Dinuclear Complexes of Rhodium and Iridium with Cyanide or Thiocyanate Bridges: Molecular Structure of $[(PMe_2Ph)_3Cl_2Ir(\mu\text{-}CN)IrCl_2(PMe_2Ph)_3][ClO_4]$ *

Antony J. Deeming and Graeme P. Proud
Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ
Helen M. Dawes and Michael B. Hursthouse
Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

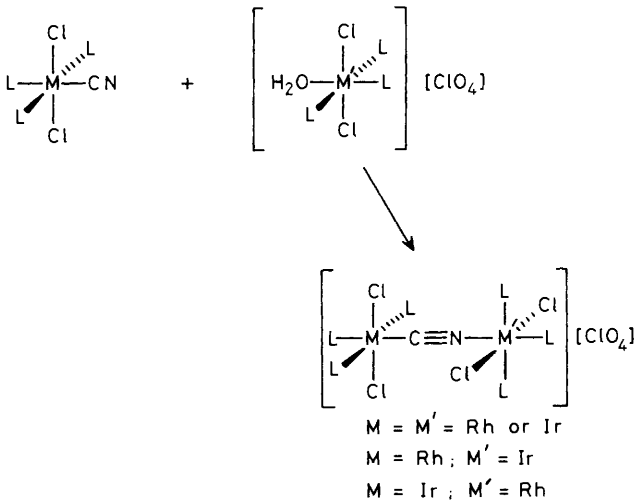
Reactions of the rhodium or iridium complexes $[MCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ with $[MCl_2(CN)(PMe_2Ph)_3]$ give the homometallic cyano-bridged compounds $[(PMe_2Ph)_3Cl_2M(CN)M'Cl_2(PMe_2Ph)_3][ClO_4]$ (M = M' = Rh or Ir) and the corresponding heterometallic isomers which do not interconvert. The crystal structure of the complex $[(PMe_2Ph)_3Cl_2Ir(CN)IrCl_2(PMe_2Ph)_3][ClO_4]$ revealed that the two $IrCl_2(PMe_2Ph)_3$ groups are symmetry related because there is a disordered distribution of IrCNIr and IrNCIr orientations. Hence, though the structure is well refined (R = 0.035), the different structural influences of the C and N atoms in the bridge could not be defined. However, ^{13}C, ^{15}N, and ^{31}P n.m.r. studies reveal that the *trans* influence of C is greater than that of the N atom. The corresponding homometallic compounds $[(PMe_2Ph)_3Cl_2M(SCN)MCl_2(PMe_2Ph)_3][ClO_4]$ (M = Rh or Ir) were obtained but attempted syntheses of the mixed Rh/Ir compounds led to a mixture of all four possible homo- and hetero-metallic species. We conclude that the thiocyanato bridges can cleave to give both S- and N-bonded mononuclear species but N-bonded cyanide monomers are inaccessible.

Bridging cyanides involving linear M–CN–M arrangements of atoms occur widely.[1] Silver cyanide is a linear polymer with two-co-ordinate silver and linear cyanide bridges,[2] which are also found in Prussian Blue (Turnball's Blue), $K[Fe_2(CN)_6]$.[3] A number of molecular species involving two metal atoms linked only by a single cyanide bridge are known. For example, the recently reported species $[(\eta\text{-}C_5H_5)(dppe)Ru(\mu\text{-}CN)Ru(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (*X*-ray structure) was prepared by displacement of the chloride ion from $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ by the nucleophilic nitrogen atom of $[Ru(CN)(dppe)(\eta\text{-}C_5H_5)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$).[4]

We have examined the co-ordinating ability of metal cyanide compounds at iridium or rhodium centres, knowing that the aqua ligands in *trans*, *mer*-$[MCl_2(H_2O)(PMe_2Ph)_3]^+$ (M = Rh or Ir),[5] being *trans* to PMe_2Ph, are readily displaced by neutral or anionic ligands.[6] Organic nitriles (RCN) readily displace H_2O, and neutral cyano complexes (MCN) were expected to behave similarly. By using the cyano compounds *trans*, *mer*-$[MCl_2(CN)(PMe_2Ph)_3]$ we were able to obtain μ-CN systems with identical metal groups, $MCl_2(PMe_2Ph)_3$ (M = Rh or Ir), at each end of the bridge and so assess the different influences of the carbon and nitrogen atoms at these metal centres. Furthermore this general route would allow isomeric RhCNIr and IrCNRh chain compounds to be made. In this paper we describe our work on the synthesis of μ-CN and related μ-SCN compounds and the crystal structure of $[(PMe_2Ph)_3Cl_2Ir(\mu\text{-}CN)IrCl_2(PMe_2Ph)_3][ClO_4]$.

Results and Discussion

Synthesis of Cyano-bridged Complexes of Rhodium and Iridium.—The chloro ligands *trans* to the tertiary phosphine in the complexes *mer*-$[MCl_3(PMe_2Ph)_3]$ (M = Rh or Ir) are labile and may be readily replaced by cyanide ion. The compound *trans*,*mer*-$[IrCl_2(CN)(PMe_2Ph)_3]$ has been reported[7] and we have prepared this by reacting the trichloride with a slight excess of KCN in refluxing methanol for several hours. The corresponding Rh compound is obtained similarly but within minutes. An excess of KCN leads to *mer*-$[Rh(CN)_3(PMe_2Ph)_3]$.



Scheme 1. L = PMe_2Ph

The aqua ligands in the cations of $[MCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (M = Rh or Ir) undergo rapidly reversible dissociations to give the intermediates $[MCl_2(PMe_2Ph)_3]^+$ which are stereochemically non-rigid.[6] These five-co-ordinate species are readily trapped by incoming nucleophiles such as CO, pyridine, or MeCN *etc*. Using the compounds *trans*, *mer*-$[MCl_2(CN)(PMe_2Ph)_3]$ as the incoming nucleophiles, the aqua complexes react in dichloromethane to give a series of cyano-bridged species, $[(PMe_2Ph)_3Cl_2M(\mu\text{-}CN)MCl_2(PMe_2Ph)_3][ClO_4]$ (Scheme 1). The homometallic dimers $[L_3Cl_2Rh(CN)RhCl_2L_3][ClO_4]$ and $[L_3Cl_2Ir(CN)IrCl_2L_3][ClO_4]$ were readily isolated while the isomeric heterometallic compounds $[L_3Cl_2Rh(CN)IrCl_2L_3][ClO_4]$ and $[L_3Cl_2Ir(CN)RhCl_2L_3][ClO_4]$

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* μ-Cyano-bis[dichlorotris(dimethylphenylphosphine)iridium] perchlorate.

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

Table 1. Infrared data for mono- and di-nuclear cyano-compounds

Compound[a]	$\nu(^{12}C^{14}N)$[b]/cm^{-1}	$\nu(^{13}C^{14}N)$[b]/cm^{-1}	$\nu(^{12}C^{15}N)$[b]/cm^{-1}
$[IrCl_2(CN)L_3]$	2 127vs	2 080	2 097
$[RhCl_2(CN)L_3]$	2 125	2 078	2 095
$[Rh(CN)_3L_3]$	2 140m		
	2 130s		
	2 120vs		
$[L_3Cl_2Ir(CN)IrCl_2L_3][ClO_4]$	2 159	2 114	2 126
$[L_3Cl_2Rh(CN)RhCl_2L_3][ClO_4]$	2 157	2 112	2 124
$[L_3Cl_2Ir(CN)RhCl_2L_3][ClO_4]$	2 157	2 111	2 125
$[L_3Cl_2Rh(CN)IrCl_2L_3][ClO_4]$	2 159	2 114	2 126
$[L_3(CN)_2Rh(CN)RhCl_2L_3][ClO_4]$	2 165vs		
	2 142m		
	2 125vs		

[a] L = PMe_2Ph. [b] Recorded in Nujol mull; strong absorptions unless stated otherwise.

Table 2. ^1H (Methyl) n.m.r. data for cyano-complexes (in $CDCl_3$)

	Doublets[b]		Triplets[c]	
Compound[a]	δ	^2J(PH)	δ	J(PH)
$[IrCl_2(CN)L_3]$	1.10	9.9	2.01	8.4
$[RhCl_2(CN)L_3]$	1.04	9.9	2.01	7.9
$[Rh(CN)_3L_3]$	1.15	10.2	2.17	7.6
$[L_3Cl_2Ir(CN)IrCl_2L_3][ClO_4]$	1.16	10.2	2.04	8.3
	1.23	11.1	2.12	8.1
$[L_3Cl_2Rh(CN)RhCl_2L_3][ClO_4]$	1.12	10.5	2.09	8.9
	1.24	11.5	2.07	8.4
$[L_3Cl_2Ir(CN)RhCl_2L_3][ClO_4]$	1.15	10.3	2.08	8.2
	1.24	11.4	2.10	8.4
$[L_3Cl_2Rh(CN)IrCl_2L_3][ClO_4]$	1.14	10.3	2.04	8.3
	1.24	11.1	2.12	7.6
$[L_3(CN)_2Rh(CN)RhCl_2L_3][ClO_4]$	1.26	10.4	2.10	7.9
	1.25	11.7	2.22	7.3

[a] L = PMe_2Ph. [b] Unique PMe_2Ph ligand. [c] *trans*-PMe_2Ph ligands; $J(PH) = |^2J(PH) + {}^4J(PH)|$ (separation of outer lines of the 1:2:1 triplets).

Table 3. ^{31}P N.m.r. data[a] for cyano-complexes

	C-bonded end[c]					N-bonded end[c]				
Compound[b]	δ_t	$J(RhP_t)$	δ_c	$J(RhP_c)$	J_{ct}	δ_t	$J(RhP_t)$	δ_c	$J(RhP_t)$	J_{ct}
$[IrCl_2(CN)L_3]$	−197.9		−186.0		22.2					
$[L_3Cl_2Ir(CN)IrCl_2L_3][ClO_4]$	−197.3		−189.8		23.9	−197.3		−184.7		20.1
$[L_3Cl_2Ir(CN)RhCl_2L_3][ClO_4]$	−197.4		−189.7		23.5	−139.0	107.7	−149.1	81.6	29.0
$[RhCl_2(CN)L_3]$	−158.4	85.4	−147.7	80.0	28.4					
$[L_3Cl_2Rh(CN)RhCl_2L_3][ClO_4]$	−155.1	86.7	−151.0	78.7	30.0	−138.8	107.7	−149.2	82.0	29.0
$[L_3Cl_2Rh(CN)IrCl_2L_3][ClO_4]$	−155.0	87.2	−151.1	78.5	30.4	−197.4		−184.7		20.2
$[L_3(CN)_2Rh(CN)RhCl_2L_3][ClO_4]$	−149.0	*d*	−146.6	73.7	26.7	−137.6	107.4	−148.7	81.4	28.9

[a] In CH_2Cl_2 solution, δ relative to $P(OMe)_3$ in C_6D_6. [b] L = PMe_2Ph. [c] Subscript c identifies the two mutually *trans* PMe_2Ph ligands *cis* to cyanide, subscript t the PMe_2Ph ligand *trans* to cyanide. [d] Obscured.

(L = PMe_2Ph) could be prepared specifically and showed no interconversion even after several days in solution at room temperature. This contrasts with the behaviour of the μ,η^2-cyanide bridges in $[Mn_2H(\mu,\eta^2\text{-}CN)(CO)_4(Ph_2PCH_2PPh_2)_2]$[8] and $[Mo_2(\mu,\eta^2\text{-}CN)(CO)_4(\eta\text{-}C_5H_5)_2]^-$[9] which rapidly oscillate between the two metal atoms on an n.m.r. time-scale. There appears to be no evidence for an intramolecular (or even intermolecular) rapid re-orientation of cyanide ligands in linear M–CN–M brides. This contrasts with what we have observed for thiocyanato bridges (see later).

We have also studied *mer*-$[Rh(CN)_3(PMe_2Ph)_3]$ as the incoming nucleophile in preparing $[(PMe_2Ph)_3(CN)_2Rh(\mu\text{-}CN)RhCl_2(PMe_2Ph)_3][ClO_4]$. The cyanide ligand *trans* to PMe_2Ph is the most basic and involved in bridge formation, and even with an excess of $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ there is no further bridging through the two cyanide ligands *trans* to each other.

The isotopically enriched species $[MCl_2(^{13}CN)(PMe_2Ph)_3]$ and $[MCl_2(C^{15}N)(PMe_2Ph)_3]$ (M = Rh or Ir), and their derived μ-CN species have been prepared from $K^{13}CN$ (90% ^{13}C) or $KC^{15}N$ (97% ^{15}N), in the same way, for ^{13}C and ^{15}N n.m.r. studies.

Characterisation of the Cyano Compounds.—The terminal and bridged CN compounds were characterised by infrared, ^1H and ^{31}P n.m.r., and for enriched samples, by ^{13}C and ^{15}N n.m.r. spectroscopy (see Tables 1—4). The value of ν(CN) for KCN (2 076 cm^{-1} in Nujol mull) is shifted to higher frequency on co-

Table 4. ^{13}C and ^{15}N n.m.r. data for the CN ligands of the cyano-complexes

Compound[a]	$\delta(^{13}C)$[b]	$^2J(PC)_{trans}$	$^2J(PC)_{cis}$	$^3J(PC)_{trans}$	$^1J(RhC)$
$[IrCl_2(CN)L_3]$	114.1	120	14		
$[L_3Cl_2Ir(CN)IrCl_2L_3][ClO_4]$	118.5	132	12	15	
$[L_3Cl_2Ir(CN)RhCl_2L_3][ClO_4]$	122.0	130	12	13	
$[RhCl_2(CN)L_3]$	131.0	146	19		38.0
$[L_3Cl_2Rh(CN)RhCl_2L_3][ClO_4]$	141.0	158	16	14	40.0
$[L_3Cl_2Rh(CN)IrCl_2L_3][ClO_4]$	137.3	159	16	12	40.5
	$\delta(^{15}N)$[c]	$^2J(PN)_{trans}$	$^2J(PN)_{cis}$	$^3J(PN)_{trans}$	$^1J(RhN)$
$[IrCl_2(CN)L_3]$	−95.9	0	0	4	
$[L_3Cl_2Ir(CN)IrCl_2L_3][ClO_4]$	−204.6	51	3	8	
$[L_3Cl_2Ir(CN)RhCl_2L_3][ClO_4]$	−178.1	56	4	8	8
$[RhCl_2(CN)L_3]$	−85.6	0	0	4	0
$[L_3Cl_2Rh(CN)RhCl_2L_3][ClO_4]$	−169.9	55	4	9	9
$[L_3Cl_2Rh(CN)IrCl_2L_3][ClO_4]$	−196.1	50	2	9	0

[a] L = PMe_2Ph. [b] Recorded in CD_2Cl_2, relative to $SiMe_4$. [c] Recorded in CH_2Cl_2 relative to neat CH_3NO_2.

ordination through the carbon atom, since a weakly antibonding C–N σ-orbital is used for donation. The opposite is observed for co-ordination of CO where π-backbonding is much more important. In forming bridges ν(CN) values are shifted to even higher frequencies, for the same reason. These effects are shown in Table 1; a shift of *ca.* 50 cm^{-1} on co-ordination is followed by a shift of 32 cm^{-1} on forming a bridge. Three ν(CN) absorptions were observed for *mer*-$[Rh(CN)_3(PMe_2Ph)_3]$ and three for $[(PMe_2Ph)_3(CN)_2Rh(\mu\text{-}CN)RhCl_2(PMe_2Ph)_3]^+$, one of these absorptions being at 2 165 cm^{-1}, in the bridging region.

^1H N.m.r. spectra (Table 2) contain the expected doublets and virtual triplets for the phosphine methyl groups, demonstrating that all the compounds reported here have *mer* geometries. ^{31}P N.m.r. results (Table 3) confirm this. It has been possible to assign ^{31}P n.m.r. signals to the C-bonded and N-bonded ends of the μ-CN molecules by comparing spectra of homometallic compounds with those of the heterometallic compounds, and by observing ^{13}C and ^{15}N couplings in the appropriate ^{13}CN and $C^{15}N$ compounds. Figure 1 shows ^{31}P n.m.r. spectra for $[L_3Cl_2Rh(CN)RhCl_2L_3][ClO_4]$ and for samples isotopically enriched at the cyanide bridge. The ^{13}C–^{31}P coupling occurs at the C-bonded end of the molecules, both to phosphines *cis* to cyanide (12—19 Hz) and *trans* to cyanide (120—160 Hz), but coupling at the N-bonded end only occurs to the phosphine *trans* to the bridge (12—15 Hz). Corresponding couplings, but lower in value, are observed for the ^{15}N-labelled species.

There are marked differences in the values of *J*(RhP) depending upon the ligand *trans* to the phosphine. The *J*(RhP) values for PMe_2Ph *trans* to CN, Cl, or H_2O are 85.4, 112.6, and 119.6 Hz respectively for the compounds $[RhCl_2(CN)L_3]$, $[RhCl_3L_3]$, and $[RhCl_2(H_2O)L_3]^+$ (L = PMe_2Ph).[6] This is a measure of the *trans* influence of these ligands, which is in the order CN > Cl > H_2O. Applying this criterion to the μ-CN species, *J*(RhP) values for phosphines *trans* to the carbon atom of the bridge are in the range 85.4—87.2 Hz, while those for phosphines *trans* to nitrogen are 107.4—107.7 Hz, leading to the conclusion that the cyanide bridges exerts a much larger *trans* influence through carbon than through nitrogen atoms. Co-ordination through nitrogen does not alter much the *trans* influence of the carbon atom, although the M–C bond is modified to some extent. For example, there are approximately 10% increases in $^2J(P^{13}C)$ and in $^3J(P^{15}N)$ values associated with the *trans*-phosphine ligand on co-ordination through nitrogen.

Examples of ^{13}C and ^{15}N n.m.r. spectra are given in Figure 2 and Table 4. Carbon-13 signals are lower by *ca.* 18 p.p.m. for RhCN compared with IrCN systems and are shifted downfield by 8—10 p.p.m. on forming bridges when N-bonded to rhodium, and by 4—6 p.p.m. when N-bonded to iridium. In contrast ^{15}N signals are shifted upfield by 80—110 p.p.m. on forming CN bridges; a large shielding of the ^{15}N nucleus in going from terminal to bridging cyanide. A large upfield shift is expected on electrophilic addition at nitrogen atoms of cyano-groups and is observed on protonation of MeCN or metal cyanides.[10] Nitrogen-15 shifts are about 27 p.p.m. higher when N-bonded to Ir than when N-bonded to Rh and about 9 p.p.m. when C-bonded to Ir than when C-bonded to Rh. Nitrogen-15 shifts are sensitive probes to the state of the CN ligand.

Crystal Structure of $[(PMe_2Ph)_3Cl_2Ir(\mu\text{-}CN)IrCl_2(PMe_2Ph)_3][ClO_4]$.—The structure was determined in order to confirm that assigned on the basis of spectroscopy, but also we hoped to establish structural differences between the C- and N-bonded ends of the cation. The structure of the cation is shown in Figure 3 and selected bond lengths and angles are given in Table 5.

The two halves of the molecule are symmetry related since the CN ligand is disordered and the molecule refined satisfactorily with 50% occupancy of N and C atoms at the cyanide sites labelled C(1) and C(1a). The configuration is that indicated in Scheme 1. The ligands are eclipsed; in particular the Cl ligands at one Ir atom are eclipsed with the PMe_2Ph ligands at the other. The C–N distance is 1.151(13) Å, close to that reported for $[(\eta\text{-}C_5H_5)(dppe)Ru(\mu\text{-}CN)Ru(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$,[4] and the IrCNIr chain is essentially linear, the Ir–C(1)–C(1a) angle being 178.0(6)°. Clearly we cannot assess how the difference in *J*(RhP) values for phosphine ligands *trans* to C or N atoms in $[L_3Cl_2Rh(CN)RhCl_2L_3][ClO_4]$ relate to the Ir–P bond lengths in $[L_3Cl_2Ir(CN)IrCl_2L_3][ClO_4]$ since those obtained represent an average of the N- and C-bonded ends of the molecule. Nonetheless Ir–P *trans* to C(1) is 0.05 Å shorter than the average of the other Ir–P bond lengths (*trans* to each other). This difference is smaller than in *mer*-$[IrCl_3(PMe_2Ph)_3]$ (0.09 Å)[11] and $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (0.13 Å)[6] and is consistent with the order of *trans* influence: CN (average of C- and N-bonding) > Cl > H_2O.

The heteronuclear species $[(PMe_2Ph)_3Cl_2Ir(\mu\text{-}CN)RhCl_2(PMe_2Ph)_3][ClO_4]$ is isostructural with the di-iridium complex and hence is likely to have disordered IrCNRh and RnNCIr orientations. Because of this diffraction data were not collected.

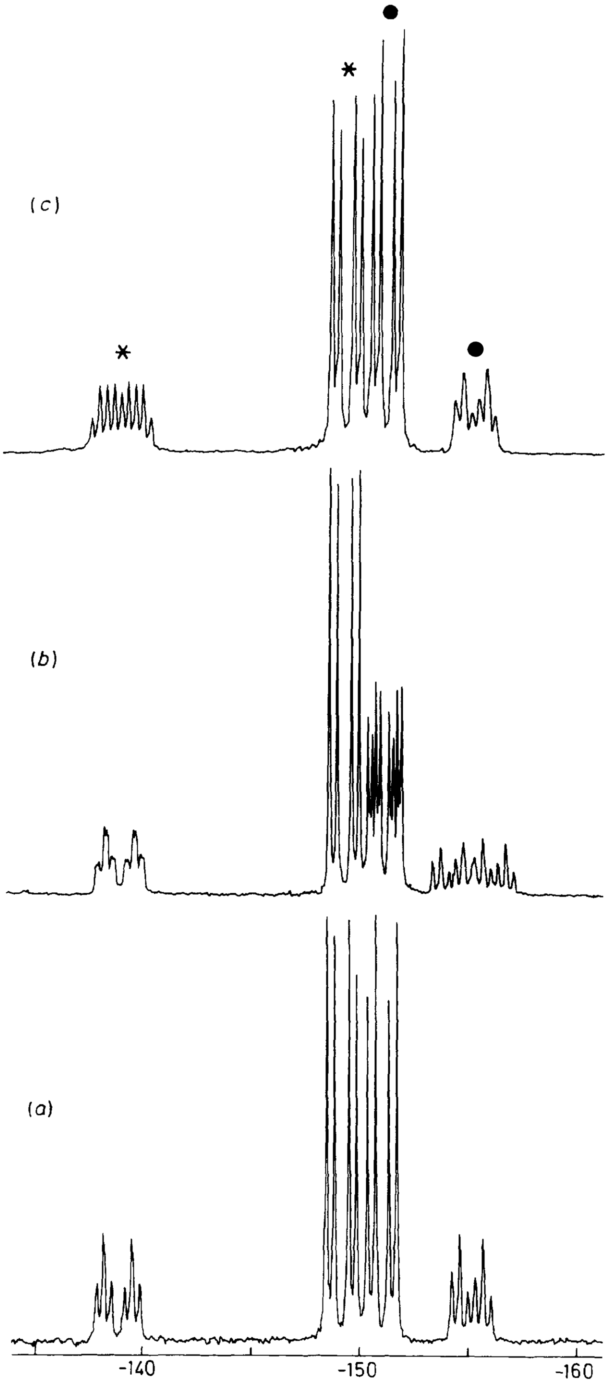


Figure 1. ^{13}P N.m.r. spectra for (*a*) $[(PMe_2Ph)_3Cl_2Rh(\mu\text{-}CN)RhCl_2(PMe_2Ph)_3][ClO_4]$, (*b*) the corresponding ^{13}CN sample (90% ^{13}C), and (*c*) the corresponding $C^{15}N$ sample (97% ^{15}N). Recorded at room temperature in CH_2Cl_2 solution. [* indicates N-bonded end and ● the C-bonded end of the molecules]

Table 5. Selected bond lengths (Å) and angles (°) for the compound $[(PMe_2Ph)_3Cl_2Ir(CN)IrCl_2(PMe_2Ph)_3][ClO_4]$

Cl(2)–Ir(1)	2.375(4)	Cl(1)–Ir(1)	2.375(4)
P(2)–Ir(1)	2.373(4)	P(1)–Ir(1)	2.391(4)
C(1)–Ir(1)	2.060(8)	P(3)–Ir(1)	2.328(4)
C(1)–C(1a)	1.151(13)		
Cl(2)–Ir(1)–Cl(1)	176.5(1)	P(1)–Ir(1)–Cl(1)	86.9(2)
P(1)–Ir(1)–Cl(2)	91.2(2)	P(2)–Ir(1)–Cl(1)	88.5(2)
P(2)–Ir(1)–Cl(2)	92.2(2)	P(3)–Ir(1)–Cl(1)	94.1(2)
P(3)–Ir(1)–Cl(2)	89.2(2)	P(2)–Ir(1)–P(1)	170.3(1)
P(3)–Ir(1)–P(1)	94.0(2)	P(3)–Ir(1)–P(2)	94.9(2)
C(1)–Ir(1)–Cl(1)	89.4(3)	C(1)–Ir(1)–Cl(2)	87.3(3)
C(1)–Ir(1)–P(1)	85.9(3)	C(1)–Ir(1)–P(2)	85.5(3)
C(1)–Ir(1)–P(3)	176.4(2)	Ir–C(1)–C(1a)	178.0(6)

C(1a) is related to C(1) by the two-fold axis at $\frac{1}{2}$, *y*, $\frac{1}{4}$.

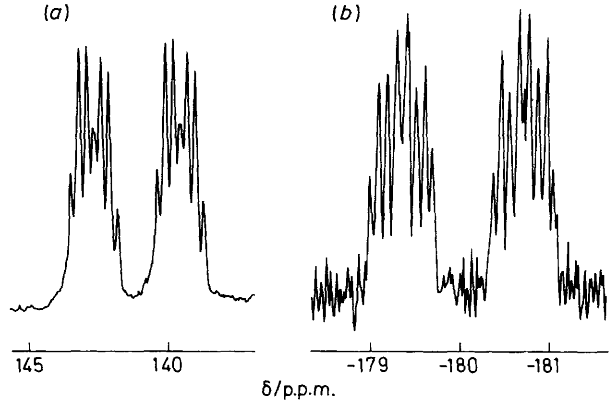


Figure 2. (*a*) ^{13}C N.m.r. spectrum of $[(PMe_2Ph)_3Cl_2Rh(^{13}CN)RhCl_2(PMe_2Ph)_3]^+$ (δ relative to $SiMe_4$) and (*b*) ^{15}N n.m.r. spectrum of $[(PMe_2Ph)_3Cl_2Ir(C^{15}N)RhCl_2(PMe_2Ph)_3]^+$ (δ relative to $MeNO_2$)

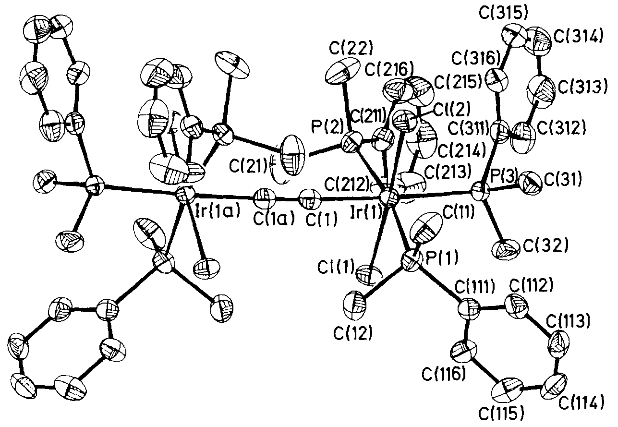


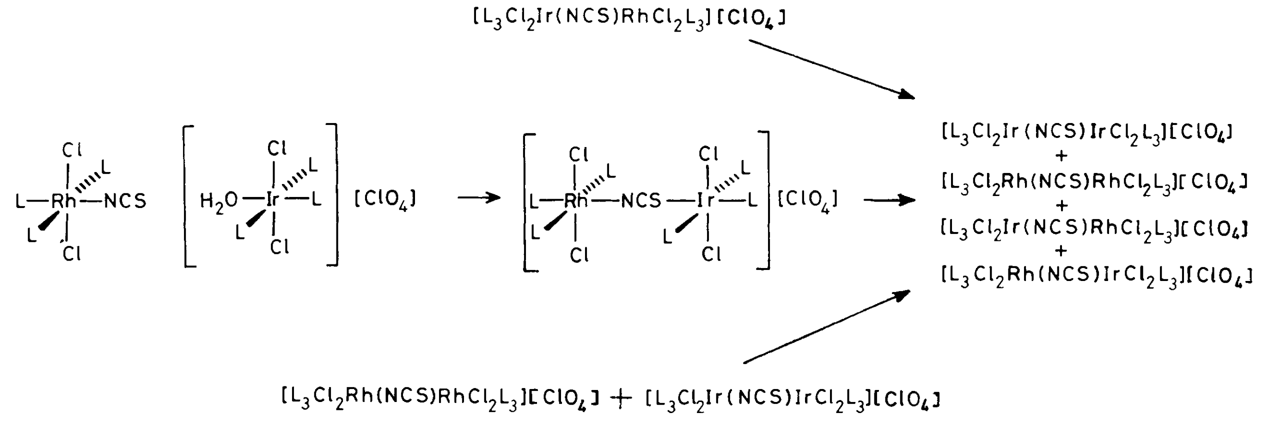
Figure 3. Molecular structure of $[(PMe_2Ph)_3Cl_2Ir(\mu\text{-}CN)IrCl_2(PMe_2Ph)_3][ClO_4]$. The atoms C(1) and C(1a) represent the CN ligand with 50% C and 50% N occupancy at each site

Thiocyanato Complexes of Rhodium and Iridium.—The complexes *trans, mer*-$[MCl_2(NCS)(PMe_2Ph)_3]$ (M = Rh or Ir) have been reported.[7,12] ^1H N.m.r. data (Table 6) establish the *mer* configurations and the Rh complex was believed to be the N-bonded form. The signals for the unique ^{13}P nuclei are expected to be a triplet (M = Ir) or a doublet of triplets (M = Rh) but we observe these signals as broad resonances (see, for *e.g.*, Figure 4) which is a result of unresolved coupling to the *trans*, quadrupolar ^{14}N nucleus ($I = 1$) of the N-bonded thiocyanate ligand. Coupling of the unique ^{31}P nucleus to ^{103}Rh and the other ^{31}P nuclei is retained. We believe that the ^{14}N nuclei in the linear M–NCS group have long relaxation times because of small electric field gradients at the nuclei. Similar line-broading has been observed in *trans*-$[PtX\{(PhO)_2$-

Table 6. Infrared[a] and ^{1}H n.m.r.[b] data for thiocyanato-complexes

		Doublets[c]		Triplets[d]	
Compound	ν(CN)/cm^{-1}	δ	^2J(PH)	δ	J(PH)
$[IrCl_2(NCS)L_3]$	2 121 2 107	1.20	11.0	1.84	8.4
$[RhCl_2(NCS)L_3]$	2 112 2 079	1.18	11.4	1.89	8.0
$[L_3Cl_2Ir(NCS)IrCl_2L_3][ClO_4]_2$	2 144 2 110				
$[L_3Cl_2Rh(NCS)RhCl_2L_3][ClO_4]_2$	2 135 2 103	1.34 1.28	11.5 12.0	1.99 1.93	7.6 7.2

[a] Nujol mulls. [b] In $CDCl_3$. [c] PMe_2Ph (L) *trans* to NCS. [d] PMe_2Ph *cis* to NCS; J(PH) = $|^2J(PH) + {}^4J(PH)|$ (separation of outer lines of the triplet).



Scheme 2. L = PMe_2Ph

$PO\}(PBu_3)_2]$ (X = NCO or NCS)[13] while in *cis*-$[Pt(NCS)(SCN)\{P(OPh)_3\}_2]$, ^2J(PN) is clearly resolved.[14]

The homometallic thiocyanato-bridged compounds $[(PMe_2Ph)_3Cl_2M(\mu\text{-}NCS)MCl_2(PMe_2Ph)_3][ClO_4]$ (M = Rh or Ir) were made in the same way as the μ-CN species. These compounds give ν(CN) above 2 100 cm^{-1} as expected for μ-NCS (Table 6). Proton and ^{31}P n.m.r. data are given in Tables 6 and 7. The heterometallic compounds, however, could not be isolated. Reaction of $[RhCl_2(NCS)(PMe_2Ph)_3]$ with $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ in dichloromethane initially gave $[L_3Cl_2Rh(NCS)IrCl_2L_3][ClO_4]$ (^{31}P n.m.r. evidence) but after 1 h at room temperature approximately equal amounts of $[L_3Cl_2Rh(NCS)RhCl_2L_3][ClO_4]$, $[L_3Cl_2Rh(NCS)IrCl_2L_3][ClO_4]$, $[L_3Cl_2Ir(NCS)IrCl_2L_3][ClO_4]$, and $[L_3Cl_2Ir(NCS)RhCl_2L_3][ClO_4]$ were all present in solution. The same mixture was obtained when starting from a mixture of the Ir–NCS compound and the Rh–H_2O cation, or of $[L_3Cl_2Rh(NCS)RhCl_2L_3][ClO_4]$ and $[L_3Cl_2Ir(NCS)IrCl_2L_3][ClO_4]$ (Scheme 2).

The intermolecular exchange of thiocyanate must be occurring *via* cleavage of M–N and M–S bonds to give transient S-bonded and N-bonded mononuclear species $[MCl_2(SCN)(PMe_2Ph)_3]$ and $[MCl_2(NCS)(PMe_2Ph)_3]$ which recombine with $[MCl_2(PMe_2Ph)_3]^+$. This is related to the rapid scrambling of rhodium atoms we have observed in solutions containing $[RhCl_3(PMe_2Ph)_3]$ and $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$[6] except that in this case the mononuclear species are preferred. The lability of μ-SCN species contrasts with the inertness of the μ-CN analogues. Opening of cyano bridges by M–C cleavage to give M–NC intermediates does not occur; scrambling would result but this is not observed. Nitrogen-bonded cyanides are not unknown. Oxidation of $[Co(CN)_5]^{3-}$ by $[Co(NH_3)_5(CN)]^{2+}$ *via* a μ-CN intermediate gives $[Co(CN)_5(NC)]^{3-}$ which converts in seconds at 25 °C to $[Co(CN)_6]^{3-}$.[15]

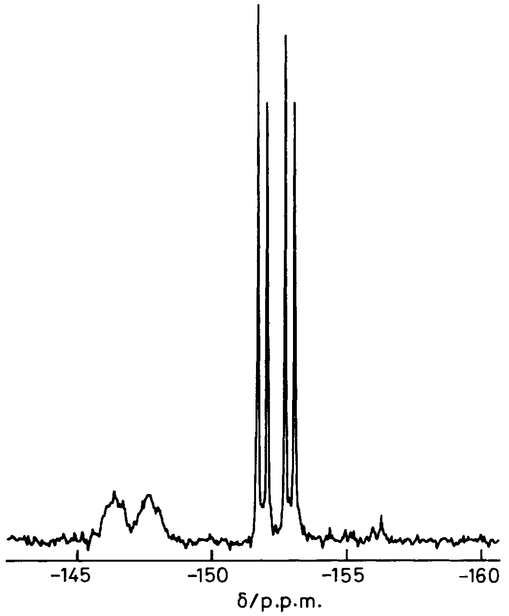


Figure 4. ^{31}P N.m.r. spectrum of *trans*, *mer*-$[RhCl_2(NCS)(PMe_2Ph)_3]$ in CH_2Cl_2 solution at room temperature

It has been reported that, on vacuum pyrolysis, $[RhCl_2(NCS)(PMe_2Ph)_3]$ isomerises to $[RhCl_2(SCN)(PMe_2Ph)_3]$.[12]

Table 7. ^{31}P N.m.r. data[a] for thiocyanato-complexes

	N-bonded end					S-bonded end				
Compound[b]	δ_t	J(RhP$_t$)	δ_c	J(RhP$_c$)	J_{ct}	δ_t	J(RhP$_t$)	δ_c	J(RhP$_c$)	J_{ct}
$[IrCl_2(NCS)L_3]$	−197.0		−180.0		19.0					
$[L_3Cl_2Ir(NCS)IrCl_2L_3][ClO_4]$	−195.2		−181.8		19.9	−184.7		−184.7		
$[L_3Cl_2Ir(NCS)RhCl_2L_3][ClO_4]$	−195.5		−181.6		19.4	−133.8	111.1	−149.5	83.6	24.4
$[RhCl_2(NCS)L_3]$	−140.0	106.0	−145.2	81.6	27.5					
$[L_3Cl_2Rh(NCS)RhCl_2L_3][ClO_4]$	−135.9	111.2	−146.9	81.8	27.6	−134.2	110.2	−149.5	83.0	25.5
$[L_3Cl_2Rh(NCS)IrCl_2L_3][ClO_4]$	−135.7	110.2	−147.2	81.8	28.0	−184.9		−184.9		

[a] In CH_2Cl_2 relative to $P(OMe)_3$ in C_6D_6. [b] L = PMe_2Ph.

However, we find the addition of catalytic quantities of $[RhCl_2(H_2O)(PMe_2Ph)_3]^+$ to a dichloromethane solution of the N-bonded isomer gave no change after 24 h at room temperature. If the S-bonded isomer were more stable thermodynamically, the aqua complex would have catalysed conversion to it *via* a μ-SCN intermediate. We have found that the action of heat on $[RhCl_2(NCS)(PMe_2Ph)_3]$ gives an intractable mixture containing $[RhCl_3(PMe_2Ph)_3]$.

Experimental

The compounds $[MCl_3(PMe_2Ph)_3]$[7,12] and $[MCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$[6] (M = Rh or Ir) were prepared as reported. $K^{13}CN$ (90% ^{13}C) and $KC^{15}N$ (97% ^{15}N) were obtained from Amersham International plc. N.m.r. spectra were recorded on a Varian XL200 spectrometer at room temperature, except for ^{15}N n.m.r. spectra which were obtained at Queen Mary College, London on a Bruker WH400 spectrometer, infrared spectra on a Perkin-Elmer 983 spectrometer, and analytical data were collected by the analytical laboratory at University College London.

Preparations.—$[IrCl_2(CN)(PMe_2Ph)_3]$. A solution of *mer*-$[IrCl_3(PMe_2Ph)_3]$ (0.634 g) and potassium cyanide (0.117 g) in methanol (25 cm^3) was refluxed for 2 h and then filtered. Evaporation of the solution to 10 cm^3 and dropwise addition of water gave the product as pale yellow needles (0.471 g), characterised by comparison of spectroscopic data with those reported.[7]

$[RhCl_2(CN)(PMe_2Ph)_3]$. This was prepared similarly from *mer*-$[RhCl_3(PMe_2Ph)_3]$ (0.311 g) and potassium cyanide (0.033 g) in refluxing methanol (30 cm^3) for 3 min. The filtered solution was evaporated to 15 cm^3 and dropwise addition of water gave the product as yellow needles (0.20 g) (Found: C, 48.55; H, 5.4; Cl, 11.7; N, 2.3. $C_{25}H_{33}Cl_2NP_3Rh$ requires: C, 48.9; H, 5.4; Cl, 11.5; N, 2.3%).

$[Rh(CN)_3(PMe_2Ph)_3]$. A solution of *mer*-$[RhCl_3(PMe_2Ph)_3]$ (0.319 g) and potassium cyanide (0.138 g) in methanol (30 cm^3) was refluxed for 40 min. Isolation of the product as above gave white needles (0.066 g) (Found: C, 53.2; H, 5.55; N, 6.75. $C_{27}H_{33}N_3P_3Rh$ requires C, 54.45; H, 5.6; N, 7.05%).

$[(PMe_2Ph)_3Cl_2Rh(\mu\text{-}CN)RhCl_2(PMe_2Ph)_3][ClO_4]$. A solution of $[RhCl_2(CN)(PMe_2Ph)_3]$ (0.053 g) and $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (0.061 g) in dichloromethane (3 cm^3) was filtered and addition of diethyl ether gave the product as orange needles (0.083 g) (Found: C, 44.9; H, 5.05; Cl, 13.75; N, 1.05. $C_{49}H_{66}Cl_5NO_4P_6Rh_2$ requires C, 45.2; H, 5.1; Cl, 13.6; N, 1.9%).

The following complexes were prepared similarly.

$[(PMe_2Ph)_3Cl_2Rh(\mu\text{-}CN)IrCl_2(PMe_2Ph)_3][ClO_4]$ as yellow needles (Found: C, 42.2; H, 4.75; Cl, 12.55; N, 1.0. $C_{49}H_{66}Cl_5IrNO_4P_6Rh$ requires C, 42.3; H, 4.8; Cl, 12.75; N, 1.0%).

$[(PMe_2Ph)_3Cl_2Ir(\mu\text{-}CN)RhCl_2(PMe_2Ph)_3][ClO_4]$ as orange needles (Found: C, 42.0; H, 4.65; Cl, 12.65; N, 1.05. $C_{49}H_{66}Cl_5IrNO_4P_6Rh$ requires C, 42.3; H, 4.8; Cl, 12.75; N, 1.0%).

$[(PMe_2Ph)_3Cl_2Ir(\mu\text{-}CN)IrCl_2(PMe_2Ph)_3][ClO_4]$ as yellow needles (Found: C, 39.5; H, 4.5; Cl, 11.75; N, 0.95. $C_{49}H_{66}Cl_5Ir_2NO_4P_6$ requires C, 39.75; H, 4.5; Cl, 11.95; N, 0.95%). Suitable crystals of this compound for an *X*-ray crystal structure determination were obtained by layering diethyl ether on to a dichloromethane solution of the compound and allowing the solutions to diffuse slowly at room temperature.

$[(PMe_2Ph)_3(CN)_2Rh(\mu\text{-}CN)RhCl_2(PMe_2Ph)_3][ClO_4]$ as orange needles (Found: C, 47.2; H, 5.15; Cl, 7.95; N, 3.4. $C_{51}H_{66}Cl_3N_3O_4P_6Rh_2$ requires C, 47.75; H, 5.2; Cl, 8.3; N, 3.25%).

The thiocyanato compound $[RhCl_2(NCS)(PMe_2Ph)_3]$ was prepared as reported.[12]

$[IrCl_2(NCS)(PMe_2Ph)_3]$. A solution of *mer*-$[IrCl_3(PMe_2Ph)_3]$ (0.324 g) and potassium thiocyanate (0.93 g) in methanol (35 cm^3) was refluxed for 3 h. Removal of the solvent under vacuum, extraction of the residue with dichloromethane until no more could be extracted, and evaporation of the dichloromethane solution gave a yellow oil. Addition of diethyl ether gave the product as a yellow microcrystalline solid (0.183 g), spectroscopically identical with the reported compound with this formulation.[7]

$[(PMe_2Ph)_3Cl_2Rh(\mu\text{-}NCS)RhCl_2(PMe_2Ph)_3][ClO_4]$. A solution of $[RhCl_2(NCS)(PMe_2Ph)_3]$ (0.152 g) and $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (0.057 g) in dichloromethane (3 cm^3) was filtered and evaporated to give an orange powder (0.093 g) (Found: C, 43.0; H, 4.95; Cl, 14.75; N, 1.15. $C_{49}H_{66}Cl_5NO_4P_6Rh_2S$ requires C, 44.1; H, 4.9; Cl, 13.3; N, 1.05%). It was not possible to recrystallise this sample to obtain an analytically pure compound. The di-iridium analogue, obtained similarly, was also difficult to crystallise and obtain analytically pure (Found: C, 39.65; H, 4.65; Cl, 11.1; N, 0.95. $C_{49}H_{66}Cl_6Ir_2NO_4P_6S$ requires, C, 38.9; H, 4.4; Cl, 11.7; N, 0.95%).

Crystal-structure Determination of $[(PMe_2Ph)_3Cl_2Ir(\mu\text{-}CN)IrCl_2(PMe_2Ph)_3][ClO_4]$.—The crystal used for the *X*-ray data collection, measuring 0.25 × 0.1 × 0.08 mm, was mounted in a capillary. Following preliminary photographic examination, unit-cell and intensity data were obtained using a CAD4 diffractometer with graphite monochromated Mo-K_α *X*-radiation (λ = 0.710 69 Å) following previously detailed procedures.[16] The structure was solved and developed *via* application of standard heavy-atom methods and refined *via* full-matrix least squares. Both the anion and cation lie on centres of symmetry and are thus disordered. For the cation, this means a mixing of CN orientations as $\frac{1}{2}$(C–N + N–C) and for the anion two orientations of the ClO_4 were found. The non-hydrogen atoms were refined anisotropically whilst hydrogen

Table 8. Fractional atomic co-ordinates (× 10^4) for $[(PMe_2Ph)_3Cl_2Ir(\mu\text{-}CN)IrCl_2(PMe_2Ph)_3][ClO_4]$

Atom	*x*	*y*	*z*
Ir(1)	4 194(0.5)	2 744(0.5)	1 665(0.5)
Cl(1)	4 356(1)	3 945(1)	545(1)
Cl(2)	4 069(1)	1 565(1)	2 851(1)
P(1)	4 017(1)	3 772(1)	3 034(1)
P(2)	4 490(1)	1 826(1)	330(1)
P(3)	3 472(1)	2 623(1)	1 003(1)
C(1)	4 824(2)	2 791(4)	2 318(5)
C(11)	3 910(3)	3 304(7)	4 347(6)
C(12)	4 474(2)	4 500(6)	3 310(7)
C(111)	3 566(2)	4 542(5)	2 815(5)
C(112)	3 192(2)	4 503(5)	3 418(6)
C(113)	2 858(2)	5 109(6)	3 246(7)
C(114)	2 901(3)	5 740(6)	2 492(8)
C(115)	3 273(3)	5 797(6)	1 882(7)
C(116)	3 607(2)	5 192(5)	2 041(6)
C(21)	5 041(3)	2 158(8)	−1(7)
C(22)	4 564(3)	714(6)	764(8)
C(211)	4 247(2)	1 754(5)	−1 041(5)
C(212)	4 210(3)	2 498(6)	−1 661(7)
C(213)	4 064(4)	2 461(7)	−2 731(7)
C(214)	3 941(3)	1 690(9)	−3 180(8)
C(215)	3 968(3)	954(8)	−2 578(8)
C(216)	4 123(3)	974(6)	−1 508(8)
C(31)	3 076(3)	2 525(6)	2 078(7)
C(32)	3 272(3)	3 520(6)	206(7)
C(311)	3 317(2)	1 670(5)	206(6)
C(312)	3 136(3)	1 725(7)	−853(7)
C(313)	2 988(3)	998(8)	−1 370(9)
C(314)	3 022(3)	203(8)	−876(10)
C(315)	3 198(3)	129(6)	166(9)
C(316)	3 343(2)	856(5)	696(7)
Cl(3)	2 500*	2 500*	5 000*
O(1)	2 572(8)	3 397(6)	5 008(25)
O(2)	2 773(11)	1 941(19)	4 400(21)
O(3)	2 320(6)	2 829(12)	3 985(11)
O(4)	2 947(5)	2 689(20)	4 893(19)

* Invariant parameter.

atoms, all of which were experimentally located, were refined isotropically (freely for Ph hydrogens and with group $U_{iso.}$ values for Me hydrogens) but with constrained C–H distances for some methyl groups.

Crystal data. $C_{49}H_{66}Cl_5Ir_2NO_4P_6$, $M = 1\,480.55$, monoclinic, $a = 30.470(4)$, $b = 15.461(3)$, $c = 12.313(1)$ Å, $\beta = 91.81(1)^\circ$, $U = 5\,797.6$ Å^3, space group $C2/c$, $Z = 4$, $D_c = 1.70$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 48.09$ cm^{-1}, $F(000) = 2\,944$. Total data recorded 5 408 ($1.5 \leqslant \theta \leqslant 25.0^\circ$, $\pm h$, $+k$, $+l$), 5 107 unique, 4 017 observed [$I > 1.5\sigma(I)$], corrected for absorption empirically. Final $R = 0.035$, $R' = 0.041$, 440 parameters, $w = [\sigma^2(F) + 0.000\,35F_o^2]^{-1}$. Final atomic positional parameters are given in Table 8.

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

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