

Contribution from Istituto di Chimica Generale ed Inorganica, and Istituto di Chimica Organica, University of Venice, Venice, Italy

Mixed-Ligand Hexacoordinate Iron(II) Complexes with Isocyanides and Phosphines

GABRIELE ALBERTIN, EMILIO BORDIGNON, ANGELO A. ORIO,*¹ and GIANGIORGIO TROILO

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The complexes of the type $[\text{FeCl}(\text{CNR})_2\text{L}_3]\text{ClO}_4$ (R = phenyl, 4-methylphenyl, 4-methoxyphenyl, 4-nitrophenyl, 2-methylphenyl, or 2,6-dimethylphenyl; L = diethyl phenylphosphonite) and of the type $[\text{FeCl}(\text{C}_6\text{H}_4\text{NC})_3(\text{PPh}_3)_2]\text{Y}$ ($\text{Y}^- = \text{ClO}_4^-$, BPh_4^- , or FeCl_4^-) and the compound $[\text{Fe}(\text{C}_6\text{H}_{11}\text{NC})_3(\text{PPh}(\text{OEt})_2)_3]\text{ClO}_4$ were synthesized, and their structures were postulated on the basis of infrared and pmr spectra. The influence of the π acidity of the phosphine and isocyanide ligands on the stability of these complexes is also discussed.

Introduction

A number of iron(II) isocyanide complexes have been isolated during the past 20 years.² While the majority are diamagnetic hexacoordinate cationic or neutral iron(II) compounds of the types $[\text{Fe}(\text{CNR})_6]^{2+}$, $[\text{FeX}(\text{CNR})_5]^+$, and $[\text{FeX}_2(\text{CNR})_4]$ (X = anionic ligand, CNR = isocyanide), tetracoordinate complexes of composition $[\text{Fe}(\text{CNR})_4]^{2+}$ and $[\text{FeCl}_2(\text{CNR})_2]$ have been proposed but not reliably characterized.³ Mixed-ligand carbonyl-isocyanide iron(II) derivatives of the type $[\text{FeX}_2(\text{CO})_n(\text{CNR})_{4-n}]$ ($n = 1, 2, \text{ or } 3$, X = Cl, Br, or I, R = *p*-tolyl or *tert*-butyl) have also been reported,⁴ but there are presently no reports of mixed-ligand isocyanide-phosphine iron(II) complexes.

In an earlier paper⁵ we have reported the synthesis and characterization of $[\text{CoL}_n(\text{CNR})_{5-n}]^+$ ($n = 2 \text{ or } 3$, L = $\text{PhP}(\text{OEt})_2$ or $\text{P}(\text{OMe})_3$), which allowed us to establish the relative σ -donor and π -acceptor abilities of phenyl-substituted isocyanides and phosphines for cobalt(I) (d^8). The effects of phenyl and/or ethoxy substituents of the isocyanide and phosphine ligands on these properties of the complex as a whole are expected to be more pronounced for iron(II) (d^6) because of its higher formal positive charge and lower d-electron density. Relevant to this hypothesis, we have prepared and characterized a number of new mixed-ligand isocyanide-phosphine complexes of iron(II) of the type $[\text{FeCl}(\text{CNR})_n\text{L}_{5-n}]\text{ClO}_4$ ($n = 2 \text{ or } 3$; R = 4- $\text{CH}_3\text{C}_6\text{H}_4$, C_6H_5 , 4- $\text{CH}_3\text{OC}_6\text{H}_4$, 2- $\text{CH}_3\text{C}_6\text{H}_4$, 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$, 4- $\text{NO}_2\text{C}_6\text{H}_4$; L = $\text{PPh}(\text{OEt})_2$ or PPh_3) and the complex $[\text{Fe}(\text{C}_6\text{H}_{11}\text{NC})_3(\text{PPh}(\text{OEt})_2)_3](\text{ClO}_4)_2$.

Experimental Section

Materials. The solvents were purified, dried by standard methods, and distilled under a stream of nitrogen just prior to use. Reagent grade $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ was dried in a vacuum oven under nitrogen at 110° or by treatment with 2,2-dimethoxypropane and used without further purification. Iron(III)-free $\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ was prepared by reaction under inert atmosphere of iron wire (12 g) with 75% perchloric acid (30 ml). The further addition of perchloric acid to the clear solution afforded light green crystals which were filtered by vacuum suction and stored under nitrogen. Ethanol solutions of $\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$, prepared from this material, contained free HClO_4 which was neutralized with NaOH prior to the addition of the ligands. Diethyl phenylphosphonite was prepared by the method of Rabinowitz and Pellon.⁶ Cyclohexyl and substituted-phenyl isocyanides were obtained by the phosgene method of Ugi, *et al.*,⁷ or by the improved Hofman carblamine syntheses.⁸

Apparatus. Magnetic susceptibilities were measured in solution by the method of Evans⁹ and corrected for diamagnetism of the ligands from tables given by Figgis and Lewis.¹⁰ Pmr measurements were made with Hitachi Perkin-Elmer, Bruker HFX-10, and/or Varian HR-220 instruments using TMS as internal reference. Conductivities of 10^{-3} M solutions of complexes in nitrobenzene at 25° were measured with an LKB bridge. Infrared spectra of KBr pellets and dichloromethane solutions were recorded on a Perkin-Elmer 621 or 225 spectrophotometer.

Syntheses of Complexes. A dry nitrogen atmosphere was employed

in all the synthetic procedures described below. Once isolated, all the complexes were found stable both in solution and as solids and no special precautions were required for the spectral and other studies performed.

Chlorobis(isocyanide)tris(diethyl phenylphosphonite)iron(II) Perchlorate. The complexes of the type $[\text{FeCl}(\text{CNR})_2\text{L}_3]\text{ClO}_4$ (R = C_6H_5 , 4- $\text{CH}_3\text{C}_6\text{H}_4$, 2- $\text{CH}_3\text{C}_6\text{H}_4$, 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$, 4- $\text{CH}_3\text{OC}_6\text{H}_4$, 4- $\text{NO}_2\text{C}_6\text{H}_4$; L = $\text{PhP}(\text{OEt})_2$) were prepared by the following general method. Anhydrous iron(II) chloride (1.27 g, 10 mmol) and diethyl phenylphosphonite (9 ml, 45 mmol) were placed in 80 ml of anhydrous ethanol and the apparatus was flushed with nitrogen. The addition of the appropriate isocyanide (22 mmol) to the magnetically stirred solution, initially at room temperature, resulted in an exothermic reaction; the color of the reaction mixture changed from orange-red to yellow-orange. After 1 hr, anhydrous lithium perchlorate (1.03 g, 10 mmol) was added and the reaction mixture was concentrated to about 30 ml. The precipitation of the crude products was effected by the addition of ether. Yields of >75% were obtained after recrystallization of the crude materials from anhydrous ethanol.

Chlorotris(4-methylphenyl isocyanide)(triphenylphosphine)iron(II)-tetrachloroiron(III). 4-Methylphenyl isocyanide (5.0 ml, 42 mmol) was slowly added to a mixture of anhydrous FeCl_2 (1.27 g, 10 mmol), triphenylphosphine (12.5 g, 45 mmol), and 30 ml of anhydrous acetone. The exothermic reaction was carried out without external cooling. A small amount (~10%) of a violet compound, identified as *trans*- $[\text{FeCl}_2(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_4]$, initially precipitated and was collected by filtration. After 4 hr the final product precipitated from the filtrate and was collected by filtration. The crude product was recrystallized from anhydrous acetone-ethanol (yield 40%). It was subsequently discovered that the FeCl_4^- counterion originated from impure (oxidized) FeCl_2 .

The corresponding tetraphenylborate derivative was precipitated by adding NaBPh_4 to the mother liquor from the previous preparation or to an acetone solution of $[\text{FeCl}(\text{CNR})_3(\text{PPh}_3)_2]\text{FeCl}_4$. The perchlorate derivative was obtained by exchanging FeCl_4^- on a Dowex 1-X4 anion exchange resin or by treating the reaction mixture with LiClO_4 in equimolar ratio if pure FeCl_2 was the starting material.

Tris(cyclohexyl isocyanide)tris(diethyl phenylphosphonite)iron(II) Perchlorate. The complex was obtained by treating anhydrous iron(II) chloride (1.27 g, 10 mmol) with phenyl diethylphosphonite (9 ml, 45 mmol) and cyclohexyl isocyanide (5 ml, 45 mmol) in anhydrous ethanol at room temperature for 1 day. The crystalline product was precipitated by slow addition of large volumes (total 2 l.) of ether to the solution. The complex was then dissolved in 20 ml of anhydrous ethanol and chromatographed on silica gel with ethanol-ether (1:1) as eluent. A single fraction was collected and the product was obtained by addition of ether. This complex is very soluble in polar and somewhat soluble in nonpolar organic solvents. For this reason the yields were lower (5%) than for the other derivatives reported in this work.

Chlorotris(4-methylphenyl isocyanide)bis(diethyl phenylphosphonite)iron(II) Perchlorate. An ethanol solution (30 ml) of 1 g of $[\text{FeCl}(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2(\text{PhP}(\text{OEt})_2)_3]\text{ClO}_4$ was refluxed for 10 hr. The final concentrated (5 ml) reaction mixture was chromatographed on silica gel (ethanol eluent) and the pure product obtained by precipitation with ether; yield 50%.

Chloropentakis(isocyanide)iron(II) Perchlorate. These compounds have been prepared several times in a similar manner. A typical preparation involved the treatment of 10 mmol (1.27 g) of anhydrous

Table I. Properties of Some Mixed-Ligand Iron(II) Complexes

Complex ^a	Color	Mp, ^b °C	Molar conduc- tance ^c	% C		% H		% N		% P		% Cl	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[FeCl(4-CH ₃ C ₆ H ₄ NC) ₂ -L ₃]ClO ₄	Yellow-orange	131	24.2	54.18	54.29	5.83	5.82	2.75	2.69	9.11	8.72	6.95	6.87
[FeCl(C ₆ H ₅ NC) ₂ L ₃]ClO ₄	Orange	84	24.6	53.29	53.17	5.59	5.53	2.82	2.74	9.37	8.91	7.16	7.18
[FeCl(4-CH ₃ OC ₆ H ₄ NC) ₂ -L ₃]ClO ₄	Orange	140	24.0	52.53	52.37	5.65	5.65	2.66	2.39	8.83	8.31	6.74	6.56
[FeCl(4-NO ₂ C ₆ H ₄ NC) ₂ -L ₃]ClO ₄	Orange	171	25.2	48.86	48.74	4.94	4.90	5.18	5.14	8.60	7.74	6.55	6.58
[FeCl(2-CH ₃ C ₆ H ₄ NC) ₂ -L ₃]ClO ₄	Orange	154	25.6	54.18	53.97	5.83	5.87	2.75	2.99	9.11	9.06	6.95	7.04
[FeCl(2,6-(CH ₃) ₂ -C ₆ H ₃ NC) ₂ L ₃]ClO ₄	Orange	158	25.1	55.03	56.04	6.06	6.35	2.67	2.65	8.87	8.28	6.77	6.76
[FeCl(4-CH ₃ C ₆ H ₄ NC) ₃ -L' ₂]ClO ₄	Orange	182	24.2	67.55	66.84	4.82	4.71	3.94	3.80	5.81	6.10	6.65	6.99
[FeCl(4-CH ₃ C ₆ H ₄ NC) ₃ -L' ₂]BPh ₄	Yellow-orange	169	13.9	78.42	77.07	5.56	5.82	3.27	3.06	4.81	4.22	2.76	2.80
[FeCl(4-CH ₃ C ₆ H ₄ NC) ₃ -L' ₂]FeCl ₄	Orange	175	21.8	61.86	62.03	4.41	4.37	3.61	3.64	5.32	5.00	15.21	15.27
[Fe(C ₂ H ₅ NC) ₃ L ₃](ClO ₄) ₂	White	228	53.5	52.05	51.91	6.68	6.67	3.57	3.62	7.89	7.54	6.02	6.31
[FeCl(4-CH ₃ C ₆ H ₄ NC) ₃]ClO ₄	Yellow	202	24.5	61.35	61.28	4.54	4.60	9.02	8.87			9.14	9.23
[FeCl(C ₆ H ₅ NC) ₃]ClO ₄	Yellow	219	24.1	59.51	58.85	3.57	3.47	9.91	9.76			10.04	10.09
[FeCl ₂ (4-CH ₃ C ₆ H ₄ NC)]	Violet	142		64.50	64.40	4.74	4.60	9.41	9.13			11.91	11.94

^a L = PPh(OEt)₂; L' = PPh₃. ^b Melting points were determined in capillaries and uncorrected. ^c Molar conductances were determined in 10⁻³ M nitrobenzene solution at 25° (in cm²/ohm mol).

iron(II) chloride and 45 mmol (6.6 ml) of triethyl phosphite in 80 ml of anhydrous ethanol with 40 mmol of the proper isocyanide for 3 hr at room temperature. The addition of 1.20 g of LiClO₄ in 20 ml of ethanol and concentration of the reaction mixture afforded a yellow precipitate which was purified by recrystallization from ethanol. Trimethyl or triphenyl phosphite in methanol or acetone, respectively, can be used instead of triethyl phosphite.

The same complexes have been obtained by treatment of Fe-(ClO₄)₂·6H₂O with diethyl phenylphosphonite and the proper isocyanide.

Results and Discussion

Products. When diethyl phenylphosphonite (PhP(OEt)₂) or triphenylphosphine is added to a light yellow solution of anhydrous iron(II) chloride in ethanol, an orange-red coloration develops which is typical of chlorophosphineiron(II) complexes. No attempt were made to isolate [FeCl₂(PhP(OEt)₂)₂] or [FeCl₂(PPh₃)₂] intermediates since similar complexes have been previously reported.¹¹ Subsequent addition of isocyanide results in an exothermic reaction, and in some cases (with 4-NO₂C₆H₄NC and 4-CH₃C₆H₄NC), the final product starts to precipitate during the addition of the lithium perchlorate solution to the reaction mixture. In other cases, oils were obtained when the reaction mixture was concentrated or diethyl ether was added to precipitate the products.

The elemental analyses, although within acceptable limits (Table I), are not sensitive to contamination of traces of Fe(III) complexes. In order to obtain reliable pmr and ir spectra, the further purification of the recrystallized complexes was achieved by chromatography of their acetone solutions on silica gel using ethanol as an eluent.

These new mixed-ligand phosphine-isocyanide iron(II) complexes are yellow or orange crystalline materials which are stable in solid state as well as in solutions of organic solvents. They are very soluble in polar solvents such as acetone, chloroform, dichloromethane, 1,2-dichloroethane, and nitrobenzene and slightly soluble in nonpolar solvents such as hydrocarbons and diethyl ether. They were characterized by elemental analyses, conductivity, magnetic measurements, and infrared and pmr spectra. The bands characteristic of phosphine and isocyanide ligands and the two typical bands of uncoordinated perchlorate ion at 1085 (vs) and 625 (s) cm⁻¹ were present in their infrared spectra.

A strong band at 377 cm⁻¹ in the spectrum of the complex [FeCl(4-CH₃C₆H₄NC)₃(PPh₃)₂]FeCl₄ due to Fe^{II}-Cl

stretching vibration and a magnetic moment of 5.8 BM are consistent with the presence of the tetrahedral FeCl₄⁻ counterion in this compound. Iron(III) contamination present in the long-stored starting iron(II) chloride samples and oxidation of iron(II) by atmospheric oxygen during the preparation of the complex are probably responsible for the formation of this anion in solution. In fact, using a different commercial sample of anhydrous iron(II) chloride, FeCl₄⁻ has not been found in the syntheses of [FeCl(CNR)₂(PPh(OEt)₂)₂]⁺ cations, and the [FeCl(CNR)₃(PPh₃)₂]Y⁻ (Y⁻ = ClO₄⁻ or BPh₄⁻) complexes can be prepared more conveniently by the simpler method, *i.e.*, by precipitation of the cation with LiClO₄ or NaBPh₄ from the reaction mixture of FeCl₂, triphenylphosphine, and isocyanide.

The nature of phosphine and isocyanide ligands and their relative σ -donor and π -accepting capacities seem to be important factors in determining the stability and therefore the composition of these complexes. At room temperature the reaction of iron(II) chloride and triphenylphosphine with 4-methylphenyl isocyanide gives the cation [FeCl(CNR)₃(PPh₃)₂]⁺, while in similar conditions diethyl phenylphosphonite afforded complexes of the type [FeCl(CNR)₂(PhP(OEt)₂)₃]⁺ (R = phenyl or substituted phenyl group), and only by refluxing for 10 hr the ethanol solution of [FeCl(4-CH₃C₆H₄NC)₂(PPh(OEt)₂)₃]ClO₄ can the complex [FeCl(4-CH₃C₆H₄NC)₃(PPh(OEt)₂)₂]ClO₄ be obtained. No analogous mixed-ligand derivatives have been obtained with the stronger π acids triphenyl, triethyl, or trimethyl phosphite. The cone angles of the ligands decrease in the order PPh₃ > P(OPh)₃ > PPh(OEt)₂ > P(OEt)₃ > P(OMe)₃,¹² whereas the Fe(d π) \rightarrow P(d π) bond ability increases in the sequence PPh₃ < PPh(OEt)₂ < P(OEt)₃ < P(OMe)₃ < P(OPh)₃. Assuming that the ordering of donor-acceptor properties and steric hindrance deduced by Tolman¹³ for tetrahedral d¹⁰ Ni(0) complexes can be applied to octahedral d⁶ iron(II) derivatives, it seems reasonable to conclude that the nature of the Fe-P bond is more important than the phosphine steric requirements in determining the formulas of complexes.

On this basis can be explained the fact that no P(OPh)₃, P(OEt)₃, or P(OMe)₃ derivatives of iron(II) have been obtained even if the cone angle of the first phosphite is between that of P(Ph)₃ and that of PPh(OEt)₂, since all three ligands are stronger π acids than triphenyl- or diethoxyphenylphosphine. d⁸ cobalt(I) cations of the type [Co(P-

Table II. $\nu(\text{CN})$ Frequencies of Iron(II) Complexes

Complex ^a	$\nu(\text{CN})$ freq, cm^{-1} , in CH_2Cl_2 soln (and solid) ^b		
$[\text{FeCl}(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_2\text{L}_3]\text{ClO}_4$		2153 s (2154 s)	2110 s (2109 s)
$[\text{FeCl}(\text{C}_6\text{H}_5\text{NC})_2\text{L}_3]\text{ClO}_4$	2173 sh	2157 s (2160 s)	2107 s (2107 s)
$[\text{FeCl}(\text{4-CH}_3\text{OC}_6\text{H}_4\text{NC})_2\text{L}_3]\text{ClO}_4$		2156 s (2162 s)	2113 (2118 s)
$[\text{FeCl}(\text{4-NO}_2\text{C}_6\text{H}_4\text{NC})_2\text{L}_3]\text{ClO}_4$	2175 sh (2171 sh)	2142 s (2143 s)	2094 s (2094 s)
$[\text{FeCl}(\text{2-CH}_3\text{C}_6\text{H}_4\text{NC})_2\text{L}_3]\text{ClO}_4$		2151 s (2145 s)	2103 s (2101 s)
$[\text{FeCl}(\text{2,6-(CH}_3)_2\text{C}_6\text{H}_3\text{NC})_2\text{L}_3]\text{ClO}_4$	(2175 sh)	2142 s (2146 s)	2104 s (2103 s)
$[\text{FeCl}(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}_2]\text{ClO}_4$		2183 s (2178 s)	2146 s (2137 s)
$[\text{FeCl}(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}'_2]\text{ClO}_4$		2164 m (2168 w)	2125 s, br (2126 s)
$[\text{FeCl}(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}'_2]\text{BPh}_4$		2164 m (2162 w)	2125 s, br (2123 s)
$[\text{FeCl}(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}'_2]\text{FeCl}_4$		2164 m (2162 w)	2125 s, br (2125 s)
$[\text{Fe}(\text{C}_6\text{H}_{11}\text{NC})_3\text{L}_3](\text{ClO}_4)_2$		2204 m (2209 m)	2170 s (2175 s)
$[\text{FeCl}(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_5]\text{ClO}_4$		2116 w (2208 w)	2173 s (2158 s)
$[\text{FeCl}(\text{C}_6\text{H}_5\text{NC})_5]\text{ClO}_4$		2214 w (2115 w)	2173 s (2170 s)
$[\text{FeCl}_2(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_4]$		2193 w (2190 w)	2151 s

^a L = PPh(OEt)₂; L' = PPh₃. ^b KBr pellets. Key: s, strong; m, medium; w, weak; br, broad; sh, shoulder.

(OMe)₃)₂(CNR)₃)⁺ (R = 4-NO₂C₆H₄, C₆H₅, 2,6-(CH₃)₂C₆H₃) have been reported,⁵ but in the present case the lower electron density on the d⁶ iron(II) atom makes the π back-donation less favorable and therefore the Fe-P(OR)₃ bond unstable even if σ -donor chloride ligand is present in the isocyanide phosphineiron(II) complexes reported in this paper. With cyclohexyl isocyanide, which is a better σ donor and a weaker π acceptor than the phenyl isocyanides, the compound $[\text{Fe}(\text{CNC}_6\text{H}_{11})_3(\text{PPh}(\text{OEt})_2)_3]^{2+}$ was afforded, instead of a chloro derivative as with the other isocyanides. It seems, therefore, that with an aliphatic isocyanide the π interaction of the diethyl phenylphosphonite is completely satisfied without the need of a strong σ -donor anionic ligand.

When iron(II) perchlorate is treated in ethanol with isocyanide in the presence of PPh(OEt)₂ or of a phosphite, $[\text{FeCl}(\text{CNR})_5]^+$ (R = phenyl or 4-methylphenyl) derivatives are obtained. A similar compound has been prepared by refluxing an acetone solution of *trans*- $[\text{FeCl}_2(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_4]$, while it is known that $\text{Fe}(\text{ClO}_4)_2$ and 4-methylphenyl isocyanide gives $[\text{Fe}(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_5\text{H}_2\text{O}]^{2+}$ or $[\text{Fe}(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_5\text{OCIO}_3]^+$ when the solvent is methanol or dichloromethane, respectively.¹⁴ We also observed the formation of the aquo complex by reaction of 4-methylphenyl isocyanide with iron(II) perchlorate in ethanol in the absence of phosphine ligands. Therefore the unexpected presence of chloride in the $[\text{FeCl}(\text{CNR})_5]^+$ complexes obtained by us can tentatively be explained assuming a perchlorate-chloride reduction by PhP(OEt)₂ or phosphite. However, this hypothesis needs further investigation.

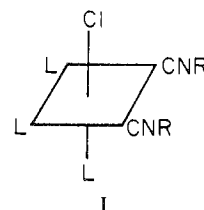
In the reaction of iron(II) chloride and triphenylphosphine with 4-methylphenyl isocyanide, some violet *trans*- $[\text{FeCl}_2(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_4]$ separates out from the ethanol solution during the addition of the isocyanide. The physical data of this compound are in good agreement with those previously reported.^{14,15} Since the same by-product has not been observed when the phosphine ligand was PPh(OEt)₂, it is likely that in the probable intermediate of the type $[\text{FeCl}_2(\text{PR}_3)_2]$ the diethyl phenylphosphonite is more strongly bonded to the iron(II) atom than triphenylphosphine.

Structures. A number of structural insights have been

obtained from ir and pmr spectra. The infrared spectra of $[\text{FeCl}(\text{CNR})_2\text{L}_3]^+$ (R = C₆H₅, 4-CH₃C₆H₄, 4-CH₃OC₆H₄, 4-NO₂C₆H₄, 2-CH₃C₆H₄, and 2,6-(CH₃)₂C₆H₃; L = PPh(OEt)₂) cations show two strong absorptions of roughly equal intensities at 2165–2140 and at 2140–2120 cm^{-1} (Table II), attributed to the symmetric (A₁) and to the antisymmetric (B₁) stretching mode of the isocyanide CN's, indicating a *cis* arrangement of the two isocyanide ligands. Furthermore, the absence of absorption in the 1800–1600- cm^{-1} region indicates that bridging isocyanides are not present and further supports a monomeric structure of these complexes. (As these complexes are ionic, it was necessary to measure solution ir spectra in dichloromethane. This polar medium thus led to broad, and in some cases poorly resolved, bands.)

The pmr spectral data of the complexes are given in Table III. The phosphine ethoxyl methyl protons in chloroform-*d* appear as a 1:4:5:2 multiplet ($J = 7$ Hz) which can be further resolved, either by using a high-resolution instrument (HR-220) or by changing solvent ((CD₃)₂CO or (CD₃)₂SO), into two 1:2:1 and 2:4:2 triplets both downfield of that observed for free phosphine, thus indicating two magnetically equivalent phosphines different from a third.

Due to the higher *trans* effect of the isocyanide ligands, the more intense triplet may be attributed to the PPh(OEt)₂ groups *trans* to the CNR ligands, since this effect would be expected to produce a magnetic environment more like that of the free PPh(OEt)₂. On this basis structure I is assigned to these $[\text{FeCl}(\text{CNR})_2\text{L}_3]^+$ cations. This assignment is further



supported by the following observations: (a) the singlets of isocyanide methyl groups in the complexes $[\text{FeCl}(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_2\text{L}_3]^+$ and $[\text{FeCl}(\text{4-CH}_3\text{OC}_6\text{H}_4\text{NC})_2\text{L}_3]^+$

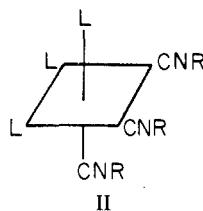
Table III. Chemical Shifts (τ) of Some Mixed-Ligand Iron(II) Complexes^a

Complex ^b	Phenyl protons (phosphine and/or isocyanide)	CH ₂ phosphine	CH ₃ isocyanide	CH ₃ phosphine
[FeCl(4-CH ₃ C ₆ H ₄ NC) ₂ L ₃]ClO ₄	2.65 br	5.95 br	7.63 s	8.76 q ^c
[FeCl(C ₆ H ₅ NC) ₂ L ₃]ClO ₄	2.70 br	5.90 br		8.75 q
[FeCl(4-CH ₃ OC ₆ H ₄ NC) ₂ L ₃]ClO ₄	2.65 br	5.95 m	6.16 s	8.75 q
	3.05 m			
[FeCl(4-NO ₂ C ₆ H ₄ NC) ₂ L ₃]ClO ₄	1.75 br	5.92 m		8.66 q
	2.00 br			
[FeCl(2-CH ₃ C ₆ H ₄ NC) ₂ L ₃]ClO ₄	2.70 br	6.05 m	7.73 s	8.76 q ^d
			7.85 s	
[FeCl(2,6-(CH ₃) ₂ C ₆ H ₃ NC) ₂ L ₃]ClO ₄	2.60 br	6.05 m	7.55 s	8.76 q ^e
			7.87 s	
[FeCl(4-CH ₃ C ₆ H ₄ NC) ₃ L ₂]ClO ₄ ^f	2.74 br	5.66 m	7.62 s	8.65 t
[FeCl(4-CH ₃ C ₆ H ₄ NC) ₃ L' ₂]ClO ₄ ^f	2.30 br		7.66 s	
	2.75 br		7.74 s	
[FeCl(4-CH ₃ C ₆ H ₄ NC) ₃ L' ₂]BPh ₄ ^f	2.30 br		7.66 s	
	2.75 br		7.74 s	
[Fe(C ₆ H ₁₁ NC) ₃ L ₃](ClO ₄) ₂ ^g	2.40 br	6.00 br		8.56 t ^h
[FeCl(C ₆ H ₅ NC) ₃]ClO ₄	2.49 br			
[FeCl(4-CH ₃ C ₆ H ₄ NC) ₃]ClO ₄ ⁱ	2.55 m		7.58 s	
			7.64 s	
[FeCl ₂ (4-CH ₃ C ₆ H ₄ NC) ₄]	2.60 br		7.50 s	
	2.90 br			

^a The spectra were measured in CDCl₃ with an Hitachi Perkin-Elmer instrument unless otherwise stated. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. The chemical shifts (τ) of the free ligands are the following. PPh(OEt)₂: 2.61 br, 6.16 m, 8.76 t; in (CD₃)₂CO, 2.34 br, 2.55 br, 6.15 m, 8.77 t. PPh₃: 2.76 br. C₆H₅NC: 2.65 br. 4-CH₃C₆H₄NC: 2.90 br, 7.76 s; in (CD₃)₂CO, 4-CH₃C₆H₄NC: 2.77 d, 3.10 s, 5.50 s. 4-NO₂C₆H₄NC: 1.62 d, 2.20 d. 2-CH₃C₆H₄NC: 2.90 br, 7.75 s. 2,6-(CH₃)₂C₆H₃NC: 2.95 br, 7.67 s. C₆H₁₁NC: 6.40 br, 8.4 br. ^b L = PPh(OEt)₂; L' = PPh₃. ^c In (CD₃)₂CO two 1:2 triplets ($J = 7$ Hz) at τ 8.65 and at 8.75. ^d In (CD₃)₂CO two 1:2 triplets ($J = 7$ Hz) at τ 8.69 and 8.76. ^e In CDCl₃ (HR-220 instrument) two 1:2 triplets ($J = 7$ Hz) at τ 8.646 and at 8.764. In (CD₃)₂CO two 1:2 triplets ($J = 7$ Hz) at τ 8.64 and at 8.78. ^f In (CD₃)₂CO. ^g Cyclohexyl methylene resonance at τ 8.33. ^h In (CD₃)₂CO one triplet ($J = 7$ Hz) at τ 8.58. ⁱ In (CD₃)₂SO. In (CD₃)₂CO (HR-220 instrument) two 4:1 pairs of doublets at τ 2.341, 2.627 and at 2.466, 2.707 and two 4:1 singlets at τ 7.614 and 7.650.

indicate that the two isocyanide ligands are equivalent and, therefore, must both be trans to a phosphine ligand; (b) two resonances are observed for the isocyanide methyl groups in the [FeCl(2,6-(CH₃)₂C₆H₃NC)₂L₃]⁺ cation. In view of the observed blue shift for ν (CN) from that of the free ligands,¹⁶ it seems reasonable to assume that the two CNR moieties are approximately linear and that the four CH₃ groups are pairwise equivalent in the equatorial plane of the molecule thus giving rise to two different signals. Moreover, the presence of two CH₃ resonances for the four methyl groups seems to exclude a rapid rotation of the phenyl rings, about the N-phenyl or the Fe-C bonds, on the nmr time scale. Finally, the fact that two 1:1 chemical shifts of the isocyanide methyl protons in the [FeCl(2-CH₃C₆H₄NC)₂L₃]⁺ cation are observed rules out the possibility of a mirror-like arrangement of the two CNR ligands in this molecule.

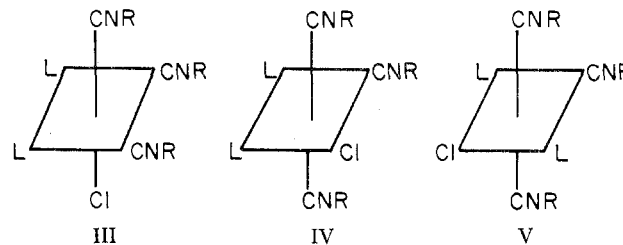
With similar reasoning the cis structure II is proposed for



the [Fe(C₆H₁₁NC)₃L₃]⁺ cation. This is supported by the fact that only a 1:2:1 triplet ($J = 7$ Hz) at τ 8.56 is shown by the methyl protons of the phosphine ligand indicating that they are equivalent. Unfortunately, the broadness of the signals due to the cyclohexyl moieties some of which overlap the phosphine ethoxy methylene protons precludes any further structural assignment from the pmr spectra of this complex. The infrared spectra showing two bands at 2204 and 2170 cm⁻¹ assigned to the A₁ and E stretching modes of isocyanide ligand are further in agreement with structure II.

Finally, the structure of the [FeCl(4-CH₃C₆H₄NC)₃L₂]⁺

(L = PPh₃ or PhP(OEt)₂) cations can be discussed in terms of the following possibilities.



The observation of two singlets (1:2) at τ 7.74 and 7.66 due to the isocyanide methyl protons in the pmr spectrum of the triphenylphosphine derivative does not allow an unambiguous differentiation of the three possibilities. However, structure IV appears to be excluded by the fact that a sharp triplet (1:2:1) at τ 8.65, due to the ethoxy methyl protons of the PhP(OEt)₂ ligand, is present in the nmr spectrum of the diethyl phenylphosphonite derivative, indicating that the two phosphine ligands are equivalent. Of the two remaining possibilities, the number and the intensity of the ν (CN) bands present in the ir spectra of both complexes (Table II) seem to favor the facial structure III.

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Registry No. [FeCl(4-CH₃C₆H₄NC)₂(PPh(OEt)₂)₃]ClO₄, 53111-46-9; [FeCl(C₆H₅NC)₂(PPh(OEt)₂)₃]ClO₄, 53111-48-1; [FeCl(4-CH₃OC₆H₄NC)₂(PPh(OEt)₂)₃]ClO₄, 53111-50-5; [FeCl(4-NO₂C₆H₄NC)₂(PPh(OEt)₂)₃]ClO₄, 53111-52-7; [FeCl(2-CH₃C₆H₄NC)₂(PPh(OEt)₂)₃]ClO₄, 53111-54-9; [FeCl(2,6-(CH₃)₂C₆H₃NC)₂(PPh(OEt)₂)₃]ClO₄, 53111-56-1; [FeCl(4-CH₃C₆H₄NC)₃(PPh(OEt)₂)₂]ClO₄, 53111-58-3; [FeCl(4-CH₃C₆H₄NC)₃(PPh₃)₂]ClO₄, 53111-60-7; [FeCl(4-

$\text{CH}_3\text{C}_6\text{H}_4\text{NC})_3(\text{PPh}_3)_2\text{BPh}_4$, 53111-61-8; $[\text{FeCl}(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_3(\text{PPh}_3)_2]\text{FeCl}_4$, 53111-62-9; $[\text{Fe}(\text{C}_6\text{H}_{11}\text{NC})_3(\text{PPh}(\text{OEt})_2)_3](\text{ClO}_4)_2$, 53111-64-1; $[\text{FeCl}(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_5]\text{ClO}_4$, 26201-85-4; $[\text{FeCl}(\text{C}_6\text{H}_5\text{NC})_3]\text{ClO}_4$, 53111-66-3; $[\text{FeCl}_2(4\text{-CH}_3\text{-C}_6\text{H}_4\text{NC})_4]$, 53111-67-4; PPh_3 , 603-35-0.

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Contribution from the Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

$t_{2g}(\pi^*)$ Electron Distribution in Some Low-Spin Mixed-Ligand Complexes of Iron(III)

P. B. MERRITHEW,* C.-C. LO, and A. J. MODESTINO

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The temperature dependence of the quadrupole splitting of $[\text{Fe}(\text{bipy})_2(\text{CN})_2]\text{ClO}_4$, $[\text{Fe}(\text{phen})_2(\text{CN})_2]\text{ClO}_4$, $\text{H}[\text{Fe}(\text{bipy})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$, and $\text{H}[\text{Fe}(\text{phen})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ was obtained in the range 80–300°. Electron paramagnetic resonance spectra were obtained at 77° on pure samples of these complexes. These data were interpreted to give the magnitude of the spin-orbit coupling constant and the splitting of the $t_{2g}(\pi^*)$ orbitals. The results are found to be consistent with earlier studies of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{Fe}(\text{bipy})_3(\text{ClO}_4)_3$.

Numerous low-spin ($S = 1/2$) iron(III) complexes of the form $[\text{FeA}_6]^{1-3}$ and $[\text{FeB}_3]^{3-9}$ where B is a bidentate ligand, have been studied by Mossbauer spectroscopy in an effort to characterize the cubic $t_{2g}(\pi^*)$ (or $t_{2g}(\pi)$) if the ligands are considered as back-bonding orbitals. The relative energies of the cubic $t_{2g}(\pi^*)$ orbitals in high-spin ($S = 2$) mixed-ligand complexes of iron(II) have also been extensively investigated by Mossbauer spectroscopy.¹⁰⁻¹² Until recently little attention had been paid to mixed-ligand complexes of iron(III). Reiff and DeSimone,¹³ in an electron paramagnetic resonance (epr) and magnetically perturbed Mossbauer spectral study of $[\text{Fe}(\text{bipy})_2(\text{CN})_2]^+$ (bipy = 2,2'-bipyridine) and $[\text{Fe}(\text{phen})_2(\text{CN})_2]^+$ (phen = 1,10-phenanthroline), suggested that the complexes exhibit trigonal distortions. We have investigated the epr spectra, Mossbauer spectroscopy quadrupole splitting data, and magnetic susceptibilities of the compounds $[\text{Fe}(\text{bipy})_2(\text{CN})_2]\text{ClO}_4$, $[\text{Fe}(\text{phen})_2(\text{CN})_2]\text{ClO}_4$, $\text{H}[\text{Fe}(\text{bipy})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$, and $\text{H}[\text{Fe}(\text{phen})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ in an attempt to characterize the perturbation of the cubic ${}^2T_{2g}$ ground term of these complexes.

Experimental Section

Preparation of Compounds. The compounds $[\text{Fe}(\text{bipy})_2(\text{CN})_2]\text{ClO}_4$, $[\text{Fe}(\text{phen})_2(\text{CN})_2]\text{ClO}_4$, $[\text{Fe}(\text{bipy})_2(\text{CN})_2]\text{NO}_3$, $[\text{Fe}(\text{phen})_2(\text{CN})_2]\text{NO}_3\cdot 4\text{H}_2\text{O}$, $\text{H}[\text{Fe}(\text{bipy})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$, and $\text{H}[\text{Fe}(\text{phen})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ were prepared according to the methods of Schilt.¹⁴

Physical Measurements. The Mossbauer spectrometer and associated cryostat have been described previously.² The reproducibility of the spectrometer over the period of a typical sample run (24 hr) is better than 0.5%. The spectrometer was calibrated by employing $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ as a standard with the quadrupole splitting taken as 1.726 mm/sec. The spectra were fitted with a least-squares program and the relative error was determined statistically.¹⁵ It is this error which is given in Table I. The absolute error, due to inadequacies in the calibration procedure, is estimated to be less than 1%.

The epr spectra of $[\text{Fe}(\text{bipy})_2(\text{CN})_2]\text{ClO}_4$ and $\text{H}[\text{Fe}(\text{bipy})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ were obtained on instrumentation described previously.⁹ A Varian E-9 spectrometer system at X-band frequency was employed

Table I. Quadrupole Splitting Data

Temp, °K	Quadrupole splitting, mm/sec	Temp, °K	Quadrupole splitting, mm/sec
$[\text{Fe}(\text{bipy})_2(\text{CN})_2]\text{ClO}_4$			
81 ± 2	1.72 ± 0.02	177	1.71 ± 0.01
96	1.73 ± 0.01	243	1.67 ± 0.02
105	1.73 ± 0.01	273	1.64 ± 0.01
119	1.73 ± 0.01	298	1.61 ± 0.01
145	1.72 ± 0.01		
$[\text{Fe}(\text{phen})_2(\text{CN})_2]\text{ClO}_4$			
81	1.55 ± 0.03	133	1.51 ± 0.02
83	1.55 ± 0.02	177	1.47 ± 0.03
96	1.55 ± 0.02	234	1.41 ± 0.03
101	1.54 ± 0.02	272	1.38 ± 0.03
116	1.53 ± 0.02	298	1.37 ± 0.01
$[\text{Fe}(\text{bipy})_2(\text{CN})_2]\text{NO}_3$			
81	1.75 ± 0.01	183	1.72 ± 0.02
118	1.74 ± 0.01	218	1.69 ± 0.01
123	1.74 ± 0.01	244	1.65 ± 0.02
157	1.74 ± 0.02	296	1.60 ± 0.02
$[\text{Fe}(\text{phen})_2(\text{CN})_2]\text{NO}_3\cdot 4\text{H}_2\text{O}$			
81	1.65 ± 0.02	192	1.58 ± 0.02
90	1.65 ± 0.01	240	1.55 ± 0.02
123	1.64 ± 0.01	271	1.51 ± 0.02
172	1.60 ± 0.02	295	1.49 ± 0.02
$\text{H}[\text{Fe}(\text{bipy})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$			
81	1.63 ± 0.01	201	1.54 ± 0.01
95	1.63 ± 0.01	233	1.51 ± 0.01
103	1.62 ± 0.01	262	1.47 ± 0.01
124	1.60 ± 0.01	279	1.43 ± 0.01
144	1.59 ± 0.01	298	1.39 ± 0.01
173	1.56 ± 0.01		
$\text{H}[\text{Fe}(\text{phen})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$			
93	1.45 ± 0.01	185	1.35 ± 0.01
103	1.44 ± 0.01	212	1.31 ± 0.01
113	1.43 ± 0.01	242	1.27 ± 0.02
160	1.39 ± 0.01	271	1.21 ± 0.02

to obtain spectra of $[\text{Fe}(\text{phen})_2(\text{CN})_2]\text{ClO}_4$ and $\text{H}[\text{Fe}(\text{phen})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$. All spectra were of pure powdered samples at 77°.