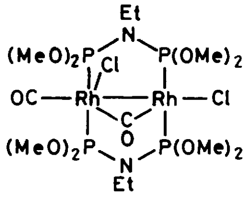
Electrophilic Attack on a Series of Dinuclear Diphosphazane-bridged Derivatives of Iron by Halogens. *X*-Ray Crystal Structures of $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ and $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]PF_6$†

John S. Field, Raymond J. Haines,* and Clifford N. Sampson
University of Natal/C.S.I.R. Unit of Metal Cluster Chemistry, Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg 3200, Republic of South Africa

Treatment of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = CH_2, Me, Pr^i, or Ph) with halogens results in the formation of $[Fe_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (X = Cl, Br, or I) which, on the basis of the structure established *X*-ray crystallographically for $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ (**A**), contains an axially co-ordinated halogen. The iron atoms in these compounds are not only bridged by the two diphosphazane ligands but are also linked through a direct iron–iron bond [Fe–Fe = 2.787(3) Å in (**A**)]. Compound (**A**), and presumably the others, adopts a staggered conformation but the extent of twisting about the iron–iron bond is small as reflected by the P(1)–Fe(1)–Fe(2)–P(2) torsion angle of 28.8°. These pentacarbonyl derivatives readily decarbonylate in solution to produce the halogeno-bridged species $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$. On the basis of a single-crystal *X*-ray diffraction study on $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]PF_6$ (**B**), these tetracarbonyl compounds, in contrast to the pentacarbonyl species, adopt an eclipsed configuration with the plane containing the two iron and four phosphorus atoms being orthogonal to a plane containing the two iron atoms, the bridging halogen, and the four terminal carbonyl groups. Although these tetracarbonyl compounds do not add halide ions to produce $[Fe_2X_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$, the tetramethoxydiphosphazane species $[Fe_2X(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ and $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ are very susceptible to halide ion attack affording the Michaelis–Arbuzov type rearrangement products $[Fe_2X\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ and $[Fe_2(\mu\text{-}X)\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ respectively. The reactions with other halogenation agents such as *N*-chloro- and *N*-bromo-succinimide, and mixed halogens (ICl) are also reported and a general mechanism for the halogenation of compounds of the type $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PYP(OR)_2\}_2]$ [R = alkyl or aryl group; Y = CH_2 or N(Et)] is proposed.

It is now universally recognised that diphosphorus ligands of the type R_2PYPR_2 (R = alkyl, aryl, alkoxy, aryloxy group, *etc.*) in which the donor atoms are linked through a single atom of Y as in CH_2, NR′(R′ = H, Me, Et, *etc.*), or O, preferentially adopt the bridging rather than the chelating co-ordination mode and as a consequence are excellent ligands for the stabilisation of dinuclear compounds to fragmentation and, in particular, of dinuclear species of unusual stereochemistry and reactivity patterns.[1,‡] One particular ligand that is being utilised extensively in this context is $Ph_2PCH_2PPh_2$ and a plethora of publications have appeared in the chemical literature in the past five to ten years describing the chemistry of dinuclear derivatives of rhodium,[1,2] iridium,[1,3] palladium,[1,4] platinum[1,5] and more of late manganese,[6] rhenium,[7] cobalt,[8] nickel,[9] and early transition metals,[10] as well as heteronuclear systems,[11] in which the metal atoms are linked by one or more molecules of this ligand.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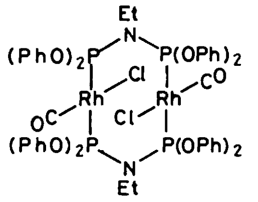
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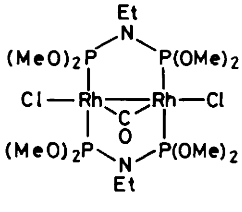
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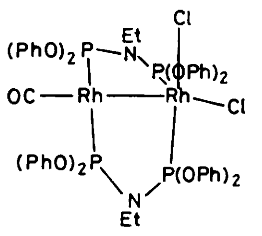
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We have appreciated the special co-ordination properties of ligands of the type R_2PYPR_2 for some time[12,13] and have employed them in the synthesis of a range of dinuclear compounds with different co-ordination numbers and stereochemistries. For particular reasons however, we have tended to concentrate on the use of phosphite-type ligands of stoicheiometry $(RO)_2POP(OR)_2$, $(RO)_2PN(R')P(OR)_2$, and $(RO)_2$-

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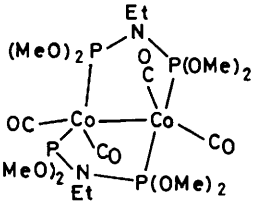
† 1,1,1,2,2-Pentacarbonyl-di-μ-(2′-ethyl-1′,1′,3′,3′-tetramethoxydiphosphazane-*PP′*)-2-iodo-di-iron hexafluorophosphate (*Fe–Fe*) and μ-bromo-di-μ-(2′-ethyl-1′,1′,3′,3′-tetraphenoxydiphosphazane-*PP′*)-bis(dicarbonyliron) hexafluorophosphate (*Fe–Fe*) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ More recent publications are represented by refs. 2—11.



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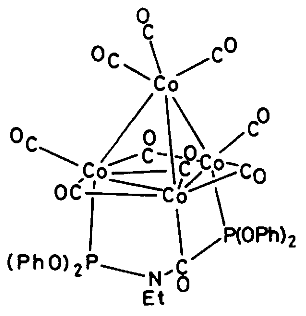

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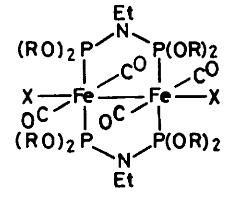

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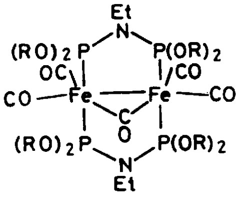

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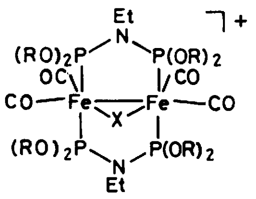
$PCH_2P(OR)_2$ (R = CH_2, Me, Et, Pr^i, or Ph; R′ = Me or Et).[14,15] One very important observation to emerge from our investigations is that the overall stereochemistry and associated chemistry of a dinuclear compound of a particular stoicheiometry is related to the nature of the co-ordinated bridging ligand R_2PYPR_2. For instance reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with $(MeO)_2PN(Et)P(OMe)_2$ and $(PhO)_2PN(Et)P(OPh)_2$ affords a product of stoicheiometry $[Rh_2Cl_2(CO)_2\{(MeO)_2PN(Et)P(OMe)_2\}_2]$ (**1**) in the case of the tetramethoxydiphosphazane ligand and a product with a related stoicheiometry, $[Rh_2Cl_2(CO)_2\{(PhO)_2PN(Et)P(OPh)_2\}_2]$ (**2**) but of a different structure, in the case of the tetraphenoxydiphosphazane ligand.[16,17] Furthermore the decarbonylation products of these compounds *viz.* $[Rh_2Cl_2(\mu\text{-}CO)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (**3**) and $[Rh_2Cl_2(CO)\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ (**4**) respectively, have also been found to adopt different structures in the crystalline state.[17,18] Also, whereas the reaction of $[Co_2(CO)_8]$ with $(MeO)_2PN(Et)P(OMe)_2$ produces only $[Co_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (**5**) irrespective of the molar ratio, that involving $(PhO)_2PN(Et)P(OPh)_2$ gives the tetranuclear product, $[Co_4(CO)_{10}\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}]$ (**6**).[19,20]

We have synthesised a wide range of di-iron compounds of the type $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]$ [R = alkyl, phenyl, alkoxy, or phenoxy group; Y = CH_2, N(Et), or O][21] and have embarked on an investigation of their reactivity towards electrophiles with the overall aim of establishing the influence of the bridging ligands. With the particular objective of synthesising dihalides of the type $[Fe_2X_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (**7**) (X = Cl, Br, or I; R = Me, Pr^i, or Ph), the halogenation reactions of the diphosphazane-bridged complexes $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (**8**) have been investigated and the results of this study are reported here; some of these have already been communicated in a preliminary form.[23]

Results and Discussion

The dinuclear diphosphazane-bridged derivatives $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me, Pr^i, or Ph), readily synthesised photochemically from $[Fe_2(CO)_9]$ and $(RO)_2PN(Et)P(OR)_2$,[21] are expected to be susceptible to attack by electrophiles and indeed have been observed to react readily with halogens at ambient temperature. Thus treatment of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ with iodine in benzene was found to result in the separation of a precipitate which on crystallisation from acetone–light petroleum in the presence of sodium tetraphenylborate and ammonium hexafluorophosphate gave crystals of compounds characterised (Table 1) as $[Fe_2(\mu\text{-}I)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]BPh_4$ (**9**,BPh_4; X = I, R = Ph) and $[Fe_2(\mu\text{-}I)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]PF_6$ (**9**,PF_6; X = I, R = Ph) respectively. The band pattern of the peaks in the terminal C–O stretching region of the i.r. spectra of these species was very similar to that for $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$, while the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra exhibited a single resonance at δ 161.2 and δ 163.1 p.p.m., respectively (relative to H_3PO_4) (Table 2). These data are interpreted in terms of the cation adopting a structure related to that of its parent with formally an 'iodinium' ion having replaced the bridging carbonyl group. Bromination and chlorination of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ led to the formation of analogous products *viz.* $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]^+$ (**9**; X = Br, R = Ph) and $[Fe_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]^+$ (**9**; X = Cl, R = Ph) respectively, again isolated as the hexafluorophosphate and tetraphenylborate salts. With the object of establishing unequivocally the structure of these compounds a single-crystal *X*-ray diffraction study was carried out on $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]PF_6$. The stereochemistry of this species is illustrated in Figure 1. The two iron atoms are bridged not only by the two diphosphazane ligands but by a bridging 'bromonium' ion as well. The Fe–Fe distance of 2.724(5) Å corresponds to a formal metal–metal bond although it is appreciably larger than the distance of 2.663(2) Å in $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(EtO)_2POP(OEt)_2\}_2]$.[14b] This difference is probably a consequence of the larger size of the bridging bromonium ion compared to that of the carbon of the bridging carbonyl group. Two of the terminal carbonyl groups are essentially orthogonal to the iron–iron vector while the other two are almost collinear with it. These four carbonyl groups, together with the bromine and iron atoms lie on a crystallographically-imposed mirror plane which is essentially orthogonal to a least-squares plane defined by the two iron atoms, the four phosphorus atoms, and the two nitrogen atoms (dihedral angle = 91.6°).



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By monitoring the reactions of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ with halogens in CH_2Cl_2 by means of i.r. spectroscopy, intermediates in the formation of (**9**; R = Ph) could be detected. All attempts to isolate these intermediates proved unsuccessful however, due to their ready conversion to the halogeno-bridged tetracarbonyl species, but the presence of 18 peaks with a characteristic AA′BB′ pattern in their $^{31}P\text{-}\{^1H\}$ n.m.r. spectra was interpreted in terms of their having the formulation $[Fe_2X(CO)_5\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]^+$ (X = Cl, Br, or I) (**10**; R = Ph) with the halogen being terminally bound to one of the iron atoms as subsequently confirmed for a tetramethoxydiphosphazane derivative (see later).

As a means of converting compound (**9**,BPh_4 or PF_6; R = Ph) to $[Fe_2X_2(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ (X = Cl, Br, or I) (**7**; R = Ph), it was treated with an excess of halide ions but no reaction was observed to occur. It was considered that

Table 1. Conductivity and microanalytical data

Compound				Λ^a/Ω^{-1} cm^2 mol^{-1}	Analysis^b (%)				
					C	H	N	P	X
$[Fe_2X(CO)_5\{\mu\text{-}(RO)_2PYP(OR)_2\}_2]Z$									
X	Y	R	Z						
Cl	N(Et)	Me	PF_6	115	22.6 (22.9)	3.8 (3.8)	3.1 (3.1)		4.1 (4.1)
Br	N(Et)	Me	PF_6	107	22.0 (21.8)	3.5 (3.6)	3.1 (3.0)		
I	N(Et)	Me	PF_6	112	20.9 (20.8)	3.5 (3.5)	2.9 (2.9)		
$[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PYP(OR)_2\}_2]Z$									
Cl	N(Et)	CH_2	BPh_4	121	46.4 (46.7)	4.3 (4.5)	2.8 (2.7)		
Br	N(Et)	CH_2	BPh_4	127	44.9 (44.7)	4.4 (4.3)	2.7 (2.6)		
I	N(Et)	CH_2	BPh_4	124	42.7 (42.9)	4.0 (4.1)	2.5 (2.5)		11.1 (11.3)
Cl	N(Et)	Me	PF_6	117	22.4 (22.3)	3.9 (3.9)	3.1 (3.3)		4.4 (4.1)
Br	N(Et)	Me	PF_6	105	21.0 (21.2)	3.7 (3.8)	3.3 (3.1)		8.5 (8.8)
I	N(Et)	Me	PF_6	110	20.4 (20.1)	3.4 (3.6)	2.9 (2.9)		12.9 (13.3)
Cl	N(Et)	Pr^i	PF_6	120	35.4 (35.7)	6.1 (5.9)	2.6 (2.4)		2.9 (3.3)
Br	N(Et)	Pr^i	PF_6	125	33.8 (34.0)	5.7 (5.8)	2.4 (2.5)		6.9 (7.1)
I	N(Et)	Pr^i	PF_6	119	32.5 (32.6)	5.5 (5.6)	2.5 (2.4)		
Cl	N(Et)	Ph	BPh_4	127	62.4 (62.6)	4.4 (4.6)	1.8 (1.8)	8.5 (8.1)	2.7 (2.3)
Br	N(Et)	Ph	BPh_4	123	60.9 (60.9)	4.3 (4.4)	1.8 (1.8)	8.2 (7.9)	5.5 (5.1)
I	N(Et)	Ph	BPh_4	129	59.0 (59.1)	4.4 (4.3)	1.6 (1.7)	7.7 (7.6)	7.4 (7.8)
Cl	N(Et)	Ph	PF_6	125	49.7 (49.5)	3.8 (3.7)	2.1 (2.1)	11.1 (11.4)	2.3 (2.6)
Br	N(Et)	Ph	PF_6	124	48.2 (47.9)	3.7 (3.6)	1.8 (2.0)	10.7 (11.1)	5.7 (5.7)
I	N(Et)	Ph	PF_6	126	46.3 (46.3)	3.5 (3.5)	1.9 (1.9)	10.4 (10.7)	8.5 (8.8)
$[Fe_2(\mu\text{-}X)\{\mu\text{-}(RO)_2PYP(O)(OR)\}(CO)_4\{\mu\text{-}(RO)_2PYP(OR)_2\}]$									
Cl	N(Et)	Me		1.31	25.9 (25.6)	4.5 (4.4)	4.0 (4.0)		
Br	N(Et)	Me		0.98	23.9 (24.1)	4.1 (4.2)	3.6 (3.8)	17.1 (16.6)	10.3 (10.7)
I	N(Et)	Me^c		1.85	22.4 (22.7)	3.9 (3.9)	3.5 (3.5)		

[a] Measured in acetone. [b] Calculated values are given in parentheses. [c] *m/e* = 794.

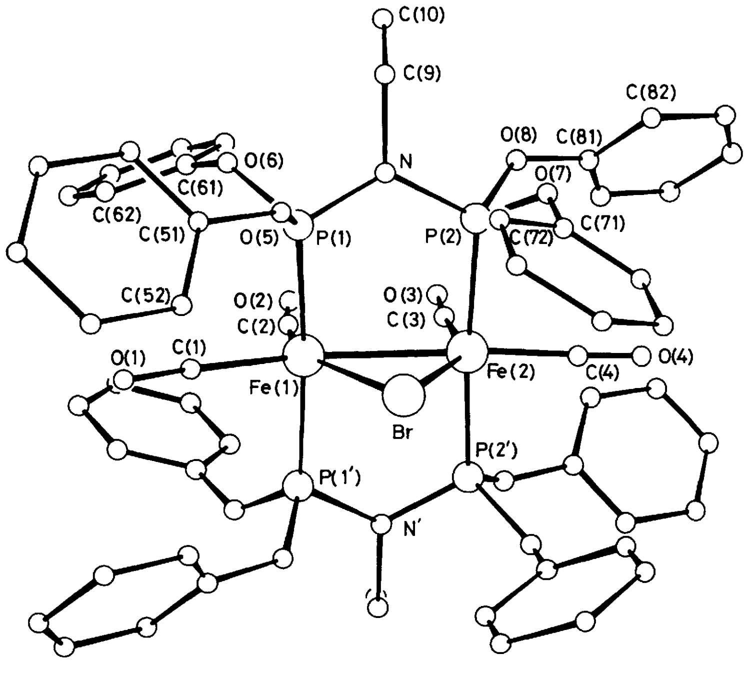


Figure 1. The stereochemistry of $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]^+$

the inability of the halogeno-bridged species to react further with halide ions might be steric in origin and as a consequence the halogenation reactions of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (**8**; R = Me) containing the less bulky tetramethoxydiphosphazane ligand were also investigated. Treatment of this compound with a twice molar amount of iodine in n-hexane was found to lead to the immediate precipitation of a yellow-orange material which exhibited a characteristic band pattern in the i.r. C–O stretching region, similar to those of the intermediates in the formation of (**9**; R = Ph), and a 12-line

Table 2. Infrared and nuclear magnetic resonance spectroscopic data

Compound				ν(CO)/cm^{-1} [a]	^{31}P-{^{1}H} [b]	^{1}H [c,d]
X	Y	R	Z			
$[Fe_2X(CO)_5\{\mu\text{-}(RO)_2PYP(OR)_2\}_2]Z$						
Cl	N(Et)	CH_2	Cl	2 060w, 2 040ms, 2 023s, 1 960w br[e]	170.7[f,g]	
Br	N(Et)	CH_2	Br	2 080w, 2 038ms, 2 024s, 1 975w br[e]	171.3[f,g]	
I	N(Et)	CH_2	I	2 080w, 2 045m, 2 022vs, 1 985w[e]	169.2[f,g]	
Cl	N(Et)	Me	PF_6	2 064w, 2 030 (sh), 2 009s, 1 975w[e] 2 074w, 2 035m, 2 011s, 1 966m[j]	161.6[f,g,h]	1.21(t) (6 H), 3.29(m) (4 H), 3.85(m) (24 H)[i]
Br	N(Et)	Me	PF_6	2 070w, 2 010s, 1 971w br[e] 2 079w, 2 035m, 2 010s br, 1 964ms[j]	157.8[f,g,h]	1.20(t) (6 H), 3.32(m) (4 H), 3.85(m) (24 H)[i]
I	N(Et)	Me	PF_6	2 068w, 2 031 (sh), 2 009s, 1 979m[e] 2 080w, 2 038m, 2 009s br, 1 964ms[j]	155.3[f,g,h]	1.31(t) (6 H), 3.31(m) (4 H), 3.99(m) (24 H)[i]
Cl	N(Et)	Pr^{i}	Cl	2 056w, 2 013s, 1 997s, 1 961w[e]	149.1[f,g]	
Br	N(Et)	Pr^{i}	Br	2 056w, 2 017s, 2 001s, 1 967w[e]	148.8[f,g]	
I	N(Et)	Pr^{i}	I	2 056w, 2 018ms, 2 000s, 1 965w[e]	151.3[f,g]	
Cl	N(Et)	Ph	Cl	2 075w, 2 041s, 2 021s, 1 982w br[e]	152.4[f,g]	
Br	N(Et)	Ph	Br	2 072w, 2 037s, 2 021vs, 1 988w br[e]	154.6[f,g]	
I	N(Et)	Ph	I	2 069w, 2 031s, 2 017s, 1 987w[e]	151.8[f,g]	
$[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PYP(OR)_2\}_2]Z$						
Cl	N(Et)	CH_2	BPh_4	2 042m, 2 010s, 1 980ms, 1 960ms[e] 2 033m, 2 003s, 1 974ms, 1 953m[j]	175.6(s)[f]	1.28(t) (6 H), 3.30(m) (4 H), 4.71(m) (16 H)[f]
Br	N(Et)	CH_2	BPh_4	2 039ms, 2 009s, 1 977ms, 1 958m[e] 2 030ms, 2 000s, 1 970m, 1 951m[j]	176.2(s)[f]	1.27(t) (6 H), 3.26(m) (4 H), 4.68(m) (16 H)[f]
I	N(Et)	CH_2	BPh_4	2 039ms, 2 007s, 1 976ms, 1 957m[e] 2 031m, 2 001s br, 1 970m, 1 952ms[j]	183.0(s)[f]	1.24(t) (6 H), 3.29(m) (4 H), 4.70(m) (16 H)[f]
Cl	N(Et)	Me	PF_6	2 030m, 1 995s, 1 970ms, 1 949w[e] 2 021m, 1 990s br, 1 961s br, 1 938m[j]	164.2(s)[f,h]	1.22(t) (6 H), 3.30(m) (4 H), 3.89(m) (24 H)[f]
Br	N(Et)	Me	PF_6	2 031m, 1 991s, 1 964ms, 1 948w[e] 2 026m, 1 998s br, 1 957s br, 1 935m[j]	164.8(s)[f,h]	1.20(t) (6 H), 3.33(m) (4 H), 3.88(m) (24 H)[f]
I	N(Et)	Me	PF_6	2 029m, 1 994s, 1 970ms, 1 950w[e] 2 023m, 1 990s br, 1 960s br, 1 938m[j]	164.1(s)[f,h]	1.33(t) (6 H), 3.35(m) (4 H), 4.02(m) (24 H)[f]
Cl	N(Et)	Pr^{i}	PF_6	2 026ms, 1 981s br, 1 960m, 1 939m[e] 2 023ms, 1 981s br, 1 956ms, 1 939ms[j]	150.7[i,h]	1.38(m) (54 H), 3.16(m) (4 H), 4.71(m) (8 H)[f]
Br	N(Et)	Pr^{i}	PF_6	2 027m, 1 980s br, 1 961m, 1 942m[e] 2 023ms, 1 980s br, 1 944ms, 1 939ms[j]	147.8[i,h]	1.38(m) (54 H), 3.15(m) (4 H), 4.69(m) (8 H)[f]
I	N(Et)	Pr^{i}	PF_6	2 028ms, 1 983s, 1 963m, 1 944w[e] 2 022ms, 1 981s br, 1 956ms, 1 941ms[j]	156.3[i,h]	1.38(m) (54 H), 3.12(m) (4 H), 4.70(m) (8 H)[f]
Cl	N(Et)	Ph	PF_6	2 041m, 2 006s, 1 981s, 1 964ms[e] 2 030m, 2 000s, 1 978ms, 1 960m[j]	158.9[f,h]	1.44(t) (6 H), 3.86(m) (4 H), 7.33(m) (40 H)[k]
			BPh_4	2 040m, 2 008s, 1 981s, 1 963ms[e] 2 027m, 1 999s, 1 979ms, 1 959m[j]	156.9[f]	1.41(t) (6 H), 3.80(m) (4 H), 7.16(m) (60 H)[k]
Br	N(Et)	Ph	PF_6	2 037m, 2 006s, 1 989ms, 1 970w[e] 2 033m, 2 001s, 1 981ms, 1 967m[j]	162.8[f,h]	1.44(t) (6 H), 3.87(m) (4 H), 7.33(m) (40 H)[k]
			BPh_4	2 037m, 2 004s, 1 983ms, 1 963w[e] 2 033m, 2 003s, 1 986ms, 1 961w[j]	157.9[f]	1.40(t) (6 H), 3.82(m) (4 H), 7.20(m) (60 H)[k]
I	N(Et)	Ph	PF_6	2 037m, 2 005s, 1 984ms, 1 962w[e] 2 030m, 2 002s, 1 980ms, 1 959w[j]	163.1[f,h]	1.46(t) (6 H), 3.87(m) (4 H), 7.34(m) (40 H)[k]
			BPh_4	2 038m, 2 004s, 1 982ms, 1 960w[e] 2 032m, 1 999s, 1 973ms, 1 954w[j]	161.2[f]	1.38(t) (6 H), 3.81(m) (4 H), 7.15(m) (60 H)[k]
Cl	CH_2	Me	PF_6	2 024m, 1 987s, 1 962ms, 1 943w[e] 2 014m, 1 983s br, 1 954ms, 1 936m[j]	162.1[f,h]	3.09(t) (4 H), 3.78(m) (24 H)[f]
Cl	CH_2	Pr^{i}	PF_6	2 020m, 1 986s, 1 959ms, 1 940w[e] 2 012m, 1 983s br, 1 951ms, 1 935m[j]	173.1[f,h]	1.31(m) (48 H), 3.05(t) (4 H), 4.82(m) (8 H)[f]
$[Fe_2X\{\mu\text{-}(RO)_2PYP(O)(OR)\}(CO)_5\{\mu\text{-}(RO)_2PYP(OR)_2\}]$						
Br	N(Et)	Me		2 052w, 2 012 (sh), 1 988s, 1 962m[e]		
I	N(Et)	Me		2 055w, 2 013 (sh), 1 990s, 1 960m[e]		
$[Fe_2(\mu\text{-}X)\{\mu\text{-}(RO)_2PYP(O)(OR)\}(CO)_4\{\mu\text{-}(RO)_2PYP(OR)_2\}]$						
Cl	N(Et)	Me		2 014m, 1 973s, 1 948m, 1 927m[l] 2 010m, 1 971s br, 1 944s, 1 921m[j]	162.5, 106.9[k,m]	1.15(t) (6 H), 3.17(m) (4 H), 3.73(m) (21 H)[k]
Br	N(Et)	Me		2 011m, 1 972s br, 1 946ms, 1 923w[l] 2 008m, 1 970s br, 1 943s, 1 918m[j]	164.5, 109.7[k,m]	1.14(t) (6 H), 3.14(m) (4 H), 3.71(m) (21 H)[k]
I	N(Et)	Me		2 012m, 1 972s, 1 947m, 1 925s[l] 2 009m, 1 970s br, 1 944s, 1 921m[j]	166.1, 112.1[k,m]	1.16(t) (6 H), 3.18(m) (4 H), 3.76(m) (21 H)[k]
$[Fe_2(\mu\text{-}X)_2(CO)_4\{\mu\text{-}(RO)_2PYP(OR)_2\}_2][Z]_2$						
Br	N(Et)	Me	Br	2 076s, 2 022s[e]		

Table 2 (*continued*)

Compound				ν(CO)/cm^{-1} [a]	^{31}P-{^{1}H} [b]	^{1}H [c,d]
X	Y	R	Z			
[$Fe_2(\mu$-X$)_2${μ-(RO)$_2$PYP(O)(OR)}(CO)$_4${μ-(RO)$_2$PYP(OR)$_2$}]Z						
Br	N(Et)	Me	Br	2 055s, 2 004s [e] 2 050s br, 2 001s br [j]		
I	N(Et)	Me	I	2 045s, 2 002s [e]		

[a] Abbreviations: vs = very strong, s = strong, ms = medium strong, m = medium, w = weak, sh = shoulder, br = broad. [b] δ scale, in p.p.m. relative to H_3PO_4. [c] Abbreviations: s = singlet, t = triplet, m = multiplet. [d] δ scale, relative to $SiMe_4$. [e] Measured in CH_2Cl_2. [f] Measured in CD_2Cl_2. [g] Midpoint of AA'BB' pattern. [h] Spectrum also contains a heptet at *ca.* δ -139 p.p.m. assigned to PF_6^-. [i] Measured in [$^2H_6$]acetone. [j] Measured as a Nujol mull. [k] Measured in $CDCl_3$. [l] Measured in n-hexane. [m] Centres of complex multiplets.

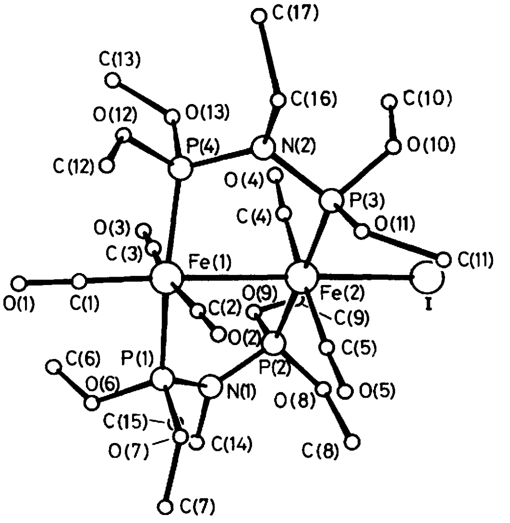
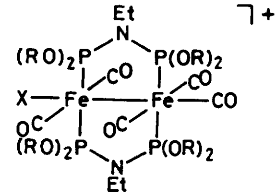


Figure 2. The stereochemistry of [$Fe_2I(CO)_5${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]$^+$

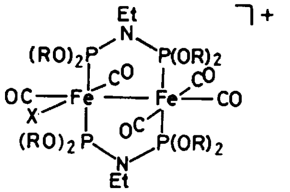
AA'BB' pattern in its ^{31}P-{^{1}H} n.m.r. spectrum. Because of its ready rearrangement, this compound could not be characterised fully but conversion by metathesis to the hexafluorophosphate salt gave a more stable compound which was characterised as [$Fe_2I(CO)_5${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]PF_6 (**10**,PF_6; X = I, R = Me).

The stereochemistry of this pentacarbonyl species, as established *X*-ray crystallographically, is illustrated in Figure 2. The two iron atoms bridged by the two diphosphazane ligands which are *trans* disposed with respect to each other, are separated by a distance of 2.787(3) Å corresponding to a formal iron–iron bond. This distance is appreciably longer than those found in [$Fe_2(\mu$-Br)(CO)$_4${μ-(PhO)$_2$PN(Et)P(OPh)$_2$}$_2$]PF_6 [2.724(5) Å] and [$Fe_2(\mu$-CO)(CO)$_4${μ-(EtO)$_2$POP(OEt)$_2$}$_2$] [2.663(2) Å][14b] which is consistent with the absence of a bridging monodentate ligand. Each iron atom in the cation is six-co-ordinate and adopts a local octahedral geometry. Four of the carbonyl groups are essentially orthogonal to the iron–iron vector while the fifth carbonyl and the iodine atom are almost collinear with it. The compound adopts a staggered conformation, to minimize steric repulsions, but undoubtedly because of constraints being placed on the cation by the bridging diphosphazane ligands, the extent of twisting about the iron–iron bond is small as reflected by the P(1)–Fe(1)–Fe(2)–P(2), P(4)–Fe(1)–Fe(2)–P(3), C(2)–Fe(1)–Fe(2)–C(5), and C(3)–Fe(1)–Fe(2)–C(4) torsion angles of 28.8, 30.3, 30.0, and 28.1° respectively.

Compound (**10**,PF_6; X = I, R = Me) is unstable in solution and slowly decarbonylates to the iodo-bridged tetracarbonyl species [$Fe_2(\mu$-I)(CO)$_4${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]PF_6 (**9**; PF_6; X = I, R = Me) of structure analogous to that of the corresponding tetraphenoxydiphosphazane derivatives according to the i.r. and ^{1}H and ^{31}P-{^{1}H} n.m.r. spectroscopic evidence.



(10a)

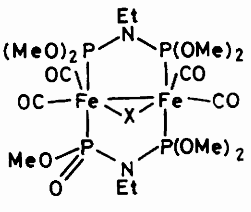


(10b)

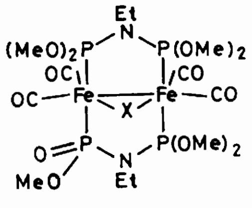
Bromination and chlorination of [$Fe_2(\mu$-CO)(CO)$_4${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$] (**8**; R = Me) in non-polar solvents was found to follow the same pattern as the iodination reaction in that the pentacarbonyl products [Fe_2X(CO)$_5${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]Z (Z = X = Br or Cl) (**10**, Z; R = Me) precipitated initially from solution and these converted to the tetracarbonyl derivatives [$Fe_2(\mu$-X)(CO)$_4${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]Z (**9**,Z; R = Me) both in solution and the solid state. For characterisation purposes these four compounds were isolated as the hexafluorophosphate salts.

Similar to that observed for the phenoxydiphosphazane species, [Fe_2X(CO)$_5${μ-(PhO)$_2$PN(Et)P(OPh)$_2$}$_2$]$^+$ (**10**; R = Ph), all three of the corresponding methoxydiphosphazane species [Fe_2X(CO)$_5${μ-MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]$^+$ (**10**; R = Me) were found to exhibit a single set of resonances with an AA'BB' pattern in their ^{31}P-{^{1}H} n.m.r. spectra indicative of these compounds occurring as a single isomer in solution. These compounds can in fact adopt two isomeric forms, either the axial isomer (**10a**) or the equatorial one (**10b**). Although the decarbonylation of (**10**) to (**9**) will presumably occur *via* the equatorial isomer, it is assumed, on the basis of the very similar band patterns of the C–O stretching peaks in the solid-state i.r. spectra of these compounds, that they all adopt the same structure in the solid state and this structure [(**10a**)] is retained in solution.

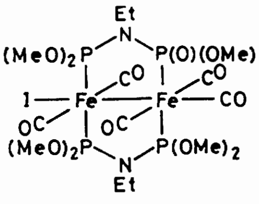
It was considered that the inability to detect neutral dihalides of the type [Fe_2X_2(CO)$_4${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$] (**7**; R = Me) in the halogenation reactions of [$Fe_2(\mu$-CO)(CO)$_4${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$] in non-polar solvents might be a consequence of the enforced precipitation of the ionic products. Monitoring of the iodination reaction in CH_2Cl_2 by means of i.r. spectroscopy revealed that (**10**; X = I, R = Me) is formed initially but that it readily rearranges to afford a reaction mixture, readily soluble in non-polar solvents such as light petroleum and with a complex band pattern in the C–O stretching region. Column chromatographic treatment of this reaction mixture led to the separation of three products, one of which was green-brown and the other two orange-red. The two orange-red products, which could be crystallised from light petroleum, exhibited identical band patterns in the C–O stretching region of their i.r. spectra, which were very similar to that of



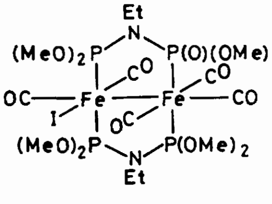
(11a)



(11b)



(12a)



(12b)

(**9**; X = I, R = Me) but at significantly lower frequency. The ^{31}P-{^{1}H} n.m.r. spectra of these species were highly complex consisting essentially of two sets of resonances, one of *ca.* 30 lines centred at δ 166.1 and the other of *ca.* 15 lines centred at δ 112.1 p.p.m. This spectral evidence together with the elemental microanalytical and mass spectra data* are consistent with these species being isomers of the Michaelis–Arbuzov type rearrangement product[23,24] $[Fe_2(\mu\text{-}I)\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ (**11**; X = I); the oxo group attached to the pentavalent phosphorus is *syn* to the bridging halogeno group in the one isomer and *anti* in the other [(**11a**) and (**11b**)]. The yellow-green product could not be isolated pure owing to its rearrangement to compounds (**11a**) and (**11b**) in solution but on the basis that it gives an i.r. spectrum with a characteristic band pattern in the C–O stretching region, very similar to that of $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**10**; X = I, R = Me), but at lower frequency, it is proposed that it is also a Michaelis–Arbuzov type rearrangement product *viz.* $[Fe_2I\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ (**12**). Confirmation that compounds (**11**) and (**12**) are indeed Arbuzov type rearrangement products and are formed by iodide ion attack on $[Fe_2(\mu\text{-}I)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**9**; X = I, R = Me) and $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**10**; X = I, R = Me) respectively, was obtained by treatment of the latter with iodide ions; compounds (**11**) and (**12**) were observed to be the respective sole products. Bromide ion attack on $[Fe_2Br(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**10**; X = Br, R = Me) and $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**9**; X = Br, R = Me) and chloride ion attack on $[Fe_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**9**; X = Cl, R = Me) were similarly found to lead to the formation of the corresponding neutral compounds consistent with the observation that bromination of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (**8**; R = Me) in dichloromethane and even benzene produces $[Fe_2Br\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ and $[Fe_2(\mu\text{-}Br)\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ *via* $[Fe_2Br(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**10**; X = Br, R = Me).

Co-ordinated phosphite ligands with secondary carbon atoms attached to the oxygens are less susceptible to halide ion attack and as a consequence the reactions of the tetraisopropoxydiphosphazane derivative $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (**8**; R = Pr^i) with halogens was investigated to establish whether the neutral dihalides $[Fe_2X_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (**7**; R = Pr^i) could be synthesised for this system. Two products were observed to be formed in each of these reactions *viz.* $[Fe_2X(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]Z$ (**10**, Z; R = Pr^i) and $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]Z$ (Z = X = Cl, Br, or I) (**9**, Z; R = Pr^i) with the former being identified by i.r. and ^{31}P-{^{1}H} n.m.r. spectroscopy only and the latter being fully characterised as the hexafluorophosphate salts. Significantly the halogeno-bridged tetracarbonyl species were found to be stable to halide ion attack and did not react at either the metal or isopropoxy centres.

It was concluded that for the formation of $[Fe_2X_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (**7**) from $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (**9**) by halide ion attack to be possible, the diphosphazane ligand must be one with minimal steric demands while at the same time resistant to nucleophilic attack. The ligand $(OCH_2CH_2O)PN(Et)P(OCH_2CH_2O)$ appeared to meet these requirements and thus the reactions of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(OCH_2CH_2O)PN(Et)P(OCH_2CH_2O)\}_2]$ (**8**; R = CH_2) were investigated. These reactions were found to parallel those of the corresponding $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ and $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ reactions, affording initially $[Fe_2X(CO)_5\{\mu\text{-}(OCH_2CH_2O)PN(Et)P(OCH_2CH_2O)\}_2]^+$ (X = Cl, Br, or I) (**10**; R = CH_2), identified by means of i.r. and ^{31}P-{^{1}H} n.m.r. spectroscopy. These pentacarbonyl species were also found to decarbonylate readily, producing the halogeno-bridged tetracarbonyl species $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(OCH_2CH_2O)PN(Et)P(OCH_2CH_2O)\}_2]^+$ (**9**; R = CH_2), isolated and characterised as the tetraphenylborate salts. These halogeno-bridged tetracarbonyl species were also found to be inert to halide ion attack which is indicative of the inability of cationic species of the type $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(R')P(OR)_2\}_2]^+$ to react further with halide ions being electronic in origin. Significantly, while the chlorination of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) by CCl_4 was found to produce $[Ru_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$, the corresponding reaction involving $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (**8**) (R = Me, Pr^i, or Ph) gave $[Fe_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]Cl$ (**9**;Cl; X = Cl)[25] which is further evidence that $[Fe_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (**7**; X = Cl) is unstable with respect to $[Fe_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]Cl$.†

A limited investigation of the reactions of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PCH_2P(OR)_2\}_2]$ (R = Me or Pr^i) with chlorine in non-polar solvents revealed that in this case the halogeno-bridged tetracarbonyl species $[Fe_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PCH_2P(OR)_2\}_2]Cl$, characterised as the hexafluorophosphate salt, precipitated from solution.

Reaction of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (**8**; R = Me) with excess bromine in dichloromethane was found to lead to the formation of not only $[Fe_2Br(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (**10**; R = Me, X = Br) but to a product which afforded two strong C–O stretching peaks at 2 076 and 2 022 cm^{-1} in its i.r. spectrum. This complex could be isolated as a red oil by *rapid* addition of excess bromine in

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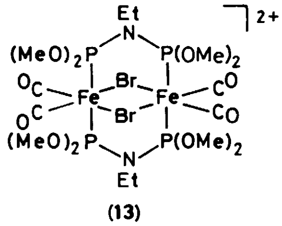
* The mass spectra exhibited molecular ion peaks of *m/e* = 794 and peaks corresponding to the loss of four carbonyl groups.

† A detailed study[25] of the reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with CCl_4 established that the mechanism of chlorination is very different to that for chlorine and does not involve ionic species as intermediates. On the other hand dissolution of $[Ru_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ in polar solvents such as CH_2Cl_2 leads to its ready rearrangement to $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]Cl$.

benzene to a benzene solution of the parent pentacarbonyl, but all attempts to obtain the compound pure proved unsuccessful. Significantly, treatment with sodium tetraphenylborate, with the object of isolating the complex as the tetraphenylborate salt, resulted instead in its reduction to $[\mathrm{Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]BPh_4}$ (**9**, $\mathrm{BPh_4}$; X = Br, R = Me).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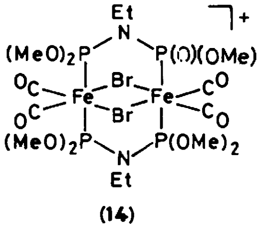
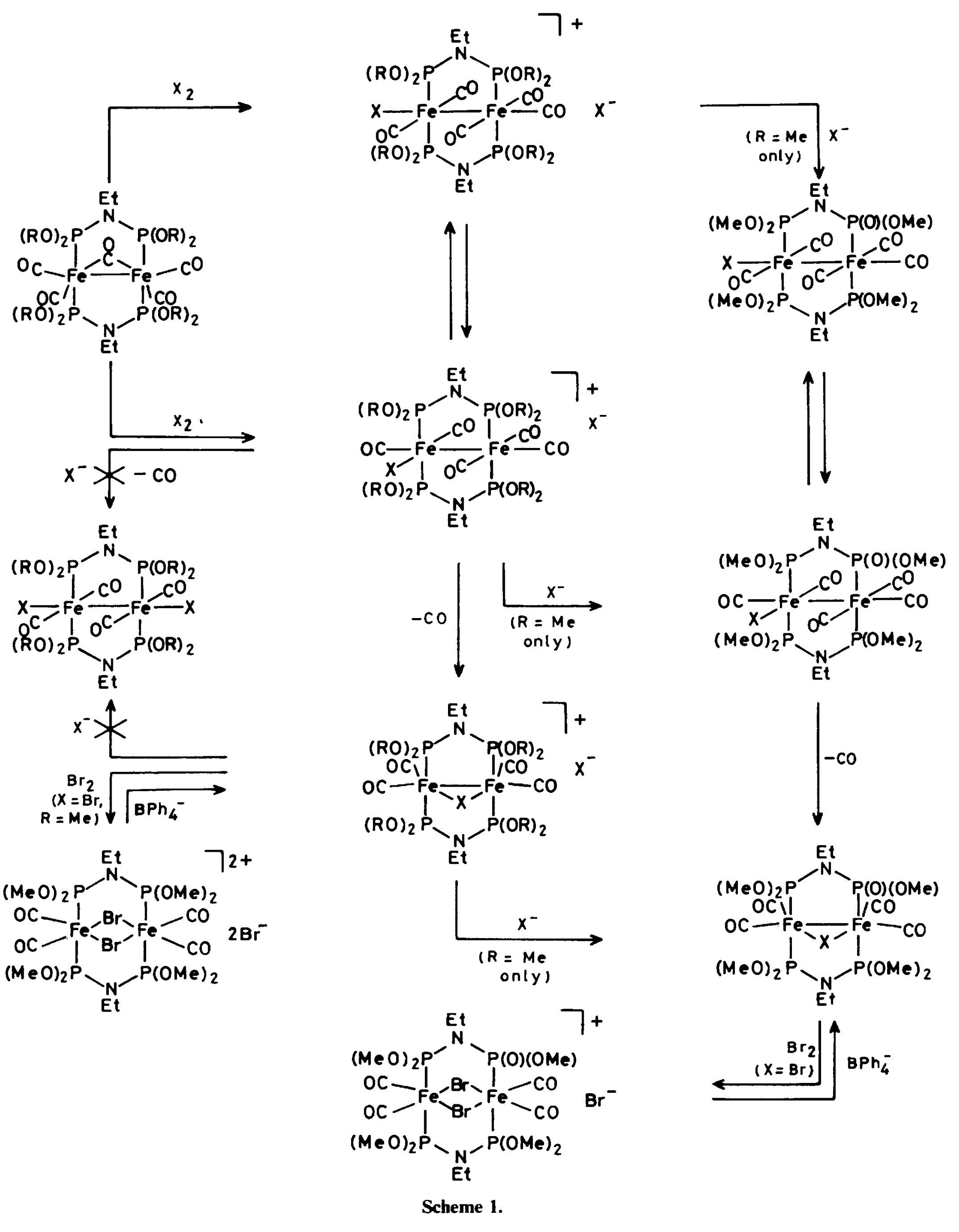
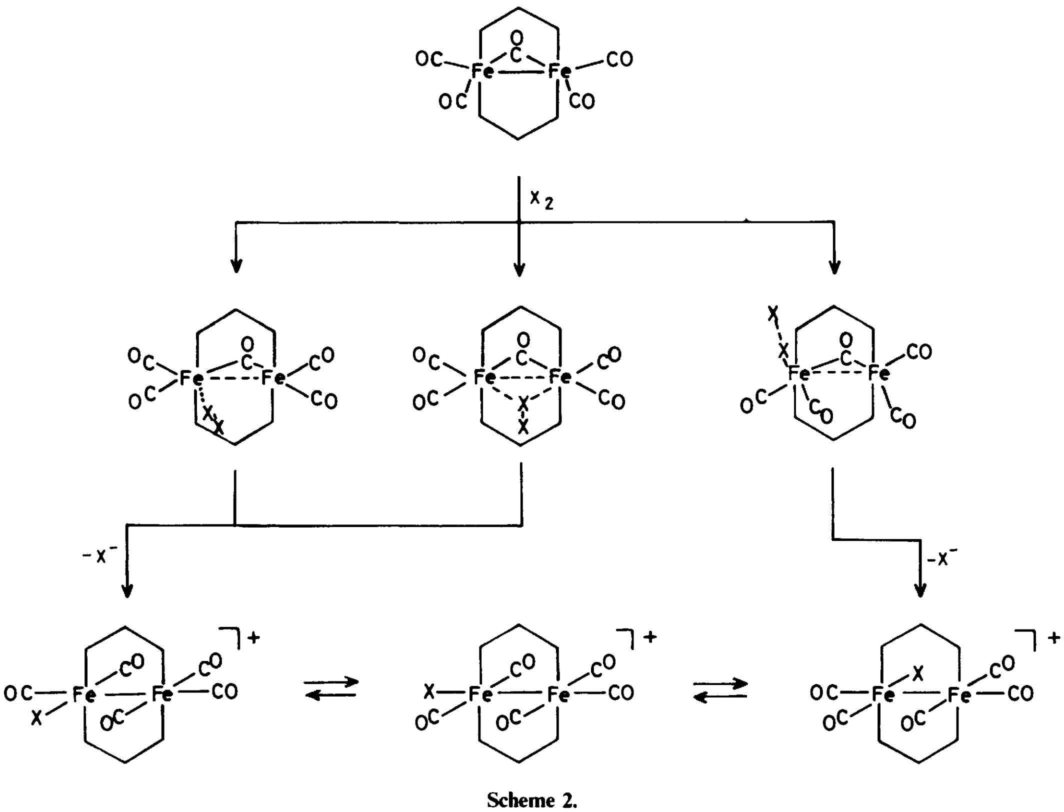

(14)

Dropwise addition of a benzene solution of excess bromine to a benzene solution of $[\mathrm{Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}]$ (**8**; R = Me) resulted in the precipitation of an orange microcrystalline material with peaks at 2 055 and 2 004 $\mathrm{cm^{-1}}$ in its i.r. spectrum. Attempts to isolate this particular species as the tetraphenylborate salt by addition of $\mathrm{NaBPh_4}$ led to the formation of $[\mathrm{Fe_2(\mu\text{-}Br)\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}}]$ (**11**; X = Br) which reacts with excess bromine to regenerate the compound with ν(C–O) at 2 055 and 2 004 $\mathrm{cm^{-1}}$. On the basis of these transformation reactions it is proposed that the compound with C–O stretching peaks of higher frequency is $[\mathrm{Fe_2(\mu\text{-}Br)_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]Br_2}$ (**13**,$\mathrm{Br_2}$) while the other is $[\mathrm{Fe_2(\mu\text{-}Br)_2\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]Br}$ (**14**,Br).



Scheme 1.

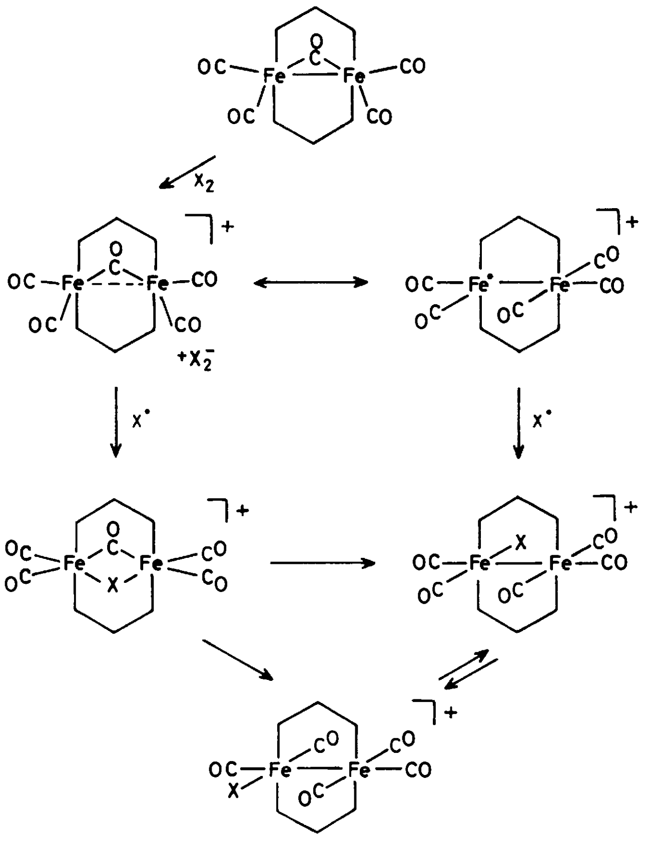


Scheme 2.

The halogenation of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ by reagents such as *N*-bromo- and *N*-chlorosuccinimide was also investigated and found to produce both the halogeno-pentacarbonyl (**10**) and halogeno-tetracarbonyl (**9**) species. This indicates that these reagents halogenate compound (**8**) by a mechanism similar to that of the halogens themselves.

Mechanism of Halogenation.—The reactions of the neutral pentacarbonyls $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me, Pr^i, Ph, or CH_2) (**8**) with halogens and the various products formed are summarised in Scheme 1.

The formation of the cationic halogeno-pentacarbonyl species (**10**) can be explained in terms of either of two mechanistic pathways. One (Scheme 2) involves electrophilic attack by the halogen molecule at one or both metal centres followed by heterolytic cleavage of the halogen–halogen bond leading to the loss of a halide ion and the formation of the cationic product. The second (Scheme 3) involves a one-electron oxidation of the parent pentacarbonyl to produce $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ followed by attack by halogen radicals on the latter to give $[Fe_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$; the halogen radicals may be considered as being derived from X_2^-. Analogous pathways have been described to interpret the halogenation reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$,[26] $[Ru_2(\eta\text{-}C_5H_5)_2(CO)_4]$,[27] $[Fe_2(\mu\text{-}SR)_2(CO)_6]$ (R = Me, *etc.*) and substituted derivatives thereof,[28] $[Mn_2(CO)_{10}]$,[29] $[Re_2(CO)_{10}]$,[29] and $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4L_2]$ [L = CO or $P(OMe)_3$][30] in polar solvents. Although the mechanism summarised in Scheme 2 might appear to be the more acceptable one, there is considerable evidence for that outlined in Scheme 3. For instance a detailed study[31] of the reaction of $[Fe_2(\mu\text{-}SR)_2(CO)_6]$ (R = Me, Et, or Ph) with $[NO]PF_6$ in the presence of $(RS)_2$ revealed that the



Scheme 3.

product of the reaction, $[Fe_2(\mu\text{-}SR)_3(CO)_6]^+$, is formed by formal insertion of a RS radical into the iron–iron bond of $[Fe_2(\mu\text{-}SR)_2(CO)_6]^+$; the latter is formed by one-electron oxidation of $[Fe_2(\mu\text{-}SR)_2(CO)_6]$ by $[NO]PF_6$. Also $[Rh_2(\mu\text{-}SC_6H_4CH_3\text{-}p)_2(\eta\text{-}C_5H_5)_2]$ was similarly found to afford $[Rh_2(\mu\text{-}SC_6H_4Me\text{-}p)_3(\eta\text{-}C_5H_5)_2]^+$ on treatment with $[NO]PF_6$ in the presence of $(p\text{-}MeC_6H_4S)_2$.[32] Furthermore earlier studies had shown that treatment of $[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ with iodine leads to the one-electron oxidation product, $[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]^+$, for a half-molar quantity of the halogen and to the iodine-bridged species, $[Fe_2(\mu\text{-}I)(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]^+$, for an excess of the iodine.[13] The one-electron oxidation step in Scheme 3 is considered to occur *via* association of the halogen molecule with the oxygen atoms of the CO ligands. This proposal is consistent with the hypothesis of Poë and co-workers[33] who, in investigating the reactions of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ with halogens, suggested this type of interaction to account for a possible weakening of the metal–metal bond by attracting electron density from the metal–metal bonding orbitals. This could lead to fission (homolytic or heterolytic) of the metal–metal bond or a single electron transfer to form $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]^+$ and X_2^- with the cation reacting rapidly with the halogen radicals present. Significantly cyclic voltametric studies indicate that $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me, Et, Pr^i, or Ph) and $[Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PCH_2PR_2)_2]$ (R = Me or Ph) are readily and reversibly oxidised to $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and $[Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PCH_2PR_2)_2]^+$, and, in the case of the ditertiary phosphine derivatives, to $[Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PCH_2PR_2)_2]^{2+}$, with E_a for the first oxidation step being in the range 0.14—0.53 V (relative to Ag–AgCl in acetone).[34]

Experimental

The neutral pentacarbonyls, $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me, Pr^i, Ph, or CH_2) and $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PCH_2P(OR)_2\}_2]$ (R = Me or Pr^i), were synthesised according to literature methods.[21] All reactions and operations were carried out under an atmosphere of nitrogen. The i.r. and n.m.r. spectra were recorded on a Perkin-Elmer model 457 spectrophotometer and on a Varian FT 80A instrument respectively. Light petroleum refers to that fraction of b.p. 60—80 °C.

Synthesis of $[Fe_2X(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ (X = Cl, Br, *or* I).—A twice molar amount of iodine (1 mmol) or bromine (1 mmol) in n-hexane (*ca.* 25 cm^3) or chlorine (1 mmol) in CCl_4 (*ca.* 5 cm^3) was added dropwise over a period of 15 min to a stirred solution of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (0.35 g, 0.5 mmol) in n-hexane and the solution stirred at room temperature for a further 20 min. The product, which separated from solution, was washed with light petroleum and dissolved in acetone (*ca.* 25 cm^3). NH_4PF_6 (0.16 g, 1 mmol) in acetone (*ca.* 40 cm^3) was added to this solution followed by water (*ca.* 40 cm^3). The acetone was quickly removed under reduced pressure resulting in the separation of the product from solution. Crystallisation was effected in the dark from ethanol–water. Yield: *ca.* 40–50%.

Synthesis of $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]Z$ (X = Cl, Br, *or* I; R = Pr^i, Ph, *or* CH_2; Z = PF_6 *or* BPh_4).—A twice molar amount of iodine (1 mmol) or bromine (1 mmol) or iodine monochloride (1 mmol) in CH_2Cl_2 (*ca.* 25 cm^3) or chlorine (1 mmol) in CCl_4 (*ca.* 5 cm^3) was added dropwise over a period of 5 min to a stirred solution of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Pr^i, Ph, or CH_2) (0.5 mmol) in CH_2Cl_2 (*ca.* 75 cm^3) and the solution stirred at room temperature for a further 3 h. The solvent was removed under reduced pressure and the oily residue washed thoroughly with aliquots of CCl_4.

The tetraphenylborate salt was obtained by adding a solution of $NaBPh_4$ (0.34 g, 1 mmol) in methanol (*ca.* 5 cm^3) to a solution of the residue $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ (X = Cl, Br, or I; R = CH_2 or Ph) in methanol (25 cm^3). The product which separated from solution was washed with cold methanol (*ca.* 10 cm^3) and crystallised from acetone–methanol. Yield: *ca.* 65—75%.

The hexafluorophosphate salt was obtained by adding a solution of NH_4PF_6 (0.16 g, 1 mmol) in acetone (*ca.* 5 cm^3) to a stirred solution of the residue $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ (X = Cl, Br, or I; R = Pr^i or Ph) in acetone (*ca.* 25 cm^3) followed by water (*ca.* 40 cm^3). The acetone was quickly removed under reduced pressure resulting in the separation of the product from solution. Crystallisation was effected from ethanol–water. Yield: 60—70%.

Synthesis of $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ (X = Cl, Br, *or* I).—$[Fe_2X(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ (X = Cl, Br, or I) was dissolved in acetone and the solution stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the product crystallised from ethanol–water. Yield: 60—70%.

Synthesis of $[Fe_2(\mu\text{-}X)\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ (X = Cl, Br, *or* I).—A twice molar amount of iodine (1 mmol) or bromine (1 mmol) in CH_2Cl_2 (*ca.* 25 cm^3) or benzene (*ca.* 25 cm^3), or chlorine (1 mmol) in CCl_4 (*ca.* 5 cm^3) was added dropwise over a period of 20 min to a stirred solution of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (0.35 g, 0.5 mmol) in CH_2Cl_2 (*ca.* 75 cm^3) or benzene (*ca.* 75 cm^3) and the solution stirred at room temperature for a further 20 h. The solvent was removed under reduced pressure and the residue chromatographed on an alumina column (acidic, activity III). Elution with $CHCl_3$ afforded a yellow-green and two orange-red bands which were collected. The yellow-green band which contains $[Fe_2X\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ was found to turn orange-red on standing and on re-elution through the column gave two orange-red bands which were found to be identical to the original two. Removal of the solvent from each of the two bands gave orange-red residues of different isomers of the title compound which were crystallised from warm (*ca.* 60 °C) light petroleum. Yields: *ca.* 20—30%.

Synthesis of $[Fe_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PCH_2P(OR)_2\}_2]PF_6$ (R = Me *or* Pr^i).—A twice molar amount of chlorine (1.0 mmol) in CCl_4 (*ca.* 5 cm^3) was added dropwise over a period of 5 min to a stirred solution of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PCH_2P(OR)_2\}_2]$ (R = Me or Pr^i) (0.5 mmol) in n-hexane (*ca.* 125 cm^3) and the solution stirred at room temperature for a further 15 min. The product which separated from solution was washed with n-hexane and dried *in vacuo* for 20 h. NH_4PF_6 (0.16 g, 1 mmol) in acetone (*ca.* 5 cm^3) was added to a solution of the product in acetone (*ca.* 40 cm^3) followed by water (*ca.* 40 cm^3). The acetone was quickly removed under reduced pressure resulting in the separation of the product from solution which was crystallised from ethanol–water. Yield: *ca.* 35—40%.

Crystal Structure Determination of $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$.—*Crystal data.* $C_{17}H_{34}F_6Fe_2IN_2O_{13}P_5$, M = 981.90, wine red crystals of dimensions 0.77 × 0.54 × 0.88 mm, orthorhombic, space group *Pbca*, a = 20.233(8), b = 15.545(6), c = 22.218(9) Å, U = 6 988.1 $Å^3$, D_m = 1.86 g cm^{-3}, Z = 8, D_c = 1.87 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 21.05 cm^{-1}, $F(000)$ = 3 904.

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for $[\mathrm{Fe_2I(CO)_5}\{\mu\text{-}(\mathrm{MeO})_2\mathrm{PN(Et)P(OMe)_2}\}_2]\mathrm{PF_6}$ with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*Z/a*	*Y/b*	*Z/c*
I	5 213(1)	2 478(1)	5 225(1)	C(9)	3 444(9)	2 790(12)	5 740(8)
Fe(2)	4 433(1)	2 513(2)	4 257(1)	C(10)	6 270(10)	2 221(13)	3 848(9)
Fe(1)	3 613(1)	2 576(1)	3 251(1)	C(11)	5 454(9)	4 722(13)	4 263(9)
P(1)	2 772(2)	2 573(3)	3 877(2)	C(12)	4 210(10)	3 768(13)	1 885(9)
P(2)	3 645(2)	1 826(3)	4 757(2)	C(13)	4 679(12)	1 116(16)	2 011(11)
P(3)	5 198(2)	3 213(3)	3 730(2)	C(14)	2 265(9)	1 768(13)	4 897(9)
P(4)	4 514(2)	2 552(3)	2 692(2)	C(15)	2 124(11)	835(15)	4 906(10)
P(5)	2 488(3)	192(4)	1 685(2)	C(16)	5 798(14)	3 052(21)	2 558(14)
O(1)	2 752(6)	2 727(7)	2 220(5)	C(17)	5 835(19)	3 929(23)	2 459(18)
O(2)	3 717(6)	4 443(8)	3 354(5)	F(1)	2 419(9)	699(12)	1 073(8)
O(3)	3 639(9)	689(8)	3 296(6)	F(2)	2 412(9)	−280(11)	2 304(7)
O(4)	4 987(6)	829(8)	3 916(5)	F(3)	2 237(9)	−642(12)	1 371(8)
O(5)	3 940(6)	4 180(8)	4 686(5)	F(4)	2 779(11)	983(14)	2 019(10)
O(6)	2 076(5)	2 241(7)	3 627(5)	F(5)	3 184(11)	−40(14)	1 497(10)
O(7)	2 559(6)	3 511(8)	4 073(5)	F(6)	1 801(12)	539(15)	1 848(11)
O(8)	3 683(5)	801(7)	4 743(5)	C(1)	3 083(8)	2 638(11)	2 635(7)
O(9)	3 577(5)	1 955(7)	5 461(5)	C(2)	3 682(8)	3 718(11)	3 322(8)
O(10)	5 954(6)	3 063(7)	3 874(5)	C(3)	3 638(8)	1 436(11)	3 288(8)
O(11)	5 177(6)	4 234(7)	3 761(5)	C(4)	4 765(8)	1 500(11)	4 032(7)
O(12)	4 452(6)	2 911(7)	2031(5)	C(5)	4 120(8)	3 520(11)	4 517(8)
O(13)	4 803(6)	1 619(8)	2 549(6)	C(6)	1 991(9)	1 386(12)	3 340(8)
N(1)	2 888(6)	2 004(8)	4 503(5)	C(7)	1 896(14)	3 880(19)	4 273(13)
N(2)	5 163(7)	3 062(9)	2 989(6)	C(8)	4 051(9)	302(12)	5 175(8)

Table 4. Interatomic distances (Å) for $[\mathrm{Fe_2I(CO)_5}\{\mu\text{-}(\mathrm{MeO})_2\mathrm{PN(Et)P(OMe)_2}\}_2]\mathrm{PF_6}$ with estimated standard deviations in parentheses

Fe(1)–Fe(2)	2.787(3)	P(2)–O(9)	1.582(11)	Fe(2)–I	2.667(2)	P(2)–O(8)	1.595(11)
Fe(1)–P(1)	2.197(4)	P(3)–O(10)	1.579(12)	F(2)–P(2)	2.217(5)	P(3)–O(11)	1.590(11)
Fe(1)–P(4)	2.206(4)	P(3)–N(2)	1.665(14)	Fe(2)–P(3)	2.225(5)	P(4)–N(2)	1.670(14)
Fe(1)–C(1)	1.741(16)	P(4)–O(12)	1.576(14)	Fe(2)–C(4)	1.782(17)	P(4)–O(13)	1.595(13)
Fe(1)–C(2)	1.789(17)	O(6)–C(6)	1.483(20)	Fe(2)–C(5)	1.785(17)	O(7)–C(7)	1.367(28)
Fe(1)–C(3)	1.774(17)	O(8)–C(8)	1.442(20)	C(4)–O(4)	1.165(17)	O(9)–C(9)	1.464(19)
C(1)–O(1)	1.148(16)	O(10)–C(10)	1.458(21)	C(5)–O(5)	1.152(18)	O(11)–C(11)	1.459(20)
C(2)–O(2)	1.131(17)	O(12)–C(12)	1.456(21)	C(3)–O(3)	1.162(18)	O(13)–C(13)	1.450(20)
P(1)–O(6)	1.599(11)	N(1)–C(14)	1.578(20)	P(1)–O(7)	1.582(12)	N(2)–C(16)	1.604(22)
P(1)–N(1)	1.665(12)	C(14)–C(15)	1.478(26)	P(2)–N(1)	1.657(12)	C(16)–C(17)	1.383(28)

Table 5. Interatomic angles (°) for $[\mathrm{Fe_2I(CO)_5}\{\mu\text{-}(\mathrm{MeO})_2\mathrm{PN(Et)P(OMe)_2}\}_2]\mathrm{PF_6}$ with estimated standard deviations in parentheses

P(1)–Fe(1)–Fe(2)	87.3(1)	P(2)–Fe(2)–Fe(1)	89.5(1)	N(1)–P(1)–Fe(1)	114.8(5)	N(1)–P(2)–Fe(2)	114.5(5)
P(4)–Fe(1)–Fe(2)	87.6(1)	P(3)–Fe(2)–Fe(1)	88.6(1)	N(1)–P(1)–O(6)	104.0(6)	N(1)–P(2)–O(8)	101.8(6)
P(1)–Fe(1)–P(4)	174.9(2)	I–Fe(2)–Fe(1)	179.1(1)	N(1)–P(1)–O(7)	107.3(6)	N(1)–P(2)–O(9)	103.6(6)
C(1)–Fe(1)–Fe(2)	178.1(5)	C(4)–Fe(2)–Fe(1)	91.8(5)	O(10)–P(3)–Fe(2)	119.6(5)	O(12)–P(4)–Fe(1)	116.9(5)
C(1)–Fe(1)–P(4)	93.9(5)	C(5)–Fe(2)–Fe(1)	90.9(5)	O(11)–P(3)–Fe(2)	116.5(5)	O(13)–P(4)–Fe(1)	115.6(5)
C(1)–Fe(1)–P(1)	91.2(5)	P(2)–Fe(2)–I	90.6(1)	O(11)–P(3)–O(10)	99.4(6)	O(13)–P(4)–O(12)	99.5(7)
C(2)–Fe(1)–Fe(2)	85.3(5)	P(3)–Fe(2)–I	91.3(1)	N(2)–P(3)–Fe(2)	114.9(5)	N(2)–P(4)–Fe(1)	114.8(5)
C(2)–Fe(1)–P(4)	90.1(5)	P(3)–Fe(2)–P(2)	178.0(2)	N(2)–P(3)–O(10)	102.9(7)	N(2)–P(4)–O(12)	105.1(7)
C(2)–Fe(1)–P(1)	90.4(5)	C(4)–Fe(2)–I	89.2(5)	N(2)–P(3)–O(11)	100.5(7)	N(2)–P(4)–O(13)	102.8(7)
C(2)–Fe(1)–C(1)	93.6(8)	C(4)–Fe(2)–P(3)	91.3(5)	P(2)–N(1)–P(1)	120.3(7)	P(3)–N(2)–P(4)	119.4(9)
C(3)–Fe(1)–Fe(2)	84.8(5)	C(4)–Fe(2)–P(2)	89.2(5)	C(14)–N(1)–P(1)	118(1)	C(16)–N(2)–P(4)	113(2)
C(3)–Fe(1)–P(4)	89.2(6)	C(5)–Fe(2)–I	88.1(5)	C(14)–N(1)–P(2)	121(1)	C(16)–N(2)–P(3)	124(2)
C(3)–Fe(1)–P(1)	89.5(6)	C(5)–Fe(2)–P(2)	90.3(5)	C(6)–O(6)–P(1)	123(1)	C(7)–O(7)–P(1)	135(2)
C(3)–Fe(1)–C(1)	96.3(8)	C(5)–Fe(2)–C(4)	177.2(8)	C(8)–O(8)–P(2)	123(1)	C(9)–O(9)–P(2)	123(1)
C(3)–Fe(1)–C(2)	170.1(7)	C(5)–Fe(2)–P(3)	89.3(5)	C(10)–O(10)–P(3)	123(1)	C(11)–O(11)–P(3)	123(1)
O(6)–P(1)–Fe(1)	117.5(4)	O(8)–P(2)–Fe(2)	115.9(5)	C(12)–O(12)–P(4)	124(1)	C(13)–O(13)–P(4)	126(1)
O(7)–P(1)–Fe(1)	112.6(5)	O(9)–P(2)–Fe(2)	119.8(5)	O(1)–C(1)–Fe(1)	176(2)	O(2)–C(2)–Fe(1)	178(2)
O(7)–P(1)–O(6)	98.9(6)	O(9)–P(2)–O(8)	98.6(6)	O(3)–C(3)–Fe(1)	178(2)	O(4)–C(4)–Fe(2)	177(2)
				O(5)–C(5)–Fe(2)	178(2)	C(15)–C(14)–N(1)	113(2)
				C(17)–C(16)–N(2)	97(3)		

Intensity data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å). A least-squares fit of high-angle reflections was used to obtain accurate cell constants. Diffraction intensities were measured in the range $2 \leqslant 2\theta \leqslant 46°$ using the ω—2θ scan technique. Three standard reflections, measured every hour, showed no decrease in intensity during data collection. Lorentz and polarisation, but no absorption corrections were applied. Of the 4 138 unique reflections measured 3 121 were classed as observed [$I > 3\sigma(I)$] and these were used for the solution and refinement of the structure.

The positions of the two Fe atoms and the iodine atom were located from a three-dimensional Patterson function.[35] The remaining non-hydrogen atoms were readily located in a subsequent electron-density map phased on the iodine and iron atoms. The structure was refined by full-matrix least-squares methods with the Fe, I, and P atoms assigned anisotropic thermal parameters, and the remaining atoms all assigned individual isotropic thermal parameters. The H atoms were not located. The refinement using unit weights converged at a final conventional R factor of 0.080. A final difference map calculated at this stage was featureless. Fractional atomic co-ordinates, interatomic distances and angles, and selected torsion angles are listed in Tables 3—6.

Table 6. Selected torsion angles (°) for $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$

Fe(1)–P(1)–P(2)–Fe(2)	27.9	Fe(1)–P(4)–P(3)–Fe(2)	29.3
P(2)–Fe(2)–Fe(1)–P(1)	28.8	P(3)–Fe(2)–Fe(1)–P(4)	30.3
C(5)–Fe(2)–Fe(1)–C(2)	30.0	C(4)–Fe(2)–Fe(1)–C(3)	28.1

Crystal Structure Determination of $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]PF_6\cdot Me_2CO$.—*Crystal data.* $C_{59}H_{56}BrF_6Fe_2N_2O_{13}P_5$, M = 1 458.47, red crystal of dimensions 0.73 × 0.65 × 0.50 mm grown from acetone–H_2O, orthorhombic, space group $Cmc2_1$, a = 16.819(6), b = 19.300(8), c = 20.824(9) Å, U = 6 759.6 Å^3, D_m = 1.47 g cm^{-3}, Z = 4, D_c = 1.44 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 13.7 cm^{-1}, $F(000)$ = 3 128.

Data were collected and accurate cell constants obtained as described for the previous compound. From a total of 2 520 intensities measured as above in the range $4 \leqslant 2\theta \leqslant 46°$, 2 060 with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. No crystal or instrument instability was detected during the measurements. The data were corrected for Lorentz and polarisation effects but not for absorption.

The two Fe atoms and the Br atom were located from a three-dimensional Patterson function, which showed that these atoms were lying on a crystallographic mirror plane.[35] The remaining non-hydrogen atoms, with the exception of a few phenyl ring carbon atoms, were readily located in an electron-density map phased on the Fe and Br atoms. Co-ordinates of the missing carbon atoms were calculated using the known geometry of phenyl rings. The structure was refined by full-matrix least-squares methods with the Fe, Br, and P atoms assigned anisotropic thermal parameters, the remaining atoms all assigned

Table 7. Fractional atomic co-ordinates (× 10^4) for $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]PF_6\cdot Me_2CO$ with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe(1)	0	602(2)	0	O(S1)*	0	2 070	2 630
Fe(2)	0	1 681(2)	−844(2)	C(S1)*	730	2 990	2 770
Br	0	1 802(1)	286(2)	C(S2)*	0	2 650	2 590
P(1)	1 326(3)	621(2)	70(3)	C(51)	1 706(9)	653(7)	1 313(6)
P(2)	1 312(3)	1 707(3)	−872(3)	C(52)	1 145(9)	865(7)	1 766(6)
P(3)	5 000	1 047(7)	426(10)	C(53)	1 134(9)	561(7)	2 374(6)
C(1)	0	16(14)	729(13)	C(54)	1 684(9)	46(7)	2 529(6)
O(1)	0	−360(11)	1 118(11)	C(55)	2 244(9)	−165(7)	2 075(6)
C(2)	0	−2(15)	−589(13)	C(56)	2 255(9)	139(7)	1 468(6)
O(2)	0	−386(10)	−1 067(10)	C(61)	1 591(7)	−725(5)	−157(6)
C(3)	0	1 082(17)	−1 482(16)	C(62)	1 338(7)	−1 229(5)	278(6)
O(3)	0	726(13)	−1 926(13)	C(63)	1 116(7)	−1 884(5)	58(6)
C(4)	0	2 496(16)	−1 228(15)	C(64)	1 149(7)	−2 036(5)	−596(6)
O(4)	0	2 993(12)	−1 519(11)	C(65)	1 402(7)	1 532(5)	−1 031(6)
N(1)	1 808(9)	1 099(8)	−453(7)	C(66)	1 624(7)	−877(5)	−812(6)
C(9)	2 725(12)	1 131(11)	−427(11)	C(71)	1 629(9)	2 869(8)	−201(7)
C(10)	3 069(16)	685(13)	−934(14)	C(72)	1 852(9)	2 689(8)	422(7)
O(5)	1 704(8)	960(7)	703(7)	C(73)	1 705(9)	3 143(8)	930(7)
O(6)	1 812(7)	−87(6)	76(6)	C(74)	1 336(9)	3 778(8)	813(7)
O(7)	1 759(8)	2 418(7)	−706(7)	C(75)	1 114(9)	3 959(8)	190(7)
O(8)	1 690(8)	1 599(7)	−1 564(7)	C(76)	1 260(9)	3 505(8)	−317(7)
F(1)	5 000	446(18)	−167(19)	C(81)	1 635(10)	2 052(8)	−2 087(7)
F(2)	4 270(19)	1 473(16)	132(17)	C(82)	2 129(10)	2 632(8)	−2 101(7)
F(3)	4 323(19)	591(17)	658(15)	C(83)	2 118(10)	3 074(8)	−2 632(7)
F(4)	5 000	1 633(22)	914(21)	C(84)	1 613(10)	2 935(8)	−3 147(7)
				C(85)	1 118(10)	2 355(8)	−3 132(7)
				C(86)	1 129(10)	1 914(8)	−2 602(7)

* Atoms of the acetone solvent molecule were located but their positions were not refined.

Table 8. Interatomic distances (Å) for $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]PF_6$ with estimated standard deviations in parentheses*

Fe(1)–Fe(2)	2.724(5)	C(1)–O(1)	1.088(30)	Fe(1)–C(2)	1.692(28)	C(2)–O(2)	1.242(31)
Fe(1)–Br	2.391(4)	C(4)–O(4)	1.136(33)	Fe(2)–Br	2.363(5)	C(3)–O(3)	1.152(35)
Fe(1)–P(1)	2.235(5)	C(9)–C(10)	1.479(32)	Fe(2)–P(2)	2.208(5)	N(1)–C(9)	1.544(23)
Fe(1)–C(1)	1.893(28)	O(6)–C(61)	1.375(14)	Fe(2)–C(3)	1.762(34)	O(5)–C(51)	1.401(16)
Fe(2)–C(4)	1.765(32)	O(8)–C(81)	1.399(18)	P(1)–N(1)	1.642(16)	O(7)–C(71)	1.383(18)
P(1)–O(5)	1.604(14)	P(3)–F(2)	1.600(32)	P(2)–N(1)	1.683(16)	P(3)–F(1)	1.694(38)
P(1)–O(6)	1.593(12)	P(3)–F(4)	1.519(44)	P(2)–O(7)	1.602(15)	P(3)–F(3)	1.518(32)
P(2)–O(8)	1.588(14)						

* All C–C distances in the phenyl rings were fixed at 1.395 Å.

Table 9. Interatomic angles (°) for $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]PF_6$ with estimated standard deviations in parentheses[a,b]

Br–Fe(1)–Fe(2)	54.6(1)	Br–Fe(2)–Fe(1)	55.5(1)	O(8)–P(2)–Fe(2)	114.9(6)	O(8)–P(2)–N(1)	100.5(8)
P(1)–Fe(1)–Fe(2)	91.7(2)	P(2)–Fe(2)–Fe(1)	92.0(2)	O(8)–P(2)–O(7)	96.9(8)	O(2)–C(2)–Fe(1)	173(2)
P(1)–Fe(1)–Br	88.2(2)	P(2)–Fe(2)–Br	91.4(2)	O(3)–C(3)–Fe(2)	176(3)	O(1)–C(1)–Fe(1)	175(3)
C(1)–Fe(1)–Fe(2)	166.8(8)	C(3)–Fe(2)–Fe(1)	89(1)	O(4)–C(4)–Fe(2)	175(3)	P(2)–N(1)–P(1)	119.4(9)
C(1)–Fe(1)–Br	112.2(8)	C(3)–Fe(2)–Br	145(1)	C(9)–N(1)–P(1)	120(1)	C(9)–N(1)–P(2)	119(1)
C(1)–Fe(1)–P(1)	87.6(2)	C(2)–Fe(2)–P(2)	89.7(2)	C(10)–C(9)–N(1)	110(2)	C(51)–O(5)–P(1)	125(1)
C(1)–Fe(1)–C(2)	100(1)	C(4)–Fe(2)–Fe(1)	167(1)	C(61)–O(6)–P(1)	129(1)	C(71)–O(7)–P(2)	129(1)
C(2)–Fe(1)–Fe(2)	93.4(9)	C(4)–Fe(2)–Br	111(1)	C(81)–O(8)–P(2)	127(1)	F(2)–P(3)–F(1)	94(2)
C(2)–Fe(1)–Br	148.0(9)	C(4)–Fe(2)–P(2)	88.1(2)	F(3)–P(3)–F(1)	80(1)	F(3)–P(3)–F(2)	81(1)
C(2)–Fe(1)–P(1)	93.4(2)	C(4)–Fe(2)–C(2)	104(1)	F(4)–P(3)–F(1)	175(2)	F(4)–P(3)–F(2)	83(3)
Fe(2)–Br–Fe(1)	69.9(1)	N(1)–P(1)–Fe(1)	117.3(6)	F(4)–P(3)–F(3)	103(2)		
O(5)–P(1)–Fe(1)	117.1(5)	O(6)–P(1)–Fe(1)	119.9(5)	C(52)–C(51)–O(5)	119.2(8)	C(62)–C(61)–O(6)	118.5(7)
O(6)–P(1)–N(1)	103.5(8)	O(6)–P(1)–O(5)	89.1(7)	C(72)–C(71)–O(7)	120.5(7)	C(82)–C(81)–O(8)	118.6(8)
N(1)–P(2)–Fe(2)	117.8(6)	O(5)–P(1)–N(1)	96.9(7)				
O(7)–P(2)–Fe(2)	118.8(6)	O(7)–P(2)–N(1)	104.6(8)				

[a] All C–C–C angles in the phenyl rings were fixed at 120°. [b] P(1)–Fe(1)–Fe(2)–P(2) torsion angle = 3.78°.

individual isotropic thermal parameters and with the phenyl rings refined as perfect hexagons. The hydrogen atoms were not located. The refinement, using unit weights, converged at a final conventional *R* factor of 0.079. A final difference map calculated at this stage was featureless. Fractional atomic co-ordinates and interatomic distances and angles are listed in Tables 7—9.

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References

1 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 99.

2 M. Cowie and S. J. Loeb, *Organometallics*, 1985, **4**, 852; P.D. Enlow and C. Woods, *Inorg. Chem.*, 1985, **24**, 1273; S. P. Deranlyagala and K. R. Grundy, *Organometallics*, 1985, **4**, 424; C. Woodcock and R. Eisenberg, *ibid.*, p. 4.

3 B. R. Sutherland and M. Cowie, *Inorg. Chem.*, 1984, **23**, 2324; J. T. Mague, C. L. Klein, R. J. Majeste, and E. D. Stevens, *Organometallics*, 1984, **3**, 1860.

4 C-L. Lee, B. R. James, D. A. Nelson, and R. T. Hallen, *Organometallics*, 1984, **3**, 1360.

5 L. Manojlović-Muir, K. W. Muir, A. A. Frew, S. S. M. Ling, M. A. Thompson, and R. J. Puddephatt, *Organometallics*, 1984, **3**, 1637; G. B. Jacobsen and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1985, 692; S. Muralidharan and J. H. Espenson, *J. Am. Chem. Soc.*, 1984, **106**, 8104; C-L. Lee, G. Besenyei, B. R. James, D. A. Nelson, and M. A. Lilga, *J. Chem. Soc., Chem. Commun.*, 1985, 1175.

6 G. Ferguson, W. J. Laws, M. Parvez, and R. J. Puddephatt, *Organometallics*, 1983, **2**, 276; A. J. Deeming and S. Donovan-Mtunzi, *ibid.*, 1985, **4**, 693.

7 F. A. Cotton, L. M. Daniels, K. R. Dunbar, L. R. Falvello, S. M. Tetrick, and R. A. Walton, *J. Am. Chem. Soc.*, 1985, **107**, 3524; K-W. Lee and T. L. Brown, *Organometallics*, 1985, **4**, 1025.

8 W. J. Laws and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1983, 1020; B. E. Hanson and J. S. Mancini, *Organometallics*, 1983, **2**, 126.

9 D. L. De Laet, D. R. Powell, and C. P. Kubiak, *Organometallics*, 1985, **4**, 954.

10 F. A. Cotton and W. J. Roth, *Inorg. Chem.*, 1983, **22**, 3654; F. A. Cotton, S. A. Duraj, and W. J. Roth, *ibid.*, 1984, **23**, 4113.

11 P. Braunstein, C. de Méric de Bellefon, M. Lanfranci, and A. Tiripicchio, *Organometallics*, 1984, **3**, 1772; B. F. Hoskins, R. J. Steen, and T. W. Turney, *J. Chem. Soc., Dalton Trans.*, 1984, 1831; J. C. Jeffery, A. G. Orpen, W. T. Robinson, F. G. A. Stone, and M. J. Went, *J. Chem. Soc., Chem. Commun.*, 1984, 396; J. A. Iggo, D. P. Markham, B. L. Shaw, and M. Thornton-Pett, *ibid.*, 1985, 432; B. Delavaux, B. Chaudret, N. J. Taylor, S. Arabi, and R. Poilblanc, *ibid.*, 1985, 805.

12 R. J. Haines, A. L. du Preez, and G. T. W. Wittman, *Chem. Commun.*, 1968, 611; R. J. Haines and A. L. du Preez, *J. Organomet. Chem.*, 1970, **21**, 181; J. A. de Beer, R. J. Haines, R. Greatrex, and N. N. Greenwood, *ibid.*, 1971, **27**, C33; J. A. de Beer, R. J. Haines, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 1971, 3271; R. J. Haines and C. R. Nolte, *J. Organomet. Chem.*, 1972, **36**, 163; J. A. de Beer and R. J. Haines, *ibid.*, 1972, **36**, 297; 1972, **37**, 173.

13 R. J. Haines and A. L. du Preez, *Inorg. Chem.*, 1972, **11**, 330.

14 (*a*) R. J. Haines, A. Pidcock, and M. Safari, *J. Chem. Soc., Dalton Trans.*, 1977, 830; A. L. du Preez, I. L. Marais, R. J. Haines, A. Pidcock, and M. Safari, *J. Organomet. Chem.*, 1977, **141**, C10; A. L. du Preez, I. L. Marais, R. J. Haines, A. Pidcock, and M. Safari, *J. Chem. Soc., Dalton Trans.*, 1981, 1918; (*b*) F. A. Cotton, R. J. Haines, B. E. Hanson, and J. C. Sekutowski, *Inorg. Chem.*, 1978, **17**, 2010.

15 R. J. Haines and E. Meintjies, *J. Chem. Soc., Dalton Trans.*, 1979, 367.

16 R. J. Haines, M. Laing, E. Meintjies, and P. Sommerville, *J. Organomet. Chem.*, 1981, **215**, C17.

17 E. Meintjies, unpublished work.

18 R. J. Haines, M. Laing, and E. Meintjies, *Inorg. Chim. Acta*, 1979, **36**, L403.

19 G. de Leeuw, unpublished work.

20 N. A. Bailey, G. de Leeuw, J. S. Field, R. J. Haines, I. C. D. Stuckenburg, and R. B. English, *S.Afr. J. Chem.*, 1985, **38**, 139.

21 G. de Leeuw, J. S. Field, R. J. Haines, B.McCulloch, E. Meintjies, C. Monberg, G. M. Olivier, P. Ramdial, C. N. Sampson, B. Sigwarth, N. D. Steen, and K. G. Moodley, *J. Organomet. Chem.*, 1984, **275**, 99.

22 G. de Leeuw, J. S. Field, R. J. Haines, B. McCulloch, E. Meintjies, C. Monberg, K. G. Moodley, G. M. Olivier, C. N. Sampson, and N. D. Steen, *J. Organomet. Chem.*, 1982, **228**, C66; J. S. Field, R. J. Haines, E. Minshall, C. N. Sampson, J. Sundermeyer, C. C. Allen, and J. C. A. Boeyens, *ibid.*, 1986, **309**, C21.

23 R. J. Haines and C. R. Nolte, *J. Organomet. Chem.*, 1970, **24**, 725; R. J. Haines, A. L. du Preez, and I. L. Marais, *ibid.*, 1971, **28**, 405.

24 T. B. Brill and S. J. Landon, *Chem. Rev.*, 1984, **84**, 577.

25 J. S. Field, R. J. Haines, C. N. Sampson, and J. Sundermeyer, *J. Organomet. Chem.*, 1986, **310**, C42.

26 R. J. Haines and A. L. du Preez, *J. Am. Chem. Soc.*, 1969, **91**, 769; R. J. Haines and A. L. du Preez, *J. Chem. Soc. A*, 1970, 2341.

27 R. J. Haines and A. L. du Preez, *J. Chem. Soc., Dalton Trans.*, 1972, 944.

28 R. J. Haines, J. A. de Beer, and R. Greatrex, *J. Chem. Soc., Dalton Trans.*, 1976, 1749.

29 S. P. Schmidt, W. C. Trogler, and F. Basolo, *J. Am. Chem. Soc.*, 1984, **106**, 1308.

30 J. C. T. R. Burckett-St. Laurent, J. S. Field, R. J. Haines, and M. McMahon, *J. Organomet. Chem.*, 1978, **153**, C19; 1979, **181**, 117.
31 C. J. Jones and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1975, 701.
32 N. G. Connelly and G. A. Johnson, *J. Chem. Soc., Dalton Trans.*, 1978, 1375.
33 S. Amer, G. Kramer, and A. J. Pöe, *J. Organomet. Chem.*, 1981, **220**, 75.
34 D. A. Kaiser, unpublished work.
35 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determinations, University of Cambridge, 1976.

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