Synthesis and Reactivity of Mixed-ligand Isocyanide–Diphosphine Iron(0) Complexes. *X*-Ray Crystal Structure of *cis*-$[Fe(dppe)(CNPh)_2\{N(Ph)=C(Me)-C=NPh\}]ClO_4$†

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Reduction of *mer*-$[FeI(L–L)(CNR)_3]I$ [(**1a**), L–L = 1,2-bis(diphenylphosphino)ethane (dppe), R = Ph; (**1b**) L–L = dppe, R = C_6H_4Me-4; (**1c**), L–L = bis(diphenylphosphino)methane, R = Ph] with sodium amalgam in tetrahydrofuran gives the very air-sensitive complexes $[Fe(L–L)(CNR)_3]$ (**2a**)—(**2c**) respectively. Compound (**2a**) reacts with NH_4PF_6 to give *mer*-$[FeH(dppe)(CNPh)_3]PF_6$ (**3**), which is readily transformed to its *fac* isomer (**4**) by heating. Reaction of (**2a**) with $SnPh_3Cl$ yields the novel heterodimetallic cation *mer*-$[Fe(SnPh_3)(dppe)(CNPh)_3]^+$ (**5**). Addition of CH_3I to toluene solutions of complexes (**2a**)—(**2c**) gives the neutral compounds $[FeI(L–L)(CNR)\{N(R)=C(Me)-C=NR\}]$ (**6a**)—(**6c**) respectively which possess a new chelating ligand. Compound (**6a**) reacts with phenyl isocyanide in the presence of $AgClO_4$ to give *cis*-$[Fe(dppe)(CNPh)_2\{N(Ph)=C(Me)-C=NPh\}]ClO_4$ (**7**) and with carbon monoxide in the presence of $TlPF_6$ to give $[Fe(dppe)(CO)(CNPh)\{N(Ph)=C(Me)-C=NPh\}]^+$. For complex (**7**), a single-crystal *X*-ray diffraction study was carried out. The iminic nitrogen in (**6a**) is easily protonated with $HClO_4$ affording the cationic complex $[FeI(dppe)(CNPh)\{N(Ph)=C(Me)-C-NHPh\}]ClO_4$. Complex (**2a**) reacts with allyl bromide to give mainly the undesired *mer*-$[FeBr(dppe)(CNPh)_3]^+$ and a small amount of the neutral complex $[FeBr(dppe)(CNPh)\{N(Ph)=C(CH_2CHCH_2)-C=NPh\}]$.

The chemistry of low-valent metal isocyanide complexes has been developed in recent years;[1,2] of particular importance are the homoleptic metal isocyanide compounds of the type $[Ni(CNR)_4]$,[3] $[Co_2(CNR)_8]$,[4] $[Fe(CNR)_5]$,[5] and $[Fe_2(CNR)_9]$[6] (R = alkyl or aryl), which are analogous to their corresponding carbonyl derivatives. Moreover, zero-valent metal isocyanide complexes have proved to react much more easily with oxidation agents than their carbonyl analogues because isocyanide ligands increase the nucleophilicity of metal centres.[1,2] In iron chemistry, compounds of the type $[Fe(CNR)_5]$ (R = Bu^t, Pr^i, Et, or $C_6H_3Me_2$-2,6), $[Fe(CNEt)_3(CNC_6H_3Me_2\text{-}2,6)_2]$, $[Fe(CNBu^t)_4(PPh_3)]$, and $[Fe_2(CNR)_9]$ (R = Et or Pr^i) have been described by Stone and co-workers.[5,6] The parent compound $[Fe(CNR)_5]$ exhibited a high reactivity toward a great variety of reagents such as MeI, EtI, Pr^{i}I, $Me_3O{\cdot}BF_4$, PhC≡CPh, *etc.*, affording new iron(II) derivatives[7] and demonstrating the large perspective of this field. We have initiated the study of the chemistry of mixed-ligand isocyanide–diphosphine iron(0) complexes by obtaining the species $[Fe(L–L)(CNR)_3]$ [(**2a**), L–L = 1,2-bis(diphenylphosphino)ethane (dppe), R = Ph; (**2b**), L–L = dppe, R = C_6H_4Me-4; (**2c**) L–L = bis(diphenylphosphino)methane (dppm), R = Ph] through sodium amalgam reduction of the corresponding cationic compounds *mer*-$[FeI(L–L)(CNR)_3]I$ (**1a**)—(**1c**), which we have recently published.[8] The reaction of these very air-sensitive species toward a variety of reagents (NH_4PF_6, $SnPh_3Cl$, MeI, CH_2=$CHCH_2Br$) to give a number of iron(II) derivatives has also been studied.

Results and Discussion

The neutral complexes $[Fe(L–L)(CNR)_3]$ (**2a**)—(**2c**), obtained by sodium amalgam reduction of the cations $[FeI(L–L)(CNR)_3]^+$ in tetrahydrofuran (thf), were very air-sensitive and could not be isolated as pure samples, precluding both analytical and crystallographic studies. However, these compounds showed a high reactivity towards electrophiles and this allowed us to obtain a number of derivatives which are in agreement with the proposed stoicheiometry for the neutral complexes (**2a**)—(**2c**).

The i.r. spectrum in thf of the representative complex (**2a**) showed a band at 2 050 cm^{-1} and two broad absorptions at 1 945 and 1 800 cm^{-1}. This last very low frequency absorption probably arises from a considerably bent isocyanide ligand, as has been shown in other iron(0) derivatives.[5] The ^{31}P-{^1H} n.m.r. spectrum of (**2a**) showed only one singlet at 93.5 p.p.m. even down to −90 °C, indicating that the phosphorus atoms of the dppe ligand are equivalent. With these data, it is not possible to distinguish between the two most probable molecular geometries for the compound: square pyramidal and trigonal bipyramidal. Moreover the existence of stereochemical non-rigidity of the molecule is probable, as it occurs in the complex $[Fe(CNBu^t)_5]$ for which only one t-butyl isocyanide environment was observed in the ^1H and ^{13}C n.m.r. spectra down to −130 °C.[5] A red solution of compound (**2a**) was also obtained by sodium amalgam reduction of $[Fe(dppe)(CNPh)_4][ClO_4]_2$[8] in thf.

As expected, reaction of (**2a**) with I_2 in thf readily afforded the parent compound (**1a**). On another hand, addition of an excess of NH_4PF_6 to a toluene solution of (**2a**) gave the cationic hydride derivative *mer*-$[FeH(dppe)(CNPh)_3]PF_6$ (**3**) (see Scheme) as a yellow precipitate. The reaction of iron(0) complexes with acids is a general way of obtaining iron(II) cationic hydrides; thus it is known that $[Fe\{P(OMe)_3\}_5]$ reacts

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† *cis*-[1,2-Bis(diphenylphosphino)ethane-*PP′*][1,2-di(phenylimino)-propyl-C^1N^2]bis(phenyl isocyanide)iron(II) perchlorate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

Table 1. Infrared and analytical data

	Compound	M.p.[a]/ °C	Λ_m[b]	Analysis (%)[c] C	H	N	ν_{CN}[d]/ cm^{-1}	Other bands[e]
(3)	*mer*-$[FeH(dppe)(CNPh)_3]PF_6$	90	123	62.6 (62.1)	4.6 (4.4)	4.2 (4.6)	2 155w 2 101s	1 805m [ν(Fe–H)]
(4)	*fac*-$[FeH(dppe)(CNPh)_3]PF_6$	90	115	63.0 (62.1)	5.0 (4.4)	4.2 (4.6)	2 147m 2 094s	
(5)	*mer*-$[Fe(SnPh_3)(dppe)(CNPh)_3]PF_6$	245	123	61.4 (62.0)	4.4 (4.3)	3.3 (3.3)	2 139w 2 092s	
(6a)	$[FeI(dppe)(CNPh)\{N(Ph){=}C(Me){-}C{=}NPh\}]$	163		63.1 (63.6)	4.6 (4.6)	4.4 (4.6)	2 056s 2 008m	1 615m 1 545m [ν(C=N)]
(6b)	$[FeI(dppe)(CNC_6H_4Me\text{-}4)\{N(C_6H_4Me\text{-}4){=}C(Me){-}C{=}NC_6H_4Me\text{-}4\}]$	179		65.4 (64.6)	5.3 (5.1)	4.1 (4.4)	2 068s 2 040s	1 620m 1 550m [ν(C=N)]
(6c)	$[FeI(dppm)(CNPh)\{N(Ph){=}C(Me){-}C{=}NPh\}]$	119		63.7 (63.3)	5.1 (4.5)	4.7 (4.7)	2 060s 2 010m	1 610m 1 550m [ν(C=N)]
(7)	*cis*-$[Fe(dppe)(CNPh)_2\{N(Ph){=}C(Me){-}C{=}NPh\}]ClO_4$	177	132	66.9 (67.3)	4.8 (4.8)	5.7 (5.7)	2 120s 2 084s	1 620m 1 560m [ν(C=N)]
(8)	$[Fe(dppe)(CO)(CNPh)\{N(Ph){=}C(Me){-}C{=}NPh\}]BPh_4$	170	108	76.7 (77.8)	5.5 (5.5)	3.7 (3.7)	2 125s	1 985s [ν(CO)], 1 615m, 1 570m [ν(C=N)]
(9)	$[FeI(dppe)(CNPh)\{N(Ph){=}C(Me){-}C{-}NHPh\}]ClO_4$	144	118	56.0 (57.2)	4.1 (4.2)	3.9 (4.1)	2 092s	3 170w [ν(N–H)], 1 610w, 1 535m [ν(C=N)]
(10)	*mer*-$[FeBr(dppe)(CNPh)_3]PF_6$	220	120	56.3 (57.1)	4.0 (3.9)	4.2 (4.2)	2 175w 2 135s	
(11)	$[FeBr(dppe)(CNPh)\{N(Ph){=}C(CH_2CHCH_2){-}C{=}NPh\}]$	168		69.0 (67.9)	5.1 (5.0)	4.7 (4.7)	2 058s 2 010m	1 607m, 1 545m [ν(C=N)]

[a] All with decomposition. [b] In acetone (5×10^{-4} mol dm^{-3}), values in Ω^{-1} cm^2 mol^{-1}. [c] Calculated values in parentheses. [d] In CH_2Cl_2. [e] In the KBr solid spectra.

with NH_4PF_6 to give $[FeH\{P(OMe_3)\}_5]PF_6$;[9] by treating $[Fe(CNBu^t)_5]$ with HBF_4, the compound $[FeH(CNBu^t)_5]BF_4$ is obtained.[10]

The i.r. spectrum in CH_2Cl_2 solution of (**3**) exhibited two absorption bands at 2 155w and 2 101s cm^{-1} in the C≡N stretching region for the isocyanides (Table 1); its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed two doublets (Table 2) due to the inequivalent phosphorus atoms of the diphosphine. These data are in agreement with the proposed *mer* arrangement of the isocyanide ligands in the compound. Moreover an i.r. band at 1 805 cm^{-1} assigned to a Fe–H stretching frequency was observed in the KBr solid spectrum of (**3**).

Compound (**3**) slowly changes into its *fac* isomer (**4**) on standing over 4 h in CH_2Cl_2 solution at room temperature and after 10 min on heating under reflux in thf. The i.r. spectrum (CH_2Cl_2) of the *fac* isomer in the C≡N region showed absorptions at 2 147m and 2 094s cm^{-1}. An analogous pattern of bands has been found in other *fac* isocyanide complexes, *e.g.* in *fac*-$[Fe\{PPh(OEt)_2\}_3(CNC_6H_{11})_3][ClO_4]_2$ which shows absorptions at 2 204m and 2 170s cm^{-1}.[11] As expected, compound (**4**) showed only one signal in its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum at 97.9 p.p.m. due to both equivalent phosphorus atoms of the diphosphine. Moreover, its ^1H n.m.r. spectrum exhibited a lowfield hydride triplet at −10.5 p.p.m. (J_{PH} = 50 Hz). No Fe–H stretching band was observed in the i.r. solid spectrum of (**4**); this is not very surprising because there are other iron(II) cationic hydrides in which this band is not observed.[12]

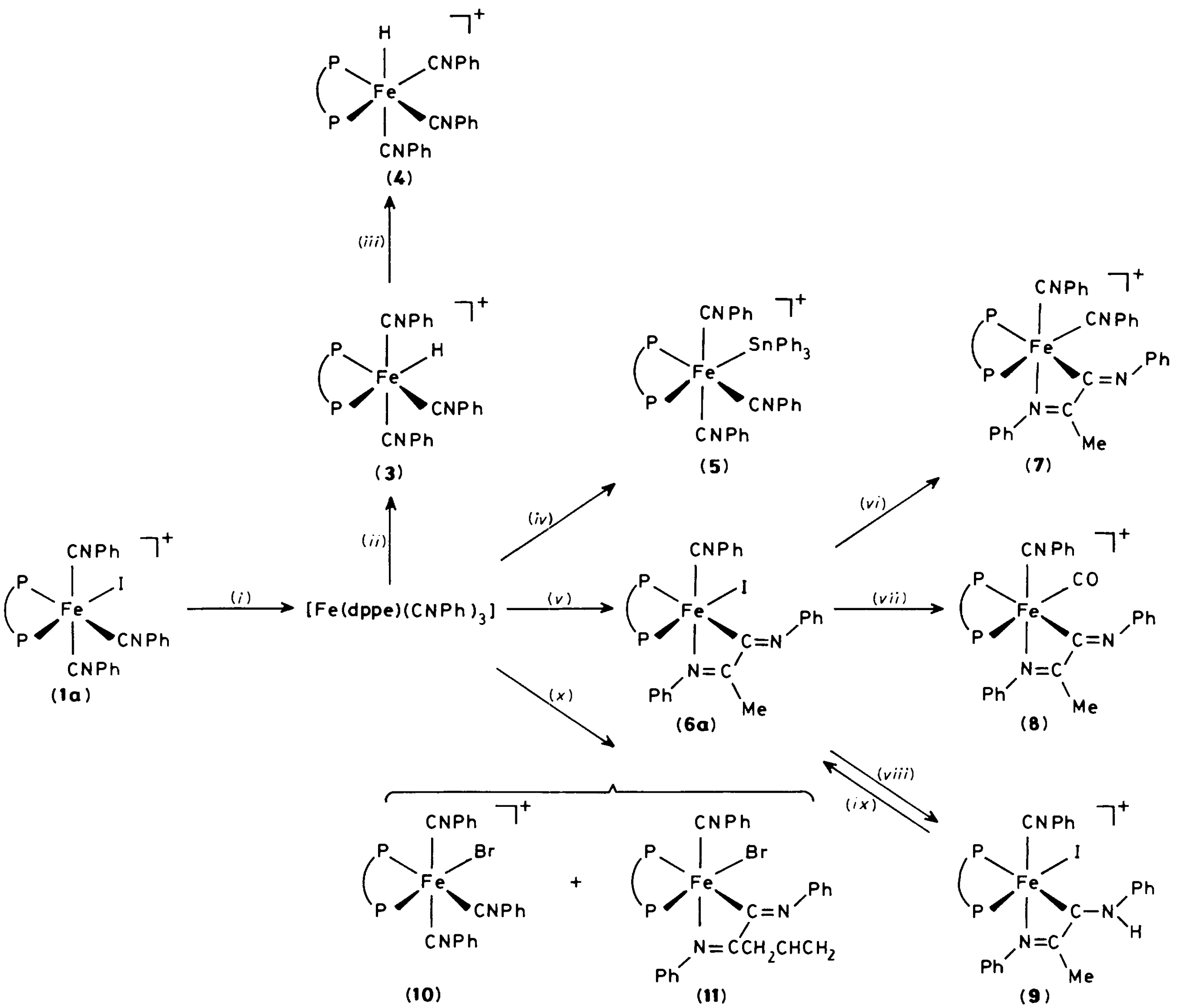
Another type of reaction accomplished with the iron(0) derivative (**2a**) was the addition of metallic species with a view to obtaining new heterobimetallic complexes. Thus, the reactions of toluene solutions of (**2a**) with $SnPh_3Cl$ readily gave a yellow precipitate corresponding to *mer*-$[Fe(SnPh_3)(dppe)(CNPh)_3]Cl$ and, after interchanging the anion with KPF_6, *mer*-$[Fe(SnPh_3)(dppe)(CNPh)_3]PF_6$ (**5**) was definitely obtained (see Scheme). The spectroscopic and analytical data are in agreement with the proposed structure for (**5**) (see Tables 1 and 2). An interesting feature of the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**5**) is the presence of weak multiplets arising from $^{117}Sn\text{-}^{31}P$ and $^{119}Sn\text{-}^{31}P$ couplings in addition to the two doublets due to the inequivalent phosphorus atoms.

Table 2. Hydrogen-1 and $^{31}P\text{-}\{^1H\}$ n.m.r. data

Compound	$^{31}P\text{-}\{^1H\}$[a]	J_{PP}/Hz	^1H[b]
(**3**)	89 (d), 77 (d)[c]	11	
(**4**)	97.9 (s)		−10.5 (t, Fe–H, J_{PH} = 50 Hz)
(**5**)	81.4 (d), 77.7 (d)	12	
(**6a**)	101.9 (s), 43.7 (s)[c]	<2	1.77 (s, C–CH_3)
(**6b**)	101 (s), 43.5 (s)	<2	1.71 (s, C–CH_3), 2.1 (s, 6 H, $C_6H_4CH_3$), 2.22 (s, 3 H, $C_6H_4CH_3$)
(**6c**)	70.8 (s, br), 11.1 (d)	3	
(**7**)	69.2 (d), 63 (d)	13	1.69 (d, C–CH_3, $^5J_{PH}$ = 2)
(**8**)	64.7 (d), 61.6 (d)	17	1.65 (d, C–CH_3, $^5J_{PH}$ = 2.5)
(**9**)	97.3 (d), 46.5 (d)	19	1.93 (s, C–CH_3)
(**11**)	94.1 (s), 41 (s)	<2	

[a] In CH_2Cl_2 as solvent; chemical shifts (p.p.m.) are positive to high frequencies relative to 85% H_3PO_4. [b] In $CDCl_3$ as solvent; chemical shifts (δ) relative to $SiMe_4$. [c] Recorded at −50 °C in CH_2Cl_2.

Efforts to obtain other heterobimetallic species were unsuccessful. Thus the reactions of (**2a**) with $[MnBr(CO)_5]$, $[Ag(PPh_3)(ClO_4)]$, and $[Au(tht)Cl]$ (tht = tetrahydrothiophene) afforded $[Mn_2(CO)_{10}]$, metallic silver, and metallic gold respectively, in addition to the corresponding iron(II) cations: $[FeBr(dppe)(CNPh)_3]^+$, $[Fe(ClO_4)(dppe)(CNPh)_3]^+$, and $[FeCl(dppe)(CNPh)_3]^+$



Scheme. (*i*) Na–Hg in thf; (*ii*) NH_4PF_6 in toluene; (*iii*) refluxing thf; (*iv*) $SnPh_3Cl$ in toluene; (*v*) MeI in toluene: (*vi*) $AgClO_4$ and phenyl isocyanide in CH_2Cl_2; (*vii*) $TlPF_6$ and CO in CH_2Cl_2; (*viii*) $HClO_4$ in CH_2Cl_2; (*ix*) KOH in CH_2Cl_2; (*x*) CH_2CHCH_2Br in toluene

As expected, organic halides reacted easily with the iron(0) compounds $[Fe(L-L)(CNR)_3]$ (**2a**)—(**2c**). In this way, when a toluene solution of $[Fe(dppe)(CNPh)_3]$ was treated with methyl iodide, a darkening of the red solution was readily observed. After crystallization from toluene–diethyl ether, red crystals of the new compound (**6a**) were obtained. Analytical data were consistent with the composition $[Fe(dppe)(CNPh)_3]\cdot MeI$. Unfortunately, we have not been able to obtain suitable crystals of (**6a**) for an *X*-ray analysis. However we have obtained suitable crystals of a derivative of (**6a**), *cis*-$[Fe(dppe)(CNPh)_2\{N(Ph){=}C(Me){-}C{=}NPh\}]ClO_4$ (**7**). This was obtained from (**6a**) by treating it with $AgClO_4$ in the presence of phenyl isocyanide. The structure of the cation is shown in Figure 1.

The structure is of an ionic type. Iron is at the centre of a very distorted cationic octahedron. Two vertices are occupied by phosphorus atoms of the dppe ligand. Two other vertices are occupied by two phenyl isocyanide molecules in mutually *cis* positions, one being *trans* to a phosphorus atom. The last two vertices are occupied by a nitrogen atom and a carbon atom of a new chelating ligand; nitrogen is *trans* to phenyl isocyanide, carbon is *trans* to phosphorus. This ligand can be described as being made of two isocyanides coupled by their carbon atoms, one of them bearing a methyl group, the other being ligated to iron so that it may result from successive insertion reactions of two isocyanide molecules into the Fe–C(methyl) σ bond, an assumption supported by the isolation of compound (**6a**). Thus, a four-membered ring Fe–N(4)–C(4)–C(3) is formed with a very small N(4)–Fe(1)–C(3) angle of 65.6(4)°.

The planarity of the Fe–C(3)–C(4)–N(4)–N(3) group (maximum deviation of 0.03 Å from the mean plane) and the short bond length C(3)–C(4) (1.46 Å) suggest some electron delocalization along the N(3)–C(3)–C(4)–N(4) chain. Atoms N(4), C(3), and C(4) are truly sp^2 with the sum of angles around them 359.7, 359.9, and 360.0° respectively. This delocalization does not seem to include phenyl rings attached to N(3) and N(4) because their planes make an angle of 62.3°. There is no significant back-bonding from Fe toward C(3) and N(4).

Some features suggested a disorder of the C(6) and C(7) atoms of dppe: Fe–P(1)–C(6)–C(7)–P(2) looks almost planar with a maximum deviation from the least-squares plane of 0.24 Å; the C(6)–C(7) bond length is abnormally short (1.43 Å); C(6) and C(7) exhibit large thermal vibration anisotropy with their

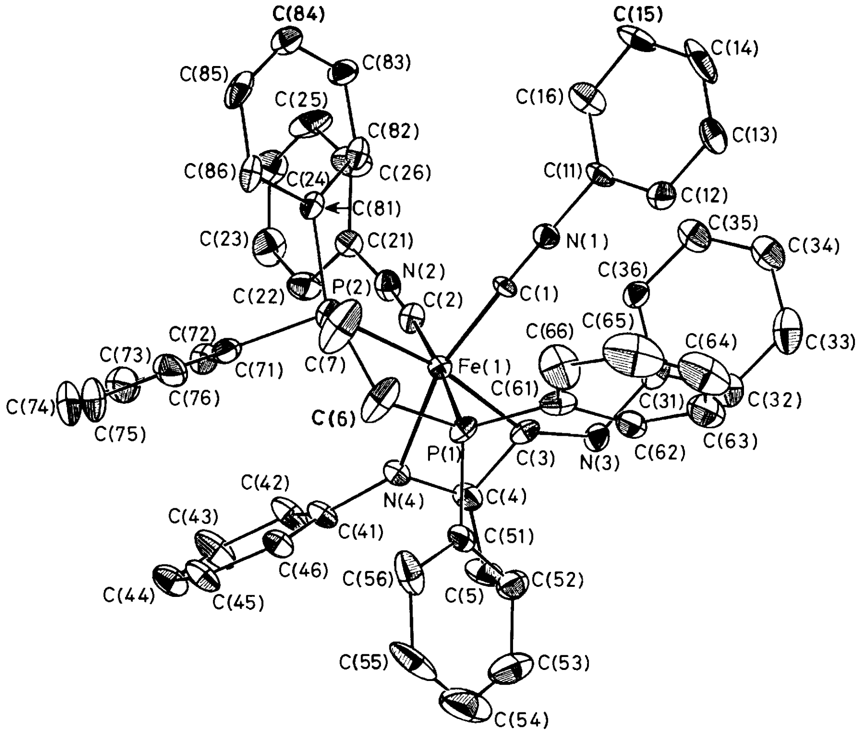


Figure. Perspective view of the cation *cis*-$[Fe(dppe)(CNPh)_2\{N(Ph)=C(Me)-C=NPh\}]^+$ with atom numbering and ellipsoids at 20% probability

largest ellipsoid axes at angles of 86.5 and 84.0° to the above mean plane. Actually both C(6) and C(7) should be out of this mean plane, one below and one above; the disorder corresponds to an average between the two possible situations for both carbon atoms. A similar situation was described for example in $[Cu_2(Me_2NCH_2CH_2NMe_2)_2(N_3)(OH)]^{2+}$,[13] involving the disordered $N-CH_2-CH_2-N$ chelating group.

On the basis of the structure of (7), the most probable structure for (**6a**) is that represented in the Scheme. It has been shown that the reaction of $[Fe(CNR)_5]$ ($R = C_6H_3Me_2$-2,6) with MeI produces the σ-iminoacyl derivative $[FeI\{C(Me)=NR\}(CNR)_4]$.[7] In our case, a further insertion reaction of isocyanide into the iron–carbon σ bond takes place to give the di-imino chelating group of (**6a**), as occurs similarly in the reaction between $[Fe(CNBu^t)_5]$ and methyl iodide.[7]

The reactions of the compounds $[Fe(dppe)(CNC_6H_4Me\text{-}4)_3]$ (**2b**) and $[Fe(dppm)(CNPh)_3]$ (**2c**) with methyl iodide afforded $[FeI(dppe)(CNC_6H_4Me\text{-}4)\{N(C_6H_4Me\text{-}4)=C(Me)-C=NC_6H_4Me\text{-}4\}]$ (**6b**) and $[FeI(dppm)(CNPh)\{N(Ph)=C(Me)-C=NPh\}]$ (**6c**) respectively which possess analogous spectroscopic characteristics to those of complex (**6a**). The solid i.r. spectra of compounds (**6**) showed absorptions at *ca.* 1 610 and 1 550 cm^{-1} due to the $\nu(C=N)$ stretching vibrations of the di-imino group. Surprisingly two absorptions were present in the region between 2 000 and 2 100 cm^{-1} for the $C\equiv N$ stretching vibrations (see Table 1). This behaviour is not common, but there are other compounds in the literature in which a lone isocyanide ligand gives two $C\equiv N$ absorptions, *e.g.* $[Cr(CO)_2(CNBu^t)(\eta^6\text{-}C_6H_5CO_2Me)]$.[14] The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of (**6a**) and (**6b**) gave two singlets arising from the two inequivalent phosphorus atoms ($J_{PP} < 2$ Hz); for (**6c**) a J_{PP} value of 3 Hz was observed (see Table 2).

It is well known in the literature that complexes with σ-iminoacyl ligands or other imino groups can be easily protonated at the iminic nitrogen to give aminocarbene complexes.[15,16] In our case, the reaction of (**6a**) with $HClO_4$ gave $[FeI(dppe)(CNPh)\{N(Ph)=C(Me)-C-NHPh\}]ClO_4$ (**9**) which possesses a chelating iminocarbene ligand (see Scheme). The i.r. spectrum of (**9**) showed only one terminal isocyanide stretching band at higher wavenumber than those observed in the spectrum of (**6a**). Moreover absorptions at 1 610 and 1 535 cm^{-1} due to the C=N stretching vibrations of the imino and carbene groups were also observed. The N–H stretching vibration gave a weak broad band at 3 170 cm^{-1}.

The protonation reaction of (**6a**) was found to be reversible; thus by treating (**9**) with KOH in CH_2Cl_2, (**6a**) was readily recovered. Another derivative of (**6a**) was obtained by abstraction of the iodide with $TlPF_6$ in the presence of carbon monoxide (see Scheme). After exchanging the anion with $NaBPh_4$, $[Fe(dppe)(CO)(CNPh)\{N(Ph)=C(Me)-C=NPh\}]BPh_4$ (**8**) was obtained. As expected, CO and CN stretching bands were present in the i.r. spectrum of (**8**). The other analytical and spectroscopic data were in agreement with the proposed structure for (**8**) (see Tables 1 and 2).

Finally, with the view to obtaining a σ-allyl iron(II) derivative, we studied the reaction of (**2a**) with allyl bromide. Unfortunately, no allyl complex was obtained; the reaction afforded the cation *mer*-$[FeBr(dppe)(CNPh)_3]^+$ (**10**) as the major product and a small amount of a neutral complex (**11**) which possess similar spectroscopic characteristics to (**6a**), and so their structures should be closely related (see Scheme and Tables 1 and 2).

Experimental

All reactions were carried out under a dry oxygen-free argon atmosphere, with solvents dried and distilled under argon prior to use. Infrared spectra were obtained on a Perkin-Elmer 298 spectrophotometer; n.m.r. spectra (^1H and $^{31}P\text{-}\{^1H\}$) were

Table 3. Final atomic co-ordinates for *cis*-[Fe(dppe)$(CNPh)_2${N(Ph)=C(Me)–C=NPh}]ClO_4

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe(1)	0.8800	0.197 9(1)	0.8000
P(1)	0.760 8(2)	0.056 9(3)	0.821 4(2)
P(2)	0.936 9(2)	0.055 2(3)	0.713 4(2)
N(1)	0.739 8(7)	0.299 1(9)	0.668 7(6)
N(2)	1.051 4(7)	0.356 7(9)	0.763 8(7)
N(3)	0.800 1(7)	0.400 2(9)	0.913 3(6)
N(4)	0.956 2(6)	0.161 0(8)	0.912 5(5)
C(1)	0.794 3(7)	0.258 9(9)	0.718 1(6)
C(2)	0.982 1(7)	0.299(1)	0.778 7(7)
C(3)	0.845 8(7)	0.307(1)	0.891 1(6)
C(4)	0.912 9(8)	0.245(1)	0.952 8(7)
C(5)	0.932(1)	0.273(1)	1.042 8(8)
C(6)	0.786(1)	−0.075(1)	0.763(1)
C(7)	0.840(1)	−0.055(2)	0.693(1)
C(11)	0.668 8(9)	0.348(1)	0.606 2(7)
C(12)	0.574(1)	0.343(1)	0.619 1(9)
C(13)	0.503(1)	0.387(2)	0.559(1)
C(14)	0.533(2)	0.435(2)	0.491(1)
C(15)	0.634(2)	0.443(2)	0.478(1)
C(16)	0.701(1)	0.400(1)	0.540(1)
C(21)	1.137 1(7)	0.409(1)	0.740 0(7)
C(22)	1.221 9(9)	0.409(1)	0.793 7(8)
C(23)	1.306 1(9)	0.464(2)	0.771(1)
C(24)	1.311(1)	0.511(2)	0.697(1)
C(25)	1.230(2)	0.508(2)	0.642(1)
C(26)	1.140(1)	0.456(2)	0.662 2(9)
C(31)	0.741 9(9)	0.478(1)	0.856 8(7)
C(32)	0.649(1)	0.505(1)	0.873 3(8)
C(33)	0.590(1)	0.579(1)	0.821(1)
C(34)	0.630(1)	0.627(1)	0.752(1)
C(35)	0.724(1)	0.603(1)	0.735 7(9)
C(36)	0.781 0(9)	0.526(1)	0.787 4(7)
C(41)	1.036 0(8)	0.087(1)	0.946 7(7)
C(42)	1.129(1)	0.143(1)	0.967 6(9)
C(43)	1.208(1)	0.072(2)	0.997(1)
C(44)	0.198(1)	−0.052(1)	1.000 8(9)
C(45)	0.108(1)	−0.104(1)	0.975 6(9)
C(46)	1.027 2(9)	−0.035(1)	0.949 1(7)
C(51)	0.751 6(8)	−0.011(1)	0.922 3(8)
C(52)	0.739(1)	0.064(2)	0.988 5(8)
C(53)	0.729(1)	0.008(3)	1.065(1)
C(54)	0.727(2)	−0.110(4)	1.077(2)
C(55)	0.743(1)	−0.185(2)	1.013(2)
C(56)	0.752(1)	−0.138(1)	0.931(1)
C(61)	0.631 1(9)	0.097(1)	0.791 2(7)
C(62)	0.589 3(9)	0.192(1)	0.831 5(8)
C(63)	0.489(1)	0.225(2)	0.815(1)
C(64)	0.433(2)	0.160(3)	0.755(2)
C(65)	0.472(2)	0.068(3)	0.717(2)
C(66)	0.572(1)	0.037(2)	0.732(1)
C(71)	1.050(1)	−0.029(1)	0.744 4(7)
C(72)	1.133(1)	0.034(2)	0.776(1)
C(73)	1.222(1)	−0.034(3)	0.797(1)
C(74)	1.224(2)	−0.158(4)	0.788(2)
C(75)	1.143(3)	−0.213(3)	0.763(2)
C(76)	1.053(2)	−0.155(1)	0.737(1)
C(81)	0.955 4(8)	0.096(1)	0.608 4(7)
C(82)	0.953 3(8)	0.216(1)	0.579 5(8)
C(83)	0.965(1)	0.241(1)	0.499 7(8)
C(84)	0.979(1)	0.150(2)	0.445 4(9)
C(85)	0.984(1)	0.030(2)	0.471 3(9)
C(86)	0.972 6(9)	0.002(1)	0.553 5(9)
Cl(1)	0.422 8(3)	0.370 5(4)	0.031 1(3)
O(1)	0.516(1)	0.308(2)	0.025(1)
O(2)	0.413(2)	0.458(2)	−0.031(1)
O(3)	0.418(2)	0.454(2)	0.101(1)
O(4)	0.348(1)	0.289(2)	0.044(1)

recorded on a Varian FT-80 instrument. The compounds *mer*-[FeI(L–L)$(CNR)_3$]I (**1a**)—(**1c**) were obtained as described previously.[8]

Preparation of a Toluene Solution of [Fe(dppe)$(CNPh)_3$] (**2a**).—To a stirred suspension of *mer*-[FeI(dppe)$(CNPh)_3$]I (**1a**) (0.2 g, 0.196 mmol), in thf (20 cm^3) was added an excess of sodium amalgam (20 g, 0.5%). After stirring for 1 h, the red solution obtained was filtered under an argon atmosphere. The solvent was removed *in vacuo* and the residue extracted with toluene (30 cm^3). After filtration, the toluene solution of [Fe(dppe)$(CNPh)_3$] (**2a**) is ready to be used as a reagent. Toluene solutions of the compounds [Fe(dppe)$(CNC_6H_4$-Me-4$)_3$] (**2b**) and [Fe(dppm)$(CNPh)_3$] (**2c**) were prepared in the same manner.

mer-[FeH(dppe)$(CNPh)_3$]PF_6 (**3**).—To a solution of [Fe(dppe)$(CNPh)_3$] (**2a**) [obtained from (**1a**) (0.2 g, 0.196 mmol)] in toluene (30 cm^3) was added NH_4PF_6 (0.05 g, 0.3 mmol) in deaerated distilled water (2 cm^3). The mixture was stirred for 2 h after which a yellow precipitate of (**3**) was formed. The precipitate was filtered off and washed with three successive portions (30 cm^3) of distilled water. Finally, the product was dried *in vacuo* (yield 0.125 g, 70%).

fac-[FeH(dppe)$(CNPh)_3$]PF_6 (**4**).—A solution of *mer*-[FeH(dppe)$(CNPh)_3$]PF_6 (**3**) (0.1 g, 0.11 mmol) in thf (20 cm^3) was refluxed for 10 min. The solvent was then evaporated *in vacuo* to a volume of 5 cm^3; after adding diethyl ether (6 cm^3), yellow crystals of (**4**) were obtained (yield 0.09 g, 90%).

mer-[Fe$(SnPh_3)$(dppe)$(CNPh)_3$]PF_6 (**5**).—A solution of $SnPh_3Cl$ (0.2 g, 0.51 mmol) in toluene (10 cm^3) was added to a solution of [Fe(dppe)$(CNPh)_3$] (**2a**) [obtained from (**1a**) (0.4 g, 0.39 mmol)] in toluene (30 cm^3). The resulting mixture was stirred at *ca.* 20 °C for 2 h. During this time, a yellow oil precipitated and the solution became colourless. The solvent was removed by evaporation and the oil which remained was washed and stirred with diethyl ether (20 cm^3) until a pale yellow solid corresponding to *mer*-[Fe$(SnPh_3)$(dppe)$(CNPh)_3$]Cl was obtained. The anion was exchanged using KPF_6 (0.1 g, 0.54 mmol), with CH_2Cl_2 (20 cm^3) and ethanol (10 cm^3) as solvents; yellow crystals of *mer*-[Fe$(SnPh_3)$(dppe)$(CNPh)_3$]PF_6 (**5**) were obtained (yield 0.27 g, 55%).

[FeI(dppe)(CNPh){N(Ph)=C(Me)–C=NPh}] (**6a**).—Freshly distilled methyl iodide (0.2 cm^3, 3.24 mmol) was added to a solution of [Fe(dppe)$(CNPh)_3$] (**2a**) [prepared from (**1a**) (0.4 g, 0.39 mmol)] in toluene (20 cm^3). Immediately a darkening in the red colour of the solution was observed. The mixture was stirred for 30 min. The solvent was then evaporated *in vacuo* down to 5 cm^3 and diethyl ether (15 cm^3) was added. After cooling, dark red crystals were obtained (yield 0.26 g, 74%).

[FeI(dppe)$(CNC_6H_4Me$-4){N(C_6H_4Me-4)=C(Me)–C=NC_6H_4Me-4}] (**6b**).—This was similarly prepared from [Fe(dppe)$(CNC_6H_4Me$-4$)_3$] (**2b**), obtained from *mer*-[FeI(dppe)$(CNC_6H_4Me$-4$)_3$]I (**1b**) (0.2 g, 0.19 mmol), and methyl iodide (0.1 cm^3, 1.62 mmol), yield 0.08 g, 44%.

[FeI(dppm)(CNPh){N(Ph)=C(Me)–C=NPh}] (**6c**).—This

Table 4. Selected interatomic distances (Å) and angles (°)

(*a*) In the cation			
Co-ordination of Fe			
Fe(1)–P(1)	2.289(3)	Fe(1)–C(2)	1.84(1)
Fe(1)–P(2)	2.294(3)	Fe(1)–C(3)	2.00(1)
Fe(1)–C(1)	1.82(1)	Fe(1)–N(4)	2.064(9)
P(2)–Fe(1)–P(1)	85.0(1)	C(3)–Fe(1)–C(1)	98.6(4)
C(1)–Fe(1)–P(1)	87.2(3)	C(3)–Fe(1)–C(2)	90.4(4)
C(1)–Fe(1)–P(2)	91.5(3)	N(4)–Fe(1)–P(1)	91.8(2)
C(2)–Fe(1)–P(1)	174.6(3)	N(4)–Fe(1)–P(2)	104.3(3)
C(2)–Fe(1)–P(2)	89.8(3)	N(4)–Fe(1)–C(1)	164.1(4)
C(2)–Fe(1)–C(1)	94.4(5)	N(4)–Fe(1)–C(2)	88.0(4)
C(3)–Fe(1)–P(1)	94.5(3)	N(4)–Fe(1)–C(3)	65.6(4)
C(3)–Fe(1)–P(2)	169.8(3)		
Others			
P(1)–C(6)	1.79(2)	P(2)–C(7)	1.79(1)
P(1)–C(51)	1.83(1)	P(2)–C(71)	1.82(1)
P(1)–C(61)	1.84(1)	P(2)–C(81)	1.82(1)
C(6)–C(7)	1.43(2)		
N(1)–C(1)	1.13(1)	N(2)–C(2)	1.18(1)
N(1)–C(11)	1.44(1)	N(2)–C(21)	1.38(1)
N(3)–C(3)	1.27(1)	C(4)–N(4)	1.30(1)
N(3)–C(31)	1.44(2)	N(4)–C(41)	1.42(1)
C(4)–C(3)	1.46(2)	C(4)–C(5)	1.50(2)
C–C (phenyl)	average 1.38(3)		
C(51)–P(1)–C(6)	100.5(6)	C(71)–P(2)–C(7)	106.9(9)
C(61)–P(1)–C(6)	106.1(8)	C(81)–P(2)–C(71)	101.7(5)
C(61)–P(1)–C(51)	101.4(5)	C(81)–P(2)–C(7)	99.0(7)
C(6)–P(1)–Fe(1)	107.2(4)	C(7)–P(2)–Fe(1)	107.1(5)
C(51)–P(1)–Fe(1)	121.7(4)	C(71)–P(2)–Fe(1)	119.9(4)
C(61)–P(1)–Fe(1)	117.7(4)	C(81)–P(2)–Fe(1)	119.8(4)
C(7)–C(6)–P(1)	115.9(11)	C(6)–C(7)–P(2)	112.3(11)
C(11)–N(1)–C(1)	178.7(11)	C(21)–N(2)–C(3)	171.3(11)
N(1)–C(1)–Fe(1)	178.0(9)	N(2)–C(2)–Fe(1)	175.1(9)
N(3)–C(3)–Fe(1)	148.5(9)	C(4)–C(3)–N(3)	118.0(9)
C(4)–C(3)–Fe(1)	93.4(7)	C(31)–N(3)–C(3)	123.2(10)
C(5)–C(4)–C(3)	128.2(10)	C(5)–C(4)–N(4)	126.5(11)
N(4)–C(4)–C(3)	105.3(9)	C(41)–N(4)–C(4)	124.5(9)
C(4)–N(4)–Fe(1)	95.7(7)	C(41)–N(4)–Fe(1)	139.5(8)
C–C–C (phenyl)	average 120(2)		
(*b*) In the anion			
Cl(1)–O(1)	1.45(2)	Cl(1)–O(3)	1.47(2)
Cl(1)–O(1)	1.39(2)	Cl(1)–O(4)	1.38(2)
O(2)–Cl(1)–O(1)	107.8(12)	O(4)–Cl(1)–O(1)	110.9(13)
O(3)–Cl(1)–O(1)	116.8(12)	O(4)–Cl(1)–O(2)	122.4(12)
O(3)–Cl(1)–O(2)	96.9(12)	O(4)–Cl(1)–O(3)	101.6(12)

was similarly prepared from [Fe(dppm)(CNPh)$_3$] **(2c)**, obtained from *mer*-[FeI(dppm)(CNPh)$_3$]I **(1c)** (0.2 g, 0.2 mmol), and methyl iodide (0.1 cm^3, 1.62 mmol), yield 0.036 g, 20%.

cis-[Fe(dppe)(CNPh)$_2${N(Ph)=C(Me)–C=NPh}]ClO$_4$ (7).—A mixture of **(6a)** (0.1 g, 0.11 mmol), CH$_2$Cl$_2$ (30 cm^3), AgClO$_4$ (0.023 g, 0.11 mmol), and phenyl isocyanide (0.1 g, 1 mmol) was stirred vigorously at *ca.* 20 °C for 30 min. The solution was then filtered and the solvent evaporated to dryness. After washing the resulting oil with diethyl ether (30 cm^3), a red solid was obtained. Recrystallization from a CH$_2$Cl$_2$–C$_2$H$_5$OH solution afforded red crystals of the product (yield 0.075 g, 70%).

[Fe(dppe)(CO)(CNPh){N(Ph)=C(Me)–C=NPh}]BPh$_4$ **(8)**.—To a stirred solution of **(6a)** (0.15 g, 0.16 mmol) in CH$_2$Cl$_2$ (20 cm^3) was added TlPF$_6$ (0.2 g, 0.57 mmol), and carbon monoxide bubbled up through the solution for 6 h at room temperature. After filtration, NaBPh$_4$ (0.055 g, 0.16 mmol) and ethanol (10 cm^3) were added to the solution. The resulting mixture was stirred for 30 min. The solvent was then evaporated to dryness *in vacuo*, and the resulting residue extracted with CH$_2$Cl$_2$ (20 cm^3). Ethanol (10 cm^3) was then added to the solution and after standing for 1 d, red crystals of the compound were obtained (yield 0.1 g, 56%).

[FeI(dppe)(CNPh){N(Ph)=C(Me)–C–NHPh}]ClO$_4$ **(9)**.—To a solution of **(6a)** (0.07 g, 0.077 mmol) in CH$_2$Cl$_2$ (20 cm^3) was added 70% aqueous perchloric acid (0.1 cm^3, 1.16 mmol). The mixture was stirred at *ca.* 20 °C for 10 min. The resulting violet solution was filtered and concentrated *in vacuo* down to 5 cm^3. Diethyl ether (5 cm^3) was then added and after cooling (−20 °C), dark violet crystals were obtained (yield 0.067 g, 86%).

Reaction of [Fe(dppe)(CNPh)$_3$] **(2a)** *with Allyl Bromide.*—To a stirred solution of [Fe(dppe)(CNPh)$_3$] **(2a)** in toluene (20 cm^3), obtained from *mer*-[FeI(dppe)(CNPh)$_3$]I **(1a)** (0.5 g, 0.49 mmol), was added allyl bromide (0.3 cm^3) dropwise. The stirring was maintained for 30 min at room temperature. After this time, a large amount of orange precipitate was obtained. The precipitate was dissolved in CH$_2$Cl$_2$ (10 cm^3) and after exchanging the anion by adding KPF$_6$ (0.2 g, 1.08 mmol) and ethanol (10 cm^3), orange crystals of *mer*-[FeBr(dppe)(CNPh)$_3$]PF$_6$ **(10)** were obtained (0.25 g, 51%). The solution was concentrated to 5 cm^3; after adding diethyl ether (5 cm^3) and on cooling down to −20 °C, red crystals of [FeBr(dppe)(CNPh){N(Ph)=C(CH$_2$CHCH$_2$)–C=NPh}] **(11)** were obtained (yield 0.03 g, 7%).

Crystal Data.—C$_{55}$H$_{47}$ClFeN$_4$O$_4$P$_2$, M = 981.2, monoclinic, a = 13.548(2), b = 10.998(3), c = 16.344(2) Å, β = 95.34(1)°, U = 2 425(2) Å^3, from least-squares refinement of 25 reflections in the θ range 14—15°, space group *Pn*, Z = 2, D_c = 1.34 g cm^{-3}. Irregularly shaped red fragment cut from a larger crystal, approximate dimensions 0.3 × 0.25 × 0.15 mm, μ(Mo-K_α) = 0.49 cm^{-1}.

Structure Solution and Refinement.—CAD4 Enraf–Nonius diffractometer; ω–2θ mode with scan width 1.10 + 0.35 tanθ; graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å); θ range 1—25°. 2 550 Reflections measured at room temperature; 2 515 with $F > 2\sigma(F)$ used for refinement. No absorption correction, as suggested by a flat ψ-scan; two standard reflections measured every 2 h. The structure was solved by direct methods (Fe and P atoms) followed by Fourier synthesis. The program CRYSTALS[17] was used for computation and provided atomic form factors. Full-matrix least-squares refinement was carried out in five blocks. Hydrogen atoms were geometrically located (C–H 0.99 Å, U = 0.075 Å^2) and not refined. All atoms, except for hydrogen and perchlorate oxygen, had anisotropic thermal parameters. The perchlorate anion was refined as a rigid body. The weighting scheme was $w = w'\{1[(F_o - F_c)/6\sigma(F_o)]^2\}^2$ where $w' = 1/\sum_{r=1,3} A_r T_r(X)$, with three coefficients A = 5.16, 1.19, 3.41 for the Chebyshev polynomial $T_r(X)$; $X = F_o/F_o(\text{max.})$.[17,18] The largest peaks (0.8 Å^3) in the last Fourier difference map were in the vicinity of the perchlorate chlorine atom; final R = 0.055, R' = 0.068. The final atomic co-ordinates are given in Table 3; selected bond distances and angles are in Table 4. A perspective view of the cation with the atom numbering scheme is shown in the Figure.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, remaining bond distances and angles.

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