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THE INFLUENCE OF PHOSPHINE LIGANDS ON THE STOICHIOMETRY OF MIXED-LIGAND HEXACOORDINATE IRON(II) COMPLEXES WITH ISOCYANIDES AND PHOSPHINES

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Summary

The synthesis and characterization of complexes of the type [FeX(4-CH_3-$C_6H_4NC)_nL_{5-n}]ClO_4$ (X = Cl, Br, or I; n = 2, 3 or 4; L = $PhPMe_2$, $PhPEt_2$, Ph_2PMe, Ph_2PEt, or $Ph_2P(OEt)$) are described. The steric hindrance by the phosphine ligand is tentatively correlated with the influence of the π-acidity of phosphine and isocyanide ligands in determining the composition of these compounds. Their structures have been postulated on the basis of infrared and PMR spectra. Mössbauer parameters have also been determined at liquid nitrogen temperature by a treatment of the data by the point-charge model.

Introduction

Mixed-ligand iron(II) complexes of the type $\{FeCl(CNR)_2[PPh(OEt)_2]_3\}$ (R = phenyl, 4-methylphenyl, 4-methoxyphenyl, 4-nitrophenyl, 2-methylphenyl, or 2,6-dimethylphenyl) have been recently described [1]. Their stoichiometry and structures have been tentatively rationalized in terms of σ-donor and π-acceptor properties of isocyanide and phosphine ligands. Since steric hindrance should also play an important role in determining the phosphine/isocyanide ratio, we have prepared a new series of mixed-ligand iron(II) complexes in which phosphines of different cone angle [2] and/or π-acceptor properties are used as ligands. The interrelationship between steric and electronic properties of ligands and stoichiometry should be apparent in these octahedral iron(II) derivatives. Furthermore with the aim of understanding the influence of the halide ligand

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on the stability of such compounds we have prepared the corresponding chloro, bromo, and iodo derivatives. Their structures have been studied by IR, NMR, and Mössbauer spectroscopy.

Experimental

Materials. Commercial reagent grade chemicals and anhydrous iron(II) halides were used without further purification. The solvents were purified, dried by standard methods, and distilled under a stream of nitrogen immediately before use. 4-Tolylisocyanide was obtained by the phosgene method of Ugi et al. [3,4] or by the improved Hofman carbilamine syntheses [4]. Ethyl diphenylphosphonite, $Ph_2P(OEt)$, was prepared by the method of Rabinowitz and Pellon [6]. Phenyldimethyl phosphine, phenyldiethylphosphine, diphenylmethylphosphine and diphenylethylphosphine were reagent grade chemicals obtained from Maybridge Chemical Co., LTD.

Apparatus. Infrared spectra of KBr pellets and dichloromethane solutions were recorded on a Perkin—Elmer 621 spectrophotometer. PMR measurements were made with a Bruker HFX-10 instrument using TMS as internal reference. Conductivities of 10^{-3} *M* solutions of complexes in nitrobenzene at 25°C, were measured with a LKB bridge. Mössbauer spectra were recorded at liquid nitrogen temperature with the spectrometer previously described [7] using a 50 mCi $^{57}Co/Rh$ source (The Radiochemical Centre-Amershan). The velocity scale was calibrated by an enriched iron foil and the centre shifts are quoted relative to sodium nitroprusside at room temperature. The complexes containing bromide and iodide showed very low count rates and small peak intensities. At room temperature, the Mössbauer effect was detected only for the $\{FeCl(4\text{-}CH_3C_6H_4NC)_3[Ph_2P(OEt)]_2\}ClO_4$ complex.

All spectra were fitted to two Lorentzian line shapes with an iterative least squares program [8] adapted for use on the Cyber 76 CDC computer. The data are accurate to ± 0.03 mm s^{-1}.

Synthesis of complexes

Preparations were carried out under nitrogen. Once isolated, all the complexes were found to be stable under normal laboratory conditions, and were manipulated without special precautions.

The complexes of the type $[FeX(4\text{-}CH_3C_6H_4NC)_nL_{5-n}]ClO_4$ (X = Cl, Br, or I; n = 2, 3, or 4; L = $PhPMe_2$, $PhPEt_2$, Ph_2PMe, Ph_2PEt, or $Ph_2P(OEt)$) were prepared by the following general procedure. A mixture of iron(II) halide (10 mmol) and the appropriate phosphine (40 mmol) in 60 ml of anhydrous ethanol was stirred at room temperature for 1 hour under nitrogen. Addition of 4-tolylisocyanide (4.7 g, 40 mmol) caused a color change from yellow or orange to red. A saturated solution of lithium perchlorate (1.07 g, 10 mmol) in anhydrous ethanol was then added, to give a precipitate, which was recrystallized from ethanol. In the case of the $\{FeX(4\text{-}CH_3C_6H_4NC)_n[Ph_2P(OEt)]_{5-n}\}ClO_4$ complexes (X = Cl or Br; n = 3 or 4) after the addition of $LiClO_4$, an oil was obtained which was chromatographed on silica gel using ethanol as eluent. A single fraction was collected and concentrated to about 20—30 ml. The crystals separated after standing overnight at room temperature and were filtered off. The yields were ⩾85%.

Results

Products. The cationic complexes described in this paper were prepared by adding 4-tolylisocyanide at room temperature to an anhydrous ethanolic solution of iron(II) halide and the appropriate phosphine or phosphite. The same compounds were obtained when the molar ratios between the iron(II) halide, the phosphine and the 4-tolylisocyanide were changed from 1/3/3 to 1/10/10. When phosphine or phosphite is added to a solution of anhydrous iron(II) halide in ethanol, $[FeX_2(PR_3)_2]$ complexes should be formed [9]. However, it was possible to isolate only the triphenyl phosphine complexes [10], probably because the complexes of other phosphines dissociate in solution, particularly in hydroxylic solvents. Moreover, the existence of octahedral iron(II) derivatives of the type $[FeX_2(PR_3)_4]$ cannot be excluded. After the addition of the isocyanide the final product was precipitated by adding a solution of lithium perchlorate. Several attempts were made to prepare chloro derivatives, but intractable oils were always obtained; however, their IR and PMR spectra seem to indicate that the chloro complexes were formed. These mixed-ligand iron(II) complexes are red-brown or orange solids which can be handled under normal laboratory conditions. In order to remove traces of iron(III) complexes to obtain reliable PMR and IR spectra, the recrystallized complexes were chromatographed on silica gel using ethanol as an eluent. These chromatographed samples are diamagnetic, 1/1 electrolytes in nitrobenzene solution (25.0 to 23.7 ohm^{-1} M^{-1} cm^2), readily soluble in polar organic solvents such as acetone, 1,2-dichloroethane and dichloromethane and are slightly soluble in diethyl ether, benzene and hydrocarbons. The yields were high ($\simeq$85%) in each case, except for $\{FeCl(4\text{-}CH_3C_6H_4NC)_3[Ph_2P(OEt)]_2\}ClO_4$, due to its relatively high solubility in ethanol. The complexes were characterized by elemental analyses (Table 1), and infrared (Table 3) and PMR spectra (Table 4).

Mössbauer spectra. The observed Mössbauer values at liquid nitrogen temperature are listed in Table 2. To rationalize the measured centre shifts (*CS*) and the quadrupole splitting (*QS*), the relation $CS = 0.21 + \Sigma(\text{pcs})_i$ [11] and the point-charge model are used. The employed partial center shift (pcs) and partial quadrupole splitting (pqs) values, at nitrogen temperature in nm s^{-1}, are respectively: Cl (0.10; —0.30), Br (0.13; —0.28), I (0.13; —0.29), Ph_2PMe, Ph_2PEt (0.07; —0.58) [12] and $4\text{-}CH_3C_6H_4NC$ (—0.02; —0.70) [13]. Because the pcs and pqs values for the PMe_3 ligand are respectively 0.06 and —0.66 mm s^{-1} [12] we tentatively assume these values for the unknown values of $PhPMe_2$ and $PhPEt_2$. Analogously the (0.04; —0.63) values [12] of $P(OEt)_3$ are assumed for the $Ph_2P(OEt)$ ligand.

The predicted centre shift values are in parentheses in Table 2. The agreement between observed and calculated values is good, allowing for the inherent errors and assumptions, in fact the $|CS_{\text{obs}} - CS_{\text{calc}}|$ differences are less than 0.2 mm s^{-1}.

The calculated quadrupole splittings and the asymmetry parameters for the *mer*-, *fac*-, and *trans*-geometrical isomers of the $[FeX(CNR)_3L_2]^+$ (X = Br or I; L = Ph_2PMe, $PhPEt_2$) and $\{FeCl(CNR)_4[Ph_2P(OEt)]\}^+$ cations are reported in Table 2 together with the *cis*- and *trans*-geometrical isomers of the $\{FeX(CNR)_4[Ph_2P(OEt)]\}^+$ (X = Br or I) cations. The choice of axes is always such as to

(continued on p. 56)

TABLE 1

SOME PROPERTIES OF $[FeX(4\text{-}CH_3C_6H_4NC)_nL_{5-n}]ClO_4$ (X = Cl, Br or I; n = 2, 3 or 4; L = phosphine) COMPLEXES

Compound	Color	M.p. [a] (°C)	Molar conductance [b]	Analysis (Found (calcd.) (%))		
				C	H	N
$\{FeI(4\text{-}CH_3C_6H_4NC)_2[PPh(Me)_2]_3\}ClO_4$	Red-brown	124	25.0	51.55 (51.60)	5.43 (5.09)	2.77 (3.01)
$\{FeBr(4\text{-}CH_3C_6H_4NC)_3[PPh(Et)_2]_2\}ClO_4$	Yellow-orange	102	24.3	57.13 (57.50)	5.75 (5.59)	4.38 (4.57)
$\{FeI(4\text{-}CH_3C_6H_4NC)_3[PPh(Et)_2]_2\}ClO_4$	Red-brown	83	24.5	54.26 (54.70)	5.78 (5.32)	3.99 (4.35)
$\{FeBr(4\text{-}CH_3C_6H_4NC)_3[P(Ph)_2Me]_2\}ClO_4$	Red-brown	182	24.4	61.37 (60.84)	4.89 (4.80)	4.18 (4.25)
$\{FeI(4\text{-}CH_3C_6H_4NC)_3[P(Ph)_2Me]_2\}ClO_4$	Red-brown	178	23.7	57.95 (58.07)	4.63 (4.58)	4.00 (4.06)
$\{FeBr(4\text{-}CH_3C_6H_4NC)_3[P(Ph)_2Et]_2\}ClO_4$	Red-brown	197	25.0	61.50 (61.52)	5.00 (5.06)	4.16 (4.14)
$\{FeI(4\text{-}CH_3C_6H_4NC)_3[P(Ph)_2Et]_2\}ClO_4$	Red-brown	188	24.2	58.54 (58.80)	5.00 (4.84)	3.85 (3.96)
$\{FeCl(4\text{-}CH_3C_6H_4NC)_3[P(Ph)_2(OEt)]_2\}ClO_4$ [c]	Yellow	179	25.0	61.39 (62.29)	5.29 (5.13)	4.42 (4.19)
$\{FeBr(4\text{-}CH_3C_6H_4NC)_4[P(Ph)_2(OEt)]\}ClO_4$	Yellow-orange	214	24.2	59.11 (59.15)	4.80 (4.64)	5.84 (6.00)
$\{FeI(4\text{-}CH_3C_6H_4NC)_4[P(Ph)_2(OEt)]\}ClO_4$	Red-orange	211	24.7	55.90 (56.31)	4.42 (4.42)	5.58 (5.71)

[a] Melting points were determined in capillaries and uncorrected. [b] Molar conductance (expressed in cm^2/ohm mol) were determined in 10^{-3} *M* nitrobenzene solution at 25°C. [c] Cl: found, 7.36; calcd., 7.07.

TABLE 2

OBSERVED AND CALCULATED (in parenthesis) MÖSSBAUER PARAMETERS AT LIQUID NITROGEN TEMPERATURE (in mm s^{-1}), FOR *mer*-, *fac*-, all-*trans*- AND *trans,cis*-ISOMERS

Compound [a]	*QS*	*QS*	*mer*		*fac* [b]	all-*trans*		*trans* [b]	*cis* [b]	
			QS	η	*QS*	*QS*	η	*QS*	*QS*	η
$\{FeI(CNR)_2[PPh(Me)_2]_3\}ClO_4$	0.37 (0.48)	0.53	(0.70	0.17)	(0.82) [c]	(0.83 [c]	0.29)			
$\{FeBr(CNR)_3[PPh(Et)_2]_2\}ClO_4$	0.33 (0.40)	0.71	(0.88	0.14)	(0.76)	(0.77	0.32)			
$\{FeI(CNR)_3[PPh(Et)_2]_2\}ClO_4$	0.21 (0.40)	0.76	(0.86	0.14)	(0.74)	(0.75	0.32)			
$\{FeBr(CNR)_3[P(Ph)_2Me]_2\}ClO_4$	0.25 (0.42)	0.68	(0.98 [c]	0.37)	(0.60)	(−0.73	0.82)			
$\{FeI(CNR)_3[P(Ph)_2Me]_2\}ClO_4$	0.22 (0.42)	0.75	(0.96 [c]	0.38)	(0.58)	(−0.71	0.78)			
$\{FeBr(CNR)_3[P(Ph)_2Et]_2\}ClO_4$	0.27 (0.42)	0.65	(0.98 [c]	0.37)	(0.60)	(−0.73	0.82)			
$\{FeI(CNR)_3[P(Ph)_2Et]_2\}ClO_4$	0.24 (0.42)	0.70	(0.96 [c]	0.38)	(0.58)	(−0.71	0.78)			
$\{FeCl(CNR)_3[P(Ph)_2(OEt)]_2\}ClO_4$	0.33 (0.33)	0.65	(0.81	0.04)	0.78	(0.78	0.08)			
$\{FeBr(CNR)_4[P(Ph)_2(OEt)]\}ClO_4$	0.40 (0.30)	0.82	—		—	—		(0.98)	(0.78	0.27)
$\{FeI(CNR)_4[P(Ph)_2(OEt)]\}ClO_4$	0.38 (0.30)	0.80	—		—	—		(0.96)	(0.76	0.28)

[a] CNR = 4-$CH_3C_6H_4NC$. [b] $\eta = 0$. [c] $||QS_{found}| - |QS_{calcd}|| < 0.20$ mm s^{-1}.

TABLE 3

ν(CN) FREQUENCIES (cm^{-1}) OF IRON(II) COMPLEXES DISCUSSED IN THIS PAPER ($CHCl_2$ solution)

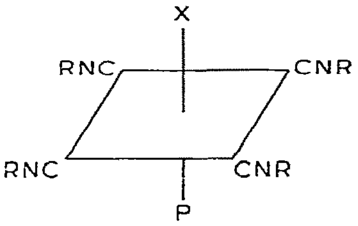
Compound [a]	ν(CN) [b]		
$\{FeI(CNR)_2[PPh(Me)_2]_3\}ClO_4$	2130s	2091s	
$\{FeBr(CNR)_3[PPh(Et)_2]_2\}ClO_4$	2167w	2129s	2112(sh)
$\{FeI(CNR)_3[PPh(Et)_2]_2\}ClO_4$	2163w	2124s	2112(sh)
$\{FeBr(CNR)_3[P(Ph)_2Me]_2\}ClO_4$	2169w	2130s	2120(sh)
$\{FeI(CNR)_3[P(Ph)_2Me]_2\}ClO_4$	2164w	2123s	
$\{FeBr(CNR)_3[P(Ph)_2Et]_2\}ClO_4$	2170w	2132s	2120(sh)
$\{FeI(CNR)_3[P(Ph)_2Et]_2\}ClO_4$	2165w	2128s	2120(sh)
$\{FeCl(CNR)_3[P(Ph)_2(OEt)]_2\}ClO_4$	2184w	2150s	2118(sh)
$\{FeBr(CNR)_4[P(Ph)_2(OEt)]\}ClO_4$	2206vw	2165s	
$\{FeI(CNR)_4[P(Ph)_2(OEt)]\}ClO_4$	2205vw	2162s	

[a] CNR = $4\text{-}CH_3C_6H_4NC$ (ν(CN) 2129 cm^{-1}). [b] Frequencies are ±0.5 cm^{-1}.

preserve the convention $|V_{XX}| \leqslant |V_{YY}| \leqslant |V_{ZZ}|$ (cf. ref. 13) for drawings and electric field gradient expressions).

From Table 2 some structural assignments may be made taking ±0.20 mm s^{-1} as satisfactory agreement between observed and calculated *QS* magnitudes [12, 14].

Structures. On the basis of IR and NMR spectra a *trans*-structure (I) is proposed for the $\{FeX(4\text{-}CH_3C_6H_4NC)_4[Ph_2P(OEt)]\}ClO_4$ (X = Br or I) complexes in solution.



(I)

A single intense ν(CN) band at 2162 (X = I) or 2165 (X = Br) cm^{-1}, which can be attributed to the e_u mode, is found in the infrared spectra (Table 3). The very weak high-frequency satellite absorption at 2205—2206 cm^{-1} may be tentatively assigned to the Raman-active a_{1g} or b_{1g} modes [15]. This seems to be consistent with Bigorgne's infrared and Raman data [16] found for analogous carbonyl complexes. Furthermore, the absence of any absorption in the 1800—1600 cm^{-1} region excludes bridging isocyanides indicating a monomeric structure for these complexes. In the PMR spectra a sharp singlet appears at τ 7.61 (X = I) or 7.58 ppm (X = Br) due to the methyl protons of the 4-tolylisocyanide ligand, indicating that these four ligands are magnetically equivalent as expected for structure I. From the observed and calculated (for *cis* and *trans* isomers) Mössbauer quadrupole splittings of I (Table 2) it is impossible to define the geometrical arrangement of ligands from the pqs alone. The theoretical values

TABLE 4

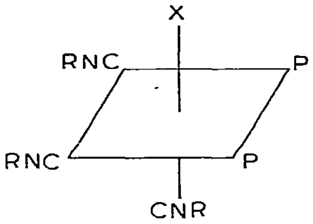
^{1}H NMR SPECTRAL DATA FOR SOME MIXED-LIGAND IRON(II) COMPLEXES [a]

Compound [b]	Chemical shifts (τ (ppm) relative to TMS internal standard)									
	Phenyl protons (phosphine and/or isocyanide)				CH_2 phosphine	CH_3 isocyanide		CH_3 phosphine		
$\{FeI(CNR)_2[PPh(Me)_2]_3\}ClO_4$ [c]	2.55d	2.72s	2.79s	3.22m	—	7.63s		8.08s	8.12s	8.16s
$\{FeBr(CNR)_3[PPh(Et)_2]_2\}ClO_4$ [d]	2.38d	2.75s	2.83s	3.00m	7.49sx	7.61s			8.84qi (8 Hz)	
$\{FeI(CNR)_3[PPh(Et)_2]_2\}ClO_4$	2.42m	2.74s	2.83s	2.99m	7.45sx	7.61s			8.87qi (8 Hz)	
$\{FeBr(CNR)_3[P(Ph)_2Me]_2\}ClO_4$	2.24m	2.67d	2.87s	3.04m	—	7.63s	7.73s		7.63t (4 Hz)	
$\{FeI(CNR)_3[P(Ph)_2Me]_2\}ClO_4$	2.25m	2.69d	2.87s	3.00m	—	7.63s	7.74s		7.49t (4 Hz)	
$\{FeBr(CNR)_3[P(Ph)_2Et]_2\}ClO_4$	2.27m	2.67s	2.84s	3.04m	7.10sx	7.64s	7.74s		9.04qi (8 Hz)	
$\{FeI(CNR)_3[P(Ph)_2Et]_2\}ClO_4$	2.30d	2.69d	2.89s	3.04m	7.02sx	7.63s	7.73s		9.12qi (8 Hz)	
$\{FeCl(CNR)_3[P(Ph)_2(OEt)]_2\}ClO_4$	2.52s			3.22m	6.34br	7.60s	7.73s		8.98t (7 Hz)	
$\{FeBr(CNR)_4[P(Ph)_2(OEt)]\}ClO_4$	2.38m			2.78s	6.31qi	7.58s			8.78t (7 Hz)	
$\{FeI(CNR)_4[P(Ph)_2(OEt)]\}ClO_4$	2.37d			2.78s	6.27qi	7.61s			8.76t (7 Hz)	

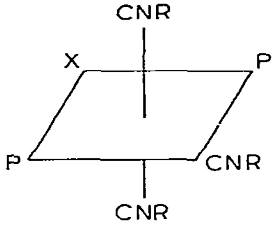
[a] The spectra were measured in $CDCl_3$. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; qi, quintet; sx, sextet; m, multiplet; br, broad.
[b] CNR = $4\text{-}CH_3C_6H_4NC$. Chemical shifts (τ, ppm): 2.90(br) (phenyl protons), 7.76s(CH_3). [c] In $(CD_3)_2CO$; CH_3 phosphine resonance appears (−20°C) as a triplet (1/2/1) at τ 8.02 ppm (4 Hz) and a doublet at τ 8.08 ppm (8 Hz). [d] In $(CD_3)_2CO$; CH_3 isocyanide resonance appears at τ 7.58 and 7.61 ppm (−60°C), and at τ 7.60 ppm (+5°C).

calculated for both *cis*- and *trans*-structures are quite close, (ratio 1/1.26) * the experimental value being intermediate between them.

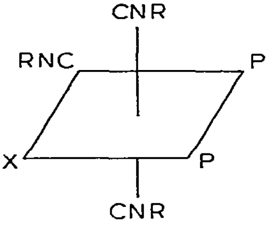
In the case of the $[FeX(4\text{-}CH_3C_6H_4NC)_3L_2]^+$ (X = Cl, Br, or I; L = Ph_2PMe, $Ph_2P(OEt)$, Ph_2PEt, or $PhPEt_2$) cations, the structural possibilities II—IV must be considered:



(II)
(fac)



(III)
(all-trans)



(IV)
(mer)

The infrared spectra in the ν(CN) stretching region shows a weak absorption at 2163—2184 cm^{-1} and an intense band at 2123—2150 cm^{-1}, which can be attributed to the a_1 and b_1 modes of the two isocyanides in *trans* positions, respectively (III or IV). The band usually present at 2120—2112 cm^{-1} may be tentatively assigned to the third isocyanide. Similar results have been previously reported [17].

Structure II should have two IR bands of comparable intensity and can be excluded on this basis. However, since the compounds are ionic, it was possible to measure their IR spectra only in polar solvents, where the bands are quite broad and inadequately resolved. The PMR spectra of the $[FeX(4\text{-}CH_3C_6H_4NC)_3(phosphine)_2]ClO_4$ complexes in $CDCl_3$ (Table 4) show two resonance lines with an intensity ratio of 2/1 in the range τ 7.60—7.74 ppm due to the isocyanide methyl protons, indicating that two isocyanides are magnetically equivalent and different from the third. A singlet is observed when the phosphine ligand is $PhPEt_2$ at τ 7.61 ppm for both the bromo and iodo derivatives. However, on lowering the temperature to —60°C this singlet is split into two resonance lines at τ 7.58 and 7.61 ppm (1/2). These data indicate that this molecule is not stereochemically rigid at room temperature. This seems to be the first example of a non-rigid hexacoordinate iron(II) complex containing only monodentate ligands. These results do not, however, allow any distinction between structures II, III, and IV.

Much better structural insights have been obtained from the signals due to the phosphine protons. The resonance lines of the phosphine methyl protons in the $[FeX(4\text{-}CH_3C_6H_4NC)_3(Ph_2PMe)_2]^+$ cations appear in chloroform-*d* as a 1/2/1 triplet at τ 7.63 (X = Br) or 7.49 ppm (X = I) with an apparent *J*(PH) of 4 Hz due to the strong "virtual" coupling between the two phosphorous nuclei. An analogous "virtual" coupling is also observed for the phenyldiethyl- and diphenylethyl-phosphine derivatives. In these last cases, the resonance lines of the methyl protons of the phosphine are observed as a 1/4/6/4/1 quintet at

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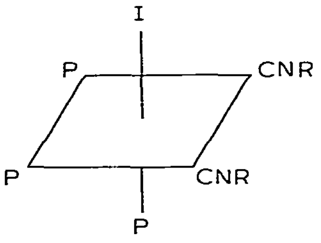
* A ratio of 1/2 was found instead for *cis,trans*-$FeX_2(4\text{-}CH_3C_6H_4NC)_4$ complexes (cf. ref. 13).

τ 8.84 (X = Br) or 8.87 (X = I) ppm for $PhPEt_2$ (apparent J 8 Hz) and at τ 9.04 (X = Br) or 9.12 ppm (X = I) for Ph_2PEt (apparent J 8 Hz) corresponding to coupling with both the methylene protons and the two phosphorous nuclei. Furthermore, a sextet between τ 7.02—7.49 ppm (apparent J 7 Hz) is observed for the methylene protons. The PMR spectrum of the $\{FeCl(4\text{-}CH_3C_6H_4NC)_3[Ph_2P(OEt)]_2\}ClO_4$ complex shows a 1/2/1 triplet at τ 8.98 ppm (J(PH) 7 Hz) due to the phosphine's methyl protons, while the methylene protons appear as an unresolved multiplet at τ 6.34 ppm.

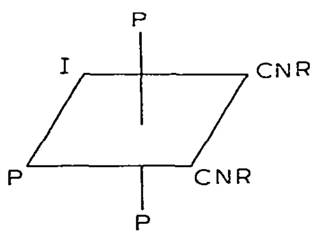
Verkade et al. [18] reported the ^{31}P—^{31}P coupling constants for over 30 complexes containing two phosphorus ligands. The repeated observations that ^{31}P—^{31}P coupling of *trans* oriented ^{31}P nuclei are large and characterized by apparent triplets in the ^1H spectra while *cis* couplings are small, leaving the J(PH) doublet unperturbated, were used as a criterion for determining the geometrical relationships between phosphorous ligands in the complexes studied. By analogy, it is reasonable to postulate that the two phosphine ligands are in *trans*-positions and to assign structure III to these complexes in solution. However, considerable caution should be exercised in using such a criterion to assign the stereochemistry of a complex. For example, many *cis*-complexes show appreciable phosphorus—phosphorus coupling as was noted in manganese complexes of the type $[Mn(CO)_3L_2X]$ (X = Cl, Br, I) where the J(PP) *cis* and J(PP) *trans* are roughly the same [18,19]. Furthermore, for chromium complexes the magnitude of J(PP) is even greater in *cis*- than in *trans* complexes [18,19]. In iron complexes, the relative magnitudes of J(PP) for *cis* and *trans* complexes are not known because the data for *cis* compounds are not available. The crystal structure of the complex, $[FeCl(4\text{-}CH_3C_6H_4NC)_3(PPh_3)_2]FeCl_4$ [20], showed the two phosphines in the *trans* position, making it reasonable to postulate a type III *trans*-structure for other $[FeX(CNR)_3L_2]^+$ cations.

In Table 2 are reported Mössbauer quadrupole splittings and the asymmetry parameters for the complexes. These data do not permit any distinction between the three possible structures.

The infrared spectrum of the cation $[FeI(4\text{-}CH_3C_6H_4NC)_2(PhPMe_2)_3]^+$ shows two strong absorptions at 2130 and 2091 cm^{-1}, which can be attributed to the symmetric (a_1) and antisymmetric (b_1) CN stretching mode of two *cis*-isocyanides. Therefore, the structure of this compound may be either V or VI.



(V)



(VI)

The PMR spectrum for the phosphine methyl protons should present two doublets (2/2; 1/1) for structure V while for structure VI a triplet (1/2/1) and a doublet (1/1) are expected. The PMR spectrum at room temperature in this region presents three resonance lines at τ 8.08, 8.12, and 8.16 ppm which do not permit an easy interpretation. By lowering the temperature to —20°C, the phosphine's methyl protons appear as a triplet (1/2/1) at τ 8.02 ppm (J_{app}(PH) 4 Hz) and a doublet (1/1) at τ 8.08 ppm (J(PH) 8 Hz), thus indicating that at this temperature a structure such as VI can be attributed to this cation. Although the room temperature PMR spectrum favours a non-rigid structure at room temperature for the $[FeI(4\text{-}CH_3C_6H_4NC)_2(PhPMe_2)_3]^+$ cation, structure VI is consistent with the structural assignment by point-charge model (see Table 2).

Discussion

The hexacoordinate(isocyanide)(phosphine)(halo)iron(II) complexes reported here are the thermodynamically determined products. No other products could be spectroscopically detected within one week at room temperature when a 10^{-2} M dichloromethane solution of the $[FeX(CNR)_nL_{5-n}]^+$ (n = 2, 3 or 4) complexes were treated with a large excess ($>10^{-1}$ M) of CNR or L entering ligand. Furthermore, the same products were obtained when a large excess of isocyanide or phosphine was used. These results should allow a correlation to be made between the π-accepting capacities and steric requirements of the phosphine and isocyanide ligands in determining the stability and stoichiometry of these complexes. In order to determine the influence of steric hindrance and the donor—acceptor properties of the tertiary phosphine ligands on the isocyanide/phosphine ratio, the bromide complexes of the type $[FeBr(4\text{-}CH_3C_6H_4NC)_nL_{5-n}]$-$ClO_4$ (n = 2, 3 or 4) were prepared. Recently Tolman [21] has shown that phosphorous ligands can be ranked in a "π-acceptor strength" series based on the a_1 carbonyl-stretching frequency of $Ni(CO)L_3$ (L = phosphine) in CH_2Cl_2. Assuming that this series, deduced for tetrahedral d^{10} nickel(0) complexes, can be applied to octahedral d^6 iron(II) derivatives, the amount of Fe($d\pi$) $\rightarrow$ P($d\pi^*$) bonding increases in the sequence: $PhPEt_2(P_2C_3) < PhPMe_2(P_3C_2) < Ph_2PEt(P_2C_3) < Ph_2PMe(P_2C_3) < PPh_3(P_2C_3) < Ph_2P(OEt)(PC_4) < PhP(OEt)_2(P_3C_2)$ (P_xC_y = ratio phosphine/isocyanide in iron(II) complexes).

The cone angles of ligands with three identical substituents were measured from models [22], but the minimum cone angle is difficult to define when the substituents are not the same. However, it is quite reasonable to assume that a ligand such as PX_2Y occupies a solid angle intermediate between PX_3 and PY_3 [2]. Hence steric hindrance should decrease in the order: $PPh_3(P_2C_3) > Ph_2PEt(P_2C_3) > Ph_2PMe(P_2C_3) > Ph_2P(OEt)(PC_4) > PPhEt_2(P_2C_3) > PhPMe_2(P_3C_2) > PhP(OEt)_2(P_3C_2)$. A correlation between the stoichiometry of these complexes and the steric and acceptor—donor series can thus be summarized: (1) P_3C_2 complexes of the type $[FeBr(4\text{-}CH_3C_6H_4NC)_2L_3]^+$ were obtained with phosphines of small steric hindrance (L = $PhPMe_2$ or $PhP(OEt)_2$) [1,13] even though the π-acceptor properties are very different. (2) If the cone angle of the phosphine ligand is greater than that of $PhPMe_2$ or $PhP(OEt)_2$, complexes in which the phosphine/isocyanide ratio is 2/3 were obtained. (3) When both the π-acceptor properties and the cone angle of the phosphine ligand increase (viz. Ph_2POEt), the number of the phosphine ligands decreases from the two to one, for example, the $\{FeBr(4\text{-}CH_3C_6H_4NC)_4[Ph_2P(OEt)]\}^+$ cation (PC_4) is obtained.

TABLE 5

M—P BOND DISTANCES (Å) IN SOME MIXED-LIGAND COMPLEXES

Compound	Length	Ref.
$\{FeCl(4\text{-}CH_3C_6H_4NC)_2[PPh(OEt)_2]_3\}ClO_4$	2.239(4)	24
$[FeCl(4\text{-}CH_3C_6H_4NC)_3(PPh_3)_2]FeCl_4$	2.309(3)	20
$\{Co(4\text{-}NO_2C_6H_4NC)_3[PPh(OEt)_2]_2\}ClO_4$	2.18(1)	25
$FeH_2[PPh(OEt)_2]_4$	2.139(2)	26
$Ni(CN)_2[PPh(OEt)_2]_3$	2.228(6)	27

It seems reasonable to conclude that steric hindrance of the tertiary phosphine ligands is more important than the nature of the Fe—P bond in determining the stoichiometry of these complexes. The Fe—P π-bonding character appears important only when the phosphine causes a large steric hindrance. The small importance of the nature of the Fe—P bond in determining the isocyanide/phosphine ratio can be explained by taking into account the effect produced by the isocyanide ligands on the iron(II) d^6 atom. The isocyanide, a strong π-acceptor, decreases the electron density on the metal, and reduces the influence of the more weakly π-accepting phosphine moiety, and the Fe—P bond should be especially long. Support for this hypothesis is shown in Table 5, in which the M—P lengths of several mixed ligand (isocyanide/phosphine) complexes are reported. In particular, it may be observed that the lengths of the Fe—P bonds (both when the phosphine is PPh_3 or $PhP(OEt)_2$) in the iron complexes described in this paper are much longer than in $FeH_2[PhP(OEt)_2]_4$.

To determine the influence of the halogen ligand, several attempts were also made to prepare the corresponding chloro and iodo derivatives. The complexes obtained suggest that the halide ligand plays an important role in determining the stoichiometry of these complexes only when the steric hindrance of the phosphine or isocyanide ligands is large. Thus, when the phosphine is PPh_3, it is possible to obtain both the Cl and Br mixed phosphine—isocyanide iron(II) derivatives, while with iodide only the iodopentakis(isonitrile) cation, $[FeI(4\text{-}CH_3C_6H_4NC)_5]^+$ [13,1] is formed. Also, when the isocyanide is $2,6\text{-}(CH_3)_2C_6H_3NC$ and the halide is iodine we have not been able to obtain any product.

Chloro and bromo derivatives may be prepared, but while a *cis* arrangement of the two isocyanides in $\{FeCl[2,6\text{-}(CH_3)_2C_6H_3NC]_2[PhP(OEt)_2]_3\}ClO_4$ is found, a distorted geometry in which the two isocyanides occupy apical positions has been postulated for the bromo derivative $\{FeBr[2,6\text{-}(CH_3)_2C_6H_3NC]_2[PhP(OEt)_2]_3\}ClO_4$ [13]. Finally, a different phosphine/isocyanide ratio is found with the ligand $Ph_2P(OEt)$, depending on whether the halide is Cl, Br, or I. Thus P_2C_3 complexes are obtained if X = Cl and PC_4 complexes when X = Br or I. The complexes $\{FeX(4\text{-}CH_3C_6H_4NC)_4[Ph_2P(OEt)]\}ClO_4$ (X = Br or I) can be compared with the previously described tetrakis(isocyanide)dihalo derivatives of the type $[FeX_2(CNR)_4]$ [13,23], which exist in two forms, α and β. The blue-colored, β form, corresponding to the *trans* isomer, is very unstable in organic solvents such as dichloromethane or 1,2-dichloroethane, since a *trans/cis* isomerisation occurs readily. Surprisingly, $\{FeX(CNR)_4[Ph_2P(OEt)]\}^+$ complexes (in which a phosphine ligand replaces a halide) are stable in solution, and presumably have a *trans* structure, according to our speculations.

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References

1 G. Albertin, E. Bordignon, A.A. Orio and G. Troilo, Inorg. Chem., 14 (1975) 238.
2 C.A. Tolman, Chem. Rev., 77 (1977) 313.
3 I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer and K. Offerman, Angew. Chem. Int. Ed. Engl., 4 (1965) 672.
4 I. Ugi, and R. Meyer, Org. Synth., 41 (1961) 101.
5 (a) W.P. Weber and G.W. Gakel, Tetrahedron Lett., 17 (1972) 1637; (b) W.P. Weber, G.W. Gokel, and I. Ugi, Angew. Chem. Int. Ed. Engl., 11 (1972) 530.
6 R. Rabinowitz and J. Pellon, J. Org. Chem., 20 (1961) 4623.
7 S. Calogero, P. Furlan, V. Peruzzo and G. Tagliavini, J. Organometal. Chem., 128 (1977) 177.
8 B.L. Chrisman and T.A. Tumolillo, Comput. Phys. Comm., 3 (1971) 322.
9 G. Booth and J. Chatt, J. Chem. Soc., (1962) 2099.
10 L. Naldini, Gazz. Chim. Ital., 90 (1960) 391; K. Issleib and G. Döll, Z. Anorg. Allgem. Chem., 305 (1960) 1.
11 G.M. Bancroft and P.L. Sears, Inorg. Chem., 14 (1975) 2716.
12 G.M. Bancroft and E.T. Libbey, J. Chem. Soc. Dalton, (1973) 2103.
13 S. Calogero, G. Albertin, A.A. Orio and G. Pelizzi, J. Organometal. Chem., 133 (1977) 327.
14 E.T. Libbey and G.M. Bancroft, J. Chem. Soc. Dalton, (1974) 87.
15 F.A. Cotton and C.S. Krajhanzel, J. Amer. Chem. Soc., 84 (1962) 4432.
16 R. Poilblanc and M. Birgogne, Bull. Soc. Chim. France, (1962) 1301.
17 R. Craig Taylor and W.D. Horrocks, Jc., Inorg. Chem., 3 (1964) 584.
18 F.B. Ogilvie, J.M. Jenkis and J.G. Verkade, J. Amer. Chem. Soc., 92 (1970) 1916.
19 R.D. Bertrand, F.B. Ogilvie and J.G. Verkade, J. Amer. Chem. Soc., 92 (1970) 1908.
20 G. Pelizzi, G. Albertin, E. Bordignon, A.A. Orio and S. Calogero, Acta Cryst., B, 33 (1977) 3761.
21 C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 2953.
22 C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 2956.
23 L. Malatesta, A. Sacco and G. Padoa, Ann. Chim. (Rome), 43 (1953) 617.
24 G. Albertin, A.A. Orio, S. Calogero, L. Di Sipio and G. Pelizzi, Acta Cryst., B, 32 (1976) 2023.
25 R. Graziani, G. Albertin, E. Forsellini, and A.A. Orio, Inorg. Chem., 15 (1976) 2422.
26 L.J. Guggenberger, D.D. Titus, M.T. Flood, R.E. Marsh, A.A. Orio, and H.B. Gray, J. Amer. Chem. Soc., 94 (1972) 1135.
27 J.K. Stalik and J.A. Ibers, Inorg. Chem., 8 (1969) 1084.