Formation and X-ray structure of a novel water-soluble tertiary–secondary phosphine complex of ruthenium(II): $[Ru\{P(CH_2OH)_3\}_2\{P(CH_2OH)_2H\}_2Cl_2]$

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The novel secondary–tertiary hydroxymethylphosphine complex, all-*trans* $[Ru\{P(CH_2OH)_3\}_2\{P(CH_2OH)_2H\}_2Cl_2]$, is formed by the room temperature reaction of excess tris(hydroxymethyl)phosphine, $P(CH_2OH)_3$, with either $RuCl_3\cdot H_2O$ or $[Ru(PPh_3)_3Cl_2]$; the X-ray crystal structure of the complex shows extensive intra- and inter-molecular hydrogen bonding consistent with the high water solubility of the complex.

The need for separation and recovery of expensive transition metal catalysts from organic products has led to the well known concept of aqueous/organic biphasic catalysis in which a catalyst that is selectively soluble in the aqueous phase is used to effect the transformation of reactants to products that are themselves selectively soluble in the organic phase.[1] Aqueous transition metal phosphine catalysts have largely been based on di or tri-sulfonated arylphosphines, such as $P(m\text{-}C_6H_4SO_3Na)_3$ (TPPTS). While highly active water-soluble analogues of triphenylphosphine complexes are known, many useful catalysts incorporate alkylphosphines and hydrophilic analogues of these are highly sought after. Tris(hydroxymethyl)phosphine (THMP), $P(CH_2OH)_3$, was initially studied by Chatt *et al.*, but after the disappointing results on the catalytic activity of rhodium complexes, this ligand was largely ignored.[2] There has recently been an upsurge of interest in THMP[3] (and related bi- and tri-dentate alkyl phosphines[4]) with the preparation of a range of complexes with applications in medicinal chemistry as well as catalysis.[5] The report that ruthenium complexes bearing the related water-soluble 1,3,5-triaza-7-phosphaadamantane (PTA) derivative[6] catalysed the reduction of aldehydes to alcohols in a biphasic organic/aqueous medium in the presence of sodium formate prompted us to synthesize tris(hydroxymethyl)phosphine complexes of ruthenium to look for similar properties. We report here that the reaction of $RuCl_3$ with excess THMP does not lead to straightforward coordination of the ligand, but rather results in the formation of a novel tertiary–secondary hydroxymethylphosphine metal complex resulting from the elimination of formaldehyde from THMP.

Addition of a fourfold excess of $P(CH_2OH)_3$ in ethanol to an ethanolic solution of $RuCl_3\cdot H_2O$ at room temperature results in the immediate formation of a green solution. The $^{31}P\{^1H\}$ NMR spectrum shows no remaining free phosphine (δ −24), but does show signals corresponding to THMP oxide (δ 45)[7] and the cation, $[P(CH_2OH)_4]^+$, at δ 24. There is a single ruthenium containing compound, **1**, which gives rise to two triplets in an A_2B_2 pattern at δ 13.5 and 9.7. The same products may be obtained upon stirring an aqueous solution of THMP with a dichloromethane solution of $[Ru(PPh_3)_3Cl_2]$ in a biphasic reaction. Removal of the solvent and recrystallisation of the resulting oil from methanol–hexane yielded yellow crystals of **1** suitable for X-ray crystallography.

The crystal structure shows that **1** is the octahedral ruthenium complex, $[Ru\{P(CH_2OH)_3\}_2\{P(CH_2OH)_2H\}_2Cl_2]$, (Fig. 1)‡ in which two of the tris(hydroxymethyl)phosphine groups have eliminated formaldehyde to give the secondary phosphine ligand $P(CH_2OH)_2H$. The asymmetric unit of the crystal structure corresponds to half a complex molecule with the ruthenium atom positioned on an inversion centre in space group $P2_1/c$. This gives rise to the all-*trans* stereochemistry for the three different ligand types. The phosphorus atom of the tertiary phosphine, P(2), is bonded to ruthenium and the carbon atoms of three hydroxymethyl groups with bond angles in the range 99.2(3)–119.2(2)°. The atom P(1) of the secondary phosphine is bonded to ruthenium, two hydroxymethyl groups and a hydrogen atom and shows a greater degree of distortion from tetrahedral geometry with bond angles in the range 105.7(3)–122.0(2)°. There is a significant difference between the two Ru–P lengths with the distance to the secondary phosphine being about 0.1 Å longer [2.414(2) *cf.* 2.318(2) Å]. The X-ray structure also shows the presence of extensive intra- and inter-molecular hydrogen bonding interactions with a total of 14 contacts per molecule in the range 2.75–3.25 Å (Fig. 2). This has also been observed for other crystallographically characterised complexes containing hydroxymethyl phosphine ligands, notably $[Pd(THMP)_4]\cdot MeOH$,[5a] which has a number of hydrogen bonds shorter than 2.8 Å.

The spectroscopic data for **1** in solution are consistent with the solid state structure.§ The higher field triplet resonance in the $^{31}P\{^1H\}$ NMR spectrum is assigned to the secondary phosphine ligand because of the large P–H coupling (J = 253 Hz) observed in the proton-coupled spectrum. The ^1H NMR spectrum shows two broad singlet resonances (δ 4.53 and 4.48) in a ratio of 1 : 0.6 due to the methylene groups in the tertiary and secondary phosphine ligands. The IR spectrum of **1**

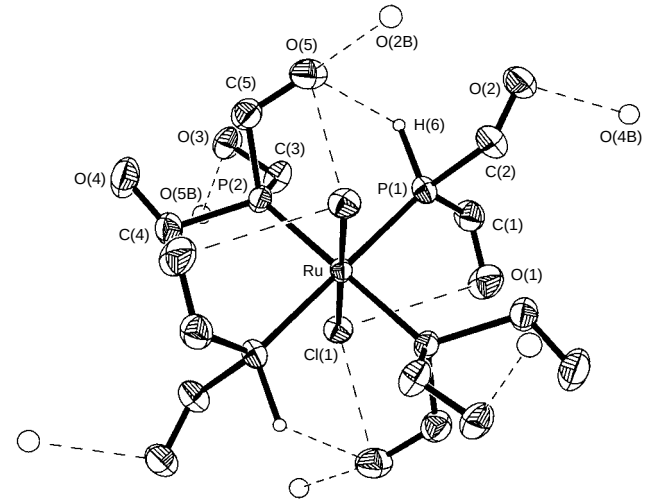

Fig. 1 View of **1** showing the atom numbering scheme and the intra- and inter-molecular hydrogen bonds (30% probability ellipsoids). Hydrogen atoms with the exception of H(6) have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru–P(1) 2.414(2), Ru–P(2) 2.318(2), Ru–Cl(1) 2.450(1), P(1)–C(1) 1.813(6), P(1)–C(2) 1.898(7), P(2)–C(3) 1.856(6), P(2)–C(4) 1.890(6), P(2)–C(5) 1.832(6), C(1)–O(1) 1.407(7), C(2)–O(2) 1.427(7), C(3)–O(3) 1.387(6), C(4)–O(4) 1.389(7), C(5)–O(5) 1.443(8); P(1)–Ru–P(1A) = P(2)–Ru–P(2A) = Cl(1)–Ru–Cl(1A) 180.0, P(1)–Ru–P(2) 85.58(6), P(1)–Ru–Cl(1) 93.12(5), P(2)–Ru–Cl(1) 86.68(5)°. Selected hydrogen bonding distances (Å): O(1)···Cl(1) 3.142(8), O(2)···O(4B) 2.709(8), O(3)···O(5B) 2.777(8), O(5)···Cl(1A) 3.226(7), O(5)···O(2B) 3.067(8).

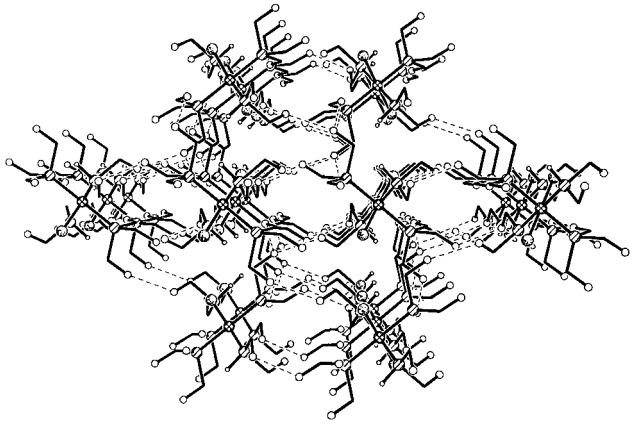

Fig. 2 View of the packing in **1** down the crystallographic *c* axis showing the hydrogen bonding

recorded in KBr shows a band at 2374 cm^{-1} which is assigned to ν(P–H).

The mechanism by which **1** is generated is not clear at present. There is no evidence for formation of the THMP complex $[Ru\{P(CH_2OH)_3\}_4Cl_2]$ nor for free secondary phosphine $P(CH_2OH)_2H$, although the elimination of formaldehyde accounts for the formation of the phosphonium cation observed by ^{31}P NMR.[8] There have been two reports of deprotonation of THMP to give metal alkoxide complexes,[9] but we can find no precedence for the formation of the secondary phosphine. This present facile route into water soluble metal complexes containing a reactive P–H bond offers great scope for further ligand functionalization.

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Notes and References

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‡ *Crystal data* for $[Ru\{P(CH_2OH)_3\}_2\{P(CH_2OH)_2H\}_2Cl_2]$ **1**: $C_{10}H_{32}Cl_2O_{10}P_4Ru$, M = 608.20, monoclinic, a = 9.367(5), b = 13.623(2), c = 9.650(1) Å, U = 1102.8(6) Å^3, T = 293 K, space group $P2_1/c$, Z = 2, μ(Mo-Kα) = 1.287 mm^{-1}. 3193 reflections collected on a Rigaku RAXIS II image plate of which 1847 were unique (R_{int} = 0.0548), 1421 had $F_o > 4\sigma(F_o)$, 5.7 < 2θ < 50.60, no absorption correction was applied. Structure solved by direct methods using SHELXS and all non-hydrogen atoms refined anisotropically using full matrix least squares (SHELXL-93).[10] $R1$ = 0.0423 (for 4σ data), $wR2$ = 0.1204, S = 1.005 (for all data). CCDC 182/861.

§ *Spectroscopic data* for $[Ru\{P(CH_2OH)_3\}_2\{P(CH_2OH)_2H\}_2Cl_2]$ **1**: NMR {270 MHz, CD_3OD, 298 K}: ^1H, δ 4.48 (br s, 8 H), 4.53 (br s, 12 H); $^{31}P\{^1H\}$, δ 9.7 (t, $^2J_{PP}$ 37.5 Hz), 13.5 (t, $^2J_{PP}$ 37.5); $^{13}C\{^1H\}$, 57.4 (vt, $|^1J_{PC} + {}^3J_{PC}|$ 27.2 Hz), 57.9 (vt, $|^1J_{PC} + {}^3J_{PC}|$ 26.8 Hz); IR (KBr, cm^{-1}), 3345s, 2966s, 2923s, 2854s, 2374m, 1627m, 1459m, 1376s, 1180m, 1023vs, 961m, 861m, 718m, 579m. Satisfactory elemental analysis (C, H) was obtained.

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