Octahedral and Trigonal-bipyramidal Complexes of Ruthenium(II) with Bidentate Phosphine Ligands

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Six- and five-co-ordinate complexes of ruthenium(II) with the unsymmetrical diphosphine ligand $Ph_2P(CH_2)_3PMe_2$ have been prepared. Phosphorus-31 n.m.r. spectroscopy indicates that octahedral complexes $[RuCl_2(P{-}P)_2]$, $[RuH(Cl)(P{-}P)_2]$, and $[RuH(CO)(P{-}P)_2]ClO_4$ (P−P = diphosphine ligand) have the all-*trans* arrangement with Me_2P *trans* to Me_2P and Ph_2P *trans* to Ph_2P. The five-co-ordinate complexes $[RuX(P{-}P)_2]BPh_4$, where X = Cl or H, are not fluxional at room temperature and have a trigonal-bipyramidal structure with axial PMe_2 groups and equatorial PPh_2 groups. Similar structures are proposed for analogous complexes of $Ph_2P(CH_2)_3PMePh$ and of $Ph_2P(CH_2)_3PPh_2$.

Relatively little work has been reported on complexes of ruthenium(II) with bidentate phosphine ligands having more than two carbon atoms in the chain forming the ligand backbone. This is surprising in view of the well known tendency for bidentate phosphines to produce five-co-ordinate complexes [1] and the considerable interest in several ruthenium(II) complexes with the simple unidentate ligand triphenylphosphine. The easily prepared compounds $[RuCl_2(PPh_3)_3]$ [2] and $[RuH(Cl)(PPh_3)_3]$ [3] have co-ordination numbers of five, most unusual for a d^6 metal ion, and they display powerful homogeneous catalytic activity in alkene hydrogenation and hydroformylation.[4] Both have been the subject of careful *X*-ray crystallographic studies [5,6] which showed the stereochemistries to be square pyramidal in the solid state. The low-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra have also been interpreted in terms of this stereochemistry in solution.[7] Indeed this stereochemistry has been predicted theoretically to be more stable than trigonal bipyramidal for a five-co-ordinate d^6 ion, and the opposite for a d^8 ion.[8]

Ruthenium(II) complexes with bidentate phosphines were first investigated in 1961 by Chatt and Hayter,[9–11] and octahedral complexes were isolated, *e.g.* *cis*- and/or *trans*-$[RuCl_2\{R_2P(CH_2)_2PR_2\}_2]$ where R = Me, Et, or Ph. In 1975 using the ligand $Ph_2P(CH_2)_3PPh_2$, similar octahedral complexes were obtained,[12–14] and also the first examples of five-co-ordinate complexes of ruthenium(II) with bidentate ligands. The $[RuX\{Ph_2P(CH_2)_3PPh_2\}_2]^+$ species where X = Cl or Br were readily isolated as PF_6^- salts, and assigned square-pyramidal geometries on the basis of the observed diamagnetism and the ready addition of CO to give *trans*-$[RuX(CO)\{Ph_2P(CH_2)_3PPh_2\}_2]^+$.[12]

We wished to investigate five-co-ordinate ruthenium(II) complexes of bidentate ligands more thoroughly in view of (*a*) the potential catalytic applications associated with co-ordinative unsaturation at ruthenium, (*b*) the scarcity of examples of five-co-ordinate complexes of d^6 metal ions, (*c*) the uncertainty as to whether the $[RuX\{Ph_2P(CH_2)_3PPh_2\}_2]^+$ species have square-pyramidal or trigonal-bipyramidal geometry, and (*d*) the implications for discussion of the S_N1 dissociation step in ligand-substitution reactions of octahedral complexes of d^6 metal ions. As well as the symmetrical ligand $Ph_2P(CH_2)_3PPh_2$, we used the unsymmetrical analogues $Ph_2P(CH_2)_3PMePh$ and $Ph_2P(CH_2)_3PMe_2$. Complexes of the last are ideally suited to study by ^{31}P n.m.r. spectroscopy, since signals from the non-equivalent phosphorus nuclei enable the many possible isomeric structures of octahedral $[RuX(Y)(P{-}P)_2]$ and five-co-ordinate $[RuX(P{-}P)_2]^+$ (P−P = diphosphine ligand) species to be distinguished.

We now report that octahedral complexes such as $[RuCl_2\{Ph_2P(CH_2)_3PMe_2\}_2]$ are non-fluxional at room temperature and are obtained as a single isomer with PMe_2 *trans* to PMe_2 and PPh_2 *trans* to PPh_2, and that halide dissociation produces five-co-ordinate species which also are non-fluxional and consist of a single isomer which is trigonal bipyramidal, not square pyramidal as previously reported.

Results and Discussion

Octahedral Complexes.—(*a*) *Preparations.* Complexes of the type $[RuCl_2(P{-}P)_2]$ have previously been prepared from reactions of either ruthenium trichloride [9] or $K_2[RuCl_5(H_2O)]$ [12] with an excess of diphosphine in ethanol or from $[RuCl_2(PPh_3)_3]$ with diphosphine in benzene [12] or acetone.[14] With our unsymmetrical diphosphines the products were very soluble in these solvents and the most convenient preparative route consisted of refluxing $[RuCl_2(PPh_3)_3]$ with the diphosphine in n-hexane to give *trans*-$[RuCl_2(P{-}P)_2]$ in >80% yield [Table, compounds (1)—(3)] as air-stable orange-yellow microcrystalline solids.

Attempts to prepare *cis*-$[RuCl_2\{Ph_2P(CH_2)_3PPh_2\}_2]$ either by thermal isomerisation [15] of the *trans* isomer (refluxed in chlorobenzene for 4 h) or by reaction of $[RuCl\{Ph_2P(CH_2)_3PPh_2\}_2]BPh_4$ with an excess of LiCl in boiling ethanol failed, starting material being recovered in each case.

Complexes of the type *trans*-$[RuH(Cl)(P{-}P)_2]$ were obtained by refluxing $[RuCl_2(PPh_3)_3]$ with the diphosphine in 2-methoxyethanol under hydrogen in the presence of trimethylamine. The products [Table, compounds (4)—(6)] were obtained in 67—78% yields as apparently air-stable pale yellow crystalline solids showing ν(RuH) close to 2 000 cm^{-1}. This type of complex has been previously prepared by reaction of $[RuH(Cl)(PPh_3)_3]\cdot dma$ with $Ph_2P(CH_2)_nPPh_2$ (n = 2—4) [13] (dma = *N*,*N*-dimethylacetamide).

The white complex $[RuH(CO)\{Ph_2P(CH_2)_3PMe_2\}_2]ClO_4$ (7) (Table) was obtained from $[RuH(Cl)(CO)(PPh_3)_3]$ and $Ph_2P(CH_2)_3PMe_2$ with $LiClO_4$ in ethanol. This synthesis failed with the other two diphosphines.

(*b*) *Structures.* For the complex $[RuCl_2\{Ph_2P(CH_2)_3PPh_2\}_2]$ a *trans* arrangement of the two chlorine atoms was assigned by Bressan and Rigo [12] on the basis of the i.r. spectrum [ν(RuCl) 315 cm^{-1}] and by Mason *et al.*[14] on the basis of the ^{31}P n.m.r. signal (singlet at δ = 145.2 p.p.m. relative to trimethyl phosphite). For complexes of our unsymmetrical diphosphines, eight isomers are possible for $[RuCl_2(P{-}P)_2]$. The complexes were characterised by visible and ^{31}P n.m.r.

Table. Analytical and spectroscopic data for the ruthenium(II) complexes

Complex	Colour	Yield (%)	M.p. (°C)	Analysis (%) [a]	$\nu_{max.}$[b]/cm^{-1}	I.r.[c] (cm^{-1})	$\delta(^{31}P)$[d]/p.p.m.	J(PP)/ Hz
(1) *trans*-$[RuCl_2\{Ph_2P(CH_2)_3PPh_2\}_2]$	Pale orange	90	196	C 64.9 (64.5) H 5.1 (5.0)	21 000 (388),[e] 26 000 (sh)	—	−4.84	—
(2) *trans*-$[RuCl_2\{Ph_2P(CH_2)_3PMePh\}_2]$	Pale orange	81	230	C 60.6 (60.6) H 5.3 (5.5) Cl 8.3 (8.1) P 13.9 (14.2)	21 600 (166)		Complex m,[f] −4.57 to −7.72	
(3) *trans*-$[RuCl_2\{Ph_2P(CH_2)_3PMe_2\}_2]$	Yellow	98	212	C 54.8 (54.5) H 5.9 (6.0) Cl 9.4 (9.5)	21 900 (90)		−3.37 (PPh_2) −9.76 (PMe_2)	38
(4) *trans*-$[RuH(Cl)\{Ph_2P(CH_2)_3PPh_2\}_2]$	Pale yellow	78	205	C 68.0 (68.2) H 5.1 (5.4)		ν(RuH) 2 000 [g]	+15.07 [h]	
(5) *trans*-$[RuH(Cl)\{Ph_2P(CH_2)_3PMePh\}_2]$	Pale yellow	73	222	C 62.7 (63.0) H 6.2 (5.9) Cl 4.0 (4.2) P 14.4 (14.8)		ν(RuH) 2 012	Complex m,[f] +27.32 to +0.09	
(6) *trans*-$[RuH(Cl)\{Ph_2P(CH_2)_3PMe_2\}_2]$	Yellow	67	245	C 57.0 (57.2) H 6.1 (6.4)		ν(RuH) 2 020	+38.46 (PPh_2) −16.09 (PMe_2)	38
(7) *trans*-$[RuH(CO)\{Ph_2P(CH_2)_3PMe_2\}_2]ClO_4$	White	33	196	C 51.8 (52.1) H 5.6 (5.6)		ν(CO) 1 990	+25.35 (PPh_2) −16.33 (PMe_2)	38
(8) $[RuCl\{Ph_2P(CH_2)_3PPh_2\}_2]BPh_4$	Brown	86	236	C 73.5 (73.2) H 5.8 (5.7)	18 200 (640), [i] 22 400 (2 030), 28 000 (sh)		+45.72 +2.95	32
(9) $[RuCl\{Ph_2P(CH_2)_3PMePh\}_2]ClO_4$	Red-brown	72	181	C 56.5 (56.4) H 5.0 (5.1) Cl 7.8 (7.6) P 13.3 (13.2)	19 100 (374), 23 100 (1 240)		Complex m,[f] around −5.0	
(10) $[RuCl\{Ph_2P(CH_2)_3PMe_2\}_2]BPh_4$	Red-brown	66	162	C 67.8 (67.5) H 6.2 (6.2) Cl 3.0 (3.4)	19 500 (226), 23 800 (sh)		+35.70 −18.89	38
(11) $[RuH\{Ph_2P(CH_2)_3PMe_2\}_2]BPh_4$	Red-brown	73	188	C 75.9 (75.7) H 5.3 (5.2)	19 700 (468), 23 300 (1 180)	ν(RuH) 2 070	+47.53 −7.43	34

[a] Calculated values in parentheses. [b] In dichloromethane solution; ε/dm^3 mol^{-1} cm^{-1} in parentheses. [c] Nujol mull. [d] In $CDCl_3$ except for complex (8) in $(CD_3)_2SO$ solution, relative to 85% H_3PO_4 external standard (+ p.p.m. is downfield). [e] Lit.,[13] 20 900 (355) and 26 000 (sh) cm^{-1}. [f] The PMePh group is chiral at phosphorus, and the complex consists of a mixture of several isomers, complicating the ^{31}P n.m.r. splitting pattern. [g] Lit.,[14] 2 000 cm^{-1}. [h] Lit.,[14] 15.59 p.p.m. [i] Lit.,[13] 18 200 (640), 22 300 (2 440), and 28 000 (sh) cm^{-1}.

spectroscopy, which showed that the all-*trans* arrangement [Figure 1(*a*)] was the only isomer present.

Sullivan and Meyer [15] have shown that the visible spectra of the *cis* and *trans* isomers of $[RuCl_2(Ph_2PCH_2PPh_2)_2]$ are quite characteristic with the lowest-energy band at 24 000 and 20 600 cm^{-1}, respectively. The data for our $[RuCl_2(P\text{-}P)_2]$ complexes closely resemble those of the *trans* isomer; they form a series with the lowest-energy absorption band moving towards the ultraviolet and decreasing in intensity as phenyl groups are replaced by methyl groups in the ligands.

In agreement with the previous report,[14] we observed a single peak in the ^{31}P n.m.r. spectrum of the complex $[RuCl_2\{Ph_2P(CH_2)_3PPh_2\}_2]$ at δ = −4.8 p.p.m. (relative to 85% H_3PO_4), consistent with four equivalent phosphorus nuclei. The complex of the unsymmetrical ligand $Ph_2P(CH_2)_3PMe_2$ shows two triplets at $\delta(PPh_2)$ = − 3.4 p.p.m. and $\delta(PMe_2)$ = −9.8 p.p.m. with $^2J(PP)$ = 38 Hz. A $^2J(PP)$ value of 30—40 Hz is typical for the coupling constant of inequivalent phosphorus nuclei *cis* to one another in ruthenium(II)-tertiary phosphine complexes. (A value about ten times larger is expected [16,17] for *trans* PP coupling.) The ^{31}P n.m.r. spectrum clearly demonstrates that only one isomer is present, with Me_2P *trans* to Me_2P as in Figure 1(*a*). This arrangement is probably the sterically preferred one to minimise overcrowding of phenyl groups.

For the complex $[RuH(Cl)\{Ph_2P(CH_2)_3PMe_2\}_2]$ ten isomers are theoretically possible, only one of which [Figure 1(*b*), the 'all-*trans*' structure] is consistent with the observed ^{31}P n.m.r. spectrum, which consists of two triplets at $\delta(PPh_2)$ = +38.5 p.p.m. and $\delta(PMe_2)$ = −16.1 p.p.m. with $^2J(PP)$ = 38 Hz. The remarkable downfield shift for $\delta(PPh_2)$ from −3.4 to +38.5 p.p.m. on replacing Cl of *trans*-$[RuCl_2\{Ph_2P(CH_2)_3PMe_2\}_2]$ by H may indicate a shorter Ru–PPh_2 bond length in the less sterically crowded hydrido-complex, since $\delta(^{31}P)$ values for phosphine ligands are well known to be strongly dependent on the metal to phosphorus bond length, *e.g.* for $[RuCl_2(PPh_3)_3]$, $\delta(^{31}P)$ = +24.1 and +75.7 p.p.m. for Ru–P bond lengths of 240 and 223 pm respectively.[5]

The 'all-*trans*' structure was clearly indicated also for $[RuH(CO)\{Ph_2P(CH_2)_3PMe_2\}_2]^+$ which again had a similar ^{31}P n.m.r. spectrum, triplets at $\delta(PPh_2)$ = +25.4 p.p.m. and $\delta(PMe_2)$ = −16.3 p.p.m. with $^2J(PP)$ = 38 Hz. The hydride ligand showed a ^1H n.m.r. signal at −6.35 p.p.m. (quintet); the two J(PH) values (H to PMe_2 and H to PPh_2) were almost identical, 16.4 Hz, so the expected triplet of triplets appeared as an almost perfect quintet.

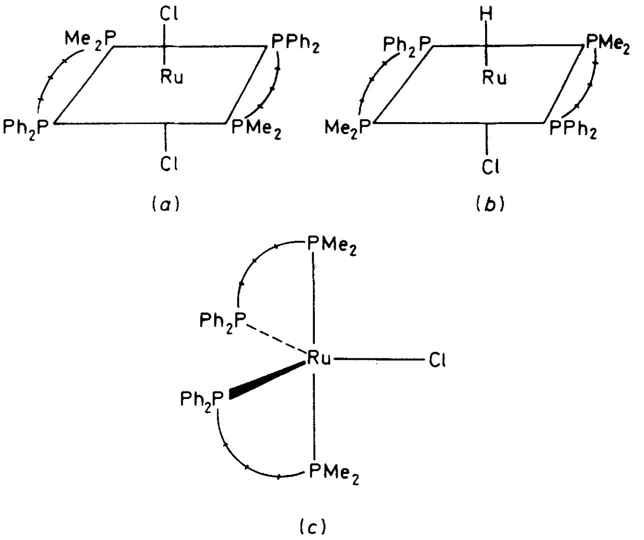

Figure 1. Structures assigned to the ruthenium(II) complexes

Five-co-ordinate Complexes.—(*a*) *Preparations.* Dissociation of Cl^- from *trans*-[$RuCl_2(P\text{-}P)_2$] to produce a trigonal-bipyramidal cation occurred quite readily. Refluxing the *trans*-[$RuCl_2(P\text{-}P)_2$] complexes in ethanol with $LiClO_4$ or $NaBPh_4$ produced dark red-brown precipitates in 66—86% yield [Table, compounds (8)—(10)]. The complex of the ligand $Ph_2P(CH_2)_3PMe_2$ reacted most quickly, and that of $Ph_2P(CH_2)_3PPh_2$ did not react with $LiClO_4$, only with $NaBPh_4$. The [$RuCl\{Ph_2P(CH_2)_3PPh_2\}_2$]$^+$ had been isolated previously as the PF_6^- salt,[12] but its ^{31}P n.m.r. spectrum was not reported.

Dissociation of Cl^- rather than of H^- occurred when [$RuH(Cl)\{Ph_2P(CH_2)_3PMe_2\}_2$] was refluxed in ethanol with $NaBPh_4$ for 1 h. The orange-brown complex [$RuH\{Ph_2P(CH_2)_3PMe_2\}_2$]$BPh_4$ (11) precipitated in 73% yield, showing ν(Ru–H) at 2 070 cm^{-1} (Table). With the corresponding $Ph_2P(CH_2)_3PMePh$ complex, a colour change occurred, but the ionic product could not be isolated in a pure state, and with the $Ph_2P(CH_2)_3PPh_2$ complex no reaction occurred.

(*b*) *Structures.* The ^{31}P n.m.r. spectrum of the [$RuCl\{Ph_2P(CH_2)_3PPh_2\}_2$]$^+$ cation contains two triplets at δ = 3.0 and 45.7 p.p.m., with a ^2J(PP) of 32 Hz (Figure 2), showing that the four PPh_2 groups surprisingly are not equivalenced by fluxional behaviour even at room temperature. Extremely fluctional behaviour for unidentate ligands is the norm in trigonal-bipyramidal complexes, equivalencing axial and equatorial groups as in PF_5,[18] [$Fe(CO)_5$],[8] [$Ru\{P(OEt)_3\}_5$],[19] and in square-pyramidal complexes, *e.g.* [$RuCl_2(PPh_3)_3$].[7] Highly fluxional behaviour for bidentate ligands has also been observed more recently in five-co-ordinate complexes of rhodium(I).[20]

The ^{31}P n.m.r. data clearly demonstrate that the four PPh_2 groups comprise two pairs of perfectly equivalent phosphorus nuclei, with very different chemical shifts. This is not consistent with a ' more or less distorted square-pyramidal geometry ' as suggested by Bressan and Rigo.[12] Such a structure is better described as trigonal bipyramidal, with two equivalent axial P atoms (δ = 3.0 p.p.m.) and two equivalent equatorial P atoms (δ = 45.7 p.p.m.). This assignment is suggested on the basis that the larger co-ordination shift, δ(complex) − δ(free ligand) * will refer to the equatorial phosphine groups which are generally closer to the metal than axial phosphine groups.[21]

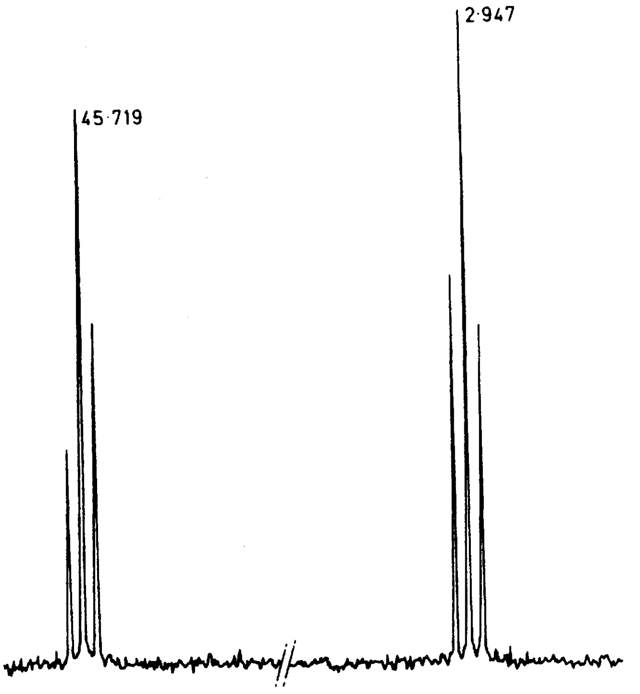

Figure 2. ^{31}P N.m.r. spectrum of [$RuCl\{Ph_2P(CH_2)_3PPh_2\}_2$]$BPh_4$

For the corresponding [$RuCl\{Ph_2P(CH_2)_3PMe_2\}_2$]$^+$ cation there are three possible trigonal-bipyramidal isomers with an equatorial chloro-group. The ^{31}P n.m.r. spectrum again consists of two triplets, δ(PMe_2) = − 18.9 p.p.m. and δ(PPh_2) = 35.7 p.p.m. with ^2J(PP) = 38 Hz, indicating again two pairs of equivalent P nuclei. The co-ordination shift for the PMe_2 groups is 34 p.p.m., which is similar to that observed for the six-co-ordinate complexes of $Ph_2P(CH_2)_3PMe_2$. The co-ordination shift for the PPh_2 group is 51 p.p.m., and this large value for a PPh_2 shift suggests that these groups are equatorial, *i.e.* as in Figure 1(*c*).† The same arrangement of PMe_2 and PPh_2 groups is indicated for the hydrido-species [$RuH\{Ph_2P(CH_2)_3PMe_2\}_2$]$^+$ on the basis of its similar ^{31}P n.m.r. spectrum, δ(axial PMe_2) = −7.4 p.p.m. and δ(equatorial PPh_2) = +47.5 p.p.m. This arrangement, Figure 1(*c*), with bulky PPh_2 groups occupying equatorial positions is also the one to be expected for steric reasons.

The visible spectra of the three [$RuCl(P\text{-}P)_2$]$^+$ species are characterised by two maxima in the visible region, due to *d*–*d* transitions. They again form a series with the bands moving to higher energy and lower intensity as phenyl groups are replaced by methyl. In the six-co-ordinate dichloro-species the bands are about 2 500 cm^{-1} to higher energy and about half as intense. Simple crystal-field theory would predict two unpaired electrons for a d^6 ion in a perfectly regular trigonal-bipyramidal stereochemistry. In these complexes, however, the trigonal symmetry is distorted by one weak-field Cl and two strong-field P ligand atoms in the equatorial plane, and the complexes are diamagnetic.

It is interesting to contrast these easily obtained [$RuXL_4$]$^+$ species (X = H or Cl, L = tertiary phosphine ligand group) with the much studied [RuX_2L_3] species. The solid-state

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* For the free ligand $Ph_2P(CH_2)_3PPh_2$, δ(PPh_2) = −16.5 p.p.m., and for $Ph_2P(CH_2)_3PMe_2$, δ(PPh_2) = 16.9 p.p.m. and δ(PMe_2) = 52.9 p.p.m.

† *Note added in proof*: selective decoupling of aromatic and aliphatic protons, respectively, confirms these assignments for δ(PPh_2) and δ(PMe_2).

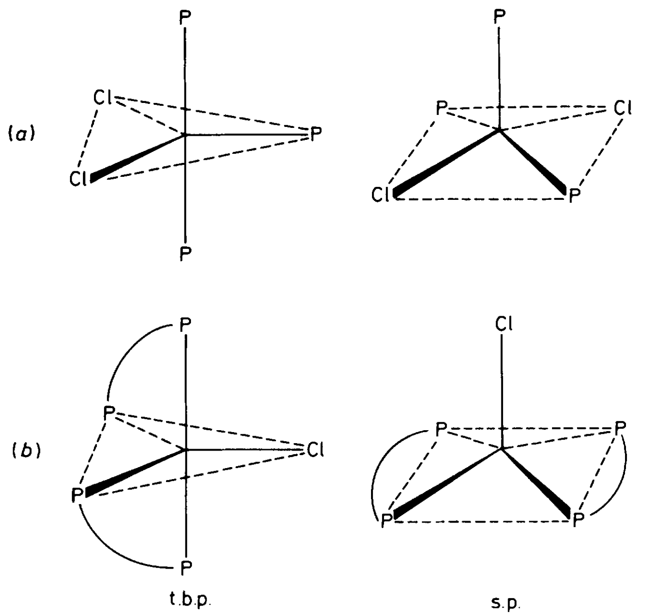

Figure 3. Possible trigonal-bipyramidal (t.b.p.) and square-pyramidal (s.p.) isomers of (*a*) $[RuCl_2L_3]$ (L = unidentate phosphine) and (*b*) $[RuCl(P^{\frown}P)_2]^+$. All have C_{2v} symmetry

structures of both $[RuCl_2(PPh_3)_3]$ and $[RuH(Cl)(PPh_3)_3]$ have been determined by *X*-ray crystallography [5,6] and they are best described as square pyramidal with the apical P–Ru distance considerably shorter than the basal P–Ru distances. For $[RuCl_2(PPh_3)_3]$ the Ru atom is 45.6 pm above the basal plane which is slightly distorted with the two *trans* P atoms 1.5 pm above.

It is difficult to ascertain whether these $[RuX_2L_3]$ complexes maintain the square-pyramidal structure in solution or whether the geometry becomes trigonal bipyramidal with the two Cl atoms equatorial. Both isomers possess C_{2v} symmetry [Figure 3(*a*)] and so cannot be distinguished by spectroscopic methods; both would give an AB_2 pattern in their ^{31}P n.m.r. spectra. In practice both $[RuCl_2(PPh_3)_3]$ and $[RuH(Cl)(PPh_3)_3]$ are highly fluxional in solution. For $[RuCl_2(PPh_3)_3]$ in CH_2Cl_2 at 2 °C, the three PPh_3 ligands are equivalent and show a sharp single $^{31}P-\{^1H\}$ n.m.r. peak at $\delta = +40.9$ p.p.m. relative to H_3PO_4, which splits in the slow-exchange limit at -97 °C into a triplet at 75.7 p.p.m. and a doublet at 24.1 p.p.m. with $^2J(PP) = 30.5$ Hz.[7] Similar data were obtained for $[RuH(Cl)(PPh_3)_3]$ [triplet at 94.0 p.p.m., doublet at 38.4 p.p.m., $^2J(PP) = 29$ Hz].[7] These data are consistent with either of the structures shown in Figure 3(*a*) yet Hoffman and Caulton [7] in 1975 interpreted the data as showing that the solid-state square-pyramidal stereochemistry persisted in solution, and also confirming Pearson's theoretical argument (based on second-order Jahn–Teller effects) [8] that d^6 ions, when they form five-co-ordinate species, produce species having the square-pyramidal rather than the trigonal-bipyramidal stereochemistry. The opposite was predicted for d^8 ions on electronic grounds and indeed most five-co-ordinate d^8 species are trigonal bipyramidal.

In contrast to the $[RuX_2L_3]$ complexes, our $[RuXL_4]^+$ species, with L_4 = two diphosphine ligands, are completely rigid in solution at room temperature. Figure 3(*b*) shows the two possible idealised stereochemistries for the diphosphine complexes, trigonal bipyramidal and square pyramidal, both again having C_{2v} symmetry. In this case however ^{31}P n.m.r. spectroscopy can distinguish the two isomers. The spectrum for $[RuCl\{Ph_2P(CH_2)_3PPh_2\}_2]^+$, Figure 2, clearly shows that the complex is trigonal pyramidal. Although it may be argued that a similar spectrum would result from a square-pyramidal structure having a basal distortion similar to that in solid $[RuCl_2(PPh_3)_3]$, *i.e.* two *trans* P atoms slightly above and two *trans* P atoms slightly below the plane, we believe that in this case a slight rocking of the bidentate ligands would be a very low-energy vibration and so would equivalence the four phosphorus atoms at room temperature. Also the huge observed difference in chemical shifts would not be expected in such a case. A large distortion of this nature of course converts the stereochemistry into trigonal bipyramidal and the rocking process then would have a high energy barrier, leading to the observed rigid structure.

If the complexes of type $[RuX_2L_3]$ do have square-pyramidal stereochemistry in solution, as has been widely assumed, then our unambiguous findings that species of the type $[RuX(P^{\frown}P)_2]^+$ are trigonal bipyramidal shows that the nature of the ligand is of prime importance in determining the stereochemistry of five-co-ordinate d^6 species. This subject is very significant for discussion of the S_N1 dissociation process in ligand-substitution reactions of octahedral complexes. In view of the inert nature of complexes of ruthenium(II) with bidentate phosphines, it is perhaps surprising that all of the above complexes are readily prepared as a pure single isomer. It appears that this isomer corresponds to both the kinetic product and the thermodynamic product, since during the preparations the first-formed complexes show no further change even on prolonged refluxing of the reaction mixture.

Chloroform solutions of the five-co-ordinate complexes catalysed hydrogenation of oct-1-ene at room temperature and pressure, but the activity was gradually lost. The six-co-ordinate complexes were inactive.

Experimental

Unless otherwise stated, reactions were carried out under a nitrogen atmosphere. The complexes $[RuCl_2(PPh_3)_3]$ and $[RuH(Cl)(CO)(PPh_3)_3]$ were prepared by the literature methods.[2,3] Unsymmetrical diphosphines, $Ph_2P(CH_2)_3PMePh$ and $Ph_2P(CH_2)_3PMe_2$, were prepared as previously described by us.[22-24] Microanalyses were carried out at U.M.I.S.T. and Manchester University microanalytical laboratories. Infrared spectra were measured on a Perkin-Elmer 457 spectrophotometer, visible spectra on a Varian Cary 210 instrument, and ^{31}P n.m.r. spectra on a Bruker WP80 FT spectrometer at 32.4 MHz.

Preparative data (yields, melting points, and elemental analyses) for the complexes are given in the Table.

trans-*Bis*[1,3-*bis(diphenylphosphino)propane*]*dichlororuthenium*(II), (1).—A suspension of $[RuCl_2(PPh_3)_3]$ (0.50 g, 0.52 mmol) and $Ph_2P(CH_2)_3PPh_2$ (0.44 g, 1.06 mmol) in n-hexane (50 cm^3) was refluxed with rapid stirring for 2 h. The black suspension gradually became pale orange. The product was filtered off while hot, washed with hot n-hexane, and dried *in vacuo*. Yield 0.47 g (90%). Further purification was unnecessary.

The analogous complexes, (2) and (3), with unsymmetrical diphosphine ligands were prepared similarly.

trans-*Bis*[1,3-*bis(diphenylphosphino)propane*]*chlorohydridoruthenium*(II), (4).—A two-necked flask (100 cm^3) was fitted with a reflux condenser and a piece of glass tubing reaching nearly to the bottom of the flask. The apparatus was flushed with nitrogen, then $[RuCl_2(PPh_3)_3]$ (0.48 g, 0.50 mmol), $Ph_2P(CH_2)_3PPh_2$ (0.42 g, 1.01 mmol), triethylamine (0.5 cm^3), and 2-methoxyethanol (8 cm^3) were placed in the flask. Hydrogen was bubbled through the black suspension during refluxing, with rapid stirring for 1 h. The suspension quickly turned brown, then orange, finally pale yellow. When cool, the complex was filtered off, washed with ethanol, then hot n-hexane, and dried *in vacuo* as yellow crystals (0.40 g, 78%).

The analogous complexes, (5) and (6), of the unsymmetrical diphosphines were made similarly.

trans-*Carbonylbis*(1-*dimethylphosphino*-3-*diphenylphosphinopropane*)*hydridoruthenium*(II) *Perchlorate*, (7).—(*i*) A suspension of [RuH(Cl)(CO)(PPh_3)$_3$] (1.14 g, 1.20 mmol) and $Ph_2P(CH_2)_3PMe_2$ (0.81 g, 2.81 mmol) in n-hexane (50 cm^3) was refluxed with rapid stirring for 2 h. The pale yellow product was filtered off while hot and washed with hot hexane. It was identified by ^1H and ^{31}P n.m.r. spectroscopy as mainly [RuH(Cl)(CO)(PPh_3){$Ph_2P(CH_2)_3PMe_2$}], yield 0.68 g (79%).

(*ii*) The product from (*i*) (0.18 g, 0.26 mmol) was dissolved in hot ethanol (20 cm^3) containing lithium perchlorate (1 mmol) and $Ph_2P(CH_2)_3PMe_2$ (0.26 mmol). The clear, pale yellow solution was refluxed for 3 h. The product was precipitated by addition of n-hexane (40 cm^3) to the cooled solution, as a white solid which was filtered off, washed with n-hexane, and dried *in vacuo*. Yield 0.07 g (33%). The i.r. spectrum showed strong absorptions at 1 990 cm^{-1} (CO) and 1 090 cm^{-1} (ClO_4).

Bis[1,3-*bis*(*diphenylphosphino*)*propane*]*chlororuthenium*(II) *Tetraphenylborate*, (8).—A suspension of *trans*-[$RuCl_2${$Ph_2P(CH_2)_3PPh_2$}$_2$] (0.21 g, 0.21 mmol) in ethanol (6 cm^3) containing sodium tetraphenylborate (1 mmol) was refluxed with stirring for several hours. The orange suspension gradually became dark brown. When cool, the product was filtered off, washed with aqueous ethanol, and dried *in vacuo*. Yield 0.23 g (86%).

The analogous complex, (10), with $Ph_2P(CH_2)_3PMe_2$ was similarly prepared.

Chlorobis(1-*diphenylphosphino*-3-*methylphenylphosphinopropane*)*ruthenium*(II) *Perchlorate*, (9).—The complex *trans*-[$RuCl_2${$Ph_2P(CH_2)_3PMePh$}$_2$] (0.45 g, 0.52 mmol) was suspended in ethanol (6 cm^3) containing lithium perchlorate (1 mmol) and refluxed with stirring for 3 h. When cool, the dark red-brown solid was filtered off, washed with aqueous ethanol, then n-hexane, and dried *in vacuo*. Yield 0.34 g (72%).

Bis(1-*dimethylphosphino*-3-*diphenylphosphinopropane*)*hydridoruthenium*(II) *Tetraphenylborate*, (11).—A suspension of *trans*-[RuH(Cl){$Ph_2P(CH_2)_3PMe_2$}$_2$] (0.16 g, 0.22 mmol) in ethanol (5 cm^3) containing sodium tetraphenylborate (2 mmol) was refluxed with stirring for 1 h. Almost immediately the pale yellow suspension turned dark red-brown. When cool the product was filtered off, washed with aqueous ethanol, and dried *in vacuo*. Yield 0.16 g (73%).

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