Structure and Fluxional Behaviour of Some Aqua-complexes of Rhodium(III) and Iridium(III)†

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The single-crystal *X*-ray structure of *trans,mer*-$[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ confirms a structure based on ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectroscopy. The weakly bonded H_2O ligand is *trans* to PMe_2Ph, a ligand with a strong *trans* influence, and has a long Ir–O bond [2.189(6) Å] and a short Ir–P bond [2.249(3) Å] *trans* to it. The phosphine ligand site exchange, apparent in the n.m.r. spectra of this compound and its rhodium analogue, is a result of rate-determining H_2O dissociation to give the five-co-ordinate intermediates $[MCl_2(PMe_2Ph)_3]^+$ (M = Rh or Ir), which are probably square-pyramidal species undergoing rapid pseudo-rotation. The rates of PMe_2Ph exchange and the rates of exchange of free and co-ordinated H_2O are similar in each case but greater for Rh than Ir.

Clark and Reimer[1] prepared the aqua-complexes $[MCl_2(H_2O)(PMe_2Ph)_3][PF_6]$ (M = Rh or Ir) by treatment of *mer*-$[MCl_3(PMe_2Ph)_3]$ with $Ag[PF_6]$ in acetone, the chloride *trans* to PMe_2Ph being precipitated as AgCl. Even when the acetone contains very little water, water molecules co-ordinate preferentially unlike in other cases such as $[MH_2(Me_2CO)_2(PPh_3)_2]^+$ (M = Rh or Ir) where acetone readily co-ordinates.[2,3] We have prepared the perchlorate analogues similarly from $Ag[ClO_4]$ and describe here the *X*-ray structure of $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$. The ^1H n.m.r. (methyl) spectrum of $[RhCl_2(H_2O)(PMe_2Ph)_3]^+$ at room temperature has been misinterpreted as a virtual triplet (mutually *trans*-PMe_2Ph ligands) overlapping a doublet (PMe_2Ph *trans* to H_2O). Our re-examination of the spectra at different temperatures has shown that the room-temperature signal is a quartet resulting from coalescence and we describe here our studies on the mechanism of phosphine-site exchange based on kinetic, spectroscopic, and structural evidence. Some of our results have been communicated briefly.[4]

Results and Discussion

Structure of $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$.—The syntheses of the aqua-complexes $[MCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (M = Rh or Ir) are given in the Experimental section. The combination of a good *trans*-bond-weakening tertiary phosphine ligand and a weakly co-ordinated aqua-ligand *trans* to it should lead to a particularly substitution-labile aqua-ligand. This leads to rapid phosphine-site exchange (see later), but initially we wished to characterise structurally the aqua-complex and to establish any distortions from octahedral geometry. We chose to examine the iridium complex in view of the known structures of *mer*-$[IrCl_3(PMe_2Ph)_3]$[5] and $[IrH_2(Me_2CO)_2(PPh_3)_2][BF_4]$.[6]

The molecular structure of $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ is shown in Figure 1 with H atoms omitted, except those for H_2O, although all were located. Selected bond lengths and angles are given in Table 1 and fractional atomic co-ordinates in Table 2. The configuration is *trans, mer* as expected. The Ir–O(1) bond length of 2.189(6) Å is particularly long since a normal Ir–OH_2 distance is expected to be around 2.02 Å.[7] The Ir–O bond length is 2.28 Å in $[IrH_2(Me_2CO)_2(PPh_3)_2][BF_4]$ and a similar situation of a weakly co-ordinating ligand (acetone) *trans* to a good *trans*-influence ligand (hydride) prevails.[6] Related to the long Ir–O(1) length in $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ is the short Ir–P(1) bond length *trans* to it [2.249(3) Å], which is shorter by 0.13 Å than the average of the other two Ir–P bonds which are *trans* to each other. This difference is 0.08 Å in *mer*-$[IrCl_3(PMe_2Ph)_3]$,[5] and 0.16 Å (average) in $[RuCl_2(PPh_3)_3]$[8] for which there is no ligand *trans* to the unique phosphine. The H_2O ligand has a weaker *trans* influence than Cl and it could be said that PMe_2Ph exerts a stronger *trans* influence on an aqua- than a chloro-ligand. The ligands *cis* to H_2O are all distorted towards it, the phosphines somewhat more than the chloro-ligands: angle O(1)–Ir–P(2) 85.2(2) and O(1)–Ir–P(3) 84.9(2)°, while O(1)–Ir–Cl(1) 86.7(2) and O(1)–Ir–Cl(2) 86.9(2)°. This might represent motion from an idealised octahedral geometry to that of the five-co-ordinate species having the water molecule dissociated.

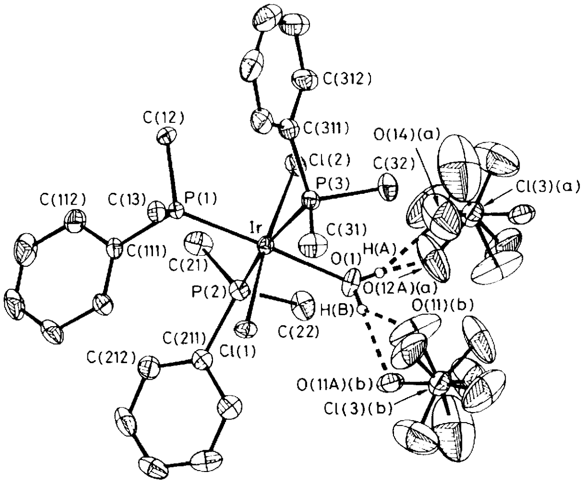

Figure 1. Molecular structure of $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ showing hydrogen bonding between co-ordinated H_2O and perchlorate ions which are disordered. Symmetry operations relating designated atoms to reference atoms at (x,y,z): (a) x, $1.0 + y$, z; (b) $-x$, $-y$, $1.0 - z$

Figure 1 shows that the water ligand is hydrogen-bonded to perchlorate. The $[ClO_4]^-$ ions are disordered with oxygen atoms located at the vertices of a cube about the Cl atoms. There

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† *Supplementary data available* (No. SUP 56637, 6 pp.): thermal parameters, H-atom co-ordinates and bond parameters, non-bonded distances. See Instructions for Authors, *J. Chem. Soc. Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Selected distances (Å) and angles (°) for $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$

Cl(1)–Ir	2.353(3)	Cl(2)–Ir	2.361(3)
P(1)–Ir	2.249(3)	P(2)–Ir	2.366(3)
P(3)–Ir	2.392(3)	O(1)–Ir	2.189(6)
C(111)–P(1)	1.819(7)	C(12)–P(1)	1.805(8)
C(13)–P(1)	1.809(7)	C(211)–P(2)	1.820(7)
C(21)–P(2)	1.814(9)	C(22)–P(2)	1.808(8)
C(311)–P(3)	1.822(8)	C(31)–P(3)	1.802(9)
C(32)–P(3)	1.836(9)	H(A)–O(1)	0.79(7)
H(B)–O(1)	0.83(7)		
O(1)–O(11A)(b)*	2.66	O(1)–O(12A)(a)	2.78
O(1)–O(14)(a)	2.85	O(1)–O(11)(b)	2.89
H(B)–O(11A)(b)	1.89	H(A)–O(12A)(a)	2.03
H(A)–O(14)(a)	2.10	H(B)–O(11)(b)	2.18
Cl(2)–Ir–Cl(1)	173.5(1)	P(1)–Ir–Cl(1)	91.4(1)
P(1)–Ir–Cl(2)	95.0(1)	P(2)–Ir–Cl(1)	93.5(1)
P(2)–Ir–Cl(2)	86.9(1)	P(3)–Ir–Cl(1)	90.8(1)
P(3)–Ir–Cl(2)	87.7(1)	P(2)–Ir–P(1)	94.6(1)
P(3)–Ir–P(1)	95.5(1)	P(3)–Ir–P(2)	168.9(1)
O(1)–Ir–Cl(1)	86.7(2)	O(1)–Ir–Cl(2)	86.9(2)
O(1)–Ir–P(1)	178.0(1)	O(1)–Ir–P(2)	85.2(2)
O(1)–Ir–P(3)	84.9(2)	C(111)–P(1)–Ir	118.2(3)
C(12)–P(1)–Ir	114.2(3)	C(13)–P(1)–Ir	113.4(3)
C(12)–P(1)–C(111)	104.8(4)	C(13)–P(1)–C(111)	100.1(4)
C(13)–P(1)–C(12)	104.4(4)	C(211)–P(2)–Ir	121.6(3)
C(21)–P(2)–Ir	114.5(3)	C(22)–P(2)–Ir	109.9(4)
C(21)–P(2)–C(211)	105.4(4)	C(22)–P(2)–C(211)	100.9(4)
C(22)–P(2)–C(21)	102.1(5)	C(311)–P(3)–Ir	122.2(3)
C(31)–P(3)–Ir	114.2(3)	C(32)–P(3)–Ir	109.9(4)
C(31)–P(3)–C(311)	104.8(4)	C(32)–P(3)–C(311)	100.8(4)
C(32)–P(3)–C(31)	102.5(5)		

* Symmetry operations as in Figure 1.

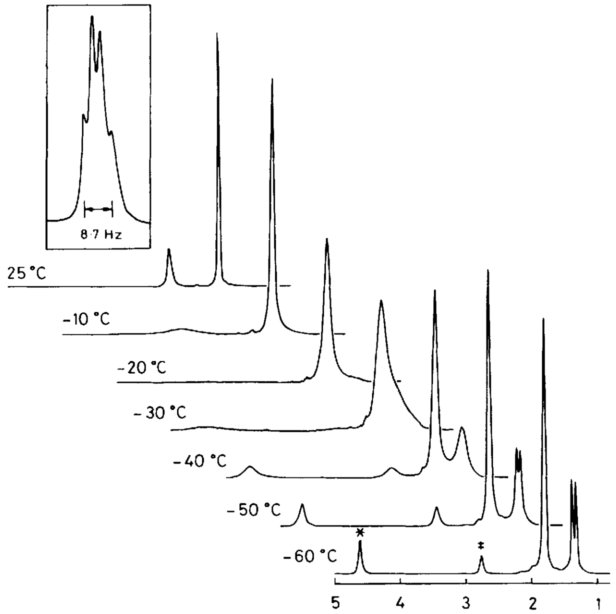

Figure 2. Proton n.m.r. spectra of $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$. The expanded spectrum in the box is that of the PMe_2Ph signals after coalescence at 25 °C (* co-ordinated H_2O; ‡ free H_2O)

is a 67% occupancy of one tetrahedral set of positions and a 33% occupancy of the remaining four vertices of the cube of oxygen atoms. Each H_2O ligand forms a hydrogen bond to one oxygen atom of each disorder orientation of each of the two neighbouring ClO_4 anions so that four such bonds are shown in Figure 1 for the two disordered orientations. The four shortest $O(1)–OClO_3$ distances are 2.66, 2.78, 2.85, and 2.89 Å, all in the range normally expected for unsymmetrical hydrogen bonds. The corresponding $H–OClO_3$ contacts in the hydrogen bonds are 1.89, 2.03, 2.10, and 2.18 Å. It is possible that these hydrogen bonds assist the high *trans*-influence phosphine in weakening the $Ir–OH_2$ bond. Possibly they also exist in ion pairs in solution and assist the labilisation of the H_2O ligand (see next section).

Kinetics and Mechanism of the Fluxional Behaviour.—The ^1H n.m.r. spectrum (methyl region) of $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ in $CDCl_3$ at 25 °C is a 1:3:3:1 quartet (δ 1.68, apparent *J* 2.9 Hz) which results from coalescence of a virtual triplet (δ 1.78, apparent *J ca.* 4 Hz) for the *trans* phosphines and a doublet (δ 1.32, *J* 12.1 Hz) for the unique phosphine, which are clearly resolved at −60 °C (Figure 2). The coalescence temperature is around −35 °C. The coalesced quartet was previously thought to be a triplet overlapping a doublet.[1] Virtual coupling and spin–spin correlation within the RhP_3 group are maintained

Table 2. Fractional atomic co-ordinates (× 10^4) for $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir	1 790(1)	2 402(1)	3 868(1)	C(216)	4 441(6)	2 852(6)	5 288(3)
Cl(1)	2 204(1)	1 230(1)	4 754(1)	C(21)	4 169(6)	3 756(6)	3 389(4)
Cl(2)	1 265(1)	3 709(1)	3 053(1)	C(22)	3 224(7)	4 795(5)	4 383(4)
P(1)	2 494(1)	1 135(1)	3 242(1)	C(311)	−726(4)	1 134(5)	2 945(3)
P(2)	3 500(1)	3 418(1)	4 081(1)	C(312)	−1 045(5)	1 855(7)	2 443(3)
P(3)	−106(1)	1 708(1)	3 700(1)	C(313)	−1 637(7)	1 461(13)	1 882(4)
O(1)	1 129(4)	3 601(4)	4 506(2)	C(314)	−1 896(7)	352(13)	1 815(5)
C(111)	4 005(4)	857(4)	3 368(3)	C(315)	−1 587(7)	−361(11)	2 301(6)
C(112)	4 684(6)	994(6)	2 895(4)	C(316)	−1 009(5)	7(7)	2 866(4)
C(113)	5 804(7)	664(8)	2 989(5)	C(31)	−430(6)	693(7)	4 276(4)
C(114)	6 247(6)	190(7)	3 547(5)	C(32)	−1 101(6)	2 849(7)	3 803(4)
C(115)	5 596(5)	47(6)	4 019(4)	Cl(3)	49(2)	−3 271(2)	4 031(1)
C(116)	4 475(5)	389(5)	3 931(3)	O(11)	359(18)	−2 796(15)	4 626(5)
C(12)	2 186(6)	1 435(6)	2 410(3)	O(12)	1 027(10)	−3 119(16)	3 734(6)
C(13)	1 954(5)	−269(5)	3 325(3)	O(13)	−614(14)	−2 728(12)	3 533(7)
C(211)	4 639(4)	2 994(4)	4 669(3)	O(14)	−77(16)	−4 436(7)	4 049(10)
C(212)	5 715(5)	2 723(5)	4 529(3)	O(11A)	−1 029(8)	−3 291(18)	4 268(6)
C(213)	6 563(6)	2 452(6)	5 003(5)	O(12A)	734(18)	−4 104(14)	4 387(12)
C(214)	6 369(7)	2 387(5)	5 607(4)	O(13A)	374(28)	−2 298(13)	4 391(11)
C(215)	5 303(8)	2 593(6)	5 755(4)	O(14A)	−600(28)	−3 977(37)	3 590(20)

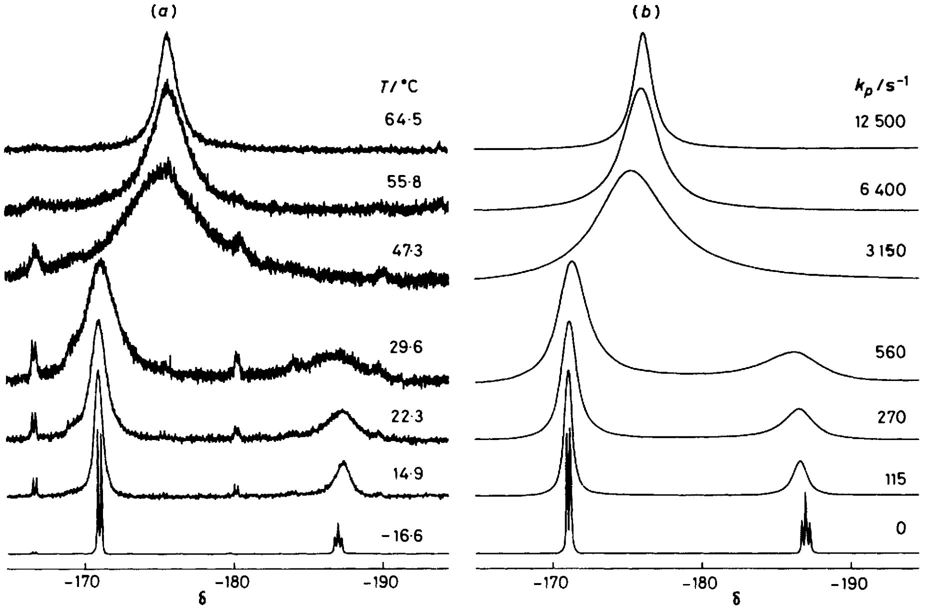

Figure 3. The $^{31}P-\{^1H\}$ n.m.r. spectra of $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (*a*) and those simulated (*b*) using the program DNMR3.[9] Weak absorptions have not been assigned but appear to be due to a species in equilibrium with the main species and coalesce at the highest temperatures examined

above coalescence and the apparent J for the coalesced quartet is 3.1 Hz when calculated from the low-temperature spectrum. Variable-temperature $^{31}P-\{^1H\}$ n.m.r. spectra for CH_2Cl_2 solutions of $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ also demonstrate phosphine-site exchange (see spectra illustrated in ref. 4). At −80 °C the expected AMX_2 spectrum is observed; J(RhP) for the unique phosphine (119.6 Hz) is greater than for the other two (83.4 Hz) as expected from the crystal structure of the iridium analogue. Coalescence occurs to give an A_3M spectrum at 20 °C. The observed value of J(RhP) above coalescence (95.7 Hz) compares with 95.5 Hz calculated from the low-temperature spectrum. We conclude that phosphine-site exchange occurs without phosphine dissociation. Furthermore separate ^1H n.m.r. signals for co-ordinated (δ 4.56) and free water (δ 2.73) were observed at −60 °C and these also coalesce at about −30 °C so that phosphine and water exchange have rather similar rates.

Table 3. Rates of phosphine-site exchange for $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (CH_2Cl_2 solution) and for $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (CH_2ClCH_2Cl solution) from $^{31}P-\{^1H\}$ spectra

Metal	T/°C	$10^{-2}k_p$*/s^{-1}
Rh	30.7	950 ± 80
	16.8	380 ± 40
	7.0	140 ± 20
	−32.6	2.75 ± 0.25
Ir	64.5	125 ± 5
	55.8	64 ± 3
	47.3	31.5 ± 1.5
	29.6	5.6 ± 0.3
	22.3	2.7 ± 0.15
	14.9	1.15 ± 0.1

* The rate at which the PMe_2Ph ligand *trans* to H_2O moves into either of the other two sites.

Similar behaviour is observed for the ^1H and $^{31}P-\{^1H\}$ n.m.r. spectra of $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ except that the coalescence temperatures are around 50 °C higher (+25 °C, ^1H n.m.r. methyl signals, $CDCl_3$) which is expected since rhodium compounds are more labile than iridium ones generally, substitution and fluxional reactions both occurring more rapidly.

The lineshapes of the $^{31}P-\{^1H\}$ n.m.r. spectra for $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (CH_2Cl_2 solution) and $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (1,2-dichloroethane solution) have been simulated (program DNMR3);[9] see Figure 3 for example. Derived rate data and activation parameters are given in Tables 3 and 4. To compare fully the rates of water exchange in $[MCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ with the rates of phosphine exchange, a complete lineshape analysis for the coalescence of the signals of free and co-ordinated water would be needed. The broadness of these signals and the variation of chemical shift with temperature have made this difficult so we have used

Table 4. Data for phosphine and H_2O exchange for $[MCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ for M = Rh (CH_2Cl_2 or CD_2Cl_2 solution) or for M = Ir (CH_2ClCH_2Cl or CD_2ClCD_2Cl solution)

M	k_p(30 °C)/s^{-1}	ln A	E_a/kJ mol^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
Rh	95 000	34	56 ± 4	55 ± 4	30 ± 13
Ir	560	38	77 ± 3	74 ± 3	52 ± 10

M	T/°C	k_H(^1H n.m.r.)/s^{-1}	k_P(^{31}P n.m.r.)/s^{-1}
Rh	−40	900[a]	125[b]
Ir	+20	800[c]	270[d]

[a] In CD_2Cl_2 solution. [b] In CH_2Cl_2 solution; estimated from data in Table 3. [c] In CD_2ClCD_2Cl solution. [d] In CH_2ClCH_2Cl solution; estimated from data in Table 3.

estimated rates at the coalescence temperatures (Table 4). The rate constant k_P is the rate at which one phosphorus nucleus moves into one of the other two sites and is the same for all nuclei, while k_H is the rate of exchange of free and co-ordinated water molecules.

Dissociation of a H_2O ligand to give a trigonal bipyramidal (t.b.p.) intermediate with three equivalent equatorial phosphines followed by a re-co-ordination of H_2O at any one of the three equivalent equatorial edges would lead to the possibility of phosphine-site exchange each time H_2O dissociates. For statistical reasons this would give $k_H = 3k_p$. Within experimental error this is what we observe. However, this would also apply if water dissociation gave a square pyramidal (s.p.) intermediate with minimum re-organisation of other ligands and if the rate of exchange of s.p. and t.b.p. forms (pseudo-rotation) were high. Our results do not distinguish these possibilities but we can rule out a s.p. intermediate with slow s.p.–t.b.p. rearrangement and also a fast proton exchange without M–O cleavage such as given by an equilibrium between $[MCl_2(H_2O)(PMe_2Ph)_3]^+$ and $[MCl_2(OH)(PMe_2Ph)_3]$. Either of these would give $k_H > 3k_p$. In the latter case of proton exchange there would be no obvious reason for the rate differences between Rh and Ir.

Although our results do not distinguish a t.b.p. intermediate from a s.p. one which is rapidly fluxional, we favour the s.p. form since this is the favourable geometry for five-co-ordinate d^6 metals. Five-co-ordinate iridium(III) compounds are believed to be s.p.[10,11] and $[RuCl_2(PPh_3)_3]$,[8] which is isoelectronic with $[RhCl_2(PPh_3)_3]^+$, has a s.p. geometry rather like that of $[IrCl_2(H_2O)(PMe_2Ph)_3]^+$ with H_2O removed and with the *trans*-chlorides and *trans*-PMe_2Ph ligands forming the basal set of ligands displaced more towards the vacant site. The complexes $[RuCl_2(PPh_3)_3]$ and $[OsCl_2(PPh_3)_3]$ are rapidly fluxional.[12] The ruthenium compound undergoes phosphine-site exchange with the rate 5 700 s^{-1} at −33.5 °C. Certainly pseudo-rotation in $[RhCl_2(PMe_2Ph)_3]^+$ might be similarly rapid and a rate >275 s^{-1} at −32.6 °C would lead to multiple pseudo-rotations each time a water ligand dissociated from an aqua-precursor. Thus a rapidly fluxional s.p. intermediate is most likely involved.

The positive $\Delta S^\ddagger$ values for phosphine exchange are consistent with a *D* mechanism; the $\Delta S^\ddagger$ values for pseudo-rotation in $[MCl_2(PPh_3)_3]$ (M = Ru or Os) are much closer to zero.[12] The major reason for the higher rates for Rh than Ir (*ca.* 170 times faster at 30 °C) is the bigger value for $\Delta H^\ddagger$ (by 20 kJ mol^{-1}) for Ir which probably reflects the differences between the Rh–O and Ir–O bond strengths. The acetone complexes $[MH_2(Me_2CO)_2(PPh_3)_2]^+$ show a similar difference in $\Delta H^\ddagger$ between Rh and Ir and also positive $\Delta S^\ddagger$ values consistent with a dissociative mechanism. The most obvious contrast is that between the rates of water exchange in $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ and in a 'classical' complex such as $[Rh(NH_3)_5(H_2O)]^{3+}$ for which exchange is *ca.* 10^{10} times slower.[13]

Experimental

The compounds *mer*-$[RhCl_3(PMe_2Ph)_3]$[14] and *mer*-$[IrCl_3(PMe_2Ph)_3]$[15] were prepared from rhodium trichloride or chloroiridic acid as reported earlier. The synthetic methods for the chlorate(VII) salts were based on those reported for $[MCl_2(H_2O)(PMe_2Ph)_3][PF_6]$ (M = Rh or Ir).[1]

Preparation of trans,mer-$[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$.—A suspension of *mer*-$[RhCl_3(PMe_2Ph)_3]$ (0.196 g) and $Ag[ClO_4]$ (0.068 g) in acetone (20 cm^3) was shaken for 40 min. The white precipitate of AgCl was filtered off and the orange filtrate evaporated to dryness under reduced pressure. The residue was recrystallised by dissolving in dichloromethane and precipitating with diethyl ether as orange needles (0.146 g) (Found: C, 40.5; H, 4.9; Cl, 15.5. $C_{24}H_{35}Cl_3O_5P_3Rh$ requires C, 40.85; H, 5.0; Cl, 15.1%).

Preparation of trans,mer-$[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$.—A suspension of *mer*-$[IrCl_3(PMe_2Ph)_3]$ (0.620 g) and $Ag[ClO_4]$ (0.181 g) in acetone (20 cm^3) was shaken for 20 min and the precipitated AgCl removed by filtration to give a clear yellow solution. Yellow needles of the product (0.456 g) were obtained as above (Found: C, 36.3; H, 4.4; Cl, 13.8. $C_{24}H_{35}Cl_3IrO_5P_3$ requires C, 36.3; H, 4.4; Cl, 13.4%).

N.M.R. and Kinetic Studies.—The line shapes of ^{31}P-$\{^1H\}$ n.m.r. spectra for $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ in dichloromethane solution and for $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ in 1,2-dichloroethane solution were simulated using the program DNMR3.[9] Temperatures were measured by measuring the difference in chemical shift (Δδ) between triphenylphosphine (0.1 mol dm^{-3}) and triphenylphosphine oxide (0.1 mol dm^{-3}) in dry $[^2H_8]$toluene; the temperature T is given by $T/°C = -30.929\ (\Delta\delta/\text{p.p.m.}) + 937.244$.[16] The temperatures were measured at the same time as the spectra by placing the thermometric solution in a 5-mm tube inside the 10-mm n.m.r. tube containing the solution studied. The kinetics of exchange of free and co-ordinated water were not studied so thoroughly because of the intrinsic broadness of the lines and the variation of chemical shift with temperature. The rates at the coalescence temperatures have been estimated from the equation $k/\text{s}^{-1} = \pi(\Delta\nu/\text{Hz})/1.414$, the intensities of the ^1H n.m.r. signals for free and co-ordinated water being equal. The temperatures were measured by using the difference of the two ^1H chemical shifts of methanol for which the variation with temperature is known.[17]

Crystal Structure of $[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$.—Good single crystals were obtained by layering diethyl ether on to a dichloromethane solution of the aqua-complex in a 5-mm tube and leaving the solvents to diffuse over several days at room temperature. The specimen used for the *X*-ray work was mounted on a fibre. Unit-cell parameters were obtained by refinement of diffractometer setting angles.

Crystal data. $C_{24}H_{35}Cl_3IrO_5P_3$, $M = 795.02$, monoclinic, $a = 11.930(4)$, $b = 11.910(2)$, $c = 21.376(4)$ Å, $\beta = 97.30(2)°$, $U = 3\,012.62$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.75$ g cm^{-3}, $F(000) = 1\,584$, $\mu(\text{Mo-}K_\alpha) = 46.78$ cm^{-1}, $\lambda = 0.710\,69$ Å. Of 5 292 unique reflections measured, 4 233 were considered observed $[I > 1.5\sigma(I)]$; $R = 0.0263$, $R' = [\Sigma(w\Delta)^2/\Delta w F_o^2]^{\frac{1}{2}} = 0.0322$, where $w = 1/[\sigma^2(F_o) + 0.000\,25\ F_o^2]$.

Solution and refinement of the structure. Intensity data were recorded on a Nonius CAD-4 diffractometer to $\theta_{\text{max.}} = 25°$ (Mo-K_α radiation) using an ω—2θ scan technique as described in a previous publication.[18] The structure was solved *via* the heavy-atom method. Refinement was carried out by full-matrix least-squares methods[19] with anisotropic thermal parameters for non-hydrogen atoms. Empirical absorption corrections were applied together with an additional correction using DIFABS.[20] All hydrogen atoms were located from Fourier difference maps and refined freely with individual isotropic thermal parameters except those of the methyl groups which were assigned group thermal parameters. Two sets of four peaks with tetrahedral geometry were visible around the chlorine atom of the perchlorate anion at distances corresponding to Cl–O bonds. Refinement indicated occupancies of 0.67 and 0.33 for the two sets of four oxygen atoms.

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