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FULL PAPER

Different co-ordination modes of the new, water-soluble, triphosphine $PhP[CH_2CH_2P(CH_2OH)_2]_2$ with Pt^{II}, Pd^{II}, Rh^{I} and Re^{V}

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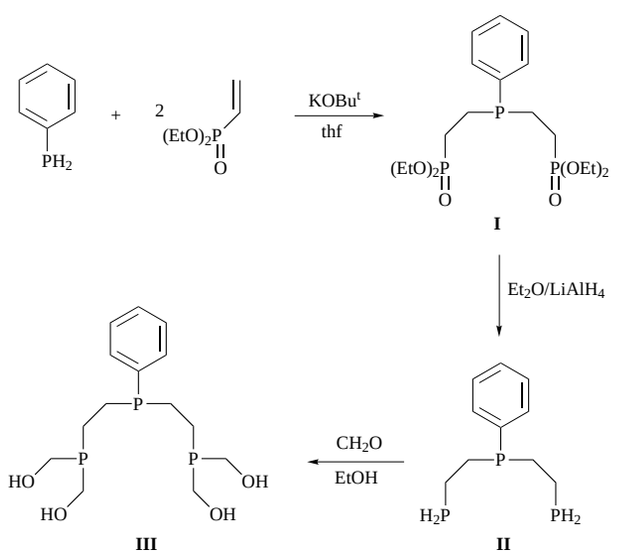
The water-soluble, triphosphine $PhP[CH_2CH_2P(CH_2OH)_2]_2$ was synthesized in good yield from $PhP(CH_2CH_2PH_2)_2$, by formylation of P–H bonds in the presence of formaldehyde and oxygen-free ethanol. When dissolved in water, it reacted readily with $[Pt(cod)]Cl_2$ (cod = cycloocta-1,5-diene), $[Pd(PhCN)_2]Cl_2$, $[\{RhCl(cod)\}_2]$ and $[ReO_2I(PPh_3)_2]$, each in CH_2Cl_2, to provide complexes **1**–**4** of Pt^{II}, Pd^{II}, Rh^{I} and Re^{V} respectively. All of the new compounds were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopies. Compound **1** was further characterized by ^{195}Pt NMR spectroscopy. The chemical constitutions of the compounds were further established by FAB mass spectrometry and elemental analysis (C and H). The results of this study demonstrate the versatility in co-ordination of the new, water-soluble, triphosphine.

There is a surge of interest in the syntheses of new tridentate ligand frameworks for use in the design and development of tripodally co-ordinated transition-metal complexes.[1–4] This stems from the possibility that tripodal ligands present the prospect of generating co-ordinatively unsaturated and catalytically active species within the same molecule, *via* reversible dissociation of one of the metal–ligand bonds in the presence of substrate molecules.[1–4] Tripodal phosphines constitute an important family of ligands for the generation of catalytically active transition-metal complexes. For example, the utility of rhodium(I) complexes derived from tripodal phosphines [*e.g.* $PhP(CH_2CH_2PPh_2)_2$] for the catalytic hydrogenation of cyclohexane and desulfurization of organosulfur compounds present in petroleum exemplifies the rich potential of transition-metal complexes derived from polydentate phosphines in catalytic applications.[4–6] While considerable effort has been devoted to understanding the co-ordination chemistry of tripodal phosphines, water-soluble tripodal phosphines and their corresponding water-soluble metallic complexes has remained largely unexplored. Such water-soluble transition-metal complexes will be unique in terms of their utility in biphasic catalysis.[7] Studies by Pringle and co-workers[8,9] have demonstrated the utility of (alkyl)hydroxyphosphine ligands as precursors toward the formation of water-soluble transition-metal complexes. As part of our ongoing investigation into the development of such compounds for catalytic and biomedical applications,[10–18] we have recently reported a novel, water-soluble, triphosphine $PhP[CH_2CH_2P(CH_2OH)_2]_2$ that demonstrated tripodal co-ordination behavior with Rh^{I} and Pt^{II}.[19] We herein report its co-ordination chemistry with Pd^{II}, Pt^{II}, Rh^{I} and Re^{V}, exemplifying the versatility of this new triphosphine.

Results and Discussion

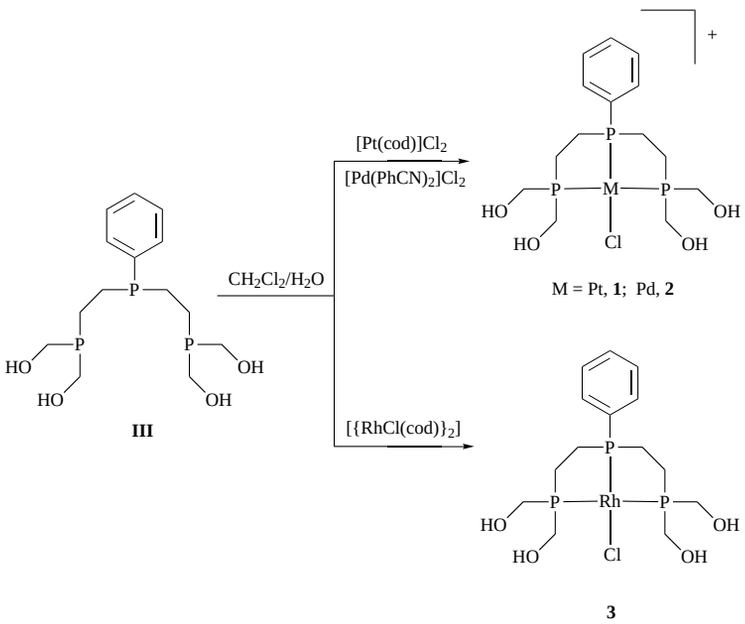
The synthesis of the triphosphine $PhP[CH_2CH_2P(CH_2OH)_2]_2$ was accomplished in a three-step procedure as described in Scheme 1. Compounds **I** and **II** were synthesized using a method similar to that reported by King *et al.*[20] The monophosphine bis(phosphonate) $PhP[CH_2CH_2P(O)(OEt)_2]_2$ **I** was prepared in 92% yield *via* the reaction of $PhPH_2$ with CH_2-$CHP(O)(OEt)_2$ in the presence of $KOBu^t$ catalyst in freshly distilled thf. The phosphine hydride $PhP(CH_2CH_2PH_2)_2$ **II** was prepared by the reduction of **I** in diethyl ether using lithium



Scheme 1

aluminium hydride. Compound **II** was isolated in pure chemical form with a yield of 94%. The (hydroxymethyl)phosphine **III** was prepared in 91% yield by formylation of P–H bonds in oxygen-free ethanol in the presence of aqueous formaldehyde.

Compounds **I**–**III** were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy. Fast atom bombardment mass spectrometry was used to identify the molecular ion for the new (hydroxyalkyl)triphosphine **III**. It showed a parent ion at $[M + H^+]$, $m/z = 351.09$. Compound **I** resonates as an AX_2 spin system in the ^{31}P NMR spectrum with a doublet centered at δ 48.6 corresponding to the $P(O)(OEt)_2$ phosphorus nuclei and a triplet centered at δ −16.5 corresponding to the PPh. The formation of the triphosphine hydride **II** was monitored by ^{31}P NMR spectroscopy. This intermediate also resonates as an AX_2 spin system with a triplet centered at δ −20.0 and a doublet centered at δ −129.8 respectively. These chemical shifts are within the normal range for those previously reported for this compound (δ −20.7 and −126.7).[20] Compound **III** shows resonances at δ −16.7 (triplet) and −20.8 (doublet) in the ^{31}P NMR spectrum corresponding to PPh and $P(CH_2OH)$ nuclei respectively. A deshielding of the ^{31}P nuclei in going from the



Scheme 2

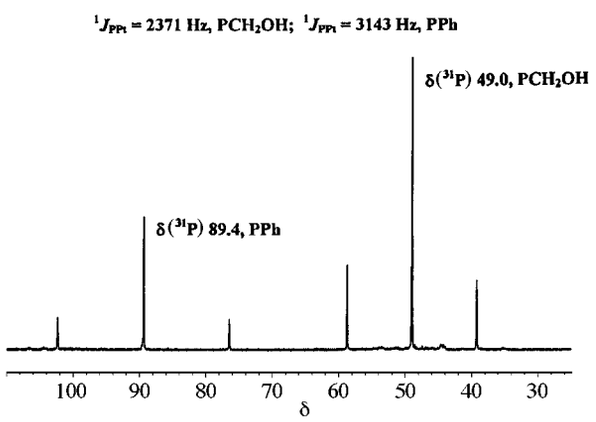


Fig. 1 The ^{31}P NMR spectrum (121.5 MHz) of complex **1**

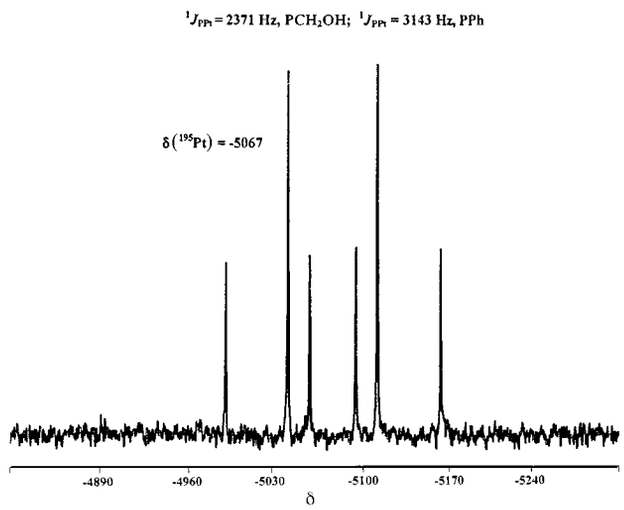


Fig. 2 The ^{195}Pt NMR spectrum (64.5 MHz) of complex **1**

phosphine hydride (δ −129.8) to the (hydroxymethyl)phosphine (δ −20.8) is of note. The three-bond coupling constants observed for each ^{31}P nucleus are 28 Hz.

Co-ordination chemistry of the tripodal triphosphine III with Pt^{II}, Pd^{II} and Rh^{I}

In order to develop a firm understanding of the co-ordination chemistry of the new (hydroxymethyl)phosphine **III**, its interactions with the late transition metals Pd^{II}, Pt^{II} and Rh^{I} were first investigated. The hydrophilic nature of this new ligand necessitated the development of its co-ordination chemistry under biphasic (aqueous–organic) reaction conditions. For example, the triphosphine **III**, upon dissolution in water, interacted with $[Pt(cod)]Cl_2$ (cod = cycloocta-1,5-diene), dissolved in CH_2Cl_2, to produce the new platinum(II) complex **1** (Scheme 2). The reaction of **III** with $[Pd(PhCN)_2]Cl_2$ was carried out under similar biphasic conditions to produce the corresponding palladium(II) complex **2** in good yield, and with the rhodium(I) precursor $[\{RhCl(cod)\}_2]$ produced the neutral, tripodal complex **3**. In all of the reactions outlined in Scheme 2 more than 99% of the platinum(II), palladium(II) and rhodium(I) precursors, from the organic phase, was transferred into the aqueous phase in the form of complexes **1**–**3**. Reaction by-products and impurities remained in the organic layer. All of the complexes were isolated from the aqueous phase upon removal of water *in vacuo*.

The new complexes were characterized by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H, ^{13}C, ^{31}P and ^{195}Pt NMR spectra of **1** were indicative of ≈98% purity. Fast atom bombardment mass spectrometric analysis showed a parent ion corresponding to $[M + H^+]$, m/z = 531.03. The ^{31}P NMR spectrum (Fig. 1) consisted of two singlet signals centered at δ 49.0 and 89.4 respectively. Platinum satellites, as a result of phosphorus coupling with the metal, are responsible for the three-line patterns ($^{1}J_{PtP}$ = 2371 Hz, PCH_2OH; $^{1}J_{PtP}$ = 3143 Hz, PPh); P–P coupling across three bonds was not evident. Absence of coupling is, however, not unexpected. For example, Meek and co-workers[21] studied a series of platinum(II)-polyphosphine complexes and observed P–P coupling of only 0.8 Hz for a triphos [= $PhP(CH_2CH_2PPh_2)_2$] complex. The ^{195}Pt NMR spectrum of **1** (Fig. 2) is diagnostic of tripodal co-ordination with 1:1 metal to ligand ratio as formulated in Scheme 2. There is a doublet of triplets, centered at δ −5067. This spectrum is consistent with the Pt coupling to two inequivalent P^{III}. The $^{1}J_{PtP}$ values of 2371 and 3143 Hz (Fig. 2) are identical to those derived from the ^{31}P NMR spectrum. Elemental analysis (C, H) further established the composition of **1**.

The fast atom bombardment mass spectrometric analysis of complex **2** showed a parent ion corresponding to $[M + H^+]$, m/z = 491.97. The ^{31}P NMR spectra consisted of two singlet signals centered at δ 54.4 and 117.7 respectively. The chemical

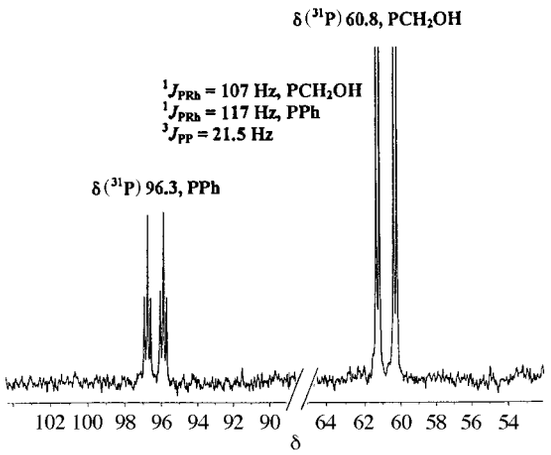


Fig. 3 The ^{31}P NMR spectrum (121.5 MHz) of complex **3**

constitution was further established by elemental analysis (C and H).

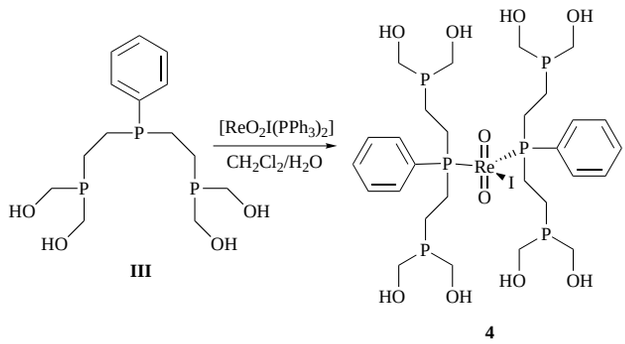
The new rhodium(I) complex **3** showed a parent ion corresponding to $[M + H^+]$, $m/z = 453.00$. The ^{31}P NMR spectrum (Fig. 3) consisted of a doublet of doublets and doublet of triplet signals centered at δ 60.8 and 96.3 respectively. The fine structure observed is due to one-bond Rh–P coupling ($^1J_{RhP}$ = 107 Hz, PCH_2OH; $^1J_{RhP}$ = 117 Hz, PPh) as well as P–P coupling ($^3J_{PP}$ = 21.5 Hz) across three bonds. These coupling constants are within the normal range of those for rhodium(I)–polyphosphine complexes.[22] The chemical constitution was further established by elemental analysis (C and H).

Phosphorus-31 NMR spectroscopy served to be a useful tool in the characterization of complexes **1**–**3**. In each case the downfield chemical shift from the free triphosphine (δ −20.8, PCH_2OH; δ −16.7, PPh) as well as the structure due to M–P coupling served to establish the tripodal co-ordinating modes of **III**. However, an interesting feature arises when comparing coupling constants for the platinum(II) and rhodium(I) complexes. The central phosphorus, PPh, is more electronegative than the terminal phosphorus centers [*i.e.* $P(CH_2OH)_2$] and, therefore, Pt–P π-back bonding is expected to be stronger with the former. The higher value of $^1J_{PtP}$ for PPh (3143 Hz) as compared to that for the $P(CH_2OH)_2$ groups (2371 Hz) complements the above description of the bonding for **1**. Furthermore, the lower *trans* influence of chlorine, as compared to phosphorus, produces stronger Pt–P bonds, hence a higher coupling constant. A similar trend in Rh–P coupling was observed for the rhodium(I) complex of triphos.[2] In this case the lower *trans* influence of chlorine, coupled with the poorer nucleophilicity of PPh_2, as compared to PPh, is presumably responsible for the higher coupling observed for the PPh. The opposite trend observed with **3** for $^1J_{RhP}$ [107 Hz, PPh; 117 Hz, $P(CH_2OH)_2$] is of note.

Co-ordination chemistry of the tripodal triphosphine with Re^V

In order to develop the co-ordination chemistry of the (hydroxymethyl)phosphine **III** with the early transition metals, its reaction with Re^V was also investigated. The triphosphine, upon dissolution in water, interacted with $[ReO_2I(PPh_3)_2]$, dissolved in CH_2Cl_2, to produce the new rhenium(V) complex **4** (Scheme 3). More than 99% of the rhenium(V) precursor, from the organic phase, was transferred into the aqueous phase in the form of the complex **4**. The complex was isolated from the aqueous phase upon removal of water *in vacuo* and characterized by conventional methods. Attempts at crystallization were unsuccessful.

Fast atom bombardment mass spectrometric analysis showed a parent ion corresponding to $[M + H^+]$, $m/z = 919.3188$. The ^{31}P NMR spectrum consisted of a triplet signal centered at



Scheme 3

δ 29.9 ($^3J_{PP}$ = 37.7 Hz) and a doublet signal centered at δ −20.1 ($^3J_{PP}$ = 37.7 Hz). This is not consistent with tripodal co-ordination of the ligand. In fact, all analytical evidence supports the structure depicted in Scheme 3. The ^{31}P NMR spectrum supports displacement of the PPh_3 ligands present in the rhenium(V) precursor. A number of reactions were performed in order to establish the co-ordination chemistry of ligand **III** with Re^V. However, in all cases, a mixture of products was obtained as established by ^{31}P NMR evidence. The reaction stoichiometry 2:1 ligand:metal served to provide the single product **4**. Its chemical constitution was further established by elemental analysis (C and H).

Conclusion

The synthesis and co-ordination chemistry of the tripodal triphosphine **III** with Pt^{II}, Pd^{II}, Rh^I and Re^V was established by various spectroscopic techniques. The disparate basicities of the phosphorus(III) centers present in this ligand system provide for a unique co-ordination among the metallic complexes investigated. Tripodal co-ordination was evident, as established by multinuclear NMR evidence, for the complexes of Pt^{II}, Pd^{II} and Rh^I. However, the investigation of the rhenium(V) chemistry with this ligand is not consistent with tripodal co-ordination. As established by ^{31}P NMR evidence, co-ordination through the PPh was the only mode of ligation with Re^V. This ligating fashion with Re^V does not complement the potential use of **III** in nuclear medicinal applications, however the different basicities of the phosphorus(III) centers may aid in the development of catalytically useful transition-metal compounds (*e.g.* **1**–**3**) wherein the weaker of the two different M–P bonds may be reversibly cleaved in the presence of a substrate molecule.

Experimental

All reactions were carried out under purified nitrogen by standard Schlenk techniques. Solvents were purified by standard methods and distilled under nitrogen prior to use. The compounds $PhPH_2$, $H_2CCHP(O)(OEt)_2$, $KOBu^t$, $LiAlH_4$, 37% aqueous formaldehyde, $[ReO_2I(PPh_3)_2]$, $[Pd(PhCN)_2]Cl_2$ and $[Pt(cod)]Cl_2$ from Aldrich Chemical Company were used without further purification as was $[\{RhCl(cod)\}_2]$ (Strem Chemical Company). Nuclear magnetic resonance spectra were recorded on a Bruker ARX-300 spectrometer using D_2O and $CDCl_3$ as solvents. The ^{1}H and ^{13}C chemical shifts are reported in ppm, downfield from external standard $SiMe_4$. The ^{31}P NMR (121.5 MHz) spectra were recorded with 85% H_3PO_4 as an external standard and positive chemical shifts lie downfield of the standard. The ^{195}Pt NMR spectra were recorded in water with chemicals shifts referenced to external $K_2[PtCl_4]$. Elemental analyses were performed by Oneida Research Services, Inc. Whitesboro, New York. There was some deviation for C and H from their calculated values for complexes **1**–**4**. Mass spectral analyses were performed by the Washington University

Resource for Biomedical and Bio Organic Mass Spectrometry, St. Louis, Missouri.

Syntheses

PhP[$CH_2CH_2P(O)(OEt)_2$]$_2$ I. A sample of $H_2CCHP(O)(OEt)_2$ (30 mmol) was placed in a solution of freshly distilled thf (100 cm^3) with stirring. The compound $PhPH_2$ (15 mmol) was added dropwise to the stirring solution. This solution was allowed to stir for 10 min, after which a catalytic amount of $KOBu^t$ (≈1 cm^3) was added. The resulting solution was stirred under nitrogen for 30 min at room temperature. The remaining thf was removed *in vacuo*. The resulting solution was dissolved in diethyl ether and filtered to remove any remaining potassium salts. Removal of solvent *in vacuo* afforded compound **I** as a colorless, viscous oil with an overall yield of 92% (6.0 g). ^{31}P NMR ($CDCl_3$): δ 31.4 (d, $^3J_{PP}$ = 48.6, $POCH_2CH_3$) and −16.5 (t, $^3J_{PP}$ = 48.6 Hz, PC_6H_5). No literature values are reported.[20]

PhP($CH_2CH_2PH_2$)$_2$ II. Compound **I** (14 mmol) was placed in dry diethyl ether (100 cm^3) and cooled at 0 °C. An ether solution of (1.0 M) lithium aluminium hydride (36 mmol, 36 cm^3) was added dropwise with constant stirring. An aqueous solution of 6 M hydrochloric acid (50 cm^3) was added to quench any remaining $LiAlH_4$. The ether layer was separated by cannula and the solvent removed *in vacuo* to afford **II** in 94% (3.0 g) yield as a colorless, viscous oil. ^{31}P NMR ($CDCl_3$): δ −20.0 (t, $^3J_{PP}$ = 14.6, PC_6H_5) and −129.8 (d, $^3J_{PP}$ = 14.6 Hz, PH_2). Literature values are δ −20.7 and −126.7.[20]

PhP[$CH_2CH_2P(CH_2OH)_2$]$_2$ III. Aqueous formaldehyde (61 mmol) was placed in oxygen-free ethanol (50 cm^3) and purged with nitrogen gas for 2 h at 25 °C. Compound **II** (13 mmol) was added dropwise with stirring at 25 °C. The reaction was complete in 2 h, as monitored by ^{31}P NMR spectroscopy. Removal of the solvent *in vacuo* afforded compound **III** in 91% (4.1 g) yield, as a colorless, viscous oil. Low-resolution FAB mass spectrum: Found [M + H^+], m/z = 351.09; Calc. for $C_{14}H_{25}O_4P_3$ 350.9 (Found: C, 47.64; H, 7.31. Calc. for $C_{14}H_{25}O_4P_3$: C, 48.01; H, 7.19%). ^{1}H NMR (D_2O): δ 1.46 (br s, 4 H, $HOH_2CPC\mathit{H}_2CH_2$), 1.82 (br s, 4 H, $HOH_2CPCH_2C\mathit{H}_2$), 3.82 (m, 8 H, $PC\mathit{H}_2OH$) and 7.35–7.5 (m, 5 H, C_6H_5). ^{31}P NMR (D_2O): δ −16.7 (t, 1 P, $^3J_{PP}$ = 28, PC_6H_5) and −20.8 (d, 2 P, $^3J_{PP}$ = 28 Hz, PCH_2OH).

Complex 1. An aqueous solution (10 cm^3) of compound **III** (0.551 mmol) was added dropwise to [Pt(cod)]Cl_2 (0.537 mmol) in dichloromethane (20 cm^3) at 25 °C with constant stirring. The stirring was continued for 30 min after which the aqueous phase was separated from the organic phase. The aqueous layer was filtered, concentrated to ≈5 cm^3 *in vacuo*, and allowed to evaporate slowly at room temperature to afford **1** as a clear, microcrystalline solid in 83% yield (0.25 g). Low-resolution FAB mass spectrum: Found [M + H^+], m/z = 531.03; Calc. for $C_{14}H_{25}ClO_4P_3Pt$ 530.03 (Found: C, 26.73; H, 4.20. Calc. for $C_{14}H_{25}Cl_2O_4P_3Pt$: C, 27.32; H, 4.10%). ^{1}H NMR (D_2O): δ 1.77 (m, 2 H, $HOH_2CPC\mathit{H}_2CH_2$), 2.63 (m, 6 H, $HOH_2CPC\mathit{H}_2CH_2$, $HOH_2CPCH_2C\mathit{H}_2$), 4.35 (m, 8 H, $PC\mathit{H}_2OH$) and 7.45–7.84 (m, 5 H, C_6H_5). ^{13}C NMR (D_2O): δ 19.4 (m, $HOH_2CPCH_2CH_2$), 27.2 (d, $^1J_{PC}$ = 40.6, $HOH_2CPCH_2CH_2$), 54.6 (m, PCH_2OH), 123 (d, $^1J_{PC}$ = 60.6, PC_6H_5), 129.3 (d, $^2J_{PC}$ = 11.3, *o*-C of C_6H_5), 133.4 (d, $^3J_{PC}$ = 11.5, *m*-C of C_6H_5) and 133.5 (s, *p*-C of C_6H_5). ^{31}P NMR (D_2O): δ 49.0 (s, 2 P, $^1J_{PtP}$ = 2371, PCH_2OH) and 89.4 (s, 1 P, $^1J_{PtP}$ = 3143 Hz, PC_6H_5).

Complex 2. An aqueous solution (10 cm^3) of compound **III** (0.460 mmol) was added dropwise to [Pd($PhCN)_2$]Cl_2 (0.409 mmol) in dichloromethane (20 cm^3) at 25 °C with constant stirring. The stirring was continued for 30 min after which the aqueous phase was separated from the organic phase. Upon filtration, the aqueous layer was concentrated to ≈5 cm^3 *in vacuo* and allowed to evaporate slowly at room temperature to afford **2** as a yellow, microcrystalline solid in 81% yield (0.17 g). Low-resolution FAB mass spectrum: Found [M + H^+], m/z = 491.97; Calc. for $C_{14}H_{25}ClO_4P_3Pd$ 490.97 (Found: C, 30.3; H, 4.51. Calc. for $C_{14}H_{25}Cl_2O_4P_3Pd$: C, 31.94; H, 4.79%). ^{1}H NMR (D_2O): δ 1.87 (m, 2 H, $HOH_2CPC\mathit{H}_2CH_2$), 2.64 (m, 6 H, $HOH_2CPC\mathit{H}_2CH_2$, $HOH_2CPCH_2C\mathit{H}_2$), 4.29 (m, 8 H, $PC\mathit{H}_2OH$) and 7.49–7.84 (m, 5 H, C_6H_5). ^{13}C NMR (D_2O): δ 18.6 (m, $HOH_2CPCH_2CH_2$), 29.1 (d, $^1J_{PC}$ = 59.5, $HOH_2CPCH_2CH_2$), 55.1 (m, PCH_2OH), 123.3 (d, $^1J_{PC}$ = 53.6, PC_6H_5), 129.5 (d, $^2J_{PC}$ = 11.3, *o*-C of C_6H_5), 133.3 (d, $^3J_{PC}$ = 11.8, *m*-C of C_6H_5) and 133.8 (s, *p*-C of C_6H_5). ^{31}P NMR (D_2O): δ 54.4 (s, 2 P, PCH_2OH) and 117.7 (s, 1 P, PC_6H_5).

Complex 3. An aqueous solution (10 cm^3) of compound **III** (0.490 mmol) was added dropwise to [{RhCl(cod)}$_2$] (0.24 mmol) in dichloromethane (20 cm^3) at 25 °C with constant stirring. The stirring was continued for 30 min after which the aqueous phase was separated from the organic phase. After filtration, the aqueous layer was concentrated to ≈5 cm^3 *in vacuo* and allowed to evaporate slowly at room temperature to afford **3** as an orange, microcrystalline solid in 66% yield (0.08 g). Low-resolution FAB mass spectrum: Found [M + H^+ − HCl], m/z = 453.00; Calc. for $C_{14}H_{25}ClO_4P_3Rh$ 487.97 (Found: C, 35.46; H, 5.48. Calc. for $C_{14}H_{25}ClO_4P_3Rh$: C, 34.43; H, 5.16%). ^{1}H NMR (D_2O): δ 1.90 (m, 2 H, $HOH_2CPC\mathit{H}_2CH_2$), 2.50 (m, 6 H, $HOH_2CPC\mathit{H}_2CH_2$, $HOH_2CPCH_2C\mathit{H}_2$), 4.30 (m, 8 H, $PC\mathit{H}_2OH$) and 7.45–7.84 (m, 5 H, C_6H_5). ^{31}P NMR (D_2O): δ 60.8 (dd, 2 P, $^1J_{RhP}$ = 117, $^3J_{PP}$ = 21.5, PCH_2OH) and 96.3 (dt, 1 P, $^1J_{RhP}$ = 107, $^3J_{PP}$ = 21.5 Hz, PC_6H_5).

Complex 4. An aqueous solution (10 cm^3) of compound **III** (0.50 mmol) was added dropwise to [$ReO_2I(PPh_3)_2$] (0.23 mmol) in dichloromethane (20 cm^3) at 25 °C with constant stirring. The stirring was continued for 30 min after which the aqueous phase was separated from the organic phase. The aqueous phase was filtered, concentrated to ≈5 cm^3 *in vacuo*, and allowed to evaporate slowly at room temperature to afford **4** as a yellow, viscous oil in 79% yield (0.19 g). High-resolution FAB mass spectrum: Found: [M + H^+ − HI], m/z = 919.1388; Calc. for $C_{28}H_{50}IO_{10}P_6Re$ 1046.0432 (Found: C, 33.32; H, 5.23. Calc. for $C_{28}H_{50}IO_{10}P_6Re$: C, 32.16; H, 4.82%). ^{1}H NMR (D_2O): δ 1.72 (m, 8 H, $PC\mathit{H}_2CH_2PC_6H_5$), 2.73 (m, 8 H, $PCH_2C\mathit{H}_2PC_6H_5$), 3.93 (m, 16 H, $PC\mathit{H}_2OH$) and 7.62–7.79 (m, 10 H, C_6H_5). ^{13}C NMR (D_2O): δ 11.0 (dd, $^1J_{PC}$ = 14.5, $^2J_{PC}$ = 5.18, $PCH_2CH_2PC_6H_5$), 14.1 (dd, $^1J_{PC}$ = 44.7, $^2J_{PC}$ = 19.1, $PCH_2CH_2PC_6H_5$), 57.3 (d, $^1J_{PC}$ = 10.6, PCH_2OH), 114.3 (d, $^1J_{PC}$ = 77.7, PC_6H_5), 129.5 (d, $^2J_{PC}$ = 64.9, *o*-C of C_6H_5), 132.1 (d, $^3J_{PC}$ = 8.3 Hz, *m*-C of C_6H_5) and 135.0 (s, *p*-C of C_6H_5). ^{31}P NMR (D_2O): δ 29.9 (t, $^3J_{PP}$ = 37.7, PC_6H_5) and −20.1 (d, $^3J_{PP}$ = 37.7 Hz, PCH_2OH).

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