New advances in the synthesis of a water-soluble triphosphine and the development of tripodally coordinated rhodium(I) and platinum(II) complexes†

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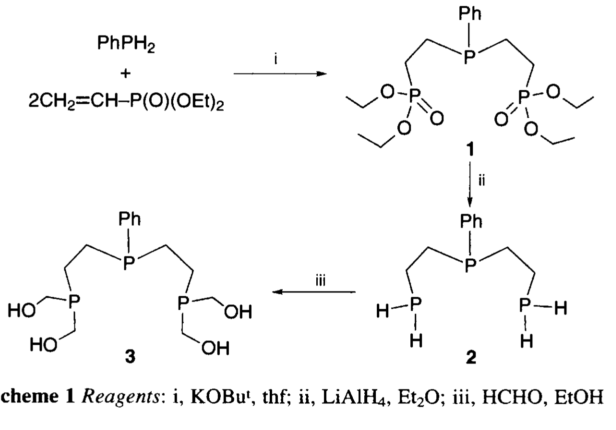
A new water-soluble triphosphine $PhP[CH_2CH_2P(CH_2OH)_2]_2$ is produced *via* the formylation of $PhP(CH_2CH_2PH_2)_2$; this triphosphine, upon interaction with $[Rh(cod)Cl]_2$ and $Pt(cod)Cl_2$ (cod = cycloocta-1,5-diene) under biphasic (water/CH_2Cl_2) conditions, produced water-soluble rhodium(I) and platinum(II) complexes respectively; ^{31}P and ^{195}Pt NMR spectroscopic data confirm the tripodal coordination of Rh^I and Pt^{II} involving > PPh and the two $-P(CH_2OH)_2$ functionalities.

Transition-metal complexes of tripodal phosphines present the prospect of generating coordinatively unsaturated (and catalytically active) species, within the same molecule, *via* reversible dissociation of one of the metal phosphine bonds in the presence of substrate molecules.[1] 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.[1–3] While considerable effort has been devoted to understanding the coordination chemistry of tripodal phosphines, the development of water-soluble tripodal phosphines and their corresponding water-soluble metal complexes have remained largely unexplored. Water-soluble transition-metal complexes derived from tripodal phosphines will be unique in terms of their utility in biphasic catalysis.[4] As part of our ongoing investigation into the development of water-soluble transition-metal compounds for catalytic and biomedical applications,[5–10] we report herein (*a*) our discovery of a novel, water-soluble, tripodal phosphine and (*b*) coordination chemistry of this new triphosphine to produce first examples of water-soluble and tripodally coordinated rhodium(I) and platinum(II) complexes (Scheme 1).

The synthesis of triphosphine, $PhP[CH_2CH_2P(CH_2OH)_2]_2$ **3**, was carried out in three steps (Scheme 1): (*a*) Michael addition of P–H bonds of $PhPH_2$ with diethyl vinylphosphonate to produce the phosphonate intermediate, $PhP[CH_2CHP(O)(OEt)_2]_2$ **1**; (*b*) reduction of this intermediate **1** using $LiAlH_4$ to produce the phosphine precursor, $PhP(CH_2CH_2PH_2)_2$ **2**[11] and (*c*) formylation of P–H bonds of **2** using formaldehyde in ethanol to produce the triphosphine **3** in near quantitative yield. The new triphosphine **3** is soluble in water and showed remarkable oxidative stability in aqueous media. Compound **3** was characterized by FABMS ($[M + H]^+$ at *m*/*z* 351.10) and ^{31}P NMR spectroscopy. The > P(Ph) resonated as a triplet at δ −16.7 [^3J(P–P) 28 Hz] and the two $-P(CH_2OH)_2$ groups resonated as a doublet at δ −20.8. HPLC analysis of **3** indicated it to be *ca.* 99% pure.

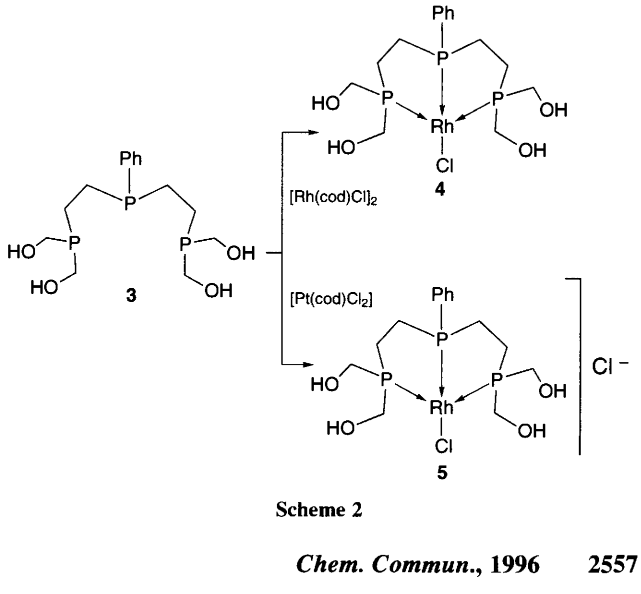


Scheme 1 *Reagents*: i, KOBu^t, thf; ii, $LiAlH_4$, Et_2O; iii, HCHO, EtOH

The reactions of **3** with rhodium(I) and platium(II) precursors under biphasic conditions (CH_2Cl_2/water), as outlined in Scheme 2, revealed tripodal coordination *via* the > P(Ph) and $-P(CH_2OH)_2$ centres. The rhodium(I) **4** and platinum(II) **5** complexes were formed in near quantitative yields demonstrating the kinetic propensity to tripodal coordination. The chemical constitutions of **4** and **5** were confirmed by elemental analysis and FAB mass spectrometry.†‡

The NMR spectroscopic data for **4** and **5** appear to be very diagnostic of tripodal coordination as proposed in Scheme 2. The ^{31}P NMR of **4** showed direct one-bond couplings with > PPh {^1J[Rh–P(Ph)] 107 Hz} and the two $-P(CH_2OH)_2$ {^1J[Rh–P(CH$_2$OH)$_2$] 117 Hz} and, therefore, confirm the tripodal coordination of Rh^I as depicted in Scheme 2. The ^{31}P NMR spectrum of **5** also confirmed the direct one-bond coupling interaction of Pt with > PPh [^1J(Pt–P) 3143 Hz] and the two $P(CH_2OH)_2$ [^1J(Pt–P) 2371 Hz] groups. The ^{195}Pt NMR of **5** consisted of a doublet of triplets fine structure as a result of direct Pt–P coupling with the > PPh [^1J(Pt–P) 3143 Hz] and the two $-P(CH_2OH)_2$ [^1J(Pt–P) 2371 Hz] groups and, therefore, tripodal coordination is evident. The ^{195}Pt NMR spectrum of **5** not only reconfirms the assignments made for ^1J(Pt–P) values for its ^{31}P NMR but also conclusively demonstrates the tripodal linking of phosphine centres.

The central phosphorus (*i.e.* > PPh) is more electronegative than the terminal phosphorus centres [*i.e.* $-P(CH_2OH)_2$] and,



Scheme 2

therefore, Pt–P π-back bonding is expected to be stronger with the former phosphine than with the two latter ones. The higher value of ^1J(Pt–P) for >PPh (3143 Hz) as compared to the two –$P(CH_2OH)_2$ groups (2171 Hz) complements the above description of bonding for **5**. The opposite trend observed in **4** for ^1J(Rh–P) {^1J(Rh–PPh) 107 Hz, ^1J[Rh–$P(CH_2OH)_2$] 117 Hz} is of note.

In addition to the water-soluble characteristics of **3**, the presence of >PPh and –$P(CH_2OH)_2$ groups of disparate basicities makes it unique as compared to the traditional triphosphines [*e.g.* triphos; $PhP(CH_2CH_2PPh_2)_2$]. The different basicities of >PPh and –$P(CH_2OH)_2$ groups in **3** may aid the development of catalytically useful transition-metal compounds (*e.g.* **4** and **5**) wherein the weaker of the two different M–P bond(s) may be reversibly cleaved in the presence of a substrate molecule.

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Footnotes

† *Synthesis of* [$RhCl\{PhP[CH_2CH_2P(CH_2OH)_2]_2\}$] **4**. An aqueous solution (10 cm^3) of compound **3** (0.49 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 removed *in vacuo* and dried to afford compound **4** as an orange viscous oil in near quantitative yield. High-resolution FABMS calc. for $C_{14}H_{25}ClO_4P_3Rh$, *m/z* 487.9709. Found for [M + H^+ − HCl], *m/z* 453.0021. Anal. calc. for $C_{14}H_{25}ClO_4P_3Rh$: C, 34.40; H, 5.15. Found: C, 34.45; H, 5.45%. ^1H NMR(D_2O): δ 1.90 (m, br, 2 H, $PhPCH_2CH_2$), 2.3–2.7 (m, 6 H, $PhPCH_2CH_2$, $PhPCH_2CH_2$), 4.30 (m, 8 H, PCH_2OH), 7.45–7.84 (m, 5 H, Ph). ^{31}P NMR(D_2O): δ 60.8 [dd, 2 P, ^1J(Rh–P) 117, ^3J(P–P) 21.5 Hz, $P(CH_2OH)_2$], 96.3 [dt, ^1J(Rh–P) 107 ^3J(P–P) 21.5 Hz, PPh].

‡ *Synthesis of* [$Pt\{PhP[CH_2CH_2P(CH_2OH)_2]_2\}$]Cl **5**. An aqueous solution (10 cm^3) of compound **3** (0.551 mmol) was added dropwise to [$PtCl_2(cod)$] (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. After filtration, the aqueous layer was removed *in vacuo* and dried to afford the compound **5** as a clear viscous oil in near quantitative yield. High-resolution FABMS. Calc. for $C_{14}H_{25}ClO_4P_3Pt$, *m/z* 580.0302. Found for *m/z* 581.0302. Anal. Calc. for $C_{14}H_{25}ClO_4P_3Pt$: C, 27.30; H, 4.10. Found: C, 26.75; H, 4.20%. ^1H NMR(D_2O): δ 1.77 (m, 2 H, $PhPCH_2CH_2$), 2.42–2.83 (m, 6 H, $PhPCH_2CH_2$, $PhPCH_2CH_2$), 4.35 (m, 8 H, PCH_2OH), 7.45–7.84 (m, 5 H, Ph). ^{31}P NMR(D_2O): δ 49.0 [s, 2 P, ^1J(Pt–P) 2371 Hz, $P(CH_2OH)_2$], 89.4 [s, ^1J(Pt–P) 3143 Hz, PPh]. ^{195}Pt NMR (D_2O): δ −4783.6 {dt, ^1J(Pt–PPh) 3143, ^1J[Pt–$P(CH_2OH)_2$] 2371 Hz}.

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