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CATIONIC OCTAHEDRAL IRON(II) COMPLEXES WITH ISOCYANIDES AND DIPHOSPHINES

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Summary

The reaction of *cis*- or *trans*-$I_2Fe(CNR)_4$ (R = phenyl or 4-methylphenyl) with diphos in refluxing toluene gave *mer*-[FeI(diphos)$(CNR)_3$]I complexes. These complexes reacted with $AgClO_4$ in dichloromethane to give *mer*-[Fe($OClO_3$)(diphos)$(CNR)_3$]ClO_4. The monodentate perchlorate group could easily be replaced in refluxing Cl_2CH_2 by neutral ligands L (L = PPh_3, NCMe, CNR and diphos) to give compounds of the type [FeL(diphos)$(CNR)_3$]$(ClO_4)_2$. The structures of the complexes is discussed on the basis of their conductivities and IR, ^1H and ^{31}P NMR spectra.

Introduction

Although a number of mixed ligand isocyanide-phosphineiron(II) derivatives 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 $Ph_2P(OEt)$) have been reported [1,2], there are currently no reports of mixed ligand isocyanide-diphosphine iron(II) complexes. With this in mind, we have initiated a study of the reactivity of *cis*- and *trans*-$I_2Fe(CNR)_4$ (R = phenyl or 4-methylphenyl) compounds, by investigating their behaviour towards the potentially bidentate diphosphines, dppm and dppe. The first complexes to be isolated in this study, *mer*-[FeI(diphos)$(CNR)_3$]I, have proved to be suitable starting compounds from which to obtain the complexes: [FeL(diphos)$(CNR)_3$]$(ClO_4)_2$ (L = PPh_3, NCMe, CNR or diphos), through the

(Continued on p. 50)

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[*] Throughout this paper the diphos = $(PhP)_2(CH_2)_n$ ligands are referred to as dppm ($n = 1$) or dppe ($n = 2$).

TABLE 1

MELTING POINTS, CONDUCTIVITY, ANALYTICAL DATA AND ν(NC) FOR COMPLEXES I-XVI

Compound [a]		M.p. (°C)	Λ_M [b]	Analysis (Found (calcd)(%))			ν(NC) [c] (cm^{-1})	
				C	H	N		
(I)	$[FeI(dppm)(CNR)_3]I$	219	120	56.1 (56.2)	4.1 (4.1)	3.7 (4.0)	2170w	2135s
(II)	$[FeI(dppm)(CNR')_3]I$	215	132	55.3 (55.0)	3.6 (3.7)	4.2 (4.2)	2170w	2135s
(III)	$[FeI(dppe)(CNR)_3]I$	218 [d]	118	55.7 (56.6)	4.3 (4.2)	3.9 (3.2)	2168w	2130s
(IV)	$[FeI(dppe)(CNR')_3]I$	219	126	55.6 (55.5)	4.2 (3.8)	4.2 (4.1)	2170w	2135s
(V)	$[Fe(OClO_3)(dppm)(CNR)_3]ClO_4$	220	220 [e]	59.4 (59.4)	4.3 (4.3)	3.9 (4.2)	2189w	2158s
(VI)	$[Fe(OClO_3)(dppm)(CNR')_3]ClO_4$	219 [d]	214	57.0 (58.2)	4.0 (3.9)	4.7 (4.4)	2190w	2157s
(VII)	$[Fe(OClO_3)(dppe)(CNR)_3]ClO_4$	220	200 [f]	58.7 (59.7)	4.7 (4.5)	4.1 (4.2)	2187w	2159s
(VIII)	$[Fe(OClO_3)(dppe)(CNR')_3]ClO_4$	221 [d]	190	59.6 (58.6)	4.6 (4.0)	4.8 (4.3)	2190w	2157s

(IX)	$[Fe(dppm)(CNR)_4](ClO_4)_2$	250[d]	240	61.6 (61.8)	4.5 (4.5)	5.0 (5.0)	2195m	2160s
(X)	$[Fe(dppm)(CNR')_4](ClO_4)_2$	240[d]	237	60.2 (60.5)	3.9 (4.0)	5.0 (5.3)	2200m	2162s
(XI)	$[Fe(dppe)(CNR')_4](ClO_4)_2$	236[d]	245	60.9 (60.8)	4.2 (4.1)	5.2 (5.2)	2200m	2162s
(XII)	$[Fe(PPh_3)(dppm)(CNR)_3](ClO_4)_2$	182	260	63.1 (64.2)	4.5 (4.6)	3.1 (3.3)	2172w	2140s
(XIII)	$[Fe(PPh_3)(dppm)(CNR')_3]ClO_4)_2$	225[d]	235	62.6 (63.4)	4.2 (4.3)	3.3 (3.4)	2175w	2140s
(XIV)	$[Fe(dppm)_2(CNR)_3](ClO_4)_2$	170	240	63.6 (64.6)	4.7 (4.7)	2.5 (3.0)	2172w	2140s
(XV)	$[Fe(dppe)_2(CNR')_3](ClO_4)_2$	120[d]	200	63.0 (64.4)	4.8 (4.6)	3.0 (3.0)	2175w	2140s
(XVI)	$[Fe(MeCN)(dppe)(CNR')_3](ClO_4)_2$	240[d]	228	58.4 (58.6)	5.3 (5.5)	4.2 (4.1)	2195w	2160s

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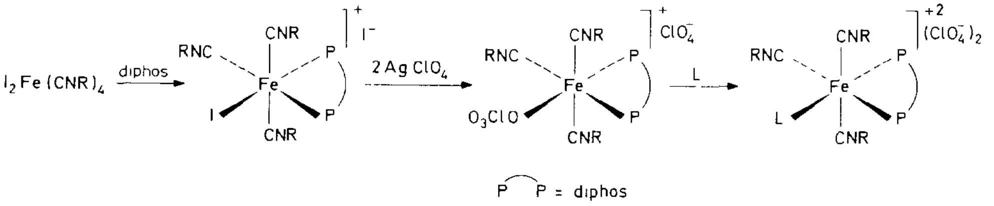
[a] R = 4-methylphenyl, R′ = phenyl. [b] Measured in acetone, 5×10^{-4} *M* (in ohm^{-1} mol^{-1} cm^2). [c] In Cl_2CH_2 solution. [d] With decomposition. [e] 24 in a 10^{-2} *M* solution in nitrobenzene. [f] 25 in a 10^{-2} *M* solution in nitrobenzene.

intermediates *mer*-[Fe(OClO$_3$)(diphos)(CNR)$_3$]ClO$_4$ by replacement of the monodentate perchlorate group.

Results and discussion

The reaction of *cis*- or *trans*-I$_2$Fe(CNR)$_4$ (R = phenyl or 4-methylphenyl) with diphosphine in refluxing toluene gave *mer*-[FeI(diphos)(CNR)$_3$]I (see Scheme 1) as a red crystalline precipitate (compounds I–IV, Table 1). The application of the Onsager equation ($\Lambda_0 - \Lambda_c = (A + WB\Lambda)c^{1/2}$) to the conductivity vs. concentration data led to the conclusion that these compounds are uni-univalent electrolytes * [3–5]. The IR spectra of the compounds I–IV in Cl$_2$CH$_2$ showed two ν(NC) stretching bands; a weak, high-frequency band and a strong one at lower frequency, due probably to the A′ and A′,A″ modes, respectively, in a *mer*-arrangement of the isocyanide ligands (pseudo *Cs* symmetry) (see Table 1). This seems to be consistent with other reports about compounds with analogous isocyanide ligands [2,6].



SCHEME 1

The ^{31}P-{^{1}H}NMR spectra of [FeI(diphos)(CNR)$_3$]$^+$ cations showed two doublets arising from the non-equivalent phosphorus atoms in the complex (see Table 2). In accordance with the general tendency found in octahedral complexes [7,8] the high-field signal is probaly due to the phosphorus atom *trans* to an isonitrile group, whereas the second one can be assigned to the phosphorus which is *trans* to the iodine atom.

It can be noted that the other possible structure which is consistent with the conductivity and analytical data, the *fac* isomers of the compounds I–IV, must be ruled out since the ^{31}P-{^{1}H} NMR spectra would show only one signal for both the equivalent phosphorus atoms.

The higher resistance of isocyanide ligands than CO towards substitution reactions is clearly shown in this work. Thus, it is well known that I$_2$Fe(CO)$_4$ reacts easily (at room temperature) with diphos, to give I$_2$Fe(CO)$_2$(diphos) [9], whereas the reaction of I$_2$Fe(CNR)$_4$ with diphos, leading to the displacement of only one isocyanide ligand, must be carried out in refluxing toluene.

On the other hand, the reaction of a dichloromethane solution of *mer*-[FeI(diphos)(CNR)$_3$]I with AgClO$_4$, in a mol ratio of 1/2, led to the formation of *mer*-[Fe(OClO$_3$)(diphos)(CNR)$_3$]ClO$_4$ (compounds V–VIII). This stoichiometry is valid only for the solid compounds, whose IR spectra show absorptions arising from perchlorate groups with both tetrahedral (1080, 625 cm^{-1}) and C_{3v} (1145, 1000 and 860 cm^{-1}) symmetry. However, the dependence upon solvent of the conductivity values found for these compounds in solution suggests the existence of the equi-

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* The values of the Onsager slope, ($A + WB\Lambda_0$), obtained from such a plot are 145 for compound II and 196 for III.

librium:

$$[\mathrm{Fe(OClO_3)(diphos)(CNR)_3}]^{+} \overset{\mathrm{sol}}{\rightleftharpoons} [\mathrm{Fe(sol)(diphos)(CNR)_3}]^{2+}$$

Thus, the values of the molar conductivity in solvents such as acetone or nitromethane (5×10^{-4} *M* concentration) are in the range which is typical of 2 : 1 electrolytes, whereas the values obtained in nitrobenzene (10^{-2} *M* concentration) are consistent with 1 : 1 electrolytes (see Table 1). An analogous equilibrium has been proposed for the complex $[\mathrm{Fe(OClO_3)(CNR)_5}]\mathrm{ClO_4}$ (R = 4-methylphenyl) [10].

The IR spectra of the compounds V–VIII in Cl_2CH_2 solution showed the same ν(NC) pattern as their parent compounds I–IV although at higher ($\simeq 20$ cm^{-1}) frequencies (see Table 1). This indicates the maintenance of the spacial arrangement of the isocyanide groups; this statement is in agreement with the ^{31}P-{^{1}H} NMR spectrum of a representative compound V, which shows two doublets due to the two non-equivalent phosphorus atoms (see Table 2).

It is well known that the monodentate perchlorate ligand can easily be replaced by neutral groups, and so we have studied the reactions of compounds V–VIII with ligands having Group IV (isocyanide) or Group V (phosphine, diphosphine, nitrile) donor atoms. The substitution reactions, carried out in refluxing Cl_2CH_2, gave the yellow compounds $[\mathrm{FeL(diphos)(CNR)_3}](\mathrm{ClO_4})_2$ (L = PPh_3, NCMe, CNR or diphos). The values of the molar conductivity in 5×10^{-4} *M* acetone solutions of these compounds are characteristic of uni-bivalent electrolytes (see Table 1).

The ^{31}P-{^{1}H} NMR spectra of IX and X showed only one signal, due to two equivalent phosphorus. Moreover, the ^{1}H NMR spectrum of compound IX showed two singlets, in the ratio 1/1, for the CH_3 resonance due to the non-equivalent isocyanide ligands.

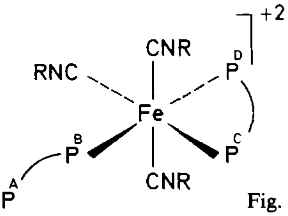

Fig. 1.

The IR spectra of compounds XII–XVI in Cl_2CH_2 solution showed the same ν(NC) pattern as compounds V–VIII, suggesting again a *mer*-arrangment of the isocyanide ligands.

In compounds XIV and XV one diphos ligand is bidentate and the other monodentate (see formula). Analogous structural dispositions of diphosphine ligands are present in tricarbonyl complexes of Mo [11] and Mn [12]. The ^{31}P-{^{1}H} NMR spectra of compounds XIV and XV showed four signals: a doublet (P^A), two double doublets (P^C and P^D) and a doublet of doublet of doublets (P^B). The values of chemical shifts and coupling constants are given in Table 2. The assignments were made on the basis of coordination chemical shifts, the inlfuence of ligands in the *trans* position and a ring contribution (ΔR), and it is in reasonable agreement with other work [13–16].

It can be noted that in the ^{31}P-{^{1}H} NMR spectra of compounds XIV and XV ΔR has the opposite sign when dppm is the chelating ligand instead of dppe. Thus,

TABLE 2

NMR SPECTROSCOPIC DATA [a] FOR SOME CHARACTERISTIC COMPOUNDS

Compound	Chemical shifts (ppm)		Coupling constants (Hz)
	^{31}P-{^{1}H}NMR	^{1}H NMR	*J*(PP)
I	40.8(d), −3.2(d)	–	67
IV	60.1(d), 97.7(d)	–	20
V	38.9(d), 1.1 (d)	–	70
IX	8.6(s)	2.25(s), 2.36(s), 5.41(t), 6–8(m)	
X	8.6(s)	–	
XII	P^B 49.5(dd), P^D 17.0(dd), P^C 6.74(dd)	–	*J*(BC) 36.7 *J*(BD) 74.4 *J*(CD) 60
XIV	P^A −28.3(d), P^B 44(ddd), P^C 5.6(dd), P^D 16.6(dd)	2.32(s,6H), 2.6(s,3H), 3.4(m), 5.18(t), 6–8(m)	*J*(AB) 63.7 *J*(BC) 39 *J*(CD) 60
XV	P^A −13.5(d), P^B 43(ddd), P^C 62.8(dd), P^D 74.2(dd)	–	*J*(AB) 30.3 *J*(BC) 36.5 *J*(BD) 67 *J*(CD) 19.8

[a] Chemical shifts, measured in DCl_3C, are positive to high frequency relative to 85% H_3PO_4 (external) for ^{31}P spectra and for ^{1}H are relative to tetramethylsilane (TMS). Multiplicity: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublet of doublets; t, triplet; m, multiplet. P^A, P^B, P^C and P^D are defined in Fig. 1

the chemical shift for P^D in the compounds XIV and XV reveals the ΔR contribution to be -27.4 ppm (dppm) and $+31.2$ ppm (dppe) by internal comparison with the chemical shift of P^B. These values are in accord with previous work in this area and with the general tendency indicated by Garrou [14] in a recent review.

On the other hand, the $^{31}P\text{-}\{^1H\}$ NMR spectrum of compound XII contains three double doublets at about the same chemical shift as that of P^B, P^C and P^D in compound XIV. No P^A signal resulting from uncoordinated phosphorus was observed (see Table 2).

As a representative ^1H NMR spectrum, that of compound XIV showed two singlets, in the ratio 1/2, for the CH_3 resonance for the 4-methylphenyl isocyanide groups the high-intensity one being due to two isocyanide groups which are *trans* to each other, and the other one to the remaining isocyanide group.

Experimental

Phenyl isocyanide (C_6H_5NC) and *p*-tolyl isocyanide ($4\text{-}CH_3C_6H_4NC$) [17], and the bidentate phosphines, dppe [18] and dppm [19] were obtained by standard literature procedures. The starting complexes, $I_2Fe(CNR)_4$ (R = phenyl and *p*-tolyl), were prepared by the reported method [20].

The reactions were carried out under argon. IR spectra were recorded on a Perkin-Elmer 298 spectrometer. ^1H and ^{31}P NMR spectra were obtained on a Varian F.T.-80 instrument.

Preparation of *mer*-$[FeI(dppm)(4\text{-}CH_3C_6H_4NC)_3]I$

A solution of $I_2Fe(4\text{-}CH_3C_6H_4NC)_4$ (*cis* or *trans*) (0.4 g, 0.51 mmol) and dppm (0.5 g, 1.3 mmol) in 50 ml of toluene was refluxed for 1 h. After this period, the red crystalline precipitate of *mer*-$[FeI(dppm)(4\text{-}CH_3C_6H_4NC)_3]I$ was filtered off and washed with diethyl ether. Yield 0.36 g (68%). Recrystallization was from Cl_2CH_2/ethanol.

The compounds II, III and IV were obtained in a similar manner.

Preparation of *mer*-$[Fe(OClO_3)(dppm)(4\text{-}CH_3C_6H_4NC)_3]ClO_4$

To a solution of *mer*-$[FeI(dppm)(4\text{-}CH_3C_6H_4NC)]I$ (0.4 g, 0.38 mmol) in 50 ml of Cl_2CH_2, $AgClO_4$ (0.159 g, 0.76 mmol) was added. After being stirred for 1 h, the orange solution was filtered to separate it from the solid yellow AgI. The volume was reduced, and petroleum ether added to precipite the orange crystalline compound V. Yield 0.34 g (92%).

The compounds VI, VII and VIII were prepared in a similar manner.

Preparation of $[Fe(dppm)(4\text{-}CH_3C_6H_4NC)_4](ClO_4)_2$

p-Tolyl isocyanide (0.1 g, 0.85 mmol) was added to a solution of *mer*-$[Fe(OClO_3)(dppm)(4\text{-}CH_3C_6H_4NC)_3]ClO_4$ (0.4 g, 0.41 mmol) in 50 ml of Cl_2CH_2. The mixture was heated under reflux for 4 h. Then the solvent was evaporated and the yellow solid product washed with diethyl ether and dried under vacuum. The compound was recrystallized from a dichloromethane/ethanol mixture to give pale yellow crystals of IX. Yield 0.32 g (70%).

Compound X and XI were prepared in a similar manner.

Preparation of mer-[Fe(PPh$_3$)(dppm)(4-CH$_3$C$_6$H$_4$NC)$_3$](ClO$_4$)$_2$

A mixture of PPh$_3$ (0.3 g, 1.14 mmol) and V (0.4 g, 0.41 mmol) was refluxed in 50 ml of Cl$_2$CH$_2$ for 5 h. The solvent was removed under reduced pressure and the solid washed with ethyl ether until the remaining PPh$_3$ had disappeared. The product was recrystallized from a Cl$_2$CH$_2$/ethanol mixture as yellow crystals. Yield 0.37 g (72%).

Compounds XIII, XIV, XV and XVI were obtained in a similar manner.

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