# Rhodium-(I) and -(III) Complexes of Diphenylphosphinous Acid and Secondary Phosphites ‡

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After shaking $[\{RhCl(C_8H_{12})\}_2]$ ($C_8H_{12}$ = cyclo-octa-1,5-diene) with $PPh_2Cl$ in methanol–water (7 : 1 v/v) for 15 min, addition of MCl gave high yields of the triple-chloride-bridged anionic complex $M[Rh_2Cl_5\{(PPh_2O)_2H\}_2]$ [M = $AsPh_4^+$ (2a) or $PPh_3(CH_2Ph)^+$ (2b)]. The structure of (2a) ($CH_2Cl_2$ trisolvate) has been verified by *X*-ray analysis. The crystals are triclinic, space group $P\bar{1}$ with $a$ = 12.157(4), $b$ = 16.191(5), $c$ = 20.523(8) Å, $\alpha$ = 96.02(3), $\beta$ = 99.88(2), $\gamma$ = 96.10(2)°, and $Z$ = 2. Variable-temperature $^{31}P-\{^1H\}$ n.m.r. spectroscopy indicates that (2a) undergoes facile intramolecular scrambling of the phosphorus nuclei at ambient temperature. Reaction of the anion (2) with $BF_3\cdot Et_2O$ leads to the formation of the $[Rh_2Cl_5\{(PPh_2O)_2BF_2\}_2]^-$ anion (3). In contrast, reaction of $[\{RhCl(C_8H_{12})\}_2]$ with $PPh_2Cl$ in methanol–water (15 : 1 v/v) gives the cations $[Rh\{PPh_2(OMe)\}_4]^+$ and $[RhH(Cl)\{PPh_2(OMe)\}_4]^+$, which do not undergo hydrolysis of the co-ordinated $PPh_2(OMe)$ ligand. The $[Rh\{PPh_2(OEt)\}_4]^+$ cation is also formed by reaction of $[RhL_2(C_8H_{12})]Y$ (Y = $ClO_4^-$ or $BPh_4^-$; $L_2$ = $Ph_2AsCH_2CH_2AsPh_2$, $PhSCH_2CH_2SPh$, or 2,2′-bipyridyl) with $PPh_2(OEt)$ whereas with the $[Rh(Ph_2PCH_2CH_2PPh_2)(C_8H_{12})]^+$ cation, $[Rh(Ph_2PCH_2CH_2PPh_2)\{PPh_2(OEt)\}_2][BPh_4]$ (4) is isolated. However, reaction of $[RhL_2(diene)][ClO_4]$ [$L_2$ = diphosphine or bis(phosphine)] with $H_2$ followed by addition of $P(OR)_2(O)H$ (R = Me or Et) gives the unstable cations $[RhL_2\{P(OR)_2OH\}_2]^+$.

Recently, we have published the full details[1] of the reactions between iridium(I) compounds such as $[\{IrCl(C_8H_{12})\}_2]$ ($C_8H_{12}$ = cyclo-octa-1,5-diene) and $[Ir(MeCN)(CO)(PPh_3)_2][ClO_4]$ with diphenylphosphinous acid or secondary phosphites. In general, these produce iridium(III) hydrido-complexes, usually containing a hydrogen-bonded $R_2POHOPR_2$ ligand (R = Ph or OMe): *e.g.* $[IrH(Cl)(C_8H_{12})\{(PPh_2O)_2H\}]$ and $[IrH(CO)(PPh_3)_2\{[P(OMe)_2O]_2H\}][ClO_4]$. To the best of our knowledge, only one report of a rhodium complex containing this type of ligand has been published, namely $[Rh(\eta\text{-}C_5H_5)(Me)\{[P(OMe)_2O]_2H\}]$.[2] In this paper we now present the full details[3] of our attempts to synthesise more rhodium complexes containing this ligand.

## Results and Discussion

As reported earlier,[1] reaction at ambient temperature of the cyclo-octa-1,5-diene complex $[\{IrCl(C_8H_{12})\}_2]$ with an excess of chlorodiphenylphosphine in a mixed methanol–water (7 : 1 v/v) solvent gave, in high yield after *ca.* 20 min, a colourless precipitate of $[IrH(Cl)(C_8H_{12})\{(PPh_2O)_2H\}]$ (1).

In contrast, shaking a suspension of $[\{RhCl(C_8H_{12})\}_2]$ with an excess of $PPh_2Cl$ in a methanol–water (7 : 1 v/v) solvent for 15 min at ambient temperature gives a red solution, from which, on addition of various salts, MCl, the yellow orange, binuclear, triple-chloride-bridged anionic complexes $M[Rh_2Cl_5\{(PPh_2O)_2H\}_2]$ [M = $AsPh_4^+$ (2a) or $PPh_3(CH_2Ph)^+$ (2b)] are precipitated in reasonable yield (*ca.* 60%).

Structure (2) has been verified by an *X*-ray analysis of the $AsPh_4^+$ salt as reported below. Suitable crystals were obtained by recrystallisation of (2a) ($CHCl_3$ disolvate) from $CH_2Cl_2$–acetone which gives $[AsPh_4][Rh_2Cl_5\{(PPh_2O)_2H\}_2]\cdot 3CH_2Cl_2$. Details of the solution of this structure are given in the Experimental section, final atomic co-ordinates in Table 1, bond lengths and angles in Table 2, and a view of the molecule in the Figure. The anion has an approximate molecular (non-crystallographic) $C_2$ axis passing through Cl(2) and the bisector of the $Rh \cdots Rh$ vector. Hence Table 2 has been drawn up to highlight the comparison of chemically equivalent ($C_2$ related) atoms. In keeping with the high *trans* influence of phosphine ligands as compared to chloride, the average Rh–Cl(bridge) bond length is 2.520 Å when *trans* to a phosphine group and 2.351 Å when *trans* to chloride. The average terminal Rh–Cl bond length is marginally shorter at 2.312 Å. Similar effects are observed in the closely related $[(PBu^n_3)_2ClRhCl_3RhCl_2(PBu^n_3)]$ structure,[4] which has corresponding Rh–Cl bond lengths of 2.513, 2.362, and 2.296 Å.

The $O(2) \cdots O(3)$ and $O(1) \cdots O(4)$ distances are 2.368 and 2.353 Å respectively. These are short compared to those found in related metal complexes[5] which range between 2.42 and 2.62 Å. However, it may be that the relatively high anisotropic thermal parameters of the oxygen atoms have introduced some shrinkage effects. Interestingly, the physically sensible refinement of the two hydroxyl hydrogen atoms shows that there are no symmetrical hydrogen bonds in the crystal. It should be noted that neutron-diffraction studies of similar $O\text{–}H \cdots O$ systems tend to show, without the constraint of any crystallographic symmetry, one short and one long O–H bond (typical values are O–H 1.01 and 1.70 Å, with an $O\text{–}H \cdots O$ angle of *ca.* 170°).[5] Here the $P(1)\text{–}O(2)\text{–}H(1) \cdots O(3)$ unit can be described as an asymmetric intramolecular hydrogen bond with O(2)–H(1) 0.97, $H(1) \cdots O(3)$ = 2.1(2) Å,§ P(1)–O(2)–H(1) 108(12), $O(2)\text{–}H(1) \cdots O(3)$ 98(13)°. However, at the other end of the molecule, the hydroxyl group adopts a different conformation and the parameters for the $P(2)\text{–}O(1)\text{–}H(2) \cdots O(4)$ unit [O(1)–H(2) 0.81, $H(2) \cdots O(4)$

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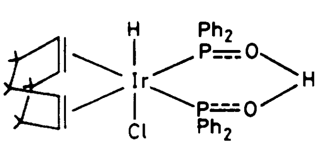
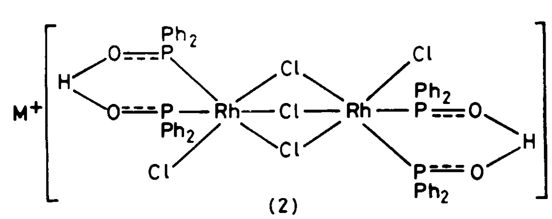
‡ *Supplementary data available* (No. SUP 23834, 33 pp.): thermal parameters, observed and calculated structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

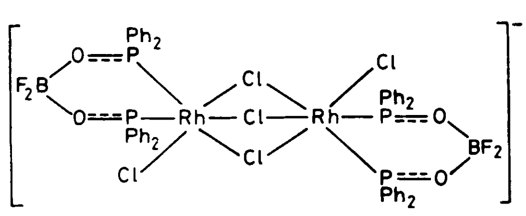
§ Similarly in $[\{RuCl_2(NO)([P(OEt)_2O]_2H)\}_2]$,[6] asymmetric intramolecular hydrogen bonds with O–H values of 1.00(5) and 1.45(5) Å are found. However, in *X*-ray structures of other complexes containing $R_2POHOPR_2$ ligands [R = Ph or OR′ (R′ = alkyl)],[7] the equality of the P–O distances has suggested the presence of symmetrical intramolecular hydrogen bonds.



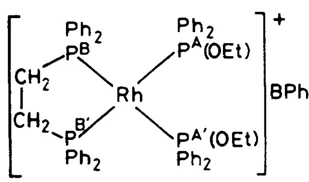
(1)



(2)



(3)



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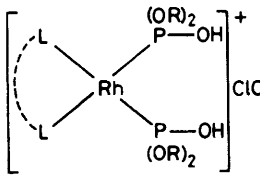

(5)

2.85(16) Å, P(2)–O(1)–H(2) 122(12), O(1)–H(2)···O(4) 45(10)°] are not consistent with the presence of a significant intramolecular hydrogen bond.

Intermolecular non-bonded interactions may perturb the intramolecular hydrogen bonding. There is a contact of 3.47 Å between O(2) and a carbon atom from $AsPh_4^+$ while at the other end of the molecule, there are O···C non-bonded contacts (of 3.34 and 3.56 Å respectively) to methylene chloride and a carbon atom of $AsPh_4^+$.

As expected for structure (2), the $^1H$ n.m.r. spectrum of (2a) in $CDCl_3$ at 298 K contains a broad resonance at δ 9.5 p.p.m. attributed to the $Ph_2PO\mathit{H}OPPh_2$ protons (*cf.* in $[IrH(Cl)(C_8H_{12})\{(PPh_2O)_2H\}]$ [1] this occurs at *ca.* δ 10.3 p.p.m.), and this disappears on addition of $D_2O$. The compounds are 1 : 1 electrolytes in $CH_2Cl_2$ and acetone.

Rather surprisingly at first sight, only one doublet is observed at ambient temperature in the $^{31}P$-$\{^1H\}$ n.m.r. spectrum of compound (2a), rather than the ABX pattern expected for structure (2). However, on cooling either $CDCl_3$ or $CH_2Cl_2$–$(CD_3)_2CO$ solutions of (2a) to *ca.* 220 K, the expected ABX pattern is observed. These changes in spectra are concentration independent, reversible with temperature, and occur with retention of Rh–P coupling. Therefore a facile intramolecular scrambling process is probably occurring, but on the available evidence it is not possible unequivocally to determine the detailed mechanism. Possibilities include facile interchange of terminal and bridging chlorides *via* double and/or single chloride-bridged transition states or intermediates (*cf.* terminal/bridge carbonyl exchange in $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ [8a] and similar hydride interchange in $[Rh_2H_4\{P(OR)_3\}_4]$ complexes [9]), or rotation of one end of the molecule with respect to the other around the three-fold axis, as recently proposed to explain the temperature-dependent n.m.r. spectra of $[Ir_2H_5(PPh_3)_4][PF_6]$ [10a] and $[Ir_2H_5\{Ph_2P(CH_2)_3PPh_2\}_2][BF_4]$.[10b] Detailed studies on the closely related $[Rh_2Cl_5(PR_3)_4]^+$ cations [11] may help to resolve this problem.

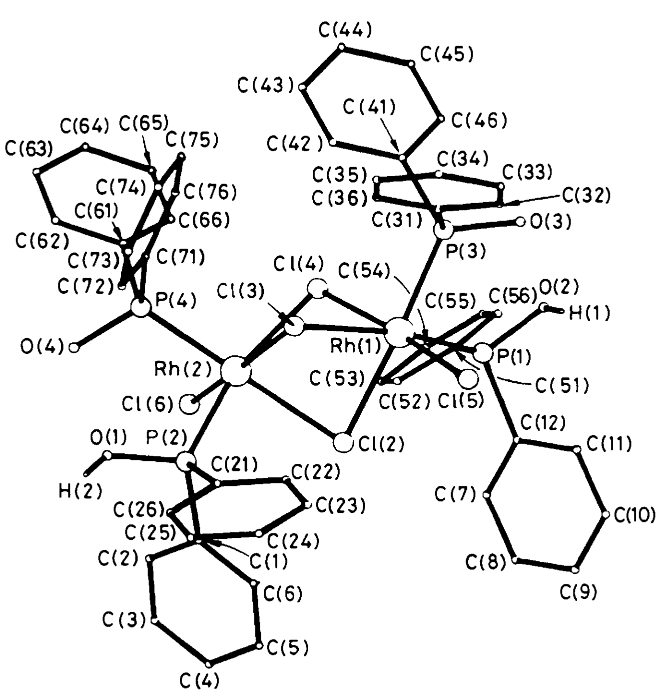

**Figure.** Molecular structure of the $[Rh_2Cl_5\{(PPh_2O)_2H\}_2]^-$ anion

A few reactions of $M[Rh_2Cl_5\{(PPh_2O)_2H\}_2]$ have been investigated. Thus, treatment with an excess of $BF_3\cdot Et_2O$ in $CHCl_3$ produces the $[Rh_2Cl_5\{(PPh_2O)_2BF_2\}_2]^-$ anion, (3). This is confirmed by the presence of additional broad bands, ν(BF), at 1 000—1 100 cm$^{-1}$ in its i.r. spectrum [7] and by examination of the $^{31}P$-$\{^1H\}$ n.m.r. spectrum of the $AsPh_4^+$ salt at 223 K in $CH_2Cl_2$–$(CD_3)_2CO$ which shows the expected ABX pattern. At ambient temperature, a broad doublet at δ 86.9 p.p.m. ($^1J_{RhP}$ = 125 Hz) is observed and this can be attributed to a combination of the quadrupolar effect of the boron nuclei and facile intramolecular interchange of the phosphorus nuclei.

Stepwise addition of $BF_3\cdot Et_2O$ to a $CH_2Cl_2$–$(CD_3)_2CO$ solution of (2a) at ambient temperature produces signals in the $^{31}P$-$\{^1H\}$ n.m.r. spectrum (see Experimental section), assigned to the intermediate anion $[\{BF_2(OPPh_2)_2\}ClRhCl_3RhCl\{(PPh_2O)_2H\}]^-$, in addition to starting material and ' bis-$BF_2$ ' product (*cf.* treatment of $[Pt\{[P(OMe)_2O]_2H\}_2]$ with $BF_3\cdot Et_2O$ which gives $[Pt\{[P(OMe)_2O]_2BF_2\}_2]$ and *in situ* n.m.r. evidence for $[Pt\{[P(OMe)_2O]_2BF_2\}\{[P(OMe)_2O]_2H\}]$.[12]

By analogy with earlier studies on binuclear, triple-halide-bridged ruthenium complexes,[13] a possible mechanism of formation of compound (2) is by facile intermolecular coupling of two co-ordinatively unsaturated monomers with the driving force being the formation of six strong rhodium(III)–ligand bonds. Clearly HCl plays an important role since, as for $[\{IrCl(C_8H_{12})\}_2]$,[1] no reaction occurs when $[\{RhCl(C_8H_{12})\}_2]$ is treated with $PPh_2(O)H$ alone.

A further complication is that unlike the $[\{IrCl(C_8H_{12})\}_2]$–$PPh_2Cl$ reaction, the nature of the product formed here is influenced by the methanol–water ratio employed. Thus, if $[\{RhCl(C_8H_{12})\}_2]$ is shaken with an excess of $PPh_2Cl$ in a

**Table 1.** Fractional atomic co-ordinates with estimated standard deviations in parentheses

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Rh(1) | 0.751 84(10) | 0.248 21(7) | 0.780 17(6) | C(21) | 0.951 1(7) | 0.069 6(6) | 0.623 8(5) |
| Rh(2) | 0.760 11(10) | 0.050 68(7) | 0.731 74(6) | C(22) | 0.963 3(7) | 0.156 9(6) | 0.632 5(5) |
| Cl(2) | 0.691 9(3) | 0.165 40(23) | 0.668 28(18) | C(23) | 1.051 8(7) | 0.202 1(6) | 0.610 9(5) |
| Cl(3) | 0.908 4(3) | 0.156 06(23) | 0.782 29(20) | C(24) | 1.127 9(7) | 0.160 1(6) | 0.580 6(5) |
| Cl(4) | 0.663 8(3) | 0.129 63(23) | 0.815 83(19) | C(25) | 1.115 7(7) | 0.072 8(6) | 0.572 0(5) |
| Cl(5) | 0.852 8(4) | 0.355 58(25) | 0.741 04(22) | C(26) | 1.027 3(7) | 0.027 5(6) | 0.593 5(5) |
| Cl(6) | 0.599 4(3) | −0.043 85(24) | 0.693 87(20) | C(31) | 0.965 9(8) | 0.345 8(8) | 0.906 2(6) |
| P(1) | 0.597 5(4) | 0.316 4(3) | 0.763 42(22) | C(32) | 1.005 4(8) | 0.431 1(8) | 0.916 3(6) |
| P(2) | 0.831 9(3) | 0.003 72(25) | 0.641 33(20) | C(33) | 1.120 6(8) | 0.457 8(8) | 0.934 9(6) |
| P(3) | 0.814 6(4) | 0.318 5(3) | 0.884 04(22) | C(34) | 1.196 4(8) | 0.399 2(8) | 0.943 5(6) |
| P(4) | 0.824 7(4) | −0.052 17(25) | 0.789 03(21) | C(35) | 1.156 8(8) | 0.313 9(8) | 0.933 5(6) |
| O(1) | 0.864 2(12) | −0.086 5(7) | 0.642 6(6) | C(36) | 1.041 6(8) | 0.287 2(8) | 0.914 8(6) |
| O(2) | 0.602 4(10) | 0.394 0(7) | 0.812 0(6) | C(41) | 0.779 6(10) | 0.260 6(7) | 0.950 3(5) |
| O(3) | 0.766 3(9) | 0.402 7(6) | 0.896 4(6) | C(42) | 0.821 2(10) | 0.185 4(7) | 0.961 5(5) |
| O(4) | 0.838 7(9) | −0.131 9(6) | 0.745 1(5) | C(43) | 0.790 9(10) | 0.142 1(7) | 1.012 5(5) |
| C(1) | 0.729 8(7) | −0.004 1(6) | 0.564 1(4) | C(44) | 0.718 9(10) | 0.174 0(7) | 1.052 2(5) |
| C(2) | 0.663 4(7) | −0.080 9(6) | 0.541 8(4) | C(45) | 0.677 3(10) | 0.249 2(7) | 1.041 1(5) |
| C(3) | 0.589 4(7) | −0.092 0(6) | 0.480 6(4) | C(46) | 0.707 6(10) | 0.292 6(7) | 0.990 1(5) |
| C(4) | 0.581 9(7) | −0.026 4(6) | 0.441 7(4) | C(61) | 0.739 0(10) | −0.092 5(8) | 0.847 7(6) |
| C(5) | 0.648 2(7) | 0.050 4(6) | 0.464 0(4) | C(62) | 0.760 3(10) | −0.170 5(8) | 0.866 3(6) |
| C(6) | 0.722 2(7) | 0.061 5(6) | 0.525 2(4) | C(63) | 0.701 1(10) | −0.206 6(8) | 0.911 1(6) |
| C(7) | 0.513 1(9) | 0.300 5(5) | 0.623 8(6) | C(64) | 0.620 7(10) | −0.164 8(8) | 0.937 3(6) |
| C(8) | 0.495 3(9) | 0.331 3(5) | 0.562 2(6) | C(65) | 0.599 4(10) | −0.086 8(8) | 0.918 7(6) |
| C(9) | 0.536 0(9) | 0.413 9(5) | 0.557 4(6) | C(66) | 0.658 5(10) | −0.050 6(8) | 0.873 9(6) |
| C(10) | 0.594 6(9) | 0.465 7(5) | 0.614 2(6) | C(71) | 0.959 9(7) | −0.015 3(6) | 0.840 2(5) |
| C(11) | 0.612 5(9) | 0.434 9(5) | 0.675 7(6) | C(72) | 1.054 9(7) | −0.023 4(6) | 0.811 3(5) |
| C(12) | 0.571 7(9) | 0.352 3(5) | 0.680 5(6) | C(73) | 1.161 6(7) | 0.009 0(6) | 0.847 4(5) |
| C(51) | 0.465 4(7) | 0.252 9(7) | 0.765 3(6) | C(74) | 1.173 3(7) | 0.049 5(6) | 0.912 2(5) |
| C(52) | 0.434 5(7) | 0.174 1(7) | 0.728 0(6) | C(75) | 1.078 3(7) | 0.057 6(6) | 0.941 0(5) |
| C(53) | 0.327 3(7) | 0.131 5(7) | 0.725 0(6) | C(76) | 0.971 6(7) | 0.025 3(6) | 0.905 0(5) |
| C(54) | 0.251 0(7) | 0.167 7(7) | 0.759 2(6) | H(1) | 0.670(16) | 0.431(12) | 0.811(10) |
| C(55) | 0.281 8(7) | 0.246 5(7) | 0.796 4(6) | H(2) | 0.912(13) | −0.103(10) | 0.623(8) |
| C(56) | 0.389 0(7) | 0.289 1(7) | 0.799 5(6) | | | | |
| Tetraphenylarsonium ion | | | | | | | |
| As(1) | 0.066 28(14) | 0.652 90(10) | 0.701 17(9) | C(91) | 0.171 0(8) | 0.749 5(6) | 0.715 1(6) |
| C(111) | −0.010 2(9) | 0.646 7(7) | 0.773 7(5) | C(92) | 0.148 6(8) | 0.816 0(6) | 0.678 9(6) |
| C(112) | −0.105 1(9) | 0.587 9(7) | 0.767 8(5) | C(93) | 0.227 9(8) | 0.887 0(6) | 0.687 2(6) |
| C(113) | −0.156 8(9) | 0.578 2(7) | 0.822 9(5) | C(94) | 0.329 7(8) | 0.891 5(6) | 0.731 6(6) |
| C(114) | −0.113 5(9) | 0.627 3(7) | 0.883 8(5) | C(95) | 0.352 1(8) | 0.824 9(6) | 0.767 8(6) |
| C(115) | −0.018 5(9) | 0.686 2(7) | 0.889 7(5) | C(96) | 0.272 8(8) | 0.753 9(6) | 0.759 5(6) |
| C(116) | 0.033 1(9) | 0.695 9(7) | 0.834 6(5) | C(101) | 0.144 0(9) | 0.557 9(6) | 0.691 8(6) |
| C(121) | −0.042 5(9) | 0.653 5(7) | 0.622 7(5) | C(102) | 0.110 3(9) | 0.484 5(6) | 0.717 1(6) |
| C(122) | −0.138 8(9) | 0.692 4(7) | 0.625 8(5) | C(103) | 0.169 9(9) | 0.416 0(6) | 0.711 0(6) |
| C(123) | −0.217 4(9) | 0.693 5(7) | 0.567 8(5) | C(104) | 0.263 2(9) | 0.420 8(6) | 0.679 6(6) |
| C(124) | −0.199 8(9) | 0.655 5(7) | 0.506 7(5) | C(105) | 0.297 0(9) | 0.494 2(6) | 0.654 3(6) |
| C(125) | −0.103 6(9) | 0.616 6(7) | 0.503 6(5) | C(106) | 0.237 4(9) | 0.562 7(6) | 0.660 4(6) |
| C(126) | −0.024 9(9) | 0.615 5(7) | 0.561 6(5) | | | | |
| Methylene chloride | | | | | | | |
| Cl(11) | 0.143 9(7) | 0.570 9(4) | 0.430 4(4) | C(202) | 0.409 2(21) | 0.252 9(16) | 0.301 1(13) |
| Cl(12) | 0.232 0(7) | 0.722 6(4) | 0.514 3(4) | Cl(15) | 0.629 7(15) | 0.451 3(9) | 0.148 2(8) |
| C(201) | 0.799 9(17) | 0.326 0(13) | 0.569 8(11) | Cl(16) | 0.465 9(17) | 0.431 9(15) | 0.061 4(13) |
| Cl(13) | 0.507 0(7) | 0.273 6(6) | 0.378 1(4) | C(203) | 0.475(6) | 0.415(4) | 0.145(3) |
| Cl(14) | 0.409 7(13) | 0.339 9(6) | 0.264 7(7) | | | | |

methanol–water (15 : 1 v/v) medium for 10 min at ambient temperature, and then $[NH_4][PF_6]$ added to the resulting orange solution,* high yields of a mixture of $[Rh\{PPh_2(OMe)\}_4][PF_6]$ and $[RhH(Cl)\{PPh_2(OMe)\}_4][PF_6]$ are precipitated. Strong evidence for these well known cations comes from their characteristic $^{31}P-\{^1H\}$ and $^1H$ n.m.r. spectra (see Experimental section and refs. 14 and 15). The size of $^2J_{PH}$ (11.1 Hz) in the rhodium(III) cation indicates that the hydrido-group is *cis* to the $PPh_2(OMe)$ ligands.

A probable explanation for the dramatic change in reaction product as the methanol–water ratio is increased is the formation of small amounts of $PPh_2(OMe)$ in addition to $PPh_2(O)H$ and HCl. It has been shown that the former will react very readily with $[\{RhCl(C_8H_{12})\}_2]$ to give the $[Rh\{PPh_2(OMe)\}_4]^+$ cation [14] which will then undergo oxidative addition with aqueous HCl to give some of the $[RhH(Cl)\{PPh_2(OMe)\}_4]^+$ cation.[15]

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* Addition of $[AsPh_4]Cl \cdot HCl$ to this reaction mixture produces no $[AsPh_4][Rh_2Cl_5\{(PPh_2O)_2H\}_2]$; conversely, addition of $[NH_4][PF_6]$ to the MeOH–$H_2O$ (7 : 1 v/v) reaction mixture gave no precipitate of $[Rh\{PPh_2(OMe)\}_4][PF_6]$ or $[RhH(Cl)\{PPh_2(OMe)\}_4][PF_6]$.

**Table 2.** Bond distances (Å) and angles (°) in $[AsPh_4][Rh_2Cl_5\{(PPh_2O)_2H\}_2]\cdot3CH_2Cl_2$

(*a*) Distances

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Rh···Rh | 3.266 2(16) | | | P(3)-C(31) | 1.811(13) | P(4)-C(61) | 1.843(13) |
| Rh(1)-Cl(2) | 2.481(4) | Rh(2)-Cl(2) | 2.510(4) | P(3)-C(41) | 1.811(12) | P(4)-C(71) | 1.796(11) |
| Rh(1)-Cl(3) | 2.538(4) | Rh(2)-Cl(4) | 2.552(4) | P(3)-O(3) | 1.555(12) | P(4)-O(4) | 1.537(11) |
| Rh(1)-Cl(4) | 2.342(4) | Rh(2)-Cl(3) | 2.359(4) | P(1)-C(12) | 1.839(11) | P(2)-C(1) | 1.820(10) |
| Rh(1)-Cl(5) | 2.310(5) | Rh(2)-Cl(6) | 2.313(4) | P(1)-C(51) | 1.819(11) | P(2)-C(21) | 1.814(11) |
| Rh(1)-P(1) | 2.272(5) | Rh(2)-P(2) | 2.272(4) | P(1)-O(2) | 1.508(13) | P(2)-O(1) | 1.555(15) |
| Rh(1)-P(3) | 2.270(5) | Rh(2)-P(4) | 2.268(4) | O(2)-H(1) | 0.97(19) | O(1)-H(2) | 0.81(16) |

(*b*) Selected bond angles

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cl(2)-Rh(1)-Cl(3) | 80.24(13) | Cl(2)-Rh(2)-Cl(4) | 78.47(13) | Rh(1)-P(1)-O(2) | 114.7(5) | Rh(2)-P(2)-O(1) | 113.5(5) |
| Cl(2)-Rh(1)-Cl(4) | 83.14(13) | Cl(2)-Rh(2)-Cl(3) | 83.20(13) | C(12)-P(1)-C(51) | 102.8(5) | C(1)-P(2)-C(21) | 102.5(5) |
| Cl(3)-Rh(1)-Cl(4) | 80.49(13) | Cl(3)-Rh(2)-Cl(4) | 79.89(13) | C(12)-P(1)-O(2) | 104.7(6) | C(1)-P(2)-O(1) | 103.6(6) |
| Cl(2)-Rh(1)-P(3) | 176.50(15) | Cl(2)-Rh(2)-P(4) | 179.08(15) | C(51)-P(1)-O(2) | 106.0(6) | C(21)-P(2)-O(1) | 107.7(6) |
| Cl(3)-Rh(1)-P(1) | 170.74(15) | Cl(4)-Rh(2)-P(2) | 166.31(15) | Rh(1)-P(3)-C(31) | 114.9(4) | Rh(2)-P(4)-C(61) | 116.8(4) |
| Cl(4)-Rh(1)-Cl(5) | 173.54(16) | Cl(3)-Rh(2)-Cl(6) | 171.19(15) | Rh(1)-P(3)-C(41) | 113.6(4) | Rh(2)-P(4)-C(71) | 110.2(4) |
| P(3)-Rh(1)-Cl(5) | 86.86(16) | P(4)-Rh(2)-Cl(6) | 85.24(15) | Rh(1)-P(3)-O(3) | 114.2(15) | Rh(2)-P(4)-O(4) | 114.7(4) |
| P(3)-Rh(1)-P(1) | 92.71(17) | P(4)-Rh(2)-P(2) | 91.74(16) | C(31)-P(3)-C(41) | 193.8(6) | C(61)-P(4)-C(71) | 104.2(5) |
| P(1)-Rh(1)-Cl(5) | 89.19(16) | P(2)-Rh(2)-Cl(6) | 89.76(15) | C(31)-P(3)-O(3) | 104.6(6) | C(61)-P(4)-O(4) | 103.0(6) |
| | | | | C(41)-P(3)-O(3) | 104.4(6) | C(71)-P(4)-O(4) | 106.8(5) |
| Rh(1)-P(1)-C(12) | 112.9(4) | Rh(2)-P(2)-C(1) | 111.9(3) | | | | |
| Rh(1)-P(1)-C(51) | 114.6(4) | Rh(2)-P(2)-C(21) | 116.2(4) | | | | |

(*c*) Selected dihedral angles

| | | | |
|---|---|---|---|
| O(4)-P(4)-Rh(2)-Cl(6) | 63 | O(3)-P(3)-Rh(1)-Cl(5) | 68 |
| C(62)-C(61)-O(4) | 35 | C(32)-C(31)-P(3)-O(3) | −11 |
| C(72)-C(71)-P(4)-O(4) | 37 | C(46)-C(41)-P(3)-O(3) | 9 |
| O(1)-P(2)-Rh(2)-Cl(6) | −69 | O(2)-P(1)-Rh(1)-Cl(5) | −72 |
| C(2)-C(1)-P(2)-O(1) | 30 | C(56)-C(51)-P(1)-O(2) | 10 |
| C(26)-C(21)-P(2)-O(1) | 21 | C(11)-C(12)-P(1)-O(2) | 29 |

Another possible approach to the synthesis of, as yet unknown, rhodium(I) hydrogenbis(diphenylphosphinito) complexes is by hydrolysis of rhodium(I) alkyl diphenylphosphinite compounds. This method has been successfully used to prepare 'oxy ring' complexes of the isoelectronic palladium(II) and platinum(II).[7] However, all our attempts to hydrolyse the $[Rh\{PPh_2(OR)\}_4]^+$ cations (R = Me or Et) in either acidic or basic media led only to recovery of starting material. This failure may be due to the fact that co-ordination of phosphorus to rhodium(I) does not withdraw sufficient electron density from the alkyl group to make it susceptible to attack by nucleophiles.

In order to investigate if a change of ligand *trans* to a co-ordinated $PPh_2(OR)$ group would facilitate hydrolysis, attempts were made to synthesis the cations $[RhL_2\{PPh_2(OEt)\}_2]^+$ by reaction of $[RhL_2(C_8H_{12})]Y$ [Y = $ClO_4^-$ or $BPh_4^-$; $L_2 = Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2AsCH_2CH_2AsPh_2$, $PhSCH_2CH_2SPh$, or 2,2′-bipyridyl] with $PPh_2(OEt)$. However, except when $L_2$ = dppe (see below), complete displacement to give $[Rh\{PPh_2(OEt)\}_4]^+$ occurred. Similarly, reaction of $[Rh(S{-}S)(C_8H_{12})]$ [S-S = $S_2CNEt_2$, $S_2PPh_2$, or $S_2P(OEt)_2$] with $PPh_2(OEt)$ gave only the $[Rh\{PPh_2(OEt)\}_4]^+$ cation.

Treatment of $[Rh(dppe)(C_8H_{12})][ClO_4]$ with $PPh_2(OEt)$ in MeOH, followed by $Na[BPh_4]$ gives $[Rh(dppe)\{PPh_2(OEt)\}_2][BPh_4]$ (4) together with a small quantity of $[Rh(dppe)_2][BPh_4]$ ($^{31}P$ n.m.r. evidence). The $^{31}P$-$\{^1H\}$ n.m.r. spectrum of (4) shows a complex AA′BB′X spin pattern and this has been successfully simulated using the NUMARIT program routine * (see Experimental section). Unfortunately all attempts then to hydrolyse compound (4) were unsuccessful.

However, if various $[RhL_2(diene)][ClO_4]$ complexes (diene = cyclo-octa-1,5-diene or norbornadiene; L = $PPh_3$, $PPh_2Me$, $PPhMe_2$, or $L_2 = Ph_2PCH_2CH_2PPh_2$) in alcohols are first treated with hydrogen {which gives the reactive intermediates $[RhL_2(solvent)_2]^+$},[16] and then two equivalents of $P(OR)_2(O)H$ (R = Et or Me) are added, careful work-up leads to the isolation of the rhodium(I) cations $[RhL_2\{P(OR)_2OH\}_2]ClO_4$ (5) in which the three-co-ordinate form of the dialkyl phosphite ligand has been stabilised. These compounds are unexpected since for platinum(II) compounds of this type deprotonation readily occurs.[7] It is likely that deprotonation fails to occur in this case because rhodium(I) is more electron rich than platinum(II), and hence does not cause the hydrogens to become as acidic. As expected, the rhodium(I) complexes with a bidentate dppe backbone are the most stable and the stability of the other complexes decreases in the order L = $PPh_3 > PPh_2Me > PPhMe_2$.

These new rhodium(I) complexes have been characterised by elemental analysis, $^1H$ n.m.r. and i.r. spectroscopic studies (see Experimental section). Thus, i.r. bands at *ca.* 1 100 cm$^{-1}$ are characteristic of unco-ordinated $ClO_4^-$ [8b] and a band at *ca.* 890 cm$^{-1}$ is assigned to ν(P-OH).[17] The cationic nature of the compounds clearly indicates that the $(RO)_2POHOP(OR)_2$ ring is not present. Unfortunately, no useful $^{31}P$-$\{^1H\}$ n.m.r. spectra could be obtained due to the facile decomposition of the compounds in solution over the time required to accumulate their Fourier-transform n.m.r. spectra. This low stability in solution also prevented all attempts to deprotonate these compounds and generate the 'oxy ring' species $[RhL_2\{[P(OR)_2O]_2H\}]$.

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* NUMARIT is a LAOCOON-type iterative n.m.r. parameter-fitting program. It was written by the University of East Anglia n.m.r. program library unit in FORTRAN to run on IBM and ICL computers. It is available from the n.m.r. program library now at Daresbury.

## Experimental

Microanalyses were by the University of Edinburgh Chemistry Department, BMAC and Galbraith Laboratories Inc. Infrared spectra were recorded in the region 200—4 000 $cm^{-1}$ on Perkin-Elmer 557 (U.E.) or 283B (W.S.U.) spectrometers either as Nujol mulls on caesium iodide plates or potassium bromide discs. Hydrogen-1 n.m.r. spectra were obtained on Varian Associates HA100 (E.U.) and Nicolet 200 (W.S.U.) spectrometers. Phosphorus-31 n.m.r. spectra ($^1H$-noise decoupled) were obtained on a JEOL-FX60Q spectrometer (E.U.) operating in the pulse and Fourier-transform mode at 22.24 MHz. Chemical shifts are reported in p.p.m. to high frequency of 85% $H_3PO_4$. Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge at 298 K. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

The compounds $[\{RhCl(C_8H_{12})\}_2]$,[18] $[RhL_2(diene)]Y$ [19] $[Y = ClO_4^-$ or $BPh_4^-$; diene = 1,5-$C_8H_{12}$ or norbornadiene ($C_7H_8$); $L_2$ = dppe, $Ph_2AsCH_2CH_2AsPh_2$, $PhSCH_2CH_2SPh$, 2,2′-bipyridyl, $2PPh_3$, $2PMePh_2$, or $2PMe_2Ph$ (not all combinations)], and $[Rh(S\text{–}S)(C_8H_{12})]$ [20] [S–S = $S_2CNEt_2$, $S_2PPh_2$, or $S_2P(OEt)_2$] were prepared by literature methods.

*Benzyltriphenylphosphonium Tri-μ-chloro-dichlorobis[hydrogenbis(diphenylphosphinito)]dirhodate*(III), (2b).—Chlorodiphenylphosphine (0.30 $cm^3$, 1.6 mmol) was hydrolysed in aqueous methanol (1 : 7 v/v) for 1 h to give an *in situ* mixture of $PPh_2(O)H$ and HCl. This mixture was then added to a suspension of $[\{RhCl(C_8H_{12})\}_2]$ (0.10 g, 0.20 mmol) in methanol (5 $cm^3$) and shaken at ambient temperature for 15 min. The red solution was filtered to remove unreacted starting materials and then an excess of $[PPh_3(CH_2Ph)]Cl$ in methanol was added to precipitate the product as an orange-yellow powder. This was washed with methanol and diethyl ether and dried *in vacuo* at 60 °C, m.p. 145—149 °C (yield 0.18 g, 56%) (Found: C, 56.2; H, 4.2. Calc. for $C_{73}H_{64}Cl_5O_4P_5Rh_2$: C, 56.8; H, 4.2%). $\Lambda_m$ ($0.88 \times 10^{-3}$ mol $dm^{-3}$): in $CH_2Cl_2$, 25.3 $\Omega^{-1}$ $cm^2$ $mol^{-1}$; in acetone, 54.0 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. $^{31}P\text{-}\{^1H\}$ N.m.r. (in $CD_2Cl_2$ at 298 K): δ 75.5 (d, ${}^1J_{RhP}$ = 120.0 Hz) and 23.0 p.p.m. (s) $[PPh_3(CH_2Ph)^+]$.

*Tetraphenylarsonium Tri-μ-chloro-dichlorobis[hydrogenbis(diphenylphosphinito)]dirhodate*(III) (2a).—This can be similarly prepared by adding a methanolic solution of $[AsPh_4]Cl\cdot HCl$ to the above red solution. Dissolution of the yellow powder (*ca.* 60% yield) in a small amount of chloroform then deposits orange microcrystals of $[AsPh_4][Rh_2Cl_5\{(PPh_2O)_2H\}_2]\cdot 2CHCl_3$ (2a), m.p. 154—157 °C. The presence of $CHCl_3$ was established by mass spectroscopic analysis (Found: C. 49.1; H, 3.4; As, 4.0. Calc. for $C_{74}H_{64}AsCl_{11}O_4P_4Rh_2$: C. 49.0; H, 3.5; As, 4.1%). $\Lambda_m$ ($0.95 \times 10^{-3}$ mol $dm^{-3}$ in $CH_2Cl_2$), 27 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. $^{31}P\text{-}\{^1H\}$ n.m.r. (in $CDCl_3$ at 298 K): 78.5 p.p.m. (d, ${}^1J_{RhP}$ = 120.0 Hz); at 223 K (ABX pattern), $\delta_A$ 77.2, $\delta_B$ 71.3 p.p.m. (${}^1J_{Rh^XP^{A,B}}$ = 122.0, ${}^2J_{P^AP^B}$ = 23.0 Hz); in $CD_2Cl_2$ at 298 K, δ 76.0 p.p.m. (d, ${}^1J_{RhP}$ = 120.0 Hz). $^1H$ N.m.r. (in $CDCl_3$ at 298 K): δ 9.50 (br, $Ph_2POHOPPh_2$), 6.90—8.00 p.p.m. (m, Ph).

Crystals suitable for *X*-ray analysis were obtained by recrystallisation of (2a) from $CH_2Cl_2$–acetone.

*Benzyltriphenylphosphonium Tri-μ-chloro-dichlorobis[bis(diphenylphosphinito)difluoroborato]dirhodate*(III), (3b).—An excess of $BF_3\cdot Et_2O$ (0.5 $cm^3$) was added to a $CHCl_3$ solution (5 $cm^3$) of $[PPh_3(CH_2Ph)][Rh_2Cl_5\{(PPh_2O)_2H\}_2]$ (0.10 g, 0.065 mmol) and the mixture shaken for 5 min. Concentration of the solution and addition of diethyl ether yielded the product as a white powder which was recrystallised from $CHCl_3$–diethyl ether, washed with methanol and diethyl ether, and dried *in vacuo* at 60 °C (yield 0.08 g, 75%) (Found: C, 53.1; H, 3.6. Calc. for $C_{73}H_{62}B_2Cl_5F_4O_4P_5Rh_2$: C, 53.4; H, 3.8%).

*Tetraphenylarsonium Tri-μ-chloro-dichlorobis[bis(diphenylphosphinito)difluoroborato]dirhodate*(III), (3a).—This was similarly prepared from $[AsPh_4][Rh_2Cl_5\{(PPh_2O)_2H\}_2]$ (0.10 g, 0.064 mmol) and an excess of $BF_3\cdot Et_2O$ (yield 0.085 g, 80%) (Found: C, 51.1; H, 3.7. Calc. for $C_{72}H_{60}AsB_2Cl_5F_4O_4P_4Rh_2$: C, 51.8; H, 3.6%). $^{31}P\text{-}\{^1H\}$ N.m.r. (in $CH_2Cl_2$–[$^2H_6$]-acetone at 298 K): δ 86.9 p.p.m. (d, br, ${}^1J_{Rh^XP}$ = 125 Hz); at 223 K (ABX pattern), $\delta_A$ 88.4, $\delta_B$ 84.3 p.p.m. (${}^1J_{Rh^XP^{A,B}}$ = 124, ${}^2J_{P^AP^B}$ = 23.5 Hz). Stepwise addition of $BF_3\cdot Et_2O$ to a $CH_2Cl_2$–$(CD_3)_2CO$ solution of $[AsPh_4][Rh_2Cl_5\{(PPh_2O)_2H\}_2]$ at 298 K gives additional $^{31}P\text{-}\{^1H\}$ n.m.r. resonances at δ 79.9 (d, ${}^1J_{RhP}$ = 122) and 76.6 p.p.m. (d, ${}^1J_{RhP}$ = 122 Hz) attributed to the intermediate $[\{BF_2(OPPh_2)_2\}ClRhCl_3RhCl\{(PPh_2O)_2H\}]^-$ anion.

*Preparation of* $[Rh\{PPh_2(OMe)\}_4][PF_6]$ *and* $[RhH(Cl)\{PPh_2(OMe)\}_4][PF_6]$ *by Reaction of* $[\{RhCl(C_8H_{12})\}_2]$ *with* $PPh_2Cl$ *in* MeOH–$H_2O$ (15 : 1 v/v).—Chlorodiphenylphosphine (0.70 $cm^3$, 3.2 mmol) was dissolved in aqueous methanol (1 : 15 v/v) and left for 1 h; this solution then was added to a suspension of $[\{RhCl(C_8H_{12})\}_2]$ (0.20 g, 0.40 mmol) in methanol (5 $cm^3$) and the mixture shaken at ambient temperature for 10 min. Addition of $[NH_4][PF_6]$ to the resultant orange solution precipitated a yellow solid (0.71 g) shown by comparison with samples made by literature methods [14,15] to consist of approximately equal amounts of $[Rh\{PPh_2(OMe)\}_4][PF_6]$ [$^{31}P\text{-}\{^1H\}$ n.m.r. in $CDCl_3$ at 298 K, $PPh_2(OMe)$ region: δ 132.2 p.p.m. (d, ${}^1J_{RhP}$ = 159 Hz)] and $[RhH(Cl)\{PPh_2(OMe)\}_4][PF_6]$ [$^{31}P\text{-}\{^1H\}$ n.m.r. in $CDCl_3$ at 298 K, $PPh_2(OMe)$ region: δ 121.7 p.p.m. (d, ${}^1J_{RhP}$ = 110 Hz). $^1H$ N.m.r. (low frequency region): δ −13.0 p.p.m. (d of quintets, ${}^1J_{RhH}$ = 18.4, ${}^2J_{PH}$ = 11.1 Hz)]. Shorter reaction times gave more of the rhodium(I) cation whereas if the reaction was continued for *ca.* 30 min before addition of $[NH_4][PF_6]$ the opposite was true. This indicates that the $[RhH(Cl)\{PPh_2(OMe)\}_4]^+$ cation is formed by oxidative addition of HCl to the $[Rh\{PPh_2(OMe)\}_4]^+$ cation.

*Reaction of* $[RhL_2(C_8H_{12})][ClO_4]$ *with* $PPh_2(OEt)$.—The compound $[Rh(Ph_2AsCH_2CH_2AsPh_2)(C_8H_{12})][ClO_4]$ (0.30 g, 0.37 mmol) was suspended in methanol (10 $cm^3$), treated with $PPh_2(OEt)$ (0.17 g, 0.74 mmol), and shaken for 10 min at ambient temperature. After filtering off any unreacted starting material, the resultant orange solution was treated with $[NH_4][PF_6]$ to give a yellow solid (0.15 g, 39%) shown by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy to be $[Rh\{PPh_2(OEt)\}_4][PF_6]$ [$^{31}P\text{-}\{^1H\}$ n.m.r. in $CDCl_3$ at 298 K, $PPh_2(OEt)$ region: δ 130.5 p.p.m. (d, ${}^1J_{RhP}$ = 156 Hz)]. Increasing the amount of $PPh_2(OEt)$ increased the yield of $[Rh\{PPh_2(OEt)\}_4][PF_6]$.

The same compound was obtained by reaction of other $[RhL_2(C_8H_{12})]^+$ cations ($L_2$ = $PhSCH_2CH_2SPh$ or 2,2′-bipyridyl) with $PPh_2(OEt)$ followed by $[NH_4][PF_6]$.

*Reaction of* $[Rh(S\text{–}S)(C_8H_{12})]$ *with* $PPh_2(OEt)$.—The compound $[Rh(S_2CNEt_2)(C_8H_{12})]$ (0.20 g, 0.56 mmol) in $CHCl_3$ (5 $cm^3$) was shaken with $PPh_2(OEt)$ (0.26 g, 1.13 mmol) at ambient temperature for 5 min. Concentration of the orange solution gave a red-orange oil which on addition of a methanolic solution of $Na[BPh_4]$ gave a bright yellow precipitate of $[Rh\{PPh_2(OEt)\}_4][BPh_4]$ ($^{31}P$ n.m.r. evidence) (0.27 g, 38%). Concentration of the filtrate led to recovery of unreacted $[Rh(S_2CNEt_2)(C_8H_{12})]$. Again the yield was increased by adding more $PPh_2(OEt)$ and the same compound was formed from other $[Rh(S\text{–}S)(C_8H_{12})]$ [S–S = $S_2PPh_2$ or $S_2P(OEt)_2$].

*[1,2-Bis(diphenylphosphino)ethane]bis(ethoxydiphenylphosphine)rhodium*(I) *Tetraphenylborate*, (4).—A suspension of [Rh(dppe)(C$_8$H$_{12}$)][ClO$_4$] (0.10 g, 0.14 mmol) in methanol (10 cm$^3$) was treated with PPh$_2$(OEt) (0.067 g, 0.29 mmol) and the mixture shaken for 10 min. Addition of an excess of Na[BPh$_4$] to the resulting red solution then precipitated the product as a yellow powder. This was recrystallised from CHCl$_3$–diethyl ether, washed with methanol and diethyl ether, and dried *in vacuo* at 60 °C (0.15 g, 83%). The product was contaminated with a small amount of [Rh(dppe)$_2$][BPh$_4$] [$^{31}$P-{$^1$H} n.m.r. in CDCl$_3$ at 298 K: $\delta$ 57.5 p.p.m.(d, $^1J_{\mathrm{RhP}}$ = 132 Hz)]. The rest of the $^{31}$P-{$^1$H} n.m.r. spectrum shows 48 resonances in two distinct, symmetrical groups centred at $\delta$ *ca.* 56 and 130 p.p.m. which correspond to the Ph$_2$*P*CH$_2$CH$_2$*P*Ph$_2$ and PPh$_2$(OEt) signals respectively. This spectrum has been simulated using the NUMARIT program routine assuming an AA′BB′X spin system. All spectral line positions have been iteratively fitted to within 0.1 Hz to give the following parameters: $\delta_{\mathrm{A}}$ 60.3, $\delta_{\mathrm{B}}$ 131.5 p.p.m.; $^1J_{\mathrm{RhP^A}} = {}^1J_{\mathrm{RhP^{A'}}} = 128.1$, $^1J_{\mathrm{RhP^{B'}}} = 161.1$, $^2J_{\mathrm{P^AP^B}} = {}^2J_{\mathrm{P^{A'}P^{B'}}} = 36.5$, $^2J_{\mathrm{P^AP^{B'}}} = {}^2J_{\mathrm{P^{A'}P^B}} = -307.0$, $^2J_{\mathrm{P^AP^{A'}}} = 20.6$, $^2J_{\mathrm{P^BP^{B'}}} = 30.2$ Hz [see structure (4) for numbering].

*Attempted Hydrolysis of* [Rh{PPh$_2$(OR)}$_4$][PF$_6$] (R = Et, *or* Me) *and* [Rh(dppe){PPh$_2$(OEt)}$_2$][BPh$_4$].—*Method* (*a*). Water (1 cm$^3$) was added to an acetone solution of [Rh{PPh$_2$(OEt)}$_4$][PF$_6$] and the mixture stirred for one week. However, on concentration of the solution and addition of diethyl ether, only [Rh{PPh$_2$(OEt)}$_4$][PF$_6$] was recovered.

*Method* (*b*). Aqueous HCl (2 cm$^3$) was added to an acetone (20 cm$^3$) solution of [Rh{PPh$_2$(OEt)}$_4$][PF$_6$] and the mixture refluxed for 4 h. However, on reducing the volume of the solution and adding diethyl ether, only the starting material was recovered. A similar negative result was obtained using a NEt$_3$–H$_2$O mixture.

*Method* (*c*). [Rh{PPh$_2$(OEt)}$_4$][PF$_6$] was refluxed in CH$_2$Cl$_2$ for 3 h with PPh$_2$(O)H in the presence of a strong nucleophile (S$_2$CNEt$_2$$^-$). However, removal of solvent led to recovery of starting materials as before.

Similarly, no hydrolysis of [Rh{PPh$_2$(OMe)}$_4$][PF$_6$] or [Rh(dppe){PPh$_2$(OEt)}$_2$][BPh$_4$] complexes was observed under these conditions.

*[1,2-Bis(diphenylphosphino)ethane]bis(dimethyl phosphite)rhodium*(I) *Perchlorate*.—The compound [Rh(dppe)(C$_7$H$_8$)][ClO$_4$] (C$_7$H$_8$ = norbornadiene) (0.38 g, 0.55 mmol) was suspended in degassed absolute methanol (100 cm$^3$). The system was evacuated and hydrogen gas admitted. After stirring for 2 h, during which time a dark orange solution formed, hydrogen was pumped away and the vessel purged with argon. A solution of dimethyl phosphite (0.12 g, 1.10 mmol) in absolute methanol (10 cm$^3$) was then added and after further stirring for 1 h, the resulting light orange solution was filtered. Reduction in volume (to 5 cm$^3$) and dropwise addition of degassed, distilled water produced an oily precipitate. This was filtered in air, washed with distilled water and diethyl ether and air dried to yield a yellow powder (0.38 g, 85%) (Found: C, 44.0; H, 5.0; P, 15.0. Calc. for C$_{30}$H$_{38}$ClO$_{10}$P$_4$Rh: C, 43.9; H, 4.7; P, 15.1%). $^1$H N.m.r. spectrum (in CDCl$_3$ at 298 K): $\delta$ 7.0—7.8 (m, Ph), 5.50 (br, P–OH), 2.6—3.8 p.p.m. [complex multiplet from Ph$_2$PC*H*$_2$CH$_2$PPh$_2$ and P(O*Me*)$_2$OH second-order pattern]. I.r. spectrum: $\nu_{\mathrm{P-OH}}$ = 875, $\nu_{\mathrm{asym}}$(ClO$_4$$^-$) = 1 095 cm$^{-1}$.

*[1,2-Bis(diphenylphosphino)ethane]bis(diethyl phosphite)rhodium*(I) *Perchlorate*.—This was prepared similarly as a yellow powder (yield 0.14 g, 73%) by reaction of [Rh(dppe)(C$_7$H$_8$)][ClO$_4$] (0.15 g, 0.22 mmol) and P(OEt)$_2$(O)H (0.061 g, 0.44 mmol) in absolute ethanol (Found: C, 46.6; H, 5.3; P, 13.2. Calc. for C$_{34}$H$_{46}$ClO$_{10}$P$_4$Rh: C, 46.6; H, 5.3; P, 14.1%). I.r. spectrum: $\nu_{\mathrm{P-OH}}$ = 875, $\nu_{\mathrm{asym}}$(ClO$_4$$^-$) = 1 090 cm$^{-1}$.

*Bis(dimethyl phosphite)bis(triphenylphosphine)rhodium*(I) *Perchlorate*.—This was prepared similarly as an orange powder (yield 0.30 g, 67%) by the reaction of [Rh(PPh$_3$)$_2$(C$_7$H$_8$)][ClO$_4$] (0.39 g, 0.48 mmol) and P(OMe)$_2$(O)H (0.106 g, 0.96 mmol) in absolute methanol. To avoid decomposition, however, the precipitate was not washed with diethyl ether (Found: C, 50.5; H, 4.9; P, 13.2. Calc. for C$_{40}$H$_{44}$ClO$_{10}$P$_4$Rh: C, 50.7; H, 4.7; P, 13.1%). $^1$H N.m.r. spectrum (in CDCl$_3$ at 298 K): $\delta$ 7.0—7.7 (m, Ph), 4.8 (br, P–OH), 3.3 p.p.m. (m, [P(O*Me*)$_2$OH]. I.r. spectrum: $\nu_{\mathrm{P-OH}}$ = 790, $\nu_{\mathrm{asym}}$(ClO$_4$$^-$) = 1 090 cm$^{-1}$.

*Bis(dimethyl phosphite)bis(methyldiphenylphosphine)rhodium*(I) *Perchlorate Diethyl Ether Solvate*.—This was prepared in analogous fashion as a tan solid (yield 0.25 g, 68%) from [Rh(PPh$_2$Me)$_2$(C$_7$H$_8$)][ClO$_4$] (0.31 g, 0.47 mmol) and P(OMe)$_2$(O)H (0.098 g, 0.94 mmol) in absolute methanol. Note that all stages of the product isolation had to be performed on a Schlenk line under an argon atmosphere to prevent extensive decomposition (Found: C, 45.8; H, 5.1; P, 13.8. Calc. for C$_{34}$H$_{50}$ClO$_{11}$P$_4$Rh: C, 45.5; H, 5.6; P, 13.8%). $^1$H N.m.r. spectrum (in CDCl$_3$ at 298 K): $\delta$ 7.0—7.9 (m, Ph), 5.8 (br, P–OH), 3.6 [m, P(O*Me*)$_2$OH], 1.9 p.p.m. (m, PPh$_2$*Me*). I.r. spectrum: $\nu_{\mathrm{P-OH}}$ = 890, $\nu_{\mathrm{asym}}$(ClO$_4$$^-$) = 1 095 cm$^{-1}$.

In the reaction of [Rh(PPhMe$_2$)$_2$(C$_7$H$_8$)][ClO$_4$] with hydrogen and P(OMe)$_2$(O)H, an extremely unstable tan powder was isolated. Although satisfactory analytical analyses could not be obtained, $^1$H n.m.r. evidence suggests that some [Rh(PPhMe$_2$)$_2${P(OMe)$_2$OH}$_2$][ClO$_4$] is formed. $^1$H N.m.r. spectrum (in CDCl$_3$ at 298 K): $\delta$ 7.2—8.0 (m, Ph), 3.7 [m, P(O*Me*)$_2$OH], 1.9 p.p.m. (m, PPh*Me*$_2$); $\delta$(P–O*H*) was not observed.

*Crystallographic Studies*.—*Crystal data for* [AsPh$_4$][Rh$_2$Cl$_5${(PPh$_2$O)$_2$H}$_2$]·3CH$_2$Cl$_2$. C$_{75}$H$_{68}$AsCl$_{11}$O$_4$P$_4$Rh$_2$, $M$ = 1 828, deep red triclinic crystals unstable in air, $a$ = 12.157(4), $b$ = 16.191(5), $c$ = 20.523(8) Å, $\alpha$ = 96.02(3), $\beta$ = 99.88(2), $\gamma$ = 96.10(2)°, $U$ = 3 926 Å$^3$, $Z$ = 2, $D_c$ = 1.55 g cm$^{-3}$, $F$(000) = 1 840, space group $P\bar{1}$ (no. 2), Mo-$K_\alpha$ radiation, $\lambda$ = 0.710 69 Å, $\mu$ = 13.5 cm$^{-1}$.

*Structure determination*. A single crystal of dimensions 0.2 × 0.2 × 0.3 mm was transferred directly from the mother-liquor into a drop of Shellac solution. The crystal was coated with Shellac (Glue) and mounted on a glass fibre. Without such treatment the crystals were found to lose solvent of crystallisation and become opaque powders within a few hours. Unit-cell dimensions and intensity data were measured on a Nonius CAD 4 diffractometer. Of the 7 192 unique reflections measured out to $\theta$ = 20°, 4 380 had $I > 2.5\sigma(I)$. An empirical absorption correction was applied.

Positions of the rhodium atoms were determined from a sharpened Patterson synthesis (SHELX).[21] Subsequent difference-Fourier maps provided positions for all non-hydrogen atoms in the cation and anion. The solvent of crystallisation was much less well defined. Various disordered models were examined in an attempt to define a number of partially occupied CH$_2$Cl$_2$ sites, none of which was satisfactory. The best refinement was achieved by giving anisotropic thermal parameters to the CCl$_2$ atoms. Despite high thermal parameters for the chlorine atoms (suggesting some sort of gross disorder), the largest residual electron density in the final difference map was only 0.7 e Å$^{-3}$. All phenyl groups were refined as idealised rigid groups with C–C bond lengths of 1.395 Å and bond angles of 120°. All other atoms (Rh, Cl, P, As, and O) were refined anisotropically. A number of hydrogen atoms on the anion also showed up on the difference maps: the two most prominent were the two hydroxyl hydrogen atoms. Positional parameters and isotropic thermal parameters for these two hydrogen atoms were also included in the refinement.

The weighting scheme $w = 1/[\sigma^2(F) + 0.000\,37\,F^2]$ gave an even distribution of variance in $|F|$ analysed in ranges of both $|F|$ and $\sin\theta$. In the final cycle of refinement the average positional shifts were less than 0.01 times their estimated standard deviations. The final $R$ factor was 0.063 ($R' = 0.074$).

Final fractional atomic co-ordinates are given in Table 1 and bond lengths and angles are in Table 2.

## Acknowledgements

We Thank N.A.T.O. for financial support of this joint research. One of us (D. M. R.) thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. Washington State University thanks the Boeing Company for a grant towards purchase of the Nicolet n.m.r. spectrometer. Thanks are due to Dr. Alan Boyd of Edinburgh University for spectral simulations. We thank the S.E.R.C. for financial support (to J. A. S. D.) and Johnson-Matthey for loans of rhodium trichloride.

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*Received 6th June* 1983; *Paper* 3/914