.05)	121	55.6
trans-[FeBr(CO){P(OEt)₃}₄]BPh₄	51.20 (51.30)	6.80 (7.05)	135	54.1
trans-[FeCl(CO){P(OEt)₃}₄][FeCl₄][b]	30.55 (30.60)	6.40 (6.15)	158	72.7
trans-[FeCl(CO){PPh(OEt)₂}₄]BPh₄	63.55 (63.40)	6.70 (6.55)	135	57.8
[FeBr(CO)₂{PPh(OEt)₂}₃]BPh₄	60.60 (60.85)	6.00 (5.95)	135	49.5
trans-[FeBr(CO){PPh(OEt)₂}₄]BPh₄	60.90 (61.20)	6.30 (6.30)	137	52.3
[FeBr(4-MeC₆H₄NC)₃{P(OMe)₃}₂]BPh₄[c]	61.65 (61.50)	5.80 (5.65)	116	57.2
[FeBr(4-MeC₆H₄NC)₃{P(OEt)₃}₂]BPh₄[d]	62.75 (63.30)	6.20 (6.30)	162	52.4
[FeBr(4-MeC₆H₄NC)₃{PPh(OEt)₂}₂]BPh₄[e]	67.70 (67.90)	6.05 (5.95)	180	48.0

[a] Calculated values in parentheses. [b] Cl, 17.20 (18.05)%. [c] N, 3.90 (4.00)%. [d] N, 3.70 (3.70)%. [e] N, 3.30 (3.50)%.
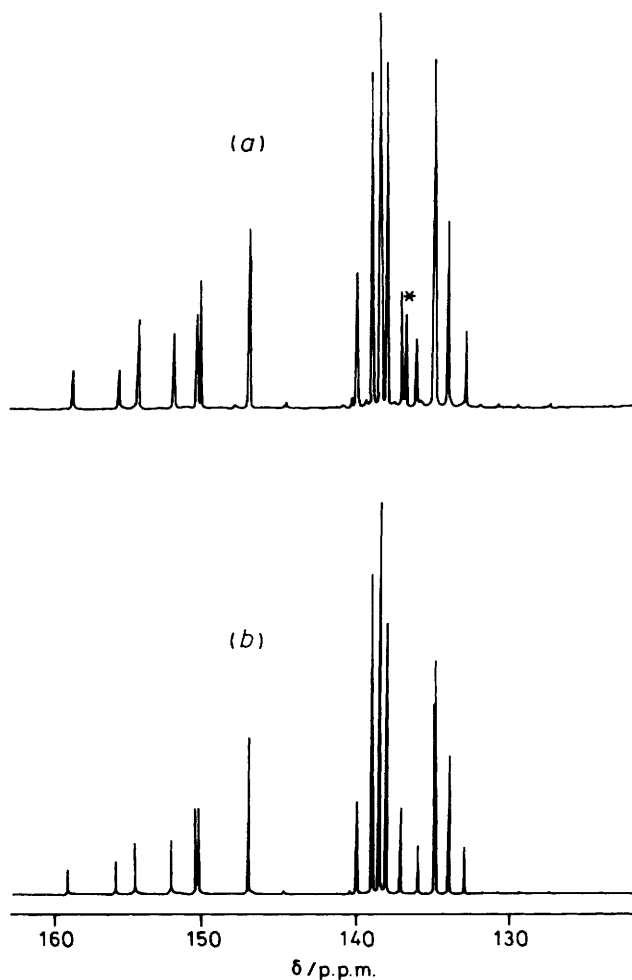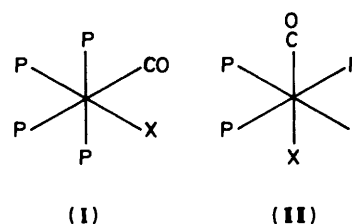

Figure. Observed (a) and calculated (b) ³¹P-{¹H} n.m.r. spectra for a (CD₃)₂CO solution of cis-[FeCl(CO){P(OEt)₃}₄]BPh₄. An impurity of trans-[FeCl(CO){P(OEt)₃}₄]BPh₄ is indicated by an asterisk

(I)   (II)

Results and Discussion

Carbon monoxide reacts at room temperature (1 atm) with FeX₂ (X = Cl or Br) solutions containing an excess of phosphite [P(OMe)₃ or P(OEt)₃] to give a mixture of cis- and trans-[FeX(CO)L₄]⁺ derivatives which can be separated by fractional crystallization. The reaction was carried out by varying the mol ratio FeX₂:L in the range 1:10—1:3 as well as by reacting with CO for several days, but in every case monocarbonyls were always obtained.

Selected properties of these complexes, which are crystalline yellow solids, stable in the solid state and in solution in polar organic solvents, are given in Table 2. The compounds are diamagnetic; conductivity values (Λ_M 52.5—56.9 S cm² mol⁻¹ in nitromethane) are in agreement with those reported for 1:1 electrolytes containing BPh_4^- as anion.[8] The ³¹P-{¹H} n.m.r. spectra of the cis-[FeX(CO)L₄]BPh₄ complexes show an AB₂X pattern [Figure (a)] at room temperature which remains unchanged from +40 to −80 °C. The experimental spectra can be simulated with the values listed in Table 2 and the good fit obtained between the observed and calculated spectra [Figure (b)] suggests the cis geometry (I) for the cations. On the other hand, the ³¹P-{¹H} spectra of the trans-[FeX(CO)L₄]⁺ derivatives in the temperature range +40 to −80 °C consist of only one peak at +136 to +140 p.p.m., indicating the presence of four equivalent phosphorus nuclei as expected for geometry (II).

The i.r. spectra of both the cis and trans isomers in the CO stretching region show only one band at 2 021—2 036 cm⁻¹ (cis) and at 1 998—1 992 cm⁻¹ (trans) in dichloromethane solution. The lowering of ν(CO) by ca. 25 cm⁻¹ in the trans complexes is attributable to the position of the halogen ligand, which lengthens the π-bond of the carbon monoxide when it is trans to this ligand. Furthermore, comparison of the i.r. spectra of these monocarbonyl Feᴵᴵ complexes with [FeX(CO)(depe)]BPh₄ (depe = Et₂PCH₂CH₂PEt₂)[1d] and [FeCl(CO)(pdma)]BPh₄

ambient temperature with a Cahn Instrument Faraday balance, using Hg[Co(NCS)₄] as standard. Solution susceptibilities were determined by the Evans' method.[7]

Table 2. Selected infrared, n.m.r., and electronic absorption data for the iron(II) complexes

Compound	v(CO)[a]/cm⁻¹	v(CN)[a]/cm⁻¹	δ(¹H)[b] CH₃ of P ligand	δ(¹H)[b] 4-MeC₆H₄NC	Spin system	³¹P-{¹H} N.m.r. δ[b,c]	³¹P-{¹H} N.m.r. J/Hz	Visible spectra[d] λmax./nm (ε/dm³ mol⁻¹ cm⁻¹)
cis-[FeCl(CO){P(OMe)₃}₄]BPh₄	2 036s (2 024s)		3.86 (m)		AB₂X	δA 140.3, δB 141.7, δX 157.3	J(AB) 141.5, J(AX) 132.2, J(BX) 122.3	368 (760), 410 (sh)
cis-[FeBr(CO){P(OMe)₃}₄]BPh₄	2 030s (2 022s)		3.86 (m)		AB₂X	δA 141.3, δB 142.2, δX 162.7	J(AB) 55.0, J(AX) 127.0, J(BX) 120.0	405 (460)
cis-[FeCl(CO){P(OEt)₃}₄]BPh₄	2 030s (2 021s)		1.33 (t), 1.30 (t)		AB₂X	δA 135.3, δB 137.4, δX 151.9	J(AB) 138.0, J(AX) 132.8, J(BX) 127.5	406 (450)
cis-[FeBr(CO){P(OEt)₃}₄]BPh₄	2 021s (2 023s)		1.37 (t), 1.35 (t)		AB₂X	δA 136.7, δB 137.6, δX 157.8	J(AB) 55.0, J(AX) 129.0, J(BX) 120.0	408 (500)
trans-[FeBr(CO){P(OMe)₃}₄]BPh₄	1 998s (1 991s)		3.91 (m)			+140.38		390 (850)
trans-[FeCl(CO){P(OEt)₃}₄]BPh₄	1 992s (1 990s)		1.32 (t)			+136.88		380 (1 300)
trans-[FeCl(CO){P(OEt)₃}₄][FeCl₄][e]	1 996s (1 995s)							313 (8 400), 365 (8 400)
trans-[FeBr(CO){P(OEt)₃}₄]BPh₄	1 996s (1 990s)		1.34 (t)			+136.54		375 (1 200)
trans-[FeCl(CO){PPh(OEt)₂}₄]BPh₄	1 972s (1 972s)		1.23 (t)			+163.86		365 (2 900)
trans-[FeBr(CO){PPh(OEt)₂}₄]BPh₄	1 975s (1 980s)		1.26 (t)			+164.0		390 (1 200)
[FeBr(CO)₂{PPh(OEt)₂}₃]BPh₄	2 065s, 2 013s (2 063s, 2 006s)		1.35 (t), 1.29 (t)		AB₂	δA 157.8, δB 156.9	J(AB) 130.0	351 (1 400), 404 (1 200)
[FeBr(4-MeC₆H₄NC)₃{P(OMe)₃}₂]BPh₄		2 185m, 2 144s, [2 187m, 2 141s, 2 040 (sh)]	3.98 (t)	2.38 (s), 2.33 (s)		+147.17		403 (1 100)
[FeBr(4-MeC₆H₄NC)₃{P(OEt)₃}₂]BPh₄		2 184m, 2 142s, 2 040 (sh) [2 183m, 2 140s, 2 038 (sh)]	1.29 (t)	2.37 (s), 2.33 (s)		+141.87		400 (1 100)
[FeBr(4-MeC₆H₄NC)₃{PPh(OEt)₂}₂]BPh₄		2 180m, 2 140s, 2 040 (sh) [2 175m, 2 132s, 2 038 (sh)]	1.33 (t)	2.37 (s)		+168.95		338 (1 400), 404 (1 100)

[a] In CH₂Cl₂ (KBr). [b] At room temperature in (CD₃)₂CO. [c] Positive shift downfield from 85% H₃PO₄. [d] In CH₂Cl₂. [e] A strong band at 377 cm⁻¹ in the i.r. spectrum due to v(Feᴵᴵᴵ–Cl) and μeff. = 5.7 confirm the presence of the [FeCl₄]⁻ anion.

[pdma = o-phenylenebis(dimethylarsine)] [1e] show increased v(CO) (90 cm⁻¹) in our derivatives, in agreement with the better π-acceptor properties of phosphites, P(OR)₃, as compared to the phosphine or arsine ligands.

Surprisingly, when employing PPh(OEt)₂, the reaction with CO depends on the nature of the starting FeX₂ salt. While with FeCl₂ only trans-[FeCl(CO){PPh(OEt)₂}₄]⁺ was obtained, reaction with FeBr₂ gave a mixture of trans-[FeBr(CO){PPh-(OEt)₂}₄]⁺ and the new dicarbonyl derivative[FeBr(CO)₂{PPh-(OEt)₂}₃]⁺. Its formulation is supported by elemental analysis, conductivity, i.r., and n.m.r. data. In CH₂Cl₂ solution the i.r. spectrum shows two strong bands at 2 065 and 2 013 cm⁻¹ indicating a cis arrangement of the two carbonyl ligands. The ³¹P-{¹H} n.m.r. spectrum is an AB₂ system (parameters reported in Table 2). Although these data do not allow us to

(III)   (IY)
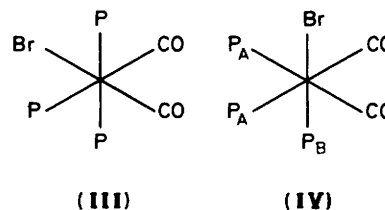
discern between mer or fac geometry, the ³¹P chemical shift values seem to indicate a mer structure (III) for the complex. Generally the ligand trans to the phosphorus atom strongly affects its ³¹P chemical shift and when the ligand is a halide, structure (IV), it causes the ³¹P resonance of the trans phosphine to shift to low field compared to a similar complex

with a carbonyl (or tertiary phosphine) *trans* to the phosphine.[9] In the *cis*-[FeX(CO)L$_4$]$^+$ derivatives also, a resonance located at *ca*. 20 p.p.m. to low field of the other two (Table 2) is observed and can be attributed to the phosphorus *trans* to the halogen. In [FeBr(CO)$_2$\{PPh(OEt)$_2$\}$_3$]BPh$_4$, the two ^{31}P chemical shifts show very close values as expected for (**III**); a *fac* structure, (**IV**), on the other hand, should show the P$_B$ resonance strongly separated from P$_A$.

The formation of octahedral monocarbonyl derivatives of iron(II) in the carbonylation reaction of FeX$_2$ solutions seems to be peculiar to the P(OMe)$_3$ and P(OEt)$_3$ phosphites used. While with tertiary phosphines (PR$_3$) and secondary phosphines (PHR$_2$), whose steric hindrance changes extensively, dicarbonyl complexes were always obtained,^{1a,f} when using the P(OMe)$_3$ and P(OEt)$_3$ phosphites of better π-acceptor properties than PR$_3$, the monocarbonyl species could be prepared. By decreasing the π-acidity using PPh(OEt)$_2$, [FeBr(CO)$_2$\{PPh(OEt)$_2$\}$_3$]$^+$ was isolated together with the monocarbonyl. With bidentate phosphine or arsine ligands (L–L), however, monocarbonyl complexes [FeX(CO)(L–L)$_2$]$^+$ have previously been obtained,^{1d,e} but in this case the bidentate nature of the ligand forces the observed stoicheiometry.

Both *cis*- and *trans*-[FeX(CO)L$_4$]$^+$ react at room temperature with 4-MeC$_6$H$_4$NC to give the mixed-ligand complexes [FeX(4-MeC$_6$H$_4$NC)$_3$L$_2$]BPh$_4$ as shown in equation (1). The

$$[FeX(CO)L_4]^+ + 3CNC_6H_4Me\text{-}4 \longrightarrow$$
$$[FeX(4\text{-}MeC_6H_4NC)_3L_2]^+ + CO + 2L \quad (1)$$
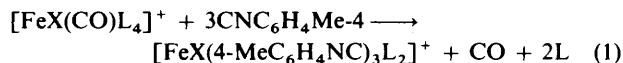
cation [FeBr(CO)$_2$\{PPh(OEt)$_2$\}$_3$]$^+$ also reacts with *p*-tolyl isocyanide to form [FeBr(4-MeC$_6$H$_4$NC)$_3$\{PPh(OEt)$_2$\}$_2$]$^+$. It can be noted, however, that while the Br derivatives were isolated in the solid state and characterized, the Cl complexes, owing to their oily nature, were only detected in solution. This reaction was also studied by changing the molar ratio between the starting compounds and the isocyanide in the range 1:1— 1:10, but in every case the formation of the tris(isocyanide) derivative was observed.

Good elemental analyses were obtained for the complexes, which are orange microcrystalline solids, diamagnetic, and 1:1 electrolytes. The i.r. spectra in dichloromethane solution show a band of medium intensity at *ca*. 2 184 cm^{-1}, a strong band at 2 142—2 144 cm^{-1}, and a weak one at 2 040 cm^{-1} in the CN stretching region. The same bands appear slightly shifted in the solid state. However, they do not allow us to distinguish clearly between a *fac* or *mer* structure. In the temperature range +40 to −80 °C the ^{31}P-\{^{1}H\} n.m.r. spectra show only one singlet, revealing the existence of two magnetically-equivalent phosphite ligands. Furthermore, the ^{1}H n.m.r. spectrum of [FeBr(4-MeC$_6$-H$_4$NC)$_3$\{P(OMe)$_3$\}$_2$]$^+$ appears, in the phosphite methyl proton region, as a triplet at δ 3.98 indicating a mutual *trans* position of the two phosphite ligands. The spectra of the P(OEt)$_3$ derivatives also agree with a *trans* arrangement. Therefore, on the basis of the n.m.r. data, *mer* structure (V) can be proposed in solution for these derivatives.

Mixed-ligand phosphine–isocyanide iron(II) complexes have previously been reported[10] by us with PPh(OEt)$_2$ or PPh$_3$ ligands, but no trimethoxy- or triethoxy-phosphine derivatives have ever been prepared. Now, by using the monocarbonyls [FeX(CO)L$_4$]$^+$ as starting materials, the synthesis of these derivatives too has been achieved.

Reaction of lithium halide with a suspension of [FeX(CO)L$_4$]$^+$ leads to an oily product whose i.r. spectra do not display any ν(CO) band, indicating substitution of CO by the halide ion.

(**V**)
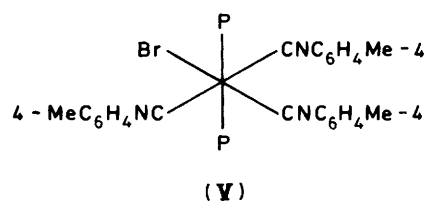
Carbon monoxide does not react with [FeX(CO)L$_4$]$^+$ at room temperature (1 atm) within a two-week period and the starting complexes can be recovered unchanged, thus supporting the hypothesis that substitution of a phosphite or halogen ligand to give a dicarbonyl complex does not take place.

Treatment with nitric oxide results in some decomposition, but no nitrosyl species is detected.

In the case of P(OMe)$_3$ or P(OEt)$_3$ derivatives, excess of phosphite gives rise to CO substitution to produce [FeXL$_5$]$^+$.[11]

An acetonitrile solution of [FeX(CO)L$_4$]$^+$ [L = P(OMe)$_3$, P(OEt)$_3$ or PPh(OEt)$_2$] is reduced by zinc dust, affording the new monohydride [FeH(CO)L$_4$]$^+$. This reaction, however, needs further investigation and will be reported in a forthcoming paper.

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