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THE REACTIONS OF A SECONDARY PHOSPHITE WITH CHLORO- AND PENTAN-2,4-DIONATO COMPLEXES OF IRIDIUM(I) AND RHODIUM(I)

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Summary

The secondary phosphite $\overline{OCH_2CMe_2CH_2OP}(O)H$ reacts with chlorobis(cyclooctene)rhodium(I) dimer to give $RhX(R_2POHOPR_2)_2(R_2POH)$ (X = H, Cl) and $RhCl_2(R_2POHOPR_2)(R_2POH)_2$, where $R_2PO = \overline{OCH_2CMe_2CH_2O}P$O. The iridium analogue yields corresponding products. The phosphite reacts with bis(cyclooctene)pentan-2,4-dionatorhodium(I) to give $Rh(R_2POHOPR_2)_3$ and with the corresponding iridium complex to produce $Ir(acac)(R_2POHOPR_2)_2$. Some of the complexes act as catalysts or catalytic precursors for the stereoselective reduction of 4-t-butylcyclohexanone.

Introduction

The catalytic reduction of unhindered cyclohexanones to axial alcohols using chloroiridic acid and dialkylphosphite in aqueous propan-2-ol has been known for a long time [1], but little information on the nature of the species present or of the actual catalyst is available. In preliminary attempts [2] to prepare well-defined dialkylphosphite complexes of iridium, which might be catalysts for the reaction, we treated chlorobis(cyclooctene)iridium(I), $[IrCl(C_8H_{14})_2]_2$ (**1**), with dimethylphosphite in benzene at 80°C, expecting to obtain hydridoiridium(III) species analogous to those we have made [2,3] by reaction of **1** successively with triphenylphosphine and dialkylphosphite under similar conditions, e.g. $IrHCl\{[MeO)_2PO]_2H\}(PPh_3)_2$. Depending on the amount of dimethylphosphite used, we were able to isolate a colourless solid and a colourless oil which analysed for $IrHCl[(MeO)_2PO][(MeO)_2POH]_2$ and $IrHCl[(MeO)_2PO][(MeO)_2POH]_3$, respectively. Neither of these showed a hydride resonance in the range δ 0– – 30 in their ^1H NMR spectra at room temperature, though they showed absorptions at 2230 cm^{-1} (CH_2Cl_2) in their IR spectra attributable to ν(Ir–H). The oil was a catalyst (precursor) for the stereoselective reduction of 4-t-butylcyclohexanone in aqueous propan-2-ol, but the solid was not. However, subsequent attempts to repeat the preparation of the oil gave products

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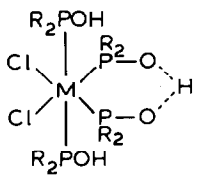
of varying elemental composition which were shown to be mixtures of several compounds by $^{31}P\{^1H\}$ NMR spectroscopy.

When chlorobis(cyclooctene)rhodium(I) dimer, $[RhCl(C_8H_{14})_2]_2$ (**2**), reacted with dimethylphosphite in boiling benzene, a pale yellow solid, soluble in dichloromethane, and a colourless solid not soluble in that solvent were obtained [2]. The yellow solid was a precursor for an even more stereoselective catalyst than the iridium-containing oil, but its $^{31}P\{^1H\}$ NMR spectrum was not very informative and it appeared to be converted to the colourless solid in solution. In view of the lability of the complexes derived from dimethylphosphite, we turned to the cyclic secondary phosphite 5,5-dimethyl-1,3-dioxa-2-phosphorinane, $\overline{OCH_2CMe_2CH_2OP}(O)H$ (**3**) and found its complexes to be soluble and stable in solution, so that informative $^{31}P\{^1H\}$ NMR spectra could be obtained. Further work has therefore been confined to reactions of **3** with iridium(I) and rhodium(I) complexes.

Results and discussion

Rhodium complexes

When **2** was heated with **3** in benzene at reflux, three major solid products were obtained, in proportions depending on reaction conditions, to which structures **4a**, **5a** and **6a** have been assigned. When four equivalents of **3** per mol of rhodium were used the main products were **4a** and **5a** and it was possible to purify **4a** by crystallisation, but not **5a**. When six or more equivalents of **3** were used, a mixture of



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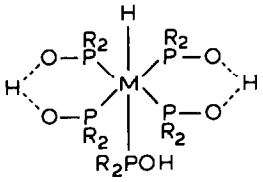

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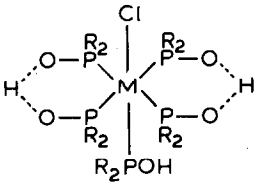

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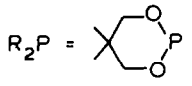
(a, M = Rh;
b, M = Ir)



4a, **5a** and **6a** was formed initially, but longer reaction time gave **5a** and **6a** only. We were unable to separate **5a** from **6a**, although the excess of **3** could easily be removed by gel permeation chromatography.

The yield of **5a** was much improved, and the formation of **4a** and **6a** was completely suppressed, by heating **2** with five equivalents of **3** in boiling benzene in the presence of triethylamine to remove hydrogen chloride. Some very minor impurities were removed by gel permeation chromatography, but we were unable to recrystallise **5a** satisfactorily despite the fact that $^{31}P\{^1H\}$ NMR indicated that it was essentially pure.

In the original reaction, in the absence of triethylamine, it seemed likely that **6a** was formed from **5a** by the action of hydrogen chloride with liberation of dihydrogen, and that this might be encouraged if a hydrogen acceptor such as cyclohexanone were present. Accordingly we heated **2** with eight equivalents of **3** in benzene at reflux in the presence of cyclohexanone and found, indeed, that **6a** was

TABLE 1

^{1}H NMR SPECTRA (δ (ppm))

Complex (R_2P = )	Solvent [a]	CH_3	CH_2	OH
$RhCl_2(R_2POHOPR_2)(R_2POH)_2$ (**4a**)	C	0.84(6H, s) 1.01(6H, s) 1.14(6H, s) 1.35(6H, s)	3.80(4H, dd, 10.5, 20.4) 3.98(4H, dd, 10.5, 14.3) 4.43(4H, d, 10.5) 4.55(4H, m)	8.5(3H, br s)
$RhH(R_2POHOPR_2)_2(R_2POH)$ [b] (**5a**)	B	0.19(3H, s) 0.38(12H, s) 1.13(12H, s) 1.38(3H, s)	3.47(10H, m) 4.36(8H, d, 11.0) 4.4 (2H, m)	9.8(3H, br s)
$RhCl(R_2POHOPR_2)_2(R_2POH)$ (**6a**)	B	0.38(3H, s) 0.42(12H, s) 1.13(12H, s) 1.23(3H, s)	3.54(2H, dd, 10.8, 19.2) 3.70(8H, m) 4.38(8H, d, 10.8) 4.4 (2H, m)	9.1(3H, br s)
$Rh(R_2POHOPR_2)_3$ (**9**)	C	0.79(18H, s) 1.25(18H, s)	3.54(10H, d, 10.7) 4.38(10H, d, 10.7)	9.9(3H, br s)
$IrCl_2(R_2POHOPR_2)(R_2POH)_2$ (**4b**)	C	0.84(6H, s) 0.92(6H, s) 1.20(6H, s) 1.33(6H, s)	3.80(4H, dd, 10.5, 20.4) 3.98(4H, dd, 10.5, 14.8) 4.21(4H, m) 4.41(4H, d, 10.5)	6.2(3H, br s)
$IrH(R_2POHOPR_2)_2(R_2POH)$ [b] (**5b**)	B	0.18(3H, s) 0.36(12H, s) 1.14(12H, s) 1.38(3H, s)	3.43(10H, m) 4.35(8H, d, 10.9) 4.4 (2H, m)	10.2(3H, br s)
$IrCl(R_2POHOPR_2)_2(R_2POH)$ (**6b**)	B	0.30(3H, s) 0.37(12H, s) 1.19(12H, s) 1.29(3H, s)	3.42(2H, dd, 10.8, 20.4) 3.60(8H, m) 4.42(8H, d, 10.8) 4.5 (2H, m)	10.7(3H, br s)
$Ir(acac)(R_2POHOPR_2)_2$ [c] (**11**)	C	0.76(6H, s) 0.79(6H, s) 1.14(6H, s) 1.28(6H, s)	3.47(4H, dd, 10.1, 19.5) 3.63(4H, dd, 10.7, 19 4.36(8H, d, 10.1)	7.7(br)

[a] C is $CDCl_3$, B is C_6D_6. [b] For hydride resonance see text. [c] Singlets at δ 5.38 (1H) and δ 1.97 (6H) for acac ligand.

now formed in good yield and that it could now be purified by crystallisation after removal of excess of **3**. During the reaction **3** underwent reaction with cyclohexanone to give $CH_2(CH_2)_4C(OH)P(OH)OCH_2CMe_2CH_2O$, so more **3** was added during the reaction to ensure it was in excess. The reaction of ketones with secondary phosphites is well known [4].

The main evidence for the structures of **4a**, **5a** and **6a** rests on their $^{31}P\{^1H\}$ and ^1H NMR spectra which are detailed in Tables 1 and 2. The $^{31}P\{^1H\}$ NMR spectrum of **4a** in $CDCl_3$ consists of two double triplets at δ 76.2 and 101.9 ppm (relative to 85% H_3PO_4) with J(RhP) values of 151 and 142 Hz, respectively. This indicates the presence of two pairs of equivalent phosphorus atoms, all the phosphorus atoms being coupled to rhodium. The ^1H NMR spectrum shows four equal methyl singlets (six hydrogens each), four methylene resonances (four hydrogens each) and a broad signal at low field attributable to one PO*H* and two PO*H*OP [5]. This is consistent with the presence of two types of phosphite or phosphonate ligand as each phosphite

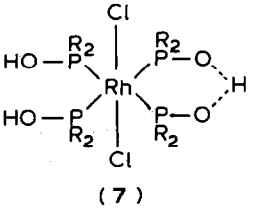
TABLE 2

^{31}P NMR SPECTRA [a]

Complex (R_2P = )	δ(P)	Multiplicity	J(P–P) (Hz)	J(Rh–P) (Hz)
$RhCl_2(R_2POHOPR_2)(R_2POH)_2$	76.2	dt	33	151
(4a)	101.9	dt	33	142
$RhH(R_2POHOPR_2)_2(R_2POH)$	109.9	dd	44.5	128
(5a)	115.1	d quin	44.5	119
$RhCl(R_2POHOPR_2)_2(R_2POH)$	84.9	d quin	35	151
(6a)	96.6	dd	35	123
$Rh(R_2POHOPR_2)_3$	97.1	d	–	118
(9)				
$IrCl_2(R_2POHOPR_2)(R_2POH)_2$	36.4	t	32	–
(4b)	67.2	t	32	–
$IrH(R_2POHOPR_2)_2(R_2POH)$	67.8	d	33.5	–
(5b)	77.2	m [b]		–
$IrCl(R_2POHOPR_2)_2(R_2POH)$	42.4	quin	30	–
(6b)	60.1	d	30	–
$Ir(acac)(R_2POHOPR_2)_2$	37.8	t	34	–
(11)	70.3	t	34	–

[a] Measured in C_6D_6. Chemical shifts are in ppm relative to 85% H_3PO_4, positive to high frequency. [b] See text.

or phosphonate ligand should show two methyl and two methylene signals (*cis* and *trans* to the exocyclic oxygen). The single very broad hydroxylic absorption may be due to overlapping resonances or to exchange of the three hydroxylic protons between the four phosphorus-containing ligands. The compound has been assigned the structure **4a** with *cis* chlorines rather than **7** which has *trans* chlorines since ^2J(PP) is small, 33 Hz, indicative of *cis* inequivalent phosphorus atoms. Typical values for coupling of *trans* inequivalent phosphorus atoms are ca. 400 Hz [6]. Also,



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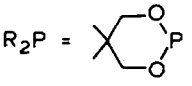


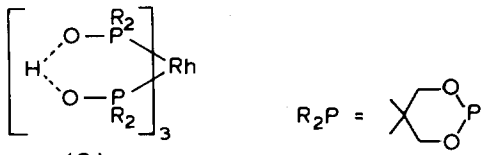
if hydroxylic proton exchange is fast then all the phosphorus ligands in structure **7** would be equivalent.

The $^{31}P\{^1H\}$ NMR spectrum of compound **5a** consists of two large doublets at δ 109.9 and two smaller overlapping quintets at 115.1 ppm. The small signal is much broader (and less well resolved) when the spectrum is run without proton decoupling, consistent with it being due to phosphorus *trans* to hydride. Stronger evidence for the nature of **5a** is provided by its ^1H NMR spectrum which shows two widely spaced double quintets (J(PH) 215.7, 8.8, J(RhH) 13.0 Hz) at δ −8.1 ppm assignable to a hydride *trans* to one phosphorus and *cis* to four others. Consistent with this are the four methyl resonances in the ratio 1/4/4/1. The methylene

resonances are not as well resolved as in **4a** consisting of a multiplet (10H) and a doublet (2H). There is also a broad three proton signal at low field which can be assigned to hydroxyl. The IR spectrum of **5a** in a Nujol mull exhibits an absorption at 1950 cm^{-1} due to ν(RhH). The fact that **5a** is also formed from Rh(acac)$(C_8H_{14})_2$ and **3** (see below) confirms that **5a** cannot contain chlorine.

A double doublet at δ 96.6 and a doublet quintet at 84.9 ppm comprise the $^{31}P\{^1H\}$ NMR spectrum of **6a** indicative of five phosphorus-containing ligands, four of which are equivalent. The value of J(RhP) for the phosphorus *trans* to chlorine is very similar to those in **4a**. As in the case of **5a**, the ^1H NMR of **6a** shows four methyl singlets in the ratio 1/4/4/1. The methylene signals also show a 1/4/4/1 ratio consisting of an eight proton doublet, which partially obscures a two proton signal, an eight proton multiplet and a two proton doublet.

When bis(cyclooctene)pentan-2,4-dionatorhodium(I) (**8**) was treated with **3** in boiling benzene, a mixture of **5a** and another compound, to which structure **9** has been assigned, was obtained. When the reaction was done in boiling toluene a much



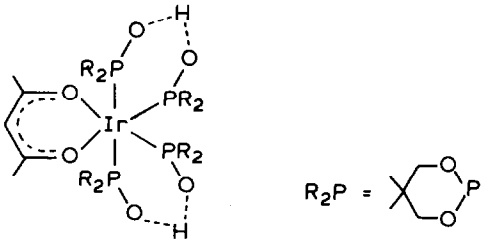
(9)

higher proportion of **9** resulted. We have not been able to crystallise **9** satisfactorily and have not obtained it in a completely pure state. Its ^1H NMR spectrum has two large methyl singlets (18H each), two methylene doublets (10H each) and a very broad low field signal (3H). Its $^{31}P\{^1H\}$ NMR spectrum consists of one doublet at δ 97.1 ppm (J(RhP) 118Hz). All this is consistent with structure **9**.

Iridium complexes

The reaction of $[IrCl(C_8H_{14})_2]_2$ (**1**) with **3** also give several products, the relative proportions of which are controlled by the ratio of **1**/**3** employed and the reaction temperature. When three equivalents of **3** per iridium were used the major product was **4b**, but a number of minor products, some of them hydrides, were also formed. No **6b** was present as judged by ^{31}P NMR spectroscopy. When the reaction was done with four equivalents of **3** and in the presence of lithium chloride, **4b** was formed in greater amount with fewer side-products and could be crystallised. Its ^1H and $^{31}P\{^1H\}$ NMR spectra are very similar to those of **4a** and are listed in Tables 1 and 2. When **1** was heated with larger amounts of **3** in benzene mixtures of **4b** and **5b** were obtained which we were unable to separate. However, when the reaction was done in boiling toluene the major product (ca. 90%) was **6b** along with some **5b**. After removal of the excess of **3** by gel permeation chromatography, it was possible to crystallise **6b**. Its ^1H and $^{31}P\{^1H\}$ NMR spectra resemble those of **6a** very closely, as can be seen from Tables 1 and 2. An attempt to increase the proportion of the hydride **5b** by treating **1** with **3** (five equivalents per iridium) in toluene, adding pyridine (to remove hydrogen chloride) and heating further was not successful. However since the rhodium hydride **5a** could be obtained by reaction of Rh(acac)$(C_8H_{14})_2$ (**8**) with **3**, we heated **3** with bis(cyclooctene)pentan-2,4-dionatoiridium(I), Ir(acac)$(C_8H_{14})_2$ (**10**), in boiling benzene. By far the major product

was the iridium(III) complex **11**, together with varying amounts of 2,2-dimethylpropan-1,3-diol (from hydrolysis of **3**); a small amount of **5b** was also formed. In



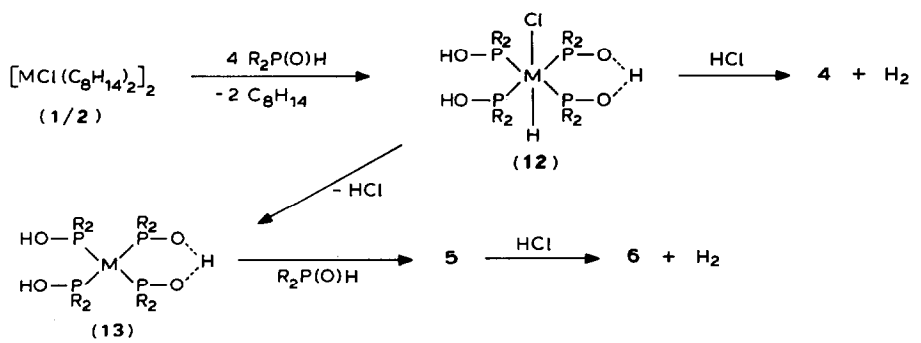
(11)

boiling toluene or xylene the yields of **5b** increased to 30 and > 90% respectively, but the product could not be completely purified. The ^{1}H NMR spectrum of **5b** exhibits a hydride resonance at δ −11.2 ppm consisting of two widely spaced quintets (J(PH) 153.6, 14.7 Hz). In other respects it is very similar to that of **5a**. The presence of hydride is confirmed by an IR absorption at 2030 cm^{-1} (Nujol). The ^{31}P{^{1}H} NMR spectrum is less clear than that of **5a** and comprises a doublet at 67.8 ppm for four phosphorus atoms and a broad unresolved multiplet at 77.2 ppm for the fifth. The latter signal splits into two multiplets (J(PH) ~ 140 Hz) when none of the protons were decoupled [7]. When only the methylene protons of the ligands were decoupled the phosphorus spectrum consists [7] of a double doublet (J(PH) ~ 14, J(PP) 33.5 Hz) and a double quintet (J(PH) ~ 150, J(PP) 33.5 Hz) quite consistent with structure **5b**.

Formation of 4, 5 and 6

A plausible scheme for the formation of compounds **4**, **5** and **6** is shown in Scheme 1.

Oxidative addition of phosphite to **1** or **2** with loss of cyclooctene to give a species such as **12** seems a very likely first step. Reductive elimination of hydrogen chloride from **12** would give **13** which in turn could undergo oxidative addition of phosphite to give **5**. The metal–hydride bonds of **12** or **5** are likely to be rapidly cleaved by hydrogen chloride to give **4** and **6** respectively plus dihydrogen. When less than five mols of phosphite are present **4** would be formed in preference to **6**. In the reaction



SCHEME 1

TABLE 3

CATALYTIC REDUCTION [a,b] OF 4-t-BUTYLCYCLOHEXANONE [c] BY VARIOUS COMPLEXES [d] IN AQUEOUS PROPAN-2-OL [e]

Complex	% Reduction	*cis/trans* 4-t-butylcyclohexanol product
4a [f]	0	–
4b	51	92/8
5a	14	98.5/1.5
5b	24	97.5/2.5
6a	12	98.5/1.5
6b	87	97.5/2.5
9	6	98/2

[a] Heated at reflux 17 h. [b] Analysis by GLC on 2-CEMS at 130°C. [c] 100 mgHg. [d] 10 mg. [e] 2 ml H_2O, 10 ml propan-2-ol. [f] Reaction done on half scale.

of **2** with phosphite removal of hydrogen chloride with base leads to formation of **5a** only.

Catalytic reduction of 4-t-butylcyclohexanone

Compounds **4a** and **b**, **5a** and **b**, **6a** and **b** and **9** were all examined as possible catalyst precursors for the reduction of 4-t-butylcyclohexanone by aqueous propan-2-ol. The results are recorded in Table 3.

The dichlororhodium compound **4a** is ineffective and the iridium analogue is active but not particularly selective. Of the monochloro and hydrido complexes the iridium species are more active, but slightly less selective than those of rhodium. This parallels the observation of Orr et al. [8] who found that chlorotris(triphenyl)phosphinerhodium(I), $RhCl(PPh_3)_3$, in the presence of an excess of trimethylphosphite gave a more selective, less reactive catalyst than sodium chloroiridate(IV) and trimethylphosphite for the reduction of steroidal ketones in aqueous propan-2-ol. Experiments involving **5a/b** and **6a/b** in dry propan-2-ol resulted in less than 1% of the ketone being reduced under the conditions of Table 3. This result suggests that the catalyst species contain ligands which have undergone hydrolysis.

Experimental

NMR spectra were recorded on a Bruker WM250 spectrometer using TMS as internal standard for ^1H spectra (250 MHz) and 85% of H_3PO_4 as external standard for ^{31}P spectra (101.27 MHz). IR spectra were recorded on a Perkin–Elmer 577 instrument. Gel permeation chromatography (GPC) was carried out on Bio-Beads S-X8 using benzene as eluant and taking the first major fraction. Microanalyses were carried out at Queen's University by W.J. Swindall and asscociates. Benzene was dried by distillation from $LiAlH_4$ and ether, toluene and xylene were dried over sodium. Reactions were carried out under dry nitrogen, although the isolated products were stable in dry air. The compounds 3,5-dimethyl-1,3-dioxa-2-phosphorinane, $OCH_2CMe_2CH_2OP(O)H$ (**3**) [9], and $[MCl(C_8H_{14})_2]_2$ (M = Rh (**2**) [10] or Ir (**1**) [11]) were made by literature methods, although in the case of **1** ammonium hexachloroiridate (IV) was used as starting material in place of hexachloroiridic acid or hydrated iridium trichloride. The pentan-2,4-dionato complexes $M(acac)(C_8H_{14})_2$

(M = Rh (**8**), Ir (**10**)) were made by treating **2** and **1** respectively with pentan-2,4-dionatothallium(I) in tetrahydrofuran, centrifuging the resulting suspension, evaporating the solutions thus obtained, extracting the consequent residues with pentane and finally removing the pentane.

Preparations

*$RhCl_2[(OCH_2CMe_2CH_2OPO)_2H][OCH_2CMe_2CH_2OPOH]_2$ (**4a**).* A mixture of $[RhCl(C_8H_{14})_2]_2$ (**2**) (0.358 g, 0.500 mmol) and **3** (0.675 g, 4.50 mmol) were heated at reflux in benzene (7 ml) for 4 h and the almost colourless solution then evaporated. The resulting sticky residue was washed with ether giving **4a** as a colourless solid (0.304 g, 39%). A portion for analysis was crystallized from dichloromethane/ether. Found: C, 30.79; H, 5.40; Cl, 8.64. $C_{20}H_{43}Cl_2O_{12}P_4Rh$ calcd.: C, 31.06; H, 5.61; Cl, 9.17%. Mol. wt. (osmometry, $CHCl_3$): Found: 806; calcd.: 773.

*$RhH[(OCH_2CMe_2CH_2OPO)_2H]_2[OCH_2CMe_2CH_2OPOH]$ (**5a**).* A mixture of $[RhCl(C_8H_{14})_2]_2$ (**2**) (0.200 g, 0.279 mmol), **3** (0.418 g, 2.789 mmol) and triethylamine (0.155 ml, 1.14 mmol) was heated in benzene (15 ml) at reflux for 7 h. The resulting pale yellow solution was filtered to remove a pale brown precipitate and the filtrate concentrated and put on a column of Bio-Beads (630 × 15 mm). Elution with benzene and evaporation of the eluate gave **5a** as an almost colourless solid (0.349 g, 73%). Found: C, 38.53; H, 6.37. $C_{25}H_{54}O_{15}P_5Rh \cdot 0.75C_6H_6$ calcd.: C, 38.90; H, 6.47%. [^{1}H NMR ($CDCl_3$) indicated the presence of 0.75 mol benzene]. Mol. wt. (osmometry, $CHCl_3$): Found: 907; calcd.: 852.

*$RhCl[(OCH_2CMe_2CH_2OPO)_2H]_2[OCH_2CMe_2CH_2OPOH]$ (**6a**).* A mixture of $[RhCl(C_8H_{14})_2]_2$ (**2**) (0.201 g, 0.280 mmol) , **3** (0.673 g, 4.49 mmol) and cyclohexanone (0.9 ml) in benzene (12 ml) was heated for 6 h at reflux. More **3** (0.400 g) was added and heating continued for 6 h. A pale yellow solution and a colourless precipitate, largely $CH_2(CH_2)_4C(OH)P(OH)OCH_2CMe_2CH_2O$, were formed. After removal of the latter by filtration, the filtrate was concentrated and subjected to GPC (as for **5a**). **6a** was obtained as a colourless solid (0.421 g, 85%); an analytical sample was crystallised from cold ether. Found: C, 34.47; H, 6.10; Cl, 4.12. $C_{25}H_{53}ClO_{15}P_5Rh$ calcd.: C, 33.86; H, 6.02; Cl, 3.99%. Mol. wt. (osmometry, $CHCl_3$): Found: 880 calcd.: 887.

*$Rh[(OCH_2CMe_2CH_2OPO)_2H]_3$ (**9**).* A mixture of **8** (0.120 g, 0.284 mmol) and **3** (0.427 g, 2.84 mmol) was heated in toluene (10 ml) at reflux for 22 h. The filtered product solution was evaporated and the residue resulting taken up in benzene and put on Bio-Beads as for **5a**. The first major solid (0.255 g, 90%) eluted with benzene was colourless. It gave C and H analyses which were in reasonable agreement for **9**; Found: C, 38.51; H, 6.79. $C_{30}H_{63}O_{18}P_6Rh \cdot 0.5C_6H_6$ calcd.: C, 38.12; H, 6.40%. NMR showed the presence of 0.5 mol benzene and traces of **5a** and **3**.

*$IrCl_2[(OCH_2CMe_2CH_2OPO)_2H][OCH_2CMe_2CH_2OPOH]_2$ (**4b**).* A mixture of $[IrCl(C_8H_{14})_2]_2$ (**1**), (0.105 g, 0.117 mmol), **3** (0.141 g, 0.939 mmol) and lithium chloride (0.300 g) was heated for 5 h in benzene (12 ml) at reflux. The solution was filtered and the filtrate concentrated and put on Bio-Beads. Elution with benzene led to the isolation of a colourless solid (0.116 g, 58%). A portion for analysis was crystallised from benzene/ether (~ 50% recovery). Found: C, 27.56; H, 5.05; Cl, 8.77. $C_{20}H_{43}Cl_2O_{12}P_4Ir$ calcd.: C, 27.85; H, 5.02; Cl, 8.22%.

*$IrH[(OCH_2CMe_2CH_2OPO)_2H]_2[OCH_2CMe_2CH_2OPOH]$ (**5b**).* A mixture of

$Ir(acac)(C_8H_{14})_2$ (**10**), (0.120 g, 0.235 mmol) and **3** (0.352 g, 2.35 mmol) was heated in xylene (5 ml) at reflux for 42 h. The resulting solution was filtered and evaporated in vacuo. The residue was dissolved in benzene and put on Bio-Beads. Elution with benzene gave colourless solid (0.224 g, 100%) as first main fraction. Found: C, 33.93; H, 5.99. $C_{25}H_{54}O_{15}P_5Ir \cdot 0.2C_6H_5$ calcd.: C, 32.90; H, 5.99% NMR showed presence of benzene and of **6b** (~ 7%).

*$IrCl[(\overline{OCH_2CMe_2CH_2OPO})_2H]_2[\overline{OCH_2CMe_2CH_2OPOH}]$ (**6b**).* A mixture of $[IrCl(C_8H_{14})_2]_2$ (0.202 g, 0.226 mmol), **3** (0.542 g, 3.611 mmol) and cyclohexanone (0.8 ml) was heated in toluene (7 ml) for 5 h at reflux. More **3** (0.271 g) was added and heating was continued for 5 h. The product solution was filtered and the filtrate was evaporated in vacuo. The resulting residue was freed from the excess of **3** by GPC giving **6b** as a colourless solid (0.434 g). A portion for analysis was crystallised from benzene/ether (~ 50% recovery). Found: C, 31.09; H, 4.53; Cl, 3.83. $C_{25}H_{53}O_{15}P_5Cl$ calcd.: C, 30.70; H, 5.67; Cl, 3.62%.

*$Ir(acac)[(\overline{OCH_2CMe_2CH_2OPO})_2H]_2$ (**11**).* A mixture of $Ir(acac)(C_8H_{14})_2$ (**10**), (0.110 g, 0.215 mmol) and **3** (0.268 g, 1.79 mmol) in benzene (5 ml) was heated at reflux for 7 h. The reaction solution was concentrated and a colourless solid (0.107 g) was isolated by GPC. Found: C, 35.48; H, 6.15. $C_{25}H_{51}O_{14}P_4Ir \cdot 0.5C_5H_{12}O_2$ calcd.: C, 35.00; H, 6.09). [The presence of 2,2-dimethylpentan-1,3-diol ($C_5H_{12}O_2$) was shown by ^1H NMR].

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