The First Examples of an Aryl Ring Substituted by Both Phosphine and Phosphonate Moieties: Synthesis and Characterization of the New Highly Water-soluble Phosphine Ligand $Na_2[Ph_2P(C_6H_4\text{-}p\text{-}PO_3)]\cdot 1.5H_2O$ and Platinum(II) Complexes

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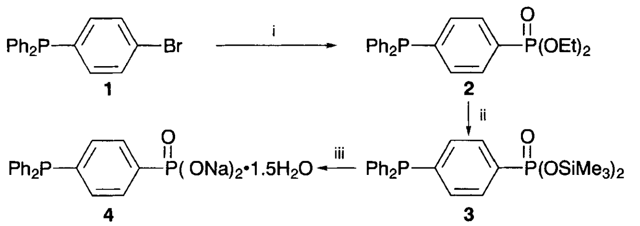
The highly water-soluble phosphine $Na_2[TPPMP]\cdot 1.5H_2O$ (TPPMP = 'triphenylphosphine monophosphonate') represents the first example of a compound containing an aryl ring which is substituted by both phosphine and anionic phosphonate moieties; the preparation and spectroscopic characterisation of the platinum(II) complexes (*trans*- and *cis*-$Na_4[PtCl_2(TPPMP)_2]\cdot 3H_2O$ is described.

The growing interest in aqueous organometallic chemistry and the application of water-soluble metal phosphine complexes in homogeneous catalysis has prompted a search for new water-soluble tertiary phosphines.[1] Although sulfonated phosphines, *e.g.* 'triphenylphosphine trisulfonate' (TPPTS), are usually the ligands of choice for homogeneous catalysis due to their high solubility and similar electronic properties to triphenylphosphine,[2] a large number of alternative ligands have been prepared containing a variety of functional groups *e.g.* $-CO_2Na$,[3] $-OH$,[4] $-PMe_3^+$,[5] $-NMe_3^+$,[6] and polyethers,[7] which render the phosphines water-soluble. Many of these have quite different steric and electronic properties to triphenylphosphine. We have been interested in the preparation of tertiary phosphine ligands containing anionic phosphonate and phosphate groups and herein describe the preparation and complexing behavior of the first ligand containing an arene ring substituted by both phosphine and phosphonate moieties, 'triphenylphosphine monophosphonate' (TPPMP) and the preparation of the first metal complex containing both anionic phosphonate and tertiary phosphine groups.

The lithiation of diphenylphosphino-*p*-bromobenzene **1** followed by reaction with an equimolar amount of diethylchlorophosphate in THF results in the formation of diphenylphosphino-*p*-benzenediethylphosphonate **2** (Scheme 1). Compound **2** was isolated from the reaction mixture after purification using flash chromatography on silica gel, as a viscous, cloudy oil in 62% yield. All attempts to crystallize the phosphonate ester, from a variety of organic solvents, were unsuccessful although the ester was spectroscopically pure by ^1H, ^{31}P and ^{13}C NMR.† Subsequent reaction of **2** with an excess of bromotrimethylsilane in dichloromethane gave the intermediate bis(trimethylsilyl) ester **3** which is characterized by two singlets in the ^{31}P NMR spectrum (CH_2Cl_2) at δ −6.4 and 0.5. Hydrolysis of **3** with 2 equiv. of water proceeded smoothly in acetone at room temperature to give the desired arylphosphonic acid which was isolated as the disodium salt **4** after neutralisation with aqueous sodium hydroxide followed by crystallisation from diethyl ether–methanol.‡ Roundhill has recently used a similar reaction sequence in the preparation of a tertiary phosphine containing a substituted alkylene phosphonate chain.[8] The ^{31}P NMR spectrum (acetone) of the unisolated free acid contains two singlets at δ −3.9 and 18.2 which are typical chemical shifts for tertiary arylphosphine and arylphosphonic acid moieties, and these resonances undergo a shift in the spectrum of the disodium salt (D_2O) to δ −5.0 and 12.9.



Scheme 1 *Reagents and conditions*: i, Bu^nLi, THF, $(EtO)_2P(O)Cl$, −70 °C to room temp. ii, $BrSiMe_3$, CH_2Cl_2, room temp.; iii, H_2O, acetone, room temp., then NaOH, H_2O, room temp.

Compound **4** has a remarkably high solubility in water and is significantly more soluble than Na(TPPMS)[9] (TPPMS = 'triphenylphosphine monosulfonate') {0.38 g ml^{-1} at 20 °C (**4**) *cf.* 0.08 g ml^{-1} at 20 °C [Na(TPPMS)]}. The enhanced solubility of **4** over the sulfonated analogue is presumably due to the dianionic nature of the phosphonate ligand.

Recrystallization of **4** from aqueous methanol gave the solvated phosphonate $Na_2[(TPPMP)(H_2O)_3(MeOH)]\cdot MeOH$ **5** and the crystal structure reveals some rather unusual features (Fig. 1). The unit cell contains two formula units bound together in a dimeric structure which is supported by multiple anion–cation interactions and bridging water molecules. There are two discrete types of sodium coordination; in the first, two sodium cations Na(2) and Na(2′) are three-coordinate and bridge two phosphonate moieties *via* phosphoryl oxygen atoms, O(1) and O(2′); and O(1′) and O(2). The second type of sodium coordination involves bonding of Na(1) and Na(1′) to O(2) and O(2′) respectively giving rise to two distinct O–Na–O–Na rings and a larger P–O–Na–O–P–O–Na–O ring *via* bridging water molecules. The cations Na(1) and Na(1′) are five-coordinate and stabilized by bonding to two further water molecules and a methanol molecule. The unit cell also contains two uncoordinated methanol molecules.

To study the binding properties of the phosphonate ligand to a late transition metal, representative platinum(II) complexes were prepared using a two-phase phosphine exchange method. A solution of $Pt(PPh_3)_2Cl_2$ in dichloromethane was rapidly stirred with an aqueous solution of **4**. Separation of the aqueous layer and work-up gave a 66:34 mixture of *trans*-$Na_4[PtCl_2(TPPMP)_2]\cdot 3H_2O$ **6** and *cis*-$Na_4[PtCl_2(TPPMP)_2]\cdot$

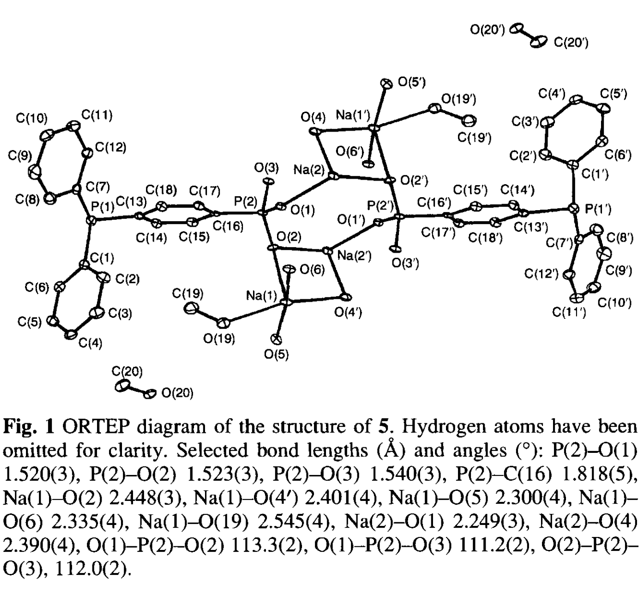


Fig. 1 ORTEP diagram of the structure of **5**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(2)–O(1) 1.520(3), P(2)–O(2) 1.523(3), P(2)–O(3) 1.540(3), P(2)–C(16) 1.818(5), Na(1)–O(2) 2.448(3), Na(1)–O(4′) 2.401(4), Na(1)–O(5) 2.300(4), Na(1)–O(6) 2.335(4), Na(1)–O(19) 2.545(4), Na(2)–O(1) 2.249(3), Na(2)–O(4) 2.390(4), O(1)–P(2)–O(2) 113.3(2), O(1)–P(2)–O(3) 111.2(2), O(2)–P(2)–O(3), 112.0(2).

$3H_2O$ **7** which could not be separated using conventional crystallisation techniques.

The ^{31}P NMR spectrum of the mixture of **6** and **7** recorded in H_2O contains two downfield triplets at δ 22.9 and 12.0 with $^2J(PtP) = 2480$ and $^2J(PtP) = 3730$ Hz, indicating *trans*- and *cis*-coordination of the phosphine ligands to platinum. Two upfield singlets at δ 10.2 and 10.0 have been assigned to the free phosphonate groups. The small shift of the phosphonate resonance from δ 12.9 in **4** to 10.2 and 10.0 in **6** and **7** respectively, and the lack of Pt–P coupling suggests an absence of coordination of the phosphonate to the metal centre. The new platinum complexes are freely soluble in water, sparingly soluble in methanol and DMSO, and are insoluble in all other common non-protic solvents.

To summarize, we have prepared and characterised a new, highly water-soluble phosphonate modified triphenylphosphine and representative transition metal complexes. The catalytic properties of **6** and **7** in water are currently under investigation.

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Footnotes

† *Spectroscopic data* for **2**: IR (NaCl, thin film): $\nu/\mathrm{cm^{-1}}$ 1163 (P=O) and 1032, 964 (P–O). ^1H NMR ($CDCl_3$): δ 7.77 (dd, J = 13.0, 5.0 Hz, 2 H, C_6H_5), 7.29 (s, 12 H, C_6H_5, C_6H_4), 4.12 (m, 4 H, CH_2) and 1.29 (t, J = 7.0 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $2C_6H_5$ at δ 135.4 (d, J_{CP} = 10.8 Hz, *i*), 133.3 (d, J_{CP} = 20.1 Hz, *o*), 128.1 (d, J_{CP} = 7.2 Hz, *m*), 128.6 (s, *p*), C_6H_4 at 127.8 (d, J_{CP} = 189.0 Hz, *i*), 132.5 (dd, J_{CP} = 15.4, 2.9 Hz, *o*), 130.8 (dd, J_{CP} = 6.0, 3.5 Hz, *m*), 142.9 (dd, J_{CP} = 14.7, 3.4 Hz, *p*), 61.5 (d, J_{CP} = 9.8 Hz, CH_2), 15.8 (d, J_{CP} = 6.8 Hz, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −3.8 (s, P) and 19.7 (s, PO).

‡ *Spectroscopic data* for **4**: IR (KBr pellet): $\nu/\mathrm{cm^{-1}}$ 1142 (P=O) and 1016–905 (P–O). ^1H NMR (D_2O): δ 7.77–7.70 (2 H of C_6H_5, C_6H_4, m), 7.37–7.20 (12 H of C_6H_5, C_6H_4, m). $^{13}C\{^1H\}$ NMR (D_2O): $2C_6H_5$ at δ 135.9 (d, J_{CP} = 7.3 Hz, *i*), 133.5 (d, J_{CP} = 19.3 Hz, *o*), 128.6 (d, J_{CP} = 7.2 Hz, *m*), 129.0 (s, *p*), C_6H_4 at 141.6 (d, J_{CP} = 166.7 Hz, *i*), 132.6 (dd, J_{CP} = 12.7, 6.2 Hz, *o*), 130.4 (dd, J_{CP} = 7.1, 1.7 Hz, *m*), 136.8 (dd, J_{CP} = 7.9, 3.0 Hz, *p*). $^{31}P\{^1H\}$ NMR (D_2O): δ −5.0 (s, P) and 12.9 (s, PO).

§ *Crystallographic data* for **5**: $C_{20}H_{28}Na_2O_8P_2$; $M = 504.34$, monoclinic, space group $P2_1/n$, $a = 6.4457(8)$, $b = 8.1226(8)$, $c = 46.351(3)$ Å, $\beta = 92.902(8)°$, $V = 2423.6(4)$ Å^3, $Z = 4$, $D_c = 1.382$ g cm^{-3}, μ(Mo-Kα) 0.257 mm^{-1}. A clear, colourless crystal with dimensions 0.50 × 0.38 × 0.08 mm was placed on an Enraf-Nonius CAD-4 diffractometer. The crystal's final cell parameters and crystal orientation matrix were determined from 25 reflections in the range $35.2 < 2\theta < 38.6°$; these constants were confirmed with axial photographs. Data were collected with ω-scans over the range $2.6 < \theta < 22.5°$ with a scan width of $(0.66 + 1.11 \tan\theta)$ and variable scan speed of 4.12–5.5° min^{-1} with each scan recorded in 96 steps with the outermost 16 steps on each end of the scan being used for background determination. Three nearly orthogonal standard reflections were monitored at 1 hour intervals of X-ray exposure with minor variations in intensity being observed; data were not corrected. Six ψ-scan reflections were collected over the range $6.3 < \theta < 16.0°$; the absorption correction was applied with transmission factors ranging from 0.2401–0.2632. Data were collected with the indices $-hk \pm l$; resulting in the measurement of 3482 reflections; 3123 unique [R(int) = 0.0673]. Data were corrected for Lorentz and Polarization factors, and reduced to $F_o{}^2$ and $\sigma(F_o{}^2)$ with direction cosines using the program XCAD4. The structure was determined using XS[10] and resulted in the location of heavy atoms. The remaining non-hydrogen atoms were found from one difference Fourier map. The structure was refined with XL[10] and hydrogen atoms attached to carbon atoms were placed in calculated positions. All of the hydrogen atoms attached to oxygen atoms were located from a second difference map and allowed to refine freely(xyzu). All of the non-hydrogen atoms were refined anisotropically and the structure was refined to convergence [$\Delta/\rho \leqslant 0.001$] with $R(F)$ = 7.80%, w$R(F^2)$ = 15.71% and GOF = 1.135 for all 3123 unique reflections [$R(F)$ = 5.05%, w$R(F^2)$ = 11.57% for those 2405 data with $F_o > 4\sigma(F_o)$]. A final difference Fourier map was featureless with residual electron density between −0.642 and 0.392 e Å^{-3}. The function minimized during the full-matrix least-squares refinement was $\Sigma w(F_o)^2 - F_c{}^2)$ where $w = 1/\sigma(F_o)^2) + (0.0539{*}P)^2 + 6.1880{*}P]$ and $P = [\max(F_o{}^2, 0) + 2{*}F_c{}^2]/3$. An empirical correction for extinction provided a negative result and was not applied [w$R(F^2)$] = $[\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ The trihydrate formulation was made on the basis of an elemental analysis of the mixture of geometric isomers: Calcd for $C_{36}H_{34}Cl_2Na_4O_9P_4Pt$: C, 39.58; H, 3.14. Found: C, 39.42; H, 3.14.

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