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*-[IrCl₂(H₂O)(PMe₂Ph)₃][ClO₄] of known crystal structure contains a highly labile H₂O ligand which is readily substituted. The corresponding ammonia and phosphine complexes *trans,mer*-[IrCl₂(EH₃)(PMe₂Ph)₃][ClO₄] (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 PH₃ is readily deprotonated, but not the one with NH₃, to give the structurally characterised neutral complex *trans,mer*-[IrCl₂(PH₂)(PMe₂Ph)₃]. The Ir-PH₃ bond is significantly shorter than the Ir-PH₂ bond and there are clear conformational changes resulting from deprotonation. Replacement of H₂O by H₂S leads to spontaneous deprotonation and formation of *trans,mer*-[IrCl₂(SH)(PMe₂Ph)₃] (crystal structure also reported). Analysis of the geometries of *trans,mer*-[IrCl₂(PMe₂Ph)₃][ClO₄] (L = H₂O, NH₃ or PH₃) and of *trans,mer*-[IrCl₂X(PMe₂Ph)₃] (X = H, Cl, SH or PH₂) 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-[$IrCl_2(H_2O)(PMe_2Ph)_3$][CIO₄],^{1.2} the fluoroborate of which had been synthesised earlier.³ This remarkable lowspin octahedral d⁶ complex undergoes dynamic exchange of the mer set of phosphine ligands to give coalescences in the ¹H and ³¹P-{¹H} NMR spectra. This coalescence behaviour is a consequence of the trans effect of PMe₂Ph on the H₂O ligand which is rapidly and reversibly displaced and of the stereochemical non-rigidity of the resulting five-co-ordinate intermediate, [IrCl₂(PMe₂Ph)₃][ClO₄]. 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 calculations⁴ and experimental work⁵ 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 PMe₂Ph on H₂O is very obvious from details of the crystal structure of trans, mer-[IrCl₂(H_2O)(PMe₂Ph)₃][ClO₄]. We have now substituted H₂O by reaction with H₂S, NH₃ and PH₃ 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-[IrCl₂(H₂O)(PMe₂Ph)₃][ClO₄] in dichloromethane,



the yellow solution lightens in colour and the ammine complex trans,mer-[IrCl₂(NH₃)(PMe₂Ph)₃][ClO₄] 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 ${}^{31}P-{}^{1}H$ 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 NH₃ resonance (δ 2.31) in the ¹H NMR spectrum when a CDCl₃ solution was treated with a large excess of D_2O over hours; slow exchange occurred over several days. Any reversible loss of NH₃ or reversible deprotonation would have given the ND₃ complex. Addition of a large excess of MeI and a three-fold excess of dbu (1,8diazabicyclo[5.4.0]undec-7-ene) leads to the slow formation of the corresponding MeNH₂ complex over 5 d. Thus the rate of the reversible loss of H⁺ to give the neutral amido complex trans,mer-[IrCl₂(NH₂)(PMe₂Ph)₃] as an intermediate is very low and the rate of NH₃ dissociation from the cation is similarly very low or negligible.

Excellent quality crystals of the complex trans,mer-[IrCl₂-(NH₃)(PMe₂Ph)₃][ClO₄] 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) Å³] 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

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

Table 1 Proton and ³¹P-{¹H} NMR data for the compounds *trans,mer*-[IrCl₂L(PMe₂Ph)₃][ClO₄] (L = H₂O, NH₃ or PH₃) and *trans,mer*-[IrCl₂X(PMe₂Ph)₃] (X = PH₂ or SH)

	¹ H ⁴				³¹ P-{ ¹ H} ^b				
L or X H ₂ O ⁴	$\frac{\delta(\mathbf{P}^{\mathbf{A}}\mathbf{M}\mathbf{e}_{2}\mathbf{P}\mathbf{h})}{1.72}$ (t)	J(PH) ^c 8.1	$\frac{\delta(\mathbf{P}^{\mathbf{B}}\mathbf{M}\mathbf{e}_{2}\mathbf{P}\mathbf{h})}{1.35 (d)}$	² <i>J</i> (PH) 11.7	Others 5.7 (br) (H ₂ O)		δ(P^A) - 46.1	δ(P^B) - 30.9	² J(P ^A P ^B) 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 "	1.71 (t)	7.8	1.88 (dd)	9.3	3.06 (ddt) (PH ₃)	¹ J(PH) 381.0	- 51.0	- 50.2	29.8
PH ₂ ^f	1.79 (dt)	8.2	1.18 (d)	9.2	1.54 (dq) (PH ₂)	$^{1}J(PH)$ 176.2	- 49.4	- 53.4	20.3
SH	1.87 (t)	8.5	1.17 (d)	10.3	— 1.08 (dt) (SH)	$^{3}J(PH) 6.7, 1.0$	-49.8	-45.8	16.9
Cl	1.88 (t)	8.7	1.23 (3)	11.0					

^a Recorded in CDCl₃ 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 CDCl₃ at room temperature relative to 85% H₃PO₄; 162 MHz spectra. ^c $J(PH) = |^2J(PH) + {}^4J(PH)]$. ^d Proton NMR spectrum recorded at -50 °C. ^e Phosphorus-31 NMR spectrum: $\delta(P^C) - 121.5$, ${}^2J(P^CP^A) = 29.8$ and ${}^2J(P^CP^B) = 403.0$ Hz. ^f Phosphorus-31 NMR spectrum: $\delta(P^C) - 150.2$, ${}^2J(P^CP^A) = 7.0$ 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) Ir-P(2) Ir-P(3) Ir-N Ir-Cl(1) Ir-Cl(2) P(1)-C(1) P(1)-C(2)	2.302(5) 2.401(5) 2.398(5) 2.15(1) 2.375(5) 2.375(5) 1.83(2) 1.81(2)	P(1)-C(11) P(2)-C(3) P(2)-C(4) P(2)-C(21) P(3)-C(5) P(3)-C(6) P(3)-C(31)	1.85(2) 1.81(2) 1.82(2) 1.83(2) 1.82(2) 1.82(2) 1.81(2) 1.83(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 $trans,mer-[IrCl_2(NH_3)-(PMe_2Ph)_3][ClO_4]$

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 NH₃ ligands and the perchlorate ion (shortest N · · · O 3.30 Å), whereas there are two hydrogen bonds per H₂O ligand in the aqua analogue. Another difference is in the conformations adopted by the PMe₂Ph ligands. In the aqua complex the Ph groups of both PMe₂Ph ligands *cis* to co-ordinated H₂O are rotated away from the H₂O ligand, whereas in the ammine complex these are



Fig. 2 A comparison of the structures of the NH_3 (left) and H_2O (right) complexes of the type *trans,mer*-[IrCl₂L(PMe₂Ph)₃][ClO₄] with views along the *trans*-P(2)-Ir-P(3) directions showing the different conformations adopted by the PMe₂Ph ligands *cis* to L

adjacent and face-on to the NH₃ ligand. Fig. 2 shows the two structures for comparison. This difference might reflect the different intrinsic affinities of benzene for NH₃ versus H₂O, for example arenes are much more soluble in ammonia than in water. Also the more extensive hydrogen bonding to H₂O might require more space around this ligand which is increased when the Ph groups are turned away from the H₂O ligand. In both the H₂O and NH₃ complexes the conformation of the PMe₂Ph trans to H₂O or NH₃ is such that all three PMe₂Ph 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 PH₃ complex *trans,mer*-[IrCl₂(PH₃)(PMe₂Ph)₃][ClO₄] as pale yellow crystals by passing PH₃ gas into a solution of the aqua complex. This gave solvent-free crystals from dichloromethane-diethyl ether mixtures. The ¹H and ³¹P-{¹H} NMR spectra (Table 1) are consistent with a non-dynamic structure corresponding to that of the NH₃ complex. The PH₃ resonance in the ³¹P 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 PH₃ 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 ³¹P (proton-coupled) NMR spectroscopy a valuable predictive tool for assigning the nature of these phosphorus atoms.^{9,10} The PH₃ resonance in the ¹H NMR spectrum is a double double



Fig. 3 Phosphorus-31 NMR spectra of the PH₃ resonance of the complex *trans,mer*- $[IrCl_2(PH_3)(PMe_2Ph)_3][ClO_4]$ in CDCl₃ with (a) and without (b) ¹H decoupling



Fig. 4 Molecular structure of the complex trans,mer-[IrCl₂(PH₃)-(PMe₂Ph)₃][ClO₄]

triplet with ${}^{1}J(PH) = 381.0$ Hz which is considerably larger than for free PH₃ (182.2 Hz).¹¹ The HPH angle in free PH₃ is 93.7°,¹² consistent with considerably greater p than sp³ character for the P–H bonds and a correspondingly substantial s character for the lone pair. This is greatly modified on coordination 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 NH₃ complex, the PH₃ complex is readily deprotonated using dbu in ethanol. Of course, co-ordinated PH₃ is expected to be considerably more acidic than coordinated NH₃. 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*-[IrCl₂(PH₂)(PMe₂Ph)₃], was initially characterised by spectroscopy, both its ¹H and ³¹P NMR properties (Table 1) displaying profoundly different, but



Fig. 5 Phosphorus-31 NMR spectra of the PH₂ resonance of the complex *trans,mer*-[$IrCl_2(PH_2)(PMe_2Ph)_3$] in CDCl₃ with (*a*) and without (*b*) ¹H decoupling

Table 3 Selected bond lengths (Å) and angles (°) for the complex trans, mer-[IrCl₂(PH₃)(PMe₂Ph)₃][ClO₄]

Ir-P(1) Ir-P(2) Ir-P(3) Ir-P(4) Ir-Cl(1) Ir-Cl(2) P(1)-C(1) P(1)-C(2)	2.46(1) 2.398(5) 2.395(4) 2.25(1) 2.382(5) 2.384(5) 1.88(2) 1.78(3)	P(1)C(11) P(2)C(3) P(2)C(4) P(2)C(21) P(3)C(5) P(3)C(6) P(3)C(31)	1.87(2) 1.82(2) 1.88(2) 1.80(2) 1.84(2) 1.77(2) 1.79(2)
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)

distinctive, characteristics to those of the parent complex. The ¹H NMR PH₂ signal in CDCl₃ appears as a double quartet with the largest coupling constant being ${}^{1}J(PH) = 176.2$ Hz, much less than that for the PH₃ complex (381.0 Hz) and much closer to that for free PH₃ (182.2 Hz). There is ample precedence for such spectroscopic modifications. Both Ebsworth¹³ and Roper⁹ and their co-workers have reported similar reductions in the values of ${}^{1}J(PH)$ upon transformation of a co-ordinated phosphine [M-PR¹R²H] into its phosphido counterpart $[M-PR^{1}R^{2}]$. The ³¹P NMR spectrum in the PH₂ 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 ${}^{1}J(PH)$ is now similar to that in free PH₃ consistent with there being a lone pair with considerable s character. This in itself would be sufficient to characterise trans, mer-[IrCl₂(PH₂)(PMe₂Ph)₃] as containing a pyramidal rather than planar phosphido igands are Both planar ¹⁴ and pyramidal ¹⁵ terminal phosphido ligands are known, having electrophilic¹⁶ and nucleophilic¹⁷ 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 PH₂ complex described here should contain a pyramidal nucleophilic PH2 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-[IrCl₂(PH₂)-(PMe₂Ph)₃]

Table 4 Selected bond lengths (Å) and angles (°) for the complex trans, mer- $[IrCl_2(PH_2)(PMe_2Ph)_3]$

Ir-P(1)	2.378(3)	P(1)-C(11) P(2)-C(3) P(2)-C(4) P(2)-C(21)	1.833(9)
Ir-P(2)	2.370(3)		1.82(1)
Ir-P(3)	2.359(2)		1.83(1)
Ir-P(4)	2.440(3)		1.84(1)
Ir - Cl(1) Ir - Cl(2) P(1) - C(1) P(1) - C(2)	2.389(2) 2.396(3) 1.82(1) 1.82(1)	P(3)-C(5) P(3)-C(6) P(3)-C(31)	1.83(1) 1.83(1) 1.84(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)



Fig. 7 Projections showing the conformations of the PH₂ and SH ligands in the complexes *trans,mer*-[IrCl₂X(PMe₂Ph)₃] (X = PH₂ 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*-PMe₂Ph ligand. In the final cycles of refinement, the P–H, Ir–H and H–H distances in the IrPH₂ 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*-PMe₂Ph ligand as illustrated in Fig. 7. Each P atom has two substituents on one side and one on the



Fig. 8 Molecular structure of the complex *trans,mer*-[$IrCl_2(SH)$ -(PMe_2Ph_3]

Table 5 Selected bond lengths (Å) and angles (°) for the complex $trans,mer-[IrCl_2(SH)(PMe_2Ph)_3]$

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(6)	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)

other side of the approximate P_4 plane, alternating around the molecule. The large substituents (Ph in PMe₂Ph and the lone pair in PH₂) share one side of the P₄ plane with another substituent avoiding clashes with the *cis*-Cl ligands. Similar arrangements are found in related molecules such as *trans*-[IrCl₂(PMe₂Ph)₄][ClO₄]. The ³¹P-{¹H} NMR spectrum even at low temperatures (-60 °C) appears as an AB₂X pattern and the PH₂ protons appear equivalent in the ¹H NMR spectrum. Rapid rotation about the Ir-P bonds is occurring.

The most notable difference between the $\bar{P}H_2$ and PH_3 structures is in the Ir–P bond lengths. Those for the mutually *trans*-PMe₂Ph 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 PH₃ and 2.440(3) Å for PH₂, an increase of over 8% on deprotonation. The Ir–P distance *trans* to PH₃ is 2.46(1) Å and that *trans* to PH₂ is 2.378(3) Å. Thus PH₃ is more closely bonded to Ir and has a stronger *trans* influence than PH₂. The coupling constants of the PH₃ ligand to the other P nuclei, J = 29.8 (*cis*) and 403.0 (*trans*) Hz, decrease considerably on deprotonation to J = 7.0

	$L = NH_3$	$L = PH_3$	$X = PH_2$	X = SH
Formula	C ₂₄ H ₃₆ Cl ₃ IrNO ₄ P ₃	C24H36Cl3IrO4P4	C ₂₄ H ₃₅ Cl ₂ IrP ₄	C ₂₄ H ₃₄ Cl ₂ IrP ₃ S
M	794.07	811.03	710.57	710.65
Crystal size/mm	$0.37 \times 0.15 \times 0.18$	$0.35 \times 0.12 \times 0.25$	$0.70 \times 0.40 \times 0.06$	$0.42 \times 0.12 \times 0.04$
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	Pbn2,	$P2_1/c$	$P2_{1}/c$
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)
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.73	1.72	1.69	1.74
$\mu(Mo-K\alpha)/cm^{-1}$	48.0	47.4	51.8	53.5
F(000)	1568	1600	1400	1400
No. orientation reflections	26	33	29	30
20 Range for orientation reflections/°	8–23	11-26	11-29	11-24
Unique data	5119	2805	4897	4785
Rejection criterion	$I_{\rm o} \leq 3\sigma(I_{\rm o})$	$I_{o} \leq 2\sigma(I_{o})$	$I_{\rm o} \leq 2\sigma(I_{\rm o})$	$I_{o} \leq 3\sigma(I_{o})$
Reflections used in refinement	3113	2172	3942	3691
No. of parameters	325	201	288	274
R ^h	0.0595	0.0496	0.0443	0.0421
<i>R</i> ′ ^c	0.0559	0.0494	0.0418	0.0442
g°	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

Table 6 Crystal data and details of data collection, structure solution and refinement for the compounds *trans,mer*-[IrCl₂L(PMe₂Ph)₃][ClO₄] (L = NH₃ or PH₃) and *trans,mer*-[IrCl₂X(PMe₂Ph)₃] (X = PH₂ or SH)^{*a*}

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

'n

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CI

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*- $[IrCl_2L(PMe_2Ph)_3][ClO_4]$

Me

С

·Me

(*cis*) and 106.2 (*trans*) Hz. This reduction in ${}^{2}J(PP)$ is most likely indicative of the substantial reduction in the s character of the Ir-PH₂ bond compared with that of Ir-PH₃ 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)(PPh₃)₂]¹⁹ and [Re(C₅H₅)(NO)(PPh₂)(PPh₃)].²⁰ Both complexes exhibit similar M-PR₂ bond lengths [Os-PHPh 2.414(7), Re-PPh₂ 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*-[IrCl₂(H₂O)(PMe₂Ph)₃][ClO₄] with H₂S in methanol gave an immediate reaction and a precipitate of the deprotonated species *trans,mer*-[IrCl₂(SH)(PMe₂Ph)₃]. The ¹H NMR spectrum shows the SH resonance at $\delta - 1.08$ as a



^{Ne} Me

CI.

Me

Fig. 10 Structure of the cation found in crystals of *trans,mer*-[IrCl₂(PMe₂Ph)₄][ClO₄]; three different conformations were found in solution

double triplet showing coupling to all three ³¹P 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*-[IrCl₂(SH)(PMe₂-Ph)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 IrCl₂S plane. Therefore the conformations of the PH₂ 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*-[IrCl₂(H₂S)(PMe₂Ph)₃][ClO₄] either in the initial reaction of H₂S or by protonation of the SH complex. Therefore the acidities of the cationic species *trans,mer*-[IrCl₂L(PMe₂Ph)₃][ClO₄] (L = H₂O, H₂S, NH₃ or PH₃) are probably in the order H₂S > PH₃ > H₂O > NH₃ as expected. A neutral SH₂ complex of ruthenium(II) has been characterised recently by X-ray diffraction²³ but the cationic SH₂ complex of iridium(III) is likely to be too acidic for straightforward isolation.

z

5752

6883(5)

5678(4)

5839(4)

4721(5)

5830(5)

5701(5)

Atom x y	Ξ
Ir 1959(1) 6177(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) = 6015(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) -1138(20) 5740(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) -1567(20) 7395(11)	10 233(17)
C(14) -1 643(22) 6 974(10)	10 957(16)
C(15) - 621(22) - 6566(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) 5447(8)	6 954(13)
C(32) -1165(17) 5616(9)	5 950(12)
$C(33) \qquad -1\ 577(22) \qquad 5\ 162(11)$	5 192(15)
C(34) -1 644(23) 4 556(11)	5 431(20)
$C(35) \qquad -1 \ 327(26) \qquad 4 \ 405(8)$	6 455(18)
C(36) -941(22) 4843(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)

Table 7 Fractional atomic coordinates $(\times 10^4)$ for the complex trans,mer-[IrCl2(NH3)(PMe2Ph)3][ClO4]

Table 8 Fractional atomic coordinates $(\times 10^4)$ for the complex trans,mer-[IrCl₂(PH₃)(PMe₂Ph)₃][ClO₄]

3598(1)

3697(5)

4645(3)

2462(3)

3620(5)

4517(3)

2674(3)

	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)
、				

General Comments on the Structures.-Fig. 9 shows the four possible conformations of the PMe₂Ph ligands of which three (A–C) are found in the solid-state structures of *trans,mer*-[IrCl₂X(PMe₂Ph)₃] (X = H,²⁴ Cl,²⁵ SH or PH₂) and *trans,mer*-[IrCl₂L(PMe₂Ph)₃][ClO₄] (L = H₂O, NH₃ 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-[IrCl₂(PMe₂Ph)₄][ClO₄]²⁶ (Fig. 10) illustrates all four arrangements, A-D, depending upon which of the four non-equivalent PMe₂Ph 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-PMe₂Ph 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-PMe₂Ph lengths trans to X or L: in increasing order Ir-P = 2.249(3) (L = H₂O), 2.278(1), 2.282(1)(X = Cl), 2.296(2) (X = SH), 2.302(5) (L = NH₃), 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 PH₃.

Experimental

Atom

Ir P(1)

P(2) P(3)

P(4)

Cl(1)

Cl(2)

х 489(1)

358(9) -1397(6)

2161(5)

2589(5)

-1611(6)

787(11)

The aqua complex trans, mer-[IrCl₂(H₂O)(PMe₂Ph)₃][ClO₄] was synthesised from mer-[IrCl₃(PMe₂Ph)₃] as previously described.^{1,2} Gaseous PH₃ was either used as supplied by Aldrich or synthesised by treatment of zinc phosphide with aqueous acid.

Syntheses.—trans,mer-[IrCl₂(NH₃)(PMe₂Ph)₃][ClO₄]. 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 cm³) 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. C₂₄H₃₆Cl₃IrNO₄P₃ 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-[IrCl₂(PH₃)(PMe₂Ph)₃][BF₄]. 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 cm³). 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-[IrCl₂(PH₂)(PMe₂Ph)₃]

• .			
Atom	x	у	Ζ
lr	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. C₂₄H₃₆BCl₂F₄IrP₄ 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-[IrCl₂(PH₂)(PMe₂Ph)₃]. 1,8-Diazabicyclo[5.4.0]-undec-7-ene (dbu) (0.0616 cm³, 0.4 mmol) was added to a suspension of [IrCl₂(PH₃)(PMe₂Ph)₃][ClO₄] (0.2194 g, 0.27 mmol) in ethanol (3 cm³). 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 cm³). 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. C₂₄H₃₅Cl₂IrP₄ 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 PH₃ complex in methanol in the dark. Good quality crystals were deposited over several hours.

trans,mer-[IrCl₂(SH)(PMe₂Ph)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. C₂₄H₃₄Cl₂IrP₃S 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-[IrCl₂(SH)(PMe₂Ph)₃]

Atom	x	у	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-[IrCl₂L(PMe₂Ph)₃][ClO₄] ($L = NH_3$ or PH₃) and trans,mer-[IrCl₂X(PMe₂Ph)₃] (X = PH₂ 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-[IrCl₂(NH₃)(PMe₂Ph)₃][ClO₄]. 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 Å²). 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-[IrCl₂(PH₃)(PMe₂Ph)₃][ClO₄]. 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 Å²). 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-[IrCl₂(PH₂)(PMe₂Ph)₃]. All non-H atoms were

refined anisotropically and the H atoms of the PMe₂Ph ligands were included in idealised positions (C-H 0.96 Å, U 0.08 Å²). 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 PH₂ co-ordination are correct.

trans,mer-[IrCl₂(SH)(PMe₂Ph)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 Å²). 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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