A Comparison of NH_3, PH_3, PH_2, OH_2 and SH as Ligands in Iridium(III) Complexes[†]

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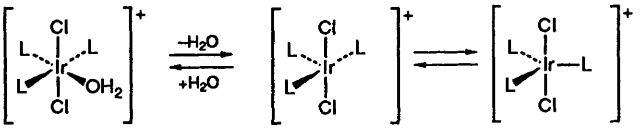
The aqua complex *trans,mer*-$[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ of known crystal structure contains a highly labile H_2O ligand which is readily substituted. The corresponding ammonia and phosphine complexes *trans,mer*-$[IrCl_2(EH_3)(PMe_2Ph)_3][ClO_4]$ (E = N or P), synthesised from the aqua complex, are inert and have been structurally characterised and compared with the aqua species. The cationic complex containing PH_3 is readily deprotonated, but not the one with NH_3, to give the structurally characterised neutral complex *trans,mer*-$[IrCl_2(PH_2)(PMe_2Ph)_3]$. The Ir–$PH_3$ bond is significantly shorter than the Ir–PH_2 bond and there are clear conformational changes resulting from deprotonation. Replacement of H_2O by H_2S leads to spontaneous deprotonation and formation of *trans,mer*-$[IrCl_2(SH)(PMe_2Ph)_3]$ (crystal structure also reported). Analysis of the geometries of *trans,mer*-$[IrCl_2L(PMe_2Ph)_3][ClO_4]$ (L = H_2O, NH_3 or PH_3) and of *trans,mer*-$[IrCl_2X(PMe_2Ph)_3]$ (X = H, Cl, SH or PH_2) has allowed the properties of these ligands, in particular their *trans* influences, to be assessed.

Some time ago we described the dynamic behaviour, spectroscopy and structure of the aqua cationic complex *trans,mer*-$[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$,[1,2] the fluoroborate of which had been synthesised earlier.[3] This remarkable low-spin octahedral d^6 complex undergoes dynamic exchange of the *mer* set of phosphine ligands to give coalescences in the ^1H and $^{31}P-\{^1H\}$ NMR spectra. This coalescence behaviour is a consequence of the *trans* effect of PMe_2Ph on the H_2O ligand which is rapidly and reversibly displaced and of the stereochemical non-rigidity of the resulting five-co-ordinate intermediate, $[IrCl_2(PMe_2Ph)_3][ClO_4]$. The measured rates of phosphine exchange and of exchange of free with co-ordinated water are consistent with a single process in which each event of water dissociation leads to total randomisation of the phosphine ligands over the three co-ordination sites. The mechanism in Scheme 1 is most likely since calculations[4] and experimental work[5] on five-co-ordinate iridium(III) complexes show that the square-pyramidal form is somewhat lower in energy than the trigonal-bipyramidal form in the absence of strongly π-donating ligands. The above aqua iridium(III) complex could hardly be more different from other rhodium and iridium octahedral d^6 complexes, $[M(H_2O)_6]^{3+}$, for which the rates of H_2O exchange are very slow for rhodium and immeasurably slow for iridium.[6–8] Therefore the total ligand set, especially the nature of the ligand *trans* to the aqua ligand, is at least as important as the identity of the metal atom and its oxidation and spin states in determining substitution rates. A strong *trans* influence of PMe_2Ph on H_2O is very obvious from details of the crystal structure of *trans,mer*-$[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$. We have now substituted H_2O by reaction with H_2S, NH_3 and PH_3 and have been able to compare the spectra and structures of a fairly complete range of directly comparable ligands based on O, S, N and P donor atoms.

Results and Discussion

Synthesis and Characterisation of the Complexes.—When ammonia gas is passed through a solution of the aqua complex *trans,mer*-$[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ in dichloromethane, the yellow solution lightens in colour and the ammine complex *trans,mer*-$[IrCl_2(NH_3)(PMe_2Ph)_3][ClO_4]$ is easily isolated in 69% yield as yellow crystals by addition of diethyl ether. Whereas the ^1H NMR spectrum of the aqua complex is very broad at room temperature because of the process in Scheme 1 and low temperatures were needed to obtain sharp well resolved signals, that of the ammine complex is sharp at room temperature (Table 1). Sharp $^{31}P-\{^1H\}$ NMR spectra are also obtained (Table 1). The process of the type in Scheme 1 must be very slow or not occurring at all. This was confirmed by the retention of the NH_3 resonance (δ 2.31) in the ^1H NMR spectrum when a $CDCl_3$ solution was treated with a large excess of D_2O over hours; slow exchange occurred over several days. Any reversible loss of NH_3 or reversible deprotonation would have given the ND_3 complex. Addition of a large excess of MeI and a three-fold excess of dbu (1,8-diazabicyclo[5.4.0]undec-7-ene) leads to the slow formation of the corresponding $MeNH_2$ complex over 5 d. Thus the rate of the reversible loss of H^+ to give the neutral amido complex *trans,mer*-$[IrCl_2(NH_2)(PMe_2Ph)_3]$ as an intermediate is very low and the rate of NH_3 dissociation from the cation is similarly very low or negligible.



Scheme 1

Excellent quality crystals of the complex *trans,mer*-$[IrCl_2(NH_3)(PMe_2Ph)_3][ClO_4]$ were obtained by the careful addition of diethyl ether to a solution in dichloromethane but these became opaque and crumbled to powder over 24 h in air probably because of loss of dichloromethane of solvation even under the vapour of this solvent. We determined the unit cell [monoclinic, $a = 27.13(1)$, $b = 8.987(2)$, $c = 30.93(1)$ Å, $\beta = 115.40(3)°$, $U = 6811(3)$ Å^3] but its large volume and the long time needed to collect the necessarily large intensity data set prevented our determining the crystal structure. However, recrystallisation by addition of diethyl ether to a 1,2-dichloroethane solution gave stable solvent-free crystals having approximately half the unit-cell volume and for which we were

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Proton and ^{31}P-{^1H} NMR data for the compounds *trans,mer*-$[IrCl_2L(PMe_2Ph)_3][ClO_4]$ (L = H_2O, NH_3 or PH_3) and *trans,mer*-$[IrCl_2X(PMe_2Ph)_3]$ (X = PH_2 or SH)

	$^1H^a$						^{31}P-{^1H}^{b}		
L or X	δ(P^AMe_2Ph)	$J(PH)^c$	δ(P^BMe_2Ph)	$^2J(PH)$	Others		δ(P^A)	δ(P^B)	$^2J(P^AP^B)$
H_2O^d	1.72 (t)	8.1	1.35 (d)	11.7	5.7 (br) (H_2O)		−46.1	−30.9	17.3
NH_3	1.68 (t)	7.0	1.80 (d)	10.0	2.31 (br) (NH_3)		−37.0	−53.7	19.5
$PH_3{}^e$	1.71 (t)	7.8	1.88 (dd)	9.3	3.06 (ddt) (PH_3)	$^1J(PH)$ 381.0 $^3J(PH)$ 7.0, 4.5	−51.0	−50.2	29.8
$PH_2{}^f$	1.79 (dt)	8.2	1.18 (d)	9.2	1.54 (dq) (PH_2)	$^1J(PH)$ 176.2 $^3J(PH)$ 8.8, 8.8	−49.4	−53.4	20.3
SH	1.87 (t)	8.5	1.17 (d)	10.3	−1.08 (dt) (SH)	$^3J(PH)$ 6.7, 1.0	−49.8	−45.8	16.9
Cl	1.88 (t)	8.7	1.23 (3)	11.0					

[a] Recorded in $CDCl_3$ at 200 or 400 MHz at room temperature unless stated otherwise; *J* in Hz; P^A = mutually *trans* P nuclei; P^B = P nuclei *trans* to X or L. [b] Recorded in $CDCl_3$ at room temperature relative to 85% H_3PO_4; 162 MHz spectra. [c] $J(PH) = |^2J(PH) + {}^4J(PH)]$. [d] Proton NMR spectrum recorded at −50 °C. [e] Phosphorus-31 NMR spectrum: δ(P^C) −121.5, $^2J(P^CP^A)$ = 29.8 and $^2J(P^CP^B)$ = 403.0 Hz. [f] Phosphorus-31 NMR spectrum: δ(P^C) −150.2, $^2J(P^CP^A)$ = 7.0 and $^2J(P^CP^B)$ = 106.2 Hz.

Table 2 Selected bond lengths (Å) and angles (°) for the complex *trans,mer*-$[IrCl_2(NH_3)(PMe_2Ph)_3][ClO_4]$

Ir–P(1)	2.302(5)	P(1)–C(11)	1.85(2)
Ir–P(2)	2.401(5)	P(2)–C(3)	1.81(2)
Ir–P(3)	2.398(5)	P(2)–C(4)	1.82(2)
Ir–N	2.15(1)	P(2)–C(21)	1.83(2)
Ir–Cl(1)	2.375(5)	P(3)–C(5)	1.82(2)
Ir–Cl(2)	2.375(5)	P(3)–C(6)	1.81(2)
P(1)–C(1)	1.83(2)	P(3)–C(31)	1.83(2)
P(1)–C(2)	1.81(2)		
N–Ir–P(2)	86.2(4)	P(1)–Ir–Cl(1)	90.1(2)
N–Ir–P(3)	87.8(4)	P(1)–Ir–Cl(2)	95.8(2)
N–Ir–Cl(1)	86.2(4)	Cl(1)–Ir–P(2)	93.4(2)
N–Ir–Cl(2)	87.8(4)	Cl(1)–Ir–P(3)	91.4(2)
P(1)–Ir–P(2)	92.5(2)	Cl(2)–Ir–P(2)	86.7(2)
P(1)–Ir–P(3)	93.7(2)	Cl(2)–Ir–P(3)	87.9(2)

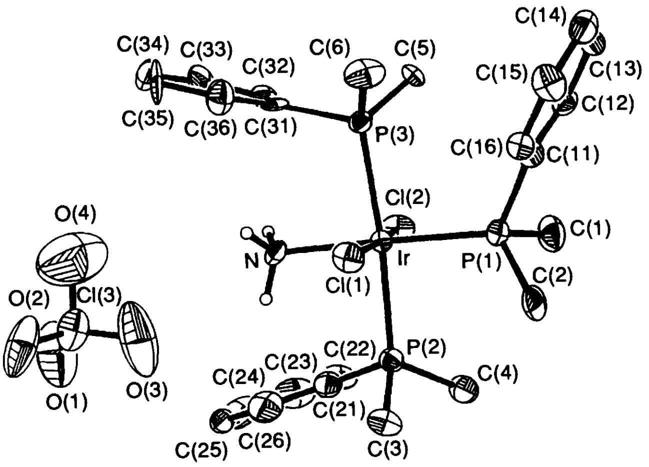

Fig. 1 Molecular structure of the complex *trans,mer*-$[IrCl_2(NH_3)(PMe_2Ph)_3][ClO_4]$

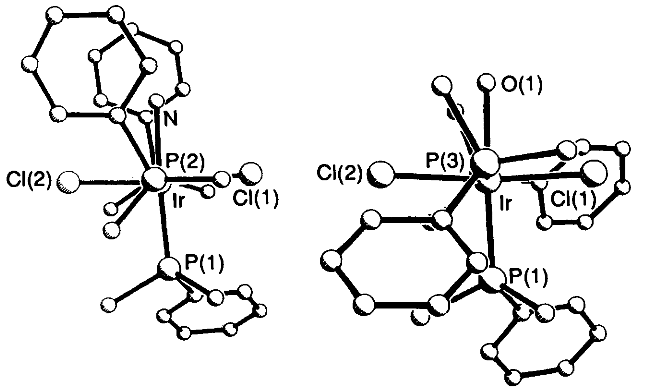

Fig. 2 A comparison of the structures of the NH_3 (left) and H_2O (right) complexes of the type *trans,mer*-$[IrCl_2L(PMe_2Ph)_3][ClO_4]$ with views along the *trans*-P(2)–Ir–P(3) directions showing the different conformations adopted by the PMe_2Ph ligands *cis* to L

able to determine the structure. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are in Table 2. Hydrogen atoms are included in idealised positions. There is a single hydrogen bond between the NH_3 ligands and the perchlorate ion (shortest N • • • O 3.30 Å), whereas there are two hydrogen bonds per H_2O ligand in the aqua analogue. Another difference is in the conformations adopted by the PMe_2Ph ligands. In the aqua complex the Ph groups of both PMe_2Ph ligands *cis* to co-ordinated H_2O are rotated away from the H_2O ligand, whereas in the ammine complex these are adjacent and face-on to the NH_3 ligand. Fig. 2 shows the two structures for comparison. This difference might reflect the different intrinsic affinities of benzene for NH_3 *versus* H_2O, for example arenes are much more soluble in ammonia than in water. Also the more extensive hydrogen bonding to H_2O might require more space around this ligand which is increased when the Ph groups are turned away from the H_2O ligand. In both the H_2O and NH_3 complexes the conformation of the PMe_2Ph *trans* to H_2O or NH_3 is such that all three PMe_2Ph ligands are different but in solution rapid rotation about the Ir–P bonds removes these differences and spectra consistent with C_{2v} symmetry are obtained.

We have similarly prepared the PH_3 complex *trans,mer*-$[IrCl_2(PH_3)(PMe_2Ph)_3][ClO_4]$ as pale yellow crystals by passing PH_3 gas into a solution of the aqua complex. This gave solvent-free crystals from dichloromethane–diethyl ether mixtures. The ^1H and ^{31}P-{^1H} NMR spectra (Table 1) are consistent with a non-dynamic structure corresponding to that of the NH_3 complex. The PH_3 resonance in the ^{31}P NMR spectrum is shown in Fig. 3, both with and without ^1H decoupling. The additional ^1H coupling in Fig. 3(*b*) gives a 1:3:3:1 pattern confirming that the ligand is indeed PH_3 and that deprotonation has not occurred. Typically values for $^1J(PH)$ for phosphines co-ordinated to late-transition-metal centres lie in the range 310–400 Hz, rendering both ^1H and ^{31}P (proton-coupled) NMR spectroscopy a valuable predictive tool for assigning the nature of these phosphorus atoms.[9,10] The PH_3 resonance in the ^1H NMR spectrum is a double double

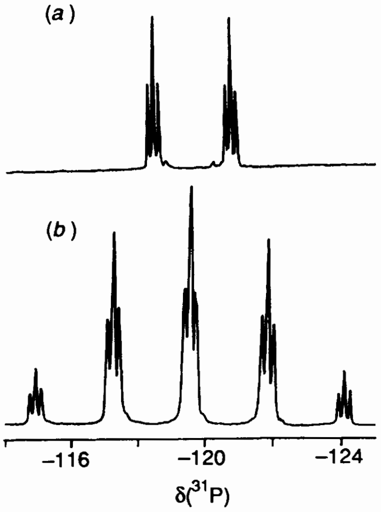

Fig. 3 Phosphorus-31 NMR spectra of the PH_3 resonance of the complex *trans,mer*-$[IrCl_2(PH_3)(PMe_2Ph)_3][ClO_4]$ in $CDCl_3$ with (*a*) and without (*b*) ^1H decoupling

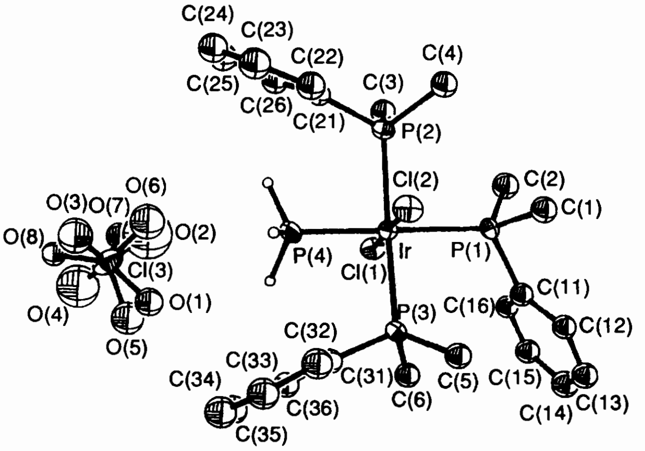

Fig. 4 Molecular structure of the complex *trans,mer*-$[IrCl_2(PH_3)(PMe_2Ph)_3][ClO_4]$

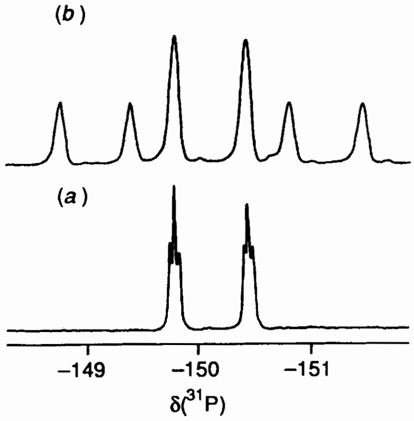

Fig. 5 Phosphorus-31 NMR spectra of the PH_2 resonance of the complex *trans,mer*-$[IrCl_2(PH_2)(PMe_2Ph)_3]$ in $CDCl_3$ with (*a*) and without (*b*) ^1H decoupling

Table 3 Selected bond lengths (Å) and angles (°) for the complex *trans,mer*-$[IrCl_2(PH_3)(PMe_2Ph)_3][ClO_4]$

Ir–P(1)	2.46(1)	P(1)–C(11)	1.87(2)
Ir–P(2)	2.398(5)	P(2)–C(3)	1.82(2)
Ir–P(3)	2.395(4)	P(2)–C(4)	1.88(2)
Ir–P(4)	2.25(1)	P(2)–C(21)	1.80(2)
Ir–Cl(1)	2.382(5)	P(3)–C(5)	1.84(2)
Ir–Cl(2)	2.384(5)	P(3)–C(6)	1.77(2)
P(1)–C(1)	1.88(2)	P(3)–C(31)	1.79(2)
P(1)–C(2)	1.78(3)		
P(4)–Ir–P(2)	89.9(3)	P(1)–Ir–Cl(1)	85.4(3)
P(4)–Ir–P(3)	91.3(3)	P(1)–Ir–Cl(2)	93.2(3)
P(4)–Ir–Cl(1)	88.5(3)	Cl(1)–Ir–P(2)	92.5(2)
P(4)–Ir–Cl(2)	92.9(3)	Cl(1)–Ir–P(3)	93.1(2)
P(1)–Ir–P(2)	89.2(3)	Cl(2)–Ir–P(2)	87.7(2)
P(1)–Ir–P(3)	90.2(3)	Cl(2)–Ir–P(3)	86.7(2)

triplet with $^1J(PH) = 381.0$ Hz which is considerably larger than for free PH_3 (182.2 Hz).[11] The HPH angle in free PH_3 is 93.7°,[12] consistent with considerably greater p than sp^3 character for the P–H bonds and a correspondingly substantial s character for the lone pair. This is greatly modified on co-ordination when much more p character is required for the M–P bond than is carried by the lone pair of the three ligand. The s character of the P–H bonds therefore increases substantially on co-ordination and this, we believe, accounts for the more than doubling of the $^1J(PH)$ value on co-ordination.

The X-ray molecular structure is shown in Fig. 4 and selected bond lengths and angles are in Table 3. No hydrogen atoms could be detected; those shown are in idealised positions. Hence we could not confirm the expected increase in the HPH angle on co-ordination. The structure including the hydrogen bonding and the conformations of the PMe_2Ph ligands are very similar to those in the NH_3 complex. The shortest P$\cdots$O distance is 3.39 Å.

Unlike the NH_3 complex, the PH_3 complex is readily deprotonated using dbu in ethanol. Of course, co-ordinated PH_3 is expected to be considerably more acidic than co-ordinated NH_3. The solution rapidly turns from pale to dark yellow on addition of base and crystals are deposited which can be recrystallised from dichloromethane by addition of ethanol. The neutral complex, *trans,mer*-$[IrCl_2(PH_2)(PMe_2Ph)_3]$, was initially characterised by spectroscopy, both its ^1H and ^{31}P NMR properties (Table 1) displaying profoundly different, but distinctive, characteristics to those of the parent complex. The ^1H NMR PH_2 signal in $CDCl_3$ appears as a double quartet with the largest coupling constant being $^1J(PH) = 176.2$ Hz, much less than that for the PH_3 complex (381.0 Hz) and much closer to that for free PH_3 (182.2 Hz). There is ample precedence for such spectroscopic modifications. Both Ebsworth[13] and Roper[9] and their co-workers have reported similar reductions in the values of $^1J(PH)$ upon transformation of a co-ordinated phosphine $[M-PR^1R^2H]$ into its phosphido counterpart $[M-PR^1R^2]$. The ^{31}P NMR spectrum in the PH_2 region shows the expected double triplet (^1H decoupled) and an additional 1:2:1 coupling when ^1H coupled. This confirms that there are only two H atoms bonded to P (Fig. 5). The value of $^1J(PH)$ is now similar to that in free PH_3 consistent with there being a lone pair with considerable s character. This in itself would be sufficient to characterise *trans,mer*-$[IrCl_2(PH_2)(PMe_2Ph)_3]$ as containing a pyramidal rather than planar phosphido group. Both planar[14] and pyramidal[15] terminal phosphido ligands are known, having electrophilic[16] and nucleophilic[17] character respectively. However, planar phosphido ligands involve multiple M–P bonding and are only encountered when the metal centre would otherwise be co-ordinatively unsaturated. Vacant metal π orbitals are also required, of course, and by both criteria the PH_2 complex described here should contain a pyramidal nucleophilic PH_2 ligand. We will report its behaviour as a nucleophile with both organic and metallic electrophiles elsewhere.[18]

The crystal structure of *trans,mer*-$[IrCl_2(PH_2)(PMe_2Ph)_3]$ is shown in Fig. 6 with selected bond lengths and angles in Table 4. The hydrogen atoms bonded to the phosphorus atoms were clearly apparent in Fourier difference maps and their positions

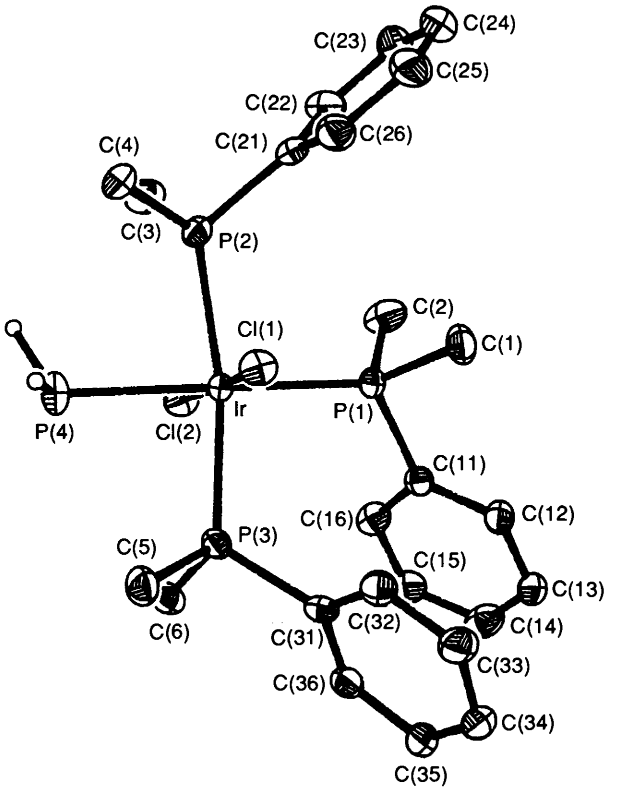

Fig. 6 Molecular structure of the complex *trans,mer*-[IrCl$_2$(PH$_2$)(PMe$_2$Ph)$_3$]

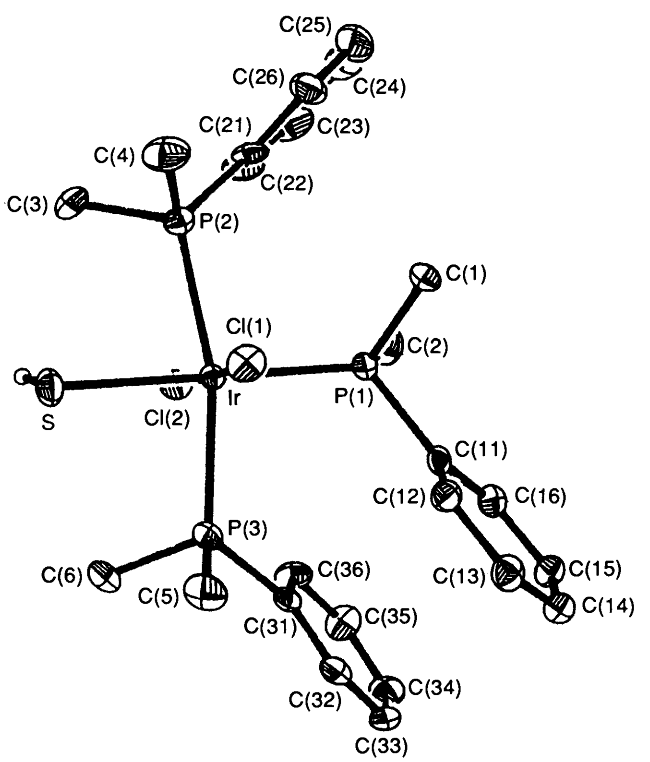

Fig. 8 Molecular structure of the complex *trans,mer*-[IrCl$_2$(SH)-(PMe$_2$Ph)$_3$]

Table 4 Selected bond lengths (Å) and angles (°) for the complex *trans,mer*-[IrCl$_2$(PH$_2$)(PMe$_2$Ph)$_3$]

Ir–P(1)	2.378(3)	P(1)–C(11)	1.833(9)
Ir–P(2)	2.370(3)	P(2)–C(3)	1.82(1)
Ir–P(3)	2.359(2)	P(2)–C(4)	1.83(1)
Ir–P(4)	2.440(3)	P(2)–C(21)	1.84(1)
Ir–Cl(1)	2.389(2)	P(3)–C(5)	1.83(1)
Ir–Cl(2)	2.396(3)	P(3)–C(6)	1.83(1)
P(1)–C(1)	1.82(1)	P(3)–C(31)	1.84(1)
P(1)–C(2)	1.82(1)		
P(4)–Ir–P(2)	84.2(1)	P(1)–Ir–Cl(1)	93.6(1)
P(4)–Ir–P(3)	84.6(1)	P(1)–Ir–Cl(2)	88.8(1)
P(4)–Ir–Cl(1)	94.1(1)	Cl(1)–Ir–P(2)	86.4(1)
P(4)–Ir–Cl(2)	83.6(1)	Cl(1)–Ir–P(3)	88.3(1)
P(1)–Ir–P(2)	96.10(1)	Cl(2)–Ir–P(2)	91.7(1)
P(1)–Ir–P(3)	95.9(1)	Cl(2)–Ir–P(3)	93.2(1)

Table 5 Selected bond lengths (Å) and angles (°) for the complex *trans,mer*-[IrCl$_2$(SH)(PMe$_2$Ph)$_3$]

Ir–P(1)	2.296(2)	P(1)–C(11)	1.823(8)
Ir–P(2)	2.366(2)	P(2)–C(3)	1.83(1)
Ir–P(3)	2.355(2)	P(2)–C(4)	1.81(1)
Ir–S	2.429(2)	P(2)–C(21)	1.823(9)
Ir–Cl(1)	2.370(2)	P(3)–C(5)	1.811(9)
Ir–Cl(2)	2.366(2)	P(3)–C(6)	1.81(1)
P(1)–C(1)	1.799(9)	P(3)–C(31)	1.83(1)
P(1)–C(2)	1.813(9)	S–H	1.00(1)
S–Ir–P(2)	83.7(1)	P(1)–Ir–Cl(1)	88.4(1)
S–Ir–P(3)	83.9(1)	P(1)–Ir–Cl(2)	94.1(1)
S–Ir–Cl(1)	84.7(1)	Cl(1)–Ir–P(2)	91.8(1)
S–Ir–Cl(2)	92.8(1)	Cl(1)–Ir–P(3)	93.5(1)
P(1)–Ir–P(2)	96.6(1)	Cl(2)–Ir–P(2)	86.3(1)
P(1)–Ir–P(3)	96.4(1)	Cl(2)–Ir–P(3)	97.9(1)

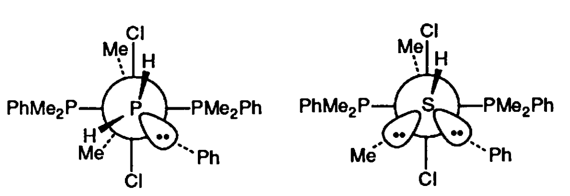

Fig. 7 Projections showing the conformations of the PH$_2$ and SH ligands in the complexes *trans,mer*-[IrCl$_2$X(PMe$_2$Ph)$_3$] (X = PH$_2$ or SH)

were allowed to refine freely. We we able to establish that there is a pyramidal geometry and that the H atoms are eclipsed with the methyl groups of the *trans*-PMe$_2$Ph ligand. In the final cycles of refinement, the P–H, Ir–H and H–H distances in the IrPH$_2$ set of atoms were fixed to maintain pyramidal geometry at phosphorus but rotation about the Ir–P(4) bond was allowed. The lone pair is stereochemically active and eclipses the Ph group of the *trans*-PMe$_2$Ph ligand as illustrated in Fig. 7. Each P atom has two substituents on one side and one on the other side of the approximate P$_4$ plane, alternating around the molecule. The large substituents (Ph in PMe$_2$Ph and the lone pair in PH$_2$) share one side of the P$_4$ plane with another substituent avoiding clashes with the *cis*-Cl ligands. Similar arrangements are found in related molecules such as *trans*-[IrCl$_2$(PMe$_2$Ph)$_4$][ClO$_4$]. The ^{31}P-{^{1}H} NMR spectrum even at low temperatures (−60 °C) appears as an AB$_2$X pattern and the PH$_2$ protons appear equivalent in the ^{1}H NMR spectrum. Rapid rotation about the Ir–P bonds is occurring.

The most notable difference between the PH$_2$ and PH$_3$ structures is in the Ir–P bond lengths. Those for the mutually *trans*-PMe$_2$Ph ligands [Ir–P(2) and Ir–P(3)] are not very different, just 0.02 to 0.03 Å shorter in the neutral complex. However, the Ir–P(4) distances are 2.25(1) Å for PH$_3$ and 2.440(3) Å for PH$_2$, an increase of over 8% on deprotonation. The Ir–P distance *trans* to PH$_3$ is 2.46(1) Å and that *trans* to PH$_2$ is 2.378(3) Å. Thus PH$_3$ is more closely bonded to Ir and has a stronger *trans* influence than PH$_2$. The coupling constants of the PH$_3$ ligand to the other P nuclei, J = 29.8 (*cis*) and 403.0 (*trans*) Hz, decrease considerably on deprotonation to J = 7.0

Table 6 Crystal data and details of data collection, structure solution and refinement for the compounds *trans,mer*-[$IrCl_2L(PMe_2Ph)_3$][ClO_4] (L = NH_3 or PH_3) and *trans,mer*-[$IrCl_2X(PMe_2Ph)_3$] (X = PH_2 or SH)[a]

	L = NH_3	L = PH_3	X = PH_2	X = SH
Formula	$C_{24}H_{36}Cl_3IrNO_4P_3$	$C_{24}H_{36}Cl_3IrO_4P_4$	$C_{24}H_{35}Cl_2IrP_4$	$C_{24}H_{34}Cl_2IrP_3S$
M	794.07	811.03	710.57	710.65
Crystal size/mm	0.37 × 0.15 × 0.18	0.35 × 0.12 × 0.25	0.70 × 0.40 × 0.06	0.42 × 0.12 × 0.04
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$Pbn2_1$	$P2_1/c$	$P2_1/c$
a/Å	10.565(8)	8.610(2)	15.937(3)	15.803(3)
b/Å	21.715(7)	16.783(5)	10.283(3)	10.2507(8)
c/Å	13.865(6)	21.675(5)	17.100(6)	16.791(3)
β/Å	106.03(5)	90	92.82(2)	92.45(2)
U/Å^3	3057(3)	3131(1)	2799(1)	2717.6(7)
D_c/g cm^{-3}	1.73	1.72	1.69	1.74
μ(Mo-Kα)/cm^{-1}	48.0	47.4	51.8	53.5
F(000)	1568	1600	1400	1400
No. orientation reflections	26	33	29	30
2θ Range for orientation reflections/°	8–23	11–26	11–29	11–24
Unique data	5119	2805	4897	4785
Rejection criterion	$I_o \leqslant 3\sigma(I_o)$	$I_o \leqslant 2\sigma(I_o)$	$I_o \leqslant 2\sigma(I_o)$	$I_o \leqslant 3\sigma(I_o)$
Reflections used in refinement	3113	2172	3942	3691
No. of parameters	325	201	288	274
R[b]	0.0595	0.0496	0.0443	0.0421
R'[c]	0.0559	0.0494	0.0418	0.0442
g[c]	0.000 262	0.000 340	0.0001	0.001 27
Maximum shift/e.s.d. in final least-squares cycles	0.001	0.05[d]	0.003	0.001
Maximum peak in final difference map/e Å^{-3}	1.64	1.01	1.84	1.73

[a] Details common to each determination: complexes are yellow, $Z = 4$; Nicolet R3v/m diffractometer; data collected at 20 °C with Mo-Kα radiation (λ = 0.710 73 Å) with scan mode ω–2θ in the range $5 \leqslant 2\theta \leqslant 50°$; direct methods solution. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o) + gF_o^2]$. [d] The maximum shift/e.s.d. was found for an oxygen atom of disordered perchlorate.

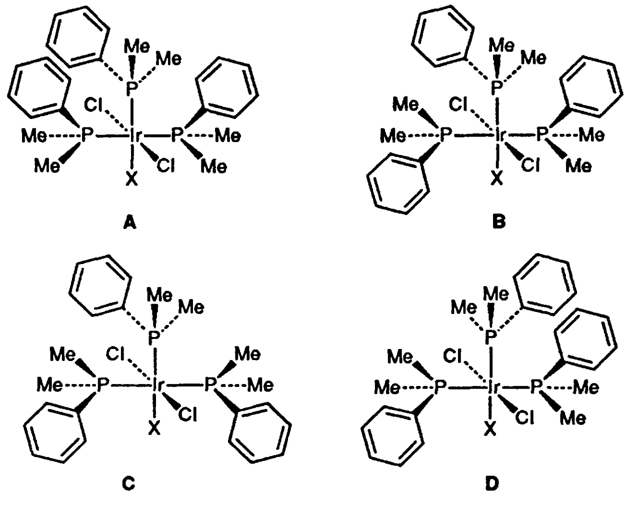

Fig. 9 Four possible conformations of the complexes *trans,mer*-[$IrCl_2X(PMe_2Ph)_3$] excluding situations with the Ph groups in the $IrCl_2P$ planes which are believed to be significantly less stable. Similar structures exist for the clusters *trans,mer*-[$IrCl_2L(PMe_2Ph)_3$][ClO_4]

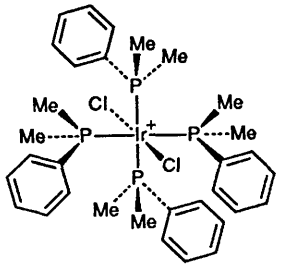

Fig. 10 Structure of the cation found in crystals of *trans,mer*-[$IrCl_2(PMe_2Ph)_4$][ClO_4]; three different conformations were found in solution

(*cis*) and 106.2 (*trans*) Hz. This reduction in ^2J(PP) is most likely indicative of the substantial reduction in the s character of the Ir–PH_2 bond compared with that of Ir–PH_3 and consequently a considerable weakening of the Ir–P bond on deprotonation. Several late-transition-metal compounds containing pyramidal phosphido ligands have been structurally characterised, including [$OsCl(CO)_2(PHPh)(PPh_3)_2$][19] and [$Re(C_5H_5)(NO)(PPh_2)(PPh_3)$].[20] Both complexes exhibit similar M–PR_2 bond lengths [Os–PHPh 2.414(7), Re–PPh_2 2.461(3) Å] to that reported here, allowing for the slight differences in the atomic radii of these third-row metal atoms.

Treatment of *trans,mer*-[$IrCl_2(H_2O)(PMe_2Ph)_3$][ClO_4] with H_2S in methanol gave an immediate reaction and a precipitate of the deprotonated species *trans,mer*-[$IrCl_2(SH)(PMe_2Ph)_3$]. The ^1H NMR spectrum shows the SH resonance at δ −1.08 as a double triplet showing coupling to all three ^{31}P nuclei. Clearly there is no observable exchange of the SH protons. Reported spectra for co-ordinated SH complexes contain signals in the range δ 1.6 to −3.0 for this proton with most having negative δ values.[21] The high-field position of this signal has been attributed to some M–H bonding to the SH group but this is unlikely.[22] The X-ray structure of *trans,mer*-[$IrCl_2(SH)(PMe_2Ph)_3$] is shown in Fig. 8 and selected bond lengths and angles are in Table 5. The SH proton position was determined by X-ray diffraction and shown to be in the $IrCl_2S$ plane. Therefore the conformations of the PH_2 and SH compounds are as shown in Fig. 7. The lone pairs preferentially occupy sites as shown rather than being eclipsed with the *cis*-Cl ligands and probably it is the potential clash with the *cis* ligands that favours the larger groups being positioned as they are.

We were unable to obtain any direct spectroscopic evidence for the cation *trans,mer*-[$IrCl_2(H_2S)(PMe_2Ph)_3$][ClO_4] either in the initial reaction of H_2S or by protonation of the SH complex. Therefore the acidities of the cationic species *trans,mer*-[$IrCl_2L(PMe_2Ph)_3$][ClO_4] (L = H_2O, H_2S, NH_3 or PH_3) are probably in the order H_2S > PH_3 > H_2O > NH_3 as expected. A neutral SH_2 complex of ruthenium(II) has been characterised recently by X-ray diffraction[23] but the cationic SH_2 complex of iridium(III) is likely to be too acidic for straightforward isolation.

Table 7 Fractional atomic coordinates ($\times 10^4$) for the complex *trans,mer*-$[IrCl_2(NH_3)(PMe_2Ph)_3][ClO_4]$

Atom	*x*	*y*	*z*
Ir	1 959(1)	6 177(1)	8 439(1)
P(1)	1 877(5)	6 943(2)	9 568(3)
P(2)	4 281(4)	6 316(2)	8 679(3)
P(3)	−377(4)	6 015(2)	7 961(3)
Cl(1)	2 267(5)	5 430(2)	9 733(3)
Cl(2)	1 647(5)	6 839(2)	7 028(3)
N	2 106(14)	5 425(6)	7 470(11)
C(1)	1 910(23)	7 726(8)	9 081(17)
C(2)	3 222(19)	6 918(10)	10 710(14)
C(3)	5 356(18)	5 923(9)	9 749(14)
C(4)	4 962(19)	7 088(8)	8 759(15)
C(5)	−1 392(16)	6 680(8)	7 465(13)
C(6)	−1 138(20)	5 740(10)	8 877(13)
C(11)	466(16)	6 956(7)	10 114(12)
C(12)	−536(17)	7 391(8)	9 783(12)
C(13)	−1 567(20)	7 395(11)	10 233(17)
C(14)	−1 643(22)	6 974(10)	10 957(16)
C(15)	−621(22)	6 566(10)	11 273(15)
C(16)	423(17)	6 538(8)	10 863(13)
C(21)	4 797(18)	6 037(9)	7 597(15)
C(22)	4 753(17)	6 421(11)	6 792(13)
C(23)	5 119(24)	6 202(18)	5 972(17)
C(24)	5 471(28)	5 639(19)	5 883(23)
C(25)	5 509(20)	5 227(13)	6 673(24)
C(26)	5 170(20)	5 417(11)	7 557(17)
C(31)	−856(20)	5 447(8)	6 954(13)
C(32)	−1 165(17)	5 616(9)	5 950(12)
C(33)	−1 577(22)	5 162(11)	5 192(15)
C(34)	−1 644(23)	4 556(11)	5 431(20)
C(35)	−1 327(26)	4 405(8)	6 455(18)
C(36)	−941(22)	4 843(9)	7 175(16)
Cl(3)	3 453(7)	1 382(3)	2 035(4)
O(1)	3 954(28)	1 357(10)	1 230(16)
O(2)	3 683(22)	1 934(8)	2 515(14)
O(3)	3 654(35)	906(2)	2 659(17)
O(4)	2 093(35)	1 359(21)	1 691(25)

General Comments on the Structures.—Fig. 9 shows the four possible conformations of the PMe_2Ph ligands of which three (**A**–**C**) are found in the solid-state structures of *trans,mer*-$[IrCl_2X(PMe_2Ph)_3]$ (X = H,[24] Cl,[25] SH or PH_2) and *trans,mer*-$[IrCl_2L(PMe_2Ph)_3][ClO_4]$ (L = H_2O, NH_3 or PH_3). Conformation **A** is found when X = Cl, SH or PH_2 or L = H_2O, conformation **B** when X = H and conformation **C** when L = NH_3 or PH_3. When L = PMe_2Ph the solid-state structure of *trans,mer*-$[IrCl_2(PMe_2Ph)_4][ClO_4]$[26] (Fig. 10) illustrates all four arrangements, **A**–**D**, depending upon which of the four non-equivalent PMe_2Ph ligands is taken to be ligand L in *trans,mer*-$[IrCl_2L(PMe_2Ph)_3][ClO_4]$. It is likely that all four conformations are present in dynamic equilibria in solutions of these species and that packing and hydrogen-bonding effects determine which crystallises.

There are distinct differences in the Ir–P bond lengths for the mutually *trans*-PMe_2Ph ligands depending upon which conformation is adopted. Lengths in the range 2.355–2.392 Å are found for conformation **A**, 2.328–2.332 Å for **B** and 2.395–2.401 Å for **C**. The only example of **B** is where X = H and it could be the small size of X that accounts for this structure being adopted and for the Ir–P distance to be short. Clearly these bond-length variations are small and much greater variation is observed for the Ir–PMe_2Ph lengths *trans* to X or L: in increasing order Ir–P = 2.249(3) (L = H_2O), 2.278(1), 2.282(1) (X = Cl), 2.296(2) (X = SH), 2.302(5) (L = NH_3), 2.363(2) (X-ray result) and 2.375(6) (neutron result) (X = H), 2.378(3) (X = PH_2) and 2.46(1) (L = PH_3) Å. This provides a reasonable *trans*-influence series for these ligands since there is almost a 10% bond-length increase on going from L = H_2O to PH_3.

Table 8 Fractional atomic coordinates ($\times 10^4$) for the complex *trans,mer*-$[IrCl_2(PH_3)(PMe_2Ph)_3][ClO_4]$

Atom	*x*	*y*	*z*
Ir	489(1)	3598(1)	5752
P(1)	358(9)	3697(5)	6883(5)
P(2)	−1397(6)	4645(3)	5678(4)
P(3)	2161(5)	2462(3)	5839(4)
P(4)	787(11)	3620(5)	4721(5)
Cl(1)	2589(5)	4517(3)	5830(5)
Cl(2)	−1611(6)	2674(3)	5701(5)
Cl(3)	2778(10)	3977(4)	2836(3)
O(1)	3158(40)	3387(18)	3294(15)
O(2)	2330(117)	4370(53)	3257(39)
O(3)	1475(54)	3696(23)	2477(21)
O(4)	4187(76)	4253(39)	2533(30)
O(5)	3989(71)	3498(33)	3085(28)
O(6)	1315(77)	3993(35)	3222(28)
O(7)	3092(47)	4789(24)	2953(19)
O(8)	2180(44)	3722(20)	2260(17)
C(1)	−1273(26)	3093(13)	7220(10)
C(2)	247(31)	4669(14)	7212(12)
C(3)	−725(22)	5651(10)	5833(18)
C(4)	−3130(26)	4559(13)	6198(11)
C(5)	1466(27)	1648(12)	6335(11)
C(6)	4068(23)	2622(13)	6123(11)
C(11)	2035(25)	3318(12)	7346(10)
C(12)	1989(26)	2643(12)	7704(10)
C(13)	3295(28)	2376(14)	8028(11)
C(14)	4583(33)	2856(15)	8028(13)
C(15)	4626(30)	3565(14)	7716(11)
C(16)	3329(25)	3805(12)	7384(10)
C(21)	−2285(24)	4723(12)	4927(10)
C(22)	−3276(30)	4124(15)	4736(12)
C(23)	−3838(34)	4100(16)	4135(13)
C(24)	−3449(31)	4743(16)	3754(13)
C(25)	−2552(32)	5294(15)	3917(12)
C(26)	−1912(27)	5304(14)	4508(11)
C(31)	2489(28)	1983(13)	5113(10)
C(32)	1467(33)	1375(15)	4871(13)
C(33)	1838(32)	983(16)	4335(13)
C(34)	3045(31)	1233(16)	3987(15)
C(35)	3976(31)	1757(14)	4175(12)
C(36)	3817(28)	2186(13)	4742(10)

Experimental

The aqua complex *trans,mer*-$[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ was synthesised from *mer*-$[IrCl_3(PMe_2Ph)_3]$ as previously described.[1,2] Gaseous PH_3 was either used as supplied by Aldrich or synthesised by treatment of zinc phosphide with aqueous acid.

Syntheses.—*trans,mer*-$[IrCl_2(NH_3)(PMe_2Ph)_3][ClO_4]$. Ammonia gas was passed through a bright yellow solution of the compound $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (0.1090 g, 1.37×10^{-4} mol) in dichloromethane (5 cm^3) for 5 min. The solution became a paler yellow and the product was crystallised as a pale yellow solid by slow addition of diethyl ether to the dichloromethane solution. This precipitate was recrystallised from this solvent mixture to give pale yellow crystals of the product (0.0658 g, 69%) (Found: C, 36.0; H, 4.2; N, 1.7. $C_{24}H_{36}Cl_3IrNO_4P_3$ requires C, 36.3; H, 4.5; N, 1.8%). These analytical data were obtained for a powder formed by keeping the crystals at low pressure for many hours to remove solvent of crystallisation. A crystal for a single-crystal structure determination was selected from those obtained by addition of diethyl ether to a solution in 1,2-dichloroethane.

trans,mer-$[IrCl_2(PH_3)(PMe_2Ph)_3][BF_4]$. Phosphine gas was bubbled through a solution of $[IrCl_2(H_2O)(PMe_2Ph)_3][BF_4]$ (0.241 g, 0.27 mmol) in dichloromethane (20 cm^3). The solution turned dark brown immediately and was left to stand overnight in a well ventilated fumehood. Decolourising charcoal was added and the suspension stirred under an atmosphere of

Table 9 Fractional atomic coordinates ($\times 10^4$) for the complex *trans,mer*-$[IrCl_2(PH_2)(PMe_2Ph)_3]$

Atom	*x*	*y*	*z*
Ir	2 212(1)	5 682(1)	2 375(1)
Cl(1)	1 142(1)	6 828(2)	1 630(1)
Cl(2)	3 233(2)	4 502(2)	3 168(1)
P(1)	2 914(2)	5 009(2)	1 248(1)
P(2)	1 257(2)	3 915(2)	2 377(2)
P(3)	2 938(2)	7 669(2)	2 541(1)
P(4)	1 635(2)	6 206(3)	3 632(2)
C(1)	2 348(6)	5 220(12)	305(6)
C(2)	3 210(7)	3 300(9)	1 260(8)
C(3)	1 543(7)	2 605(10)	3 050(7)
C(4)	209(6)	4 384(11)	2 663(6)
C(5)	2 294(7)	9 008(9)	2 884(6)
C(6)	3 793(6)	7 624(10)	3 293(6)
C(11)	3 946(5)	5 718(9)	1 087(5)
C(12)	4 132(7)	6 325(9)	392(6)
C(13)	4 937(7)	6 813(10)	284(6)
C(14)	5 541(7)	6 708(10)	873(8)
C(15)	5 368(6)	6 115(10)	1 578(7)
C(16)	4 575(6)	5 620(9)	1 685(6)
C(21)	960(6)	3 052(9)	1 465(6)
C(22)	1 218(6)	1 786(10)	1 299(7)
C(23)	946(7)	1 156(12)	617(7)
C(24)	425(8)	1 787(13)	76(7)
C(25)	164(8)	3 040(13)	217(7)
C(26)	436(7)	3 669(10)	901(6)
C(31)	3 368(6)	8 523(8)	1 706(6)
C(32)	2 830(6)	8 817(10)	1 052(6)
C(33)	3 098(7)	9 597(9)	451(6)
C(34)	3 915(7)	10 053(10)	476(6)
C(35)	4 452(6)	9 758(10)	1 100(6)
C(36)	4 185(6)	8 978(9)	1 705(6)

nitrogen for 60 min. After filtering the resulting solution through Celite, a pale yellow filtrate remained, which was evaporated to dryness under reduced pressure to give a yellow oily residue. Crystallisation of the product from a mixture of dichloromethane and diethyl ether gave the required product as yellow needles (0.176 g, 80%) (Found: C, 36.25; H, 4.5; P, 15.95. $C_{24}H_{36}BCl_2F_4IrP_4$ requires C, 36.1; H, 4.55; P, 15.5%). The perchlorate salt was synthesised correspondingly and recrystallised from dichloromethane–diethyl ether to give crystals suitable for the crystal structure determination and for the synthesis of the deprotonated derivative.

trans,mer-$[IrCl_2(PH_2)(PMe_2Ph)_3]$. 1,8-Diazabicyclo[5.4.0]-undec-7-ene (dbu) (0.0616 cm^3, 0.4 mmol) was added to a suspension of $[IrCl_2(PH_3)(PMe_2Ph)_3][ClO_4]$ (0.2194 g, 0.27 mmol) in ethanol (3 cm^3). The pale yellow suspension gave a deep yellow solution on addition of the base. The solution was stirred vigorously under an atmosphere of nitrogen for 90 min and the deep yellow solid which precipitated from solution was collected by filtration and washed with ethanol (10 cm^3). Crystallisation from a mixture of dichloromethane and ethanol gave the product as a microcrystalline solid (0.163 g, 71%) (Found: C, 39.55; H, 4.7; P, 18.1. $C_{24}H_{35}Cl_2IrP_4$ requires C, 40.5; H, 4.85; P, 17.45%). Crystals suitable for a crystal structure determination were obtained by addition of a few drops of dbu to a saturated solution of the PH_3 complex in methanol in the dark. Good quality crystals were deposited over several hours.

trans,mer-$[IrCl_2(SH)(PMe_2Ph)_3]$. Hydrogen sulfide gas was bubbled through a solution of $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (0.306 g, 0.40 mmol) in a minimum of methanol until a dirty yellow precipitate started to form. When precipitation was complete the solid was filtered off and recrystallised from a mixture of dichloromethane and diethyl ether to give the product as yellow crystals (78%) (Found: C, 40.45; H, 4.8; Cl, 9.7; P, 13.2; S, 4.3. $C_{24}H_{34}Cl_2IrP_3S$ requires C, 40.55; H, 4.8; Cl, 10.0; P, 13.1; S, 4.5%).

Table 10 Fractional atomic coordinates ($\times 10^4$) for the complex *trans,mer*-$[IrCl_2(SH)(PMe_2Ph)_3]$

Atom	*x*	*y*	*z*
Ir	2223(1)	4397(1)	2375(1)
P(1)	2902(1)	5034(2)	1257(1)
P(2)	1261(1)	6164(2)	2392(1)
P(3)	2937(1)	2393(2)	2548(1)
Cl(1)	3253(2)	5571(2)	3152(1)
Cl(2)	1142(1)	3255(2)	1649(1)
S	1637(2)	3866(3)	3649(1)
C(1)	3177(7)	6736(9)	1237(7)
C(2)	2310(6)	4802(12)	318(5)
C(3)	216(6)	5659(10)	2711(7)
C(4)	1572(8)	7432(10)	3092(6)
C(5)	3788(6)	2446(10)	3304(5)
C(6)	2263(7)	1128(10)	2927(6)
C(11)	3931(5)	4309(7)	1083(5)
C(12)	4568(6)	4418(8)	1676(6)
C(13)	5376(6)	3910(9)	1564(5)
C(14)	5540(6)	3299(10)	857(6)
C(15)	4924(6)	3200(10)	270(5)
C(16)	4129(6)	3686(9)	373(5)
C(21)	951(5)	7021(9)	1474(5)
C(22)	397(6)	6 408(10)	926(6)
C(23)	145(8)	7 005(14)	227(7)
C(24)	414(8)	8 274(15)	75(7)
C(25)	946(8)	8 875(13)	609(8)
C(26)	1 221(3)	8 289(5)	1307(3)
C(31)	3 357(6)	1 504(10)	1706(5)
C(32)	4 168(6)	1 029(10)	1709(5)
C(33)	4 431(7)	260(9)	1097(6)
C(34)	3 883(7)	−29(10)	457(6)
C(35)	3 087(7)	460(10)	440(6)
C(36)	2 799(6)	1231(9)	1054(5)

Crystal Structure Determinations for the Complexes trans,mer-$[IrCl_2L(PMe_2Ph)_3][ClO_4]$ ($L = NH_3$ *or* PH_3) *and trans,mer*-$[IrCl_2X(PMe_2Ph)_3]$ ($X = PH_2$ *or* SH).—A selected crystal of each of these four compounds was mounted on a glass fibre and fixed to a goniometer of a Nicolet R3v/m diffractometer. Essential details of the crystal data of each, and the data collections and structure solutions are given in Table 6. Unit cells were determined by autoindexing and least-squares fitting of a set of orientation reflections taken from a rotation photograph. The cell parameters and crystal systems were checked by taking axial photographs. The intensity data were collected at 20–23 °C and corrected for Lorentz and polarization effects and for minimal crystal decay and instrument stability based on the intensities of three standard reflections measured periodically during the collection. Empirical absorption corrections were based on series of intensity data obtained by psi scans. Structures were solved in the space groups given in Table 6 by direct methods and refined by alternating cycles of full-matrix least squares and by Fourier difference synthesis.

trans,mer-$[IrCl_2(NH_3)(PMe_2Ph)_3][ClO_4]$. All non-H atoms were refined anisotropically and H atoms were included in idealised positions (C–H 0.96 and N–H 0.90 Å, $U = 0.08$ Å^2). There was an indication of some disorder of the perchlorate since extra weak peaks were observed at the appropriate distances from the Cl atoms, but these were considered to be too weak to be included in the model.

trans,mer-$[IrCl_2(PH_3)(PMe_2Ph)_3][ClO_4]$. Only the Ir and P atoms were refined anisotropically because of a lack of data; H atoms started to appear in the Fourier difference map in the later stages of the refinement but were included in idealised positions (C–H 0.96 and P–H 1.42 Å, U 0.08 Å^2). The perchlorate ion was disordered and modelled by two interlocking tetrahedra of oxygen atoms, O(1)–O(4) and O(5)–O(8). Site occupancies were refined but finally fixed at 0.58 and 0.42. Apart from this constraint the oxygen atoms were freely refined.

trans,mer-$[IrCl_2(PH_2)(PMe_2Ph)_3]$. All non-H atoms were refined anisotropically and the H atoms of the PMe_2Ph ligands were included in idealised positions (C–H 0.96 Å, U 0.08 $Å^2$). The two H atoms at P(4) were located in a Fourier difference map and their positions were refined freely at first but in the final cycles of refinement P–H distances were fixed at 1.49, Ir–H at 3.20 and the H–H distance at 2.53 Å. Although there is some uncertainty in these H-atom positions, we believe that the overall conformational features of the PH_2 co-ordination are correct.

trans,mer-$[IrCl_2(SH)(PMe_2Ph)_3]$. All non-H atoms were refined anisotropically and all H atoms except that bonded to S were included in idealised positions (C–H 0.96 Å, U 0.08 $Å^2$). The SH atom position [S–H 1.00(1) Å] and its isotropic thermal parameter [U 0.13(5) $Å^2$] were refined.

Fractional atomic coordinates for the above four compounds are given in Tables 7–10 respectively. Calculations were carried out using a MicroVax II computer running SHELXTL PLUS.[27]

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

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