Synthesis and Characterization of Palladium(II) and Platinum(II) Complexes Containing Water-Soluble Hybrid Phosphine−Phosphonate Ligands

Terence L. Schull,[†] James C. Fettinger,[‡] and D. Andrew Knight*,[†]

Department of Chemistry, The George Washington University, 725 21st Street, N.W. Washington, D.C. 20052, and Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

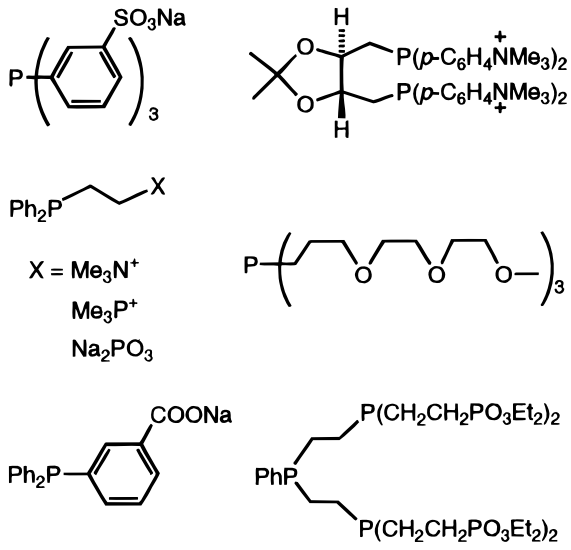
Received May 9, 1996[⊗]

Water-soluble phosphonate-functionalized triaryl phosphine ligands $Na_2[Ph_2P(4\text{-}C_6H_4PO_3)]\cdot 1.5H_2O$ (**4a**), $Na_2[Ph_2P(3\text{-}C_6H_4PO_3)]\cdot 2H_2O$ (**4b**), and $Na_2[Ph_2P(2\text{-}C_6H_4PO_3)]\cdot 2H_2O$ (**4c**), were prepared in 54−56% yields by the transesterification and hydrolysis of the appropriate phosphonic acid diethyl ester precursors. The solubilities of **4a**−**c** in water are compared and the spectroscopic properties studied in detail. The crystal structure of $Na_2[Ph_2P(4\text{-}C_6H_4PO_3)(H_2O)_3(CH_3OH)]\cdot CH_3OH$ (monoclinic, $P2_1/n$, $a = 6.4457(8)$ Å, $b = 8.1226(8)$ Å, $c = 46.351(3)$ Å, $\beta = 92.902(8)°$, $Z = 4$) shows a dimeric association via two bridging water molecules and four sodium ions. Reaction of **4a** with $PtCl_2(PPh_3)_2$ in a biphasic H_2O/CH_2Cl_2 mixture gives *cis*- and *trans*-$Na_4[PtCl_2\{Ph_2P(4\text{-}C_6H_4PO_3)\}_2]\cdot 3H_2O$. Palladium dichloride and **4a** in H_2O/benzene catalyzes the carbonylation of benzyl chloride to give phenylacetic acid (91%).

Introduction

Highly functionalized triarylphosphine ligands continue to dominate the field of homogeneous transition metal catalysis as the demand for greater activity and selectivity (especially enantioselectivity) in organic transformations continues to rise. Virtually every common organic functional group (e.g. alkene, alkyne, ether, alcohol, ester, crown-ether, carboxylic acid, ketone, amine, amide, imine, nitrile, sulfide, sulfoxide, sulfonate, phosphine oxide, phosphate, and phosphonate[1−18]) and many more complex structural forms (e.g. metalloporphyrin, silsesquioxanes, organic polymer, inorganic polymer, fullerenes, calixarenes, cyclodextrins, sugars, proteins, and organometallic molecules[19−28]) have been used to modify the chemical and physical properties of phosphines.

Chart 1. Hydrophilic Phosphine Ligands



[†] The George Washington University.
[‡] University of Maryland.
[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

(1) (a) Casey, C.; Whiteaker, G. T. *J. Org. Chem.* **1990**, *55*, 1394. (b) Bookham, J. C.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1990**, 484.
(2) Blenkiron, P.; Pillete, D.; Corrigan, J. F.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2165. (b) Scott, L. T.; Unno, M. *J. Am. Chem. Soc.* **1990**, *112*, 7823.
(3) (a) Lindner, E.; Kemmler, M.; Schneller, T.; Mayer, H. *Inorg. Chem.* **1995**, *34*, 5489 (b) Lindner, E.; Geprags, M.; Gierling, K.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1995**, *34*, 6106 and references therein.
(4) (a) Bank, J.; Gevert, O.; Wolfsberger, W.; Werner, H. *Organometallics* **1995**, *14*, 4972. (b) Braunstein, P.; Matt, D.; Mathey, F.; Thavard, D. J. *J. Chem. Res., Synop.* **1978**, 232. (c) Empsall, H. D.; Hyde, E. L.; Pawson, D.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1292.
(5) Balch, A. L.; Rowley, S. P. *J. Am. Chem. Soc.* **1990**, *112*, 6139.
(6) (a) Taqui Khan, M. M.; Nazeeruddin, M. K. *Inorg. Chim. Acta.* **1988**, *147*, 33. (b) Okada, Y.; Miuami, T.; Sasaki, Y.; Umezu, Y.; Yamaguchi, M. *Tetrahedron Lett. 31,* 3905.
(7) (a) Crochet, P.; Demerseman, B. *Organometallics* **1995**, *14*, 2173. (b) Knight, D. A.; Cole-Hamilton, D. J.; Cupertino, D. C. *J. Chem. Soc., Dalton Trans.* **1990**, 3051. (c) Bouadoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765.
(8) (a) Cooper, M. K.; Downes, J. M.; Duckworth, P. A. *Inorg. Synth.* **1989**, *25*, 129. (b) Hosmane, M. S.; Lu, K.-J.; Cowley, A. H.; Mardones, M. A. *Inorg. Chem.* **1991**, *30*, 1325.
(9) (a) Feher, F. J.; Schwab, J. J.; Phillips, S. H.; Eklund, A.; Martinez, E. *Organometallics* **1995**, *14*, 4452. (b) Hedden, D.; Roundhill, M. D. *Inorg. Synth.* **1990**, *27*, 322.
(10) (a) Grotjahn, D. B.; Joubran, C. *Organometallics* **1995**, *14*, 5171. (b) Ecke, A.; Keim, W.; Bonnet, M. C.; Tkatchenko, I.; Dahan, F. *Organometallics* **1995**, *14*, 5302.
(11) (a) Wolfsberger, W. *Chem. Ztg.* **1990**, *114*, 353. (b) Blinn, D. A.; Bulton, R. S.; Farazi, V.; Neeb, M. K.; Tapley, C. L.; Trehearne, T. E.; West, S. D.; Kruger, T. L.; Storhoff, B. N. *J. Organomet. Chem.* **1990**, *393*, 143. (c) Ravindar, V.; Hemling, H.; Schumann, H.; Blum, J. *Synth. Comm.* **1992**, *22*, 841.
(12) (a) Liu, S.-T.; Wang, H.-E.; Cheng, M.-C.; Peng, S.-M. *J. Organomet. Chem.* **1989**, *374*, 21. (b) Pascal, R. A.; West, A. P.; Van Engen, D. *J. Am. Chem. Soc.* **1990**, *112*, 6406.
(13) Febiéne, F.; Riant, O.; Ricard, L.; Kagan, H. B.; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 568.
(14) Kuntz, E. G. *CHEMTECH* **1987**, *17*, 570.
(15) Abu-Gnim, C.; Amer, I. *J. Chem. Soc., Chem. Commun.* **1994**, 115.
(16) Farin, F.; Van Gaal, H. L. M.; Bonting, S. L.; Daemen, F. J. M. *Biochim. Biophys. Acta* **1982**, *711*, 336.
(17) (a) Ganguly, S.; Mague, J .T.; Roundhill, D. M. *Inorg. Chem.* **1992**, *31*, 3500. (b) Callahan, K. P.; DiGiacomo P. M.; Dines, M. B. (Occidental Research Corp.) U.S. Pat. 4386013, A 830531.
(18) Reddy, V. S.; Berning, D. E.; Katti, K. V.; Barnes, C. L.; Volkert, W. A.; Ketring, A. R. *Inorg. Chem.* **1996**, *35*, 1753.

S0020-1669(96)00506-X CCC: $12.00

A special subgroup of this class of ligand is the tertiary phosphine containing a polar hydrophilic functional group which imparts a degree of water-solubility to the ligand. The synthesis of water-soluble tertiary phosphine ligands and their transition metal complexes for use in aqueous and biphasic homogeneous catalysis has become the focus of attention for many academic and industrial research groups in the last two decades.[29] The advantages of using water-soluble phosphines are well documented: (1) in single phase aqueous systems the need for an organic solvent is obviated, and (2) in biphasic systems the catalyst can easily be separated from the reaction mixture and recycled. While sulfonated phosphine ligands such as TPPTS ("triphenylphosphinetrisulfonate") remain the most widely used, many phosphines containing alternative hydrophilic functional groups have been prepared which show varying degrees of water-solubility (Chart 1).[30] Such ligands often provide different steric and electronic properties to triphenylphosphine and its sulfonated analog, TPPTS.

Our interest in the synthesis of new hydrophilic phosphonic acid functionalized phosphine ligands and their corresponding salts grew from several different perspectives. First, the anionic phosphonate functional group has been previously used to render alkylphosphines water-soluble[17] but to the best of our knowledge has not been used in conjunction with a *triaryl*phosphine, which remains one of the most widely used of all phosphine ligands for homogenous catalytic reactions. Second, the phosphonic acid functional group represents an ideal locus of attachment for an inorganic surface such as silica or titania and may provide us with a useful route to heterogenized transition metal phosphine catalysts. Finally, organic phosphonic acids are known to form two- and three-dimensional networks with suitable hard metal precursors such as Zn(II) and Zr(IV),[31] and we are interested in studying the formation of hybrid inorganic−organometallic networks which may find application in the synthesis of organometallic thin films and supported organometallic molecules for bifunctional catalysis.

In this paper we report (1) the synthesis and characterization of three new water-soluble triarylphosphines, (2) the preparation of representative examples of late transition metal complexes containing the *p*-TPPMP (*p*-triphenylphosphinemonophosphonate) ligand, (3) a crystal structure analysis of *p*-TPPMP which displays a rather unique dimeric association in the solid state, and (4) the use of *p*-TPPMP in the biphasic catalytic carbonylation of benzyl chloride. A portion of this work has been previously communicated.[32]

Experimental Section

General Data. All reactions were conducted under dry, prepurified N_2 using standard Schlenk-line and catheter-tubing techniques unless otherwise stated. IR spectra were recorded on a Mattson Galaxy 6020 (FT) spectrometer. All ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC-300 spectrometer and referenced to internal tetramethylsilane (^{1}H), $CDCl_3$ (^{13}C), and external H_3PO_4 (^{31}P). Microanalyses were performed by Atlantic Microlab. Melting points were determined in evacuated capillaries.[33]

Solvents were purified as follows: THF and ether, distilled from sodium/benzophenone; pentane and CH_2Cl_2, distilled from CaH_2; ethyl acetate, ligroin, methanol, acetone (Fisher), and $CDCl_3$ (Cambridge Isotope Laboratories), used as received. Silica gel (Scientific Products, 230−400 mesh) and sodium sulfate (Fisher) were used as received.

Reagents were obtained as follows: 2-dibromobenzene (Eastman), bromotrimethylsilane (Aldrich), sodium hydroxide (JT Baker), sodium methoxide (Fisher), used as received; chlorodiphenylphosphine and diethyl chlorophosphate (Aldrich), vacuum distilled prior to use; *tert*-butyllithium (Aldrich), 1.7 M solution in pentane, used as received; *n*-butyllithium (Aldrich), 1.60 M solution in hexane, standardized as previously described. Sodium tetrachloroplatinate and sodium tetrachloropalladate (Johnson Matthey) were used as received.

$Ph_2P(2\text{-}C_6H_4Br)$ (1c). A three-necked Schlenk flask was charged with 1,2-dibromobenzene, ether (20 mL), pentane (20 mL) a stirrer bar, and a thermometer and cooled to −113 °C (ether/N_2). Then, *t*-BuLi (11.7 mL, 20.0 mmol, 1.7 M in pentane) was added dropwise with stirring, maintaining the temperature below −107 °C. The reaction mixture was stirred for 10 min. Chlorodiphenylphosphine (3.6 mL, 20 mmol) in ether/pentane (40 mL, 50:50) was added dropwise with stirring, maintaining the temperature below −110 °C. The solution was warmed to −80 °C (acetone/CO_2) and stirred for 40 min. The cold bath was removed and water (50 mL) and ether (100 mL) were added. The organic phase was separated and dried over $NaSO_4$. The solvent was removed on a rotary evaporator and the resulting solid crystallized from ether/ligroin to give **1c** (3.55 g, 10.4 mmol, 52%).[34]

$Ph_2P(2\text{-}C_6H_4PO_3Et_2)$ (2c). A Schlenk flask was charged with **1c** (3.4 g, 10 mmol), THF (20 mL), and a stirrer bar and cooled to −78 °C (2-propanol/CO_2). Then, *n*-BuLi (6.50 mL, 10.4 mmol, 1.60 M in hexane) was added dropwise with stirring over a period of 30 min. The resulting solution was transferred via catheter to a stirred solution of diethyl chlorophosphate (1.6 mL, 10 mmol) in THF (30 mL) cooled to −78 °C (2-propanol/CO_2). The cold bath was removed and the solution allowed to warm to room temperature. The solution was stirred for a further 45 min. The reaction was quenched by the addition of methanol (1 mL), and the solvent was removed by rotary evaporation. Crystallization from ether/pentane gave **2c** as white needles (2.37 g, 5.95 mmol, 60%), mp 82−83 °C. Anal. Calcd for $C_{22}H_{24}O_3P_2$: C, 66.33; H, 6.07. Found: C, 66.43; H, 6.12. IR (NaCl, thin film): ν(P═O) 1237 cm^{-1}, ν(P−O) 1046, 1027, 978 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.20−7.10 (m, 14H, C_6H_5, C_6H_4), 4.10 (m, 2H, CH_2), 3.95 (m, 2H, CH'_2), 1.15 (t, J = 7.1 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): 140.6−129.6 (C_6H_5, C_6H_4), 61.4 (d, J_{CP} = 5.1 Hz, CH_2), 15.5 (d, J_{CP} = 6.5 Hz, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −8.3 (s, P), 18.9 (s, PO).

$Na_2[Ph_2P(4\text{-}C_6H_4PO_3)]\cdot 1.5H_2O$ (4a). A Schlenk flask was charged with diethyl chlorophosphate (1.6 mL, 10 mmol) in THF (50 mL), a stirrer bar and cooled to −78 °C (acetone/CO_2). Then, ((*p*-diphenyl-

(19) Märkel, G.; Reiss, M.; Kreitmeier, P.; Nöth, H. *Angew. Chem., Int Ed. Engl.* **1995**, *34*, 2230.
(20) Feher, F. J.; Schwab, J. J.; Phillips, S. H.; Eklund, A.; Martinez, E. *Organometallics* **1995**, *14*, 4452.
(21) (a) Malstrom, T.; Weigl, H.; Andersson, C. *Organometallics* **1995**, *14*, 2597.
(22) Hartley, F. R. *Supported Metal Complexes*; D. Reidel Publishing Company: Dordrecht, The Netherlands, 1985.
(23) Yamago, S.; Yanagawa, M.; Nakamura, E. *J. Chem. Soc., Chem. Commun.* **1994**, 2093.
(24) (a) Cameron, B. R.; Van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Org. Chem.* **1995**, 2802. (b) Loeber, C.; Matt, D.; Cian, A.; Fisher, J. *J. Organomet. Chem.* **1994**, *475*, 297.
(25) Reetz, M. T.; Rudolph, J. *Tetrahedron: Asymmetry* **1993**, *4*, 2405.
(26) Mitchell, T. N.; Heesche-Wagner, J. *J. Organomet. Chem.* **1992**, *436*, 43.
(27) Sunjic, W.; Habus, I.; Snatzke, G. *J. Organomet. Chem.* **1989**, *370*, 295.
(28) Nishibayashi, Y.; Segawa, K.; Ohe, K.; Uemura, S. *Organometallics* **1995**, *14*, 5486.
(29) For recent a recent review see: Cornils, B; Wiebus, E. *CHEMTECH* **1995**, *25*, 33.
(30) (a) Tóth, I.; Hanson, B. E.; Davis, M. E. *Tetrahedron: Asymmetry* **1990**, 913. (b) Herring, A. M.; Steffey, B. D.; Miedaner, A.; Wander, S. A.; DuBois, D. L. *Inorg. Chem.* **1995**, *34*, 1100. (c) Okano, T.; Moriyama, Y.; Konishi, H.; Kiji, J. *Chem. Lett.* **1986**, 1463. (d) Renaud, E.; Russell, R. B.; Fortier, S.; Brown, S. J.; Baird, M. C. *J. Organomet. Chem.* **1991**, *419*, 403. (e) Smith, R. T.; Ungar, R. K.; Sanderson, L. J.; Baird, M. C. *Organometallics* **1983**, *2*, 1138. (f) Ellis, J. W.; Harrison, K. N.; Hoye, P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *Inorg. Chem.* **1992**, *31*, 3026. (g) Darensbourg, D. J.; Joó, F.; Kannisto, M.; Kathó, A.; Reibenspies, J. H.; Daigle, D. J. *Inorg. Chem.* **1994**, *33*, 200.
(31) Clearfield, A. *Comments Inorg. Chem.* **1990**, *10*, 89.
(32) Schull, T. L.; Fettinger, J. C.; Knight, D. A. *J. Chem. Soc., Chem. Commun.* **1995**, 1487.
(33) G. V. D. Tiers, *J. Chem. Educ.* **1990**, *67*, 258.
(34) Our procedure gives a significant improvement in yield over the literature procedures; see: (a) Gilman, H.; Gorisch, R. D. *J. Am. Chem. Soc.* **1956**, *78*, 2217. (b) Hart, F. A. *J. Chem. Soc.* **1960**, 3325.

phosphino)phenyl)lithium[35] (27 mL, 10 mmol, 0.37 M in hexane/THF) was added dropwise over 75 min via cannula. The cold bath was removed and the solution was allowed to warm to room temperature. After 12 h, methanol (0.5 mL) was added via syringe and the solvent removed by oil-pump vacuum. The residue was dissolved in CH_2Cl_2 and the solution chromatographed on a 50 mm diameter column (142 g, CH_2Cl_2). The solvent was removed from the eluate to give an oil which was rechromatographed (150 g, ethyl acetate). The solvent was removed from the eluate under oil-pump vacuum to give $Ph_2P(4\text{-}C_6H_4\text{-}PO_3Et_2)$ (**2a**) as a spectroscopically pure oil (2.5 g, 63%). IR (NaCl, thin film): 1252 cm^{-1} ν(P═O) 1163 cm^{-1}, ν(P−O) 1032, 964 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.77 (dd, J = 13.0, 5.0 Hz, 2H of C_6H_5), 7.29 (s, 12H of C_6H_5, C_6H_4), 4.12 (m, 4H, CH_2), 1.29 (t, J = 7.0 Hz, 6H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −3.8 (s, P), 19.7 (s, PO). A Schlenk flask was charged with a portion of **2a** (2.02 g, 5.10 mmol), CH_2Cl_2, (20 mL) and a stirrer bar. Then bromotrimethylsilane (3.0 mL, 23 mmol) was added via syringe and the solution stirred for 3 h. The solvent was removed by oil-pump vacuum and the residue dissolved in acetone (20 mL). Water (0.20 mL, 11.1 mmol) was added via syringe, and the solution was stirred for 1.5 h. The solvent was removed by oil-pump vacuum and the residue dissolved in methanol (20 mL). Then NaOH (40%, w/w) was added and a precipitate immediately formed. The mixture was stored at −23 °C overnight and additional solid formed, which was collected by filtration. Crystallization from ether/MeOH gave **4a** as white chunks (1.09 g, 2.64 mmol, 66%), mp >300 °C. Anal. Calcd for $C_{18}H_{17}Na_2O_{4.5}P_2$: C, 52.32; H, 4.15. Found: C, 52.38; H, 4.19. IR (KBr pellet): ν(P−O) 1142, 1016−905 cm^{-1}. ^1H NMR (D_2O): δ 7.77−7.70 (2H of C_6H_5, C_6H_4, m), 7.37−7.20 (12H 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), 12.9 (s, PO).

$Na_2[Ph_2P(3\text{-}C_6H_4PO_3)]\cdot 2H_2O$ (4b). Diethyl chlorophosphate (9.5 mL, 60 mmol), THF (100 mL) and ((*m*-diphenylphosphino)phenyl)-lithium[35] (88 mL, 60 mmol, 0.68 M in hexane/THF) were combined in a procedure analogous to that given for **4a**. After 12 h, the solvent was removed by rotary evaporation. The residue was chromatographed on a 50 mm diameter silica gel column (200 g, ether). The solvent was removed from the eluate to give $Ph_2P(3\text{-}C_6H_4PO_3Et_2)$ (**2b**) as a spectroscopically pure oil (19.0 g, 79%). IR (NaCl, thin film): ν(P═O) 1254 cm^{-1}, ν(P−O) 1051, 1025, 966 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.80−7.15 (m, 14H, C_6H_5, C_6H_4), 4.00 (m, 4H, CH_2), 1.13 (m, 6H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −4.8 (s, P), 18.9 (s, PO). A Schlenk flask was charged with a portion of **2b** (18.0 g, 45.0 mmol), CH_2Cl_2, (100 mL) and a stirrer bar. Then bromotrimethylsilane (17.9 mL, 135 mmol) was added via syringe and the solution stirred for 7 h. The solvent was removed by oil-pump vacuum and the residue dissolved in acetone (100 mL). Water (1.62 mL, 90.0 mmol) was added via syringe, and the solution was stirred for 12 h. The solvent was removed by rotary evaporation and the residue dissolved in methanol (75 mL). Then NaOH (50%, w/v) was added and a precipitate immediately formed. The mixture was cooled to −23 °C for several minutes and additional solid formed which was collected by filtration. Two crystallizations from acetone/water gave **4b** as white needles (10.3 g, 24.4 mmol, 54%), mp >300 °C. Anal. Calcd for $C_{18}H_{18}Na_2O_5P_2$: C, 51.20; H, 4.30. Found: C, 51.14; H, 4.27. IR (KBr pellet): ν(P−O) 1093, 1051, 966 cm^{-1}. ^1H NMR (D_2O): δ 7.83−7.18 (14H, C_6H_5, C_6H_4, m). $^{31}P\{^1H\}$ NMR (D_2O): δ −5.7 (s, P), 11.5 (s, PO).

$Na_2[Ph_2P(2\text{-}C_6H_4PO_3)]\cdot 2H_2O$ (*p*-TPPMP) (4c). A Schlenk tube was charged with **2c** (1.5 g, 3.0 mmol), CH_2Cl_2 (15 mL) and a stirrer bar. Bromotrimethylsilane (1.2 mL, 9.0 mmol) was added via syringe and the solution was stirred for 12 h. The solvent was removed under oil-pump vacuum and the residue was dissolved in acetone (10 mL) Distilled, deionized water (0.11 mL, 6.11 mmol) was added via syringe and a white suspension formed. The solvent was removed under oil-pump vacuum and the residue dissolved in methanol (10 mL). Sodium methoxide (0.325 g, 6.02 mmol) was added to the solution which became a thick suspension within seconds. The solvent was removed under oil-pump vacuum and the resulting solid was crystallized from acetone/water to give **4c** as off-white needles (0.778 g, 1.84 mmol, 61%), mp >300 °C. Anal. Calcd for $C_{18}H_{18}Na_2O_5P_2$: C, 51.20; H, 4.30. Found: C, 51.11; H, 4.30. IR (KBr, pellet): ν(P−O) 1161, 1140, 1115, 1080, 1043, 1026, 905 cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.00−7.06 (14H, C_6H_5, C_6H_4, m). $^{13}C\{^1H\}$ NMR (CH_3OD): $2C_6H_5$ 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 ($CDCl_3$): δ −9.4 (s, P), 12.1 (s, PO).

$(4\text{-}C_6H_4PPh_2)_3PO$ (3). A 200-mL three-neck round-bottom flask was charged with *n*-BuLi (10 mmol, 6.3 mL, 1.6 M in hexane), THF (25 mL), a pressure-equalizing addition funnel, a low-temperature thermometer and a stirrer bar and cooled to −78 °C (acetone/CO_2) Then, (*p*-bromophenyl)diphenylphosphine (3.41 g, 10.0 mmol) in THF (25 mL) was added dropwise over 30 min. After the addition was complete, a solution of diethyl chlorophosphate (1.6 mL, 10 mmol) in THF (20 mL) was added dropwise. The cooling bath was removed and the solution was allowed to warm to room temperature. The solution was stirred for 3 h and the solvent was removed under oil-pump vacuum to give a viscous yellow residue. The residue was taken up in a minimum amount of CH_2Cl_2 and chromatographed on a 50 mm diameter column (102 g, CH_2Cl_2). An unidentified high R_f band eluted from the column. The eluant was changed to 10% methanol−dichloromethane, and a second band was obtained. Solvent was removed by rotary evaporation and oil-pump vacuum to give a yellow oil. Acetone was added to precipitate a white solid which was crystallized twice from ethanol-chloroform to give **3** as white prisms. Crude yield: 3.85 g. IR: ν(P═O) 1200 cm^{-1} $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 4.4 (s, P), 29.7 (s, PO). MS: *m/e*, 830 (M^+).

$Na_4[PtCl_2\{Ph_2P(4\text{-}C_6H_4PO_3)\}_2]\cdot 3H_2O$ (5). A Schlenk tube was charged with $PtCl_2(PPh_3)_2$ (0.395 g, 0.500 mmol)[36] dichloromethane (15 mL) and a stir bar. Then, a solution of **4a** (0.455 g, 1.05 mmol) in water (15 mL) was added and the reaction mixture was stirred overnight. The aqueous phase was separated and water removed under oil-pump vacuum to give a yellow solid **5** (0.539 g, 0.493 mmol, 99%, *cis*/*trans*, 64/36). Anal. Calcd for $C_{36}Cl_2H_{34}Na_4O_9P_4Pt$: C, 39.58; H, 3.14. Found: C, 39.42; H, 3.14. $^{31}P\{^1H\}$ NMR (CD_3OD, *cis*/*trans*): δ 25.7/14.8 (t/t, J_{PtP} = 3630/2486 Hz, P), 12.7/12.0 (s/s, PO).

Catalytic Carbonylation of Benzyl Chloride. A Schlenk tube was charged with $PdCl_2$ (0.0064 g, 0.0036 mmol), water (15 mL), benzene (10 mL), **4a** (0.0030 g, 0.0072 mmol), and a stir bar. The flask was then evacuated, flushed with CO several times, and pressurized with CO to ca. 8 psi. Then, NaOH (1.25 M, 0.8 mL) was added, followed by benzyl chloride (0.42 mL, 3.6 mmol). The flask was placed in an oil bath and heated at 55°C for 12 h with stirring. The reaction mixture was then allowed to cool to room temperature, acidified with 3 M HCl (10 mL), and filtered through a pad of Celite. The phases were separated, and the aqueous phase was extracted with ether (3 × 30 mL). The combined organic phases were dried ($MgSO_4$), and the solvent was removed by rotary evaporation and oil-pump vacuum. ^1H NMR yield ($CDCl_3$; toluene, internal standard): 91%.

Crystal Structure of $Na_2[Ph_2P(4\text{-}C_6H_4PO_3)(H_2O)_3(CH_3OH)]\cdot CH_3OH$. A colorless prism was grown by slowly cooling a warm CH_3OH/H_2O solution of **4a** to room temperature, and it was mounted for data collection 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 < 2θ < 38.6°; these constants were confirmed with axial photographs. Data were collected with ω-scans over the range 2.6 < θ < 22.5° with a scan width of (0.66 + 1.11 tan θ) and a 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 h 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 26.3 < θ < 16.0°; the absorption correction was applied with transmission factors ranging from 0.2401−0.2632. Data were collected

(35) Ravindar, V.; Hemling, H.; Schumann, H.; Blum J. *Synth. Comm.* **1992**, *22*, 841.

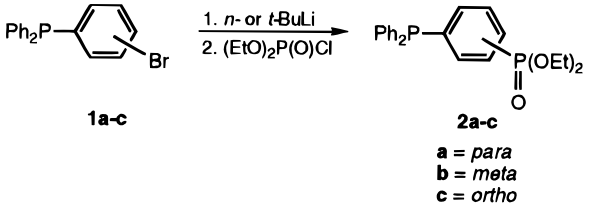
(36) Gillard, R. D.; Pilbrow, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, 2320.

with the indices $-hk\pm l$ resulting in the measurement of 3482 reflections; 3123 were 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 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 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 [$\Delta/\sigma \leq 0.001$] with $R(F) = 7.80\%$, $R_w(F^2) = 15.71\%$, and GOF = 1.135 for all 3123 unique reflections [$R(F) = 5.05\%$, $R_w(F^2) = 11.57\%$ for those 2405 data with $F_o > 4\sigma(F_o)$]. A final difference Fourier map was featureless with $|\Delta/\sigma| \leq 0.392$ e Å^{-3}. The function minimized during the full-matrix least-squares refinement was $\sum w(F_o^2 - F_c^2)$ where $w = 1/[\sigma(F_o^2) + (0.0539P)^2 + 6.1880P]$ and $P = (\max(F_o^2, 0) + 2F_c^2)/3$. An empirical correction for extinction provided a negative result and was not applied ($R_w(F^2) = [\sigma(wF_o^2 - F_c^2)^2/\sigma(wF_o^2 - F_c^2)^2]^{0.5}$).

Results and Discussion

Syntheses and Properties. The (*p*-, (*m*-, and (*o*-diphenylphosphino)bromobenzenes (**1a**−**c**) were lithiated using *n*-BuLi or *t*-BuLi and added to an equimolar amount of diethylchlorophosphate in THF to give, after workup, (see Experimental Section), the corresponding diethyl ((*p*-, ((*m*-, and ((*o*-diphenylphosphino)phenyl)phosphonates **2a**−**c** in 60−79% yields (Scheme 1). While the *meta* and *para* isomers could only be obtained as viscous oils, the *ortho* isomer could be purified by crystallization from ether/pentane. All three isomers were characterized using ^{31}P, ^{1}H NMR and IR spectroscopies (see Experimental Section). When chlorodiethylphosphate was treated with an excess of (diphenylphosphino)-*p*-bromobenzene *i.e.* the inverse addition, a white solid was isolated from the reaction mixture which was characterized as the mixed triphosphine−phosphine oxide **3**. After two recrystallizations form ethanol/chloroform, compound **3** was pure by ^{1}H NMR although a very minor phosphorus containing impurity which could not be identified (29.1 ppm) was observed in the ^{31}P NMR spectrum. One possible explanation for the formation of **3** involves the initial reaction of the aryllithium reagent with chlorodiethylphosphate to give the desired diethyl ((diphenylphosphino)-phenyl)phosphonate followed by successive nucleophilic substitutions at the phosphoryl phosphorus by the aryllithium, which is present in large excess, resulting in elimination of ethoxide anion and formation of the triarylphosphine oxide (Scheme 2). Compound **3** has a ^{31}P chemical shift of 29.7 ppm, and a strong absorption in the IR spectrum at 1200 cm^{-1}, both characteristic of a triarylphosphine oxide.[37]

Scheme 1. Synthesis of Diethyl Arylphosphonates **2**



Phosphonic acid esters can be hydrolyzed using a variety of methods such as base catalyzed hydrolysis in refluxing aqueous NaOH or via transesterification with bromotrimethylsilane (Br-TMS) and subsequent hydrolysis under mild conditions. We chose the latter route due to the presence of the moderately sensitive phosphine moiety. Roundhill has also used a similar reaction sequence in the preparation of a tertiary phosphine containing a substituted alkylene phosphonate chain.[17] Thus, compound **2a** could be successfully de-ethylated via transesterification using Br-TMS and hydrolysis in aqueous acetone to give the desired mixed triarylphosphine−phosphonic acid. Subsequent neutralization with aqueous sodium hydroxide and crystallization from ether/methanol afforded the hydrated disodium salt **4a** in 66% yield (Scheme 3). The sodium salts **4b** and **4c** were prepared in a similar fashion. Compounds **4a**−**c** contain two singlets in the ^{31}P NMR spectra corresponding to the phosphine and phosphonate moieties respectively and no homonuclear coupling is observed; this is not altogether surprising as ^{3}J and ^{4}J P−P coupling in 1,2-disubstituted substituted aryl rings can often be small or not observed.[38] All three isomers contain several broad, intense bands in the 1180−900 cm^{-1} region of the IR spectra which have been assigned to the phosphonate group.

The sodium salts show a distinct variation in aqueous solubility. The *ortho* isomer **4c** has the lowest solubility (< 0.035 g/mL), the *meta* isomer **4b** has an intermediate solubility (0.19 g/mL) and the *para* isomer **4a** has the highest solubility (0.38−0.41 g/mL). Solubilities were recorded by taking a known amount of solute and adding water at 20 °C until a clear solution was obtained. The solubility of **4c** varied slightly between two separate batches possibly due to loss of water of crystallization on standing. The solubilities of organic compounds in aqueous solution have been widely studied, and certain generalizations can be made concerning the factors which affect solubility.[39] For example, molecular size and shape, the degree of self and coassociation of the solute and the extent of solvation can all play a significant role in solubility. Second, it is well established that the solubility of a crystalline solute in water, for example the salt of a phosphonic acid, can be at least partially dependent on crystal properties such as the degree of molecular packing.[40] One must also take into account the extent of hydrogen bonding in both the crystal structure and between the solute and solvent. However, we are tempted to suggest that the relatively low aqueous solubility in **4c** may in fact be determined by the extent of solvation of the phosphonate anion, the dominating effect being the steric encumbrance encountered due to the *ortho*-substituted diphenylphosphine group. It should be noted that **4**b is significantly more soluble than the sulfonated analog Na[*m*-TPPMS][29] (TPPMS = "triphenylphosphinemonosulfonate") (0.08 g/mL at 20 °C). The enhanced solubility of **4**b over the sulfonate is presumably due to the dianionic nature of the phosphonate ligand.

Crystal Structure Analysis of $Na_2[Ph_2P(4\text{-}C_6H_4PO_3)(H_2O)_3(CH_3OH)]\cdot CH_3OH$. Recrystallization of **4a** from aqueous methanol yielded colorless crystals of the solvated phosphine which was characterized by X-ray crystallographic analysis. Exposure of the crystals to air for short periods of time resulted in etching of the crystal surface, presumably due to partial desolvation. The ORTEP representation is shown in Figure 1 and crystallographic data, selected bond distances and angles are listed in Tables 1 and 2. The structure shows some interesting and unique features. For example, the compound is dimeric and contains two formula units in the unit cell which

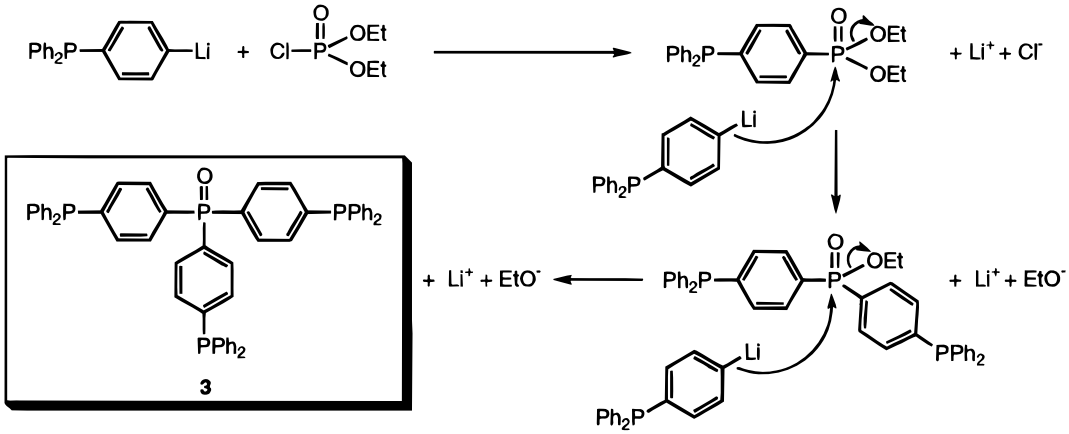
(37) Emsley, J. *The Chemistry of Phosphorus*; Harper and Row: London, 1976.

(38) Bowmaker, G. A.; Herr, R.; Schmidbaur, H. *Chem. Ber.* **1983**, *116*, 3567.

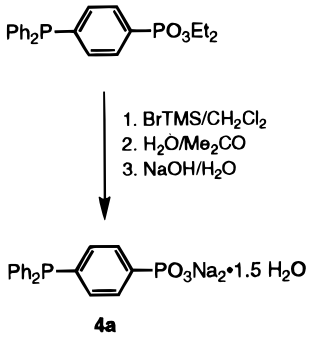
(39) Grant, D. J. W. *Solubility Behavior of Organic Compounds: Techniques of Chemistry;* Wiley Interscience: New York, 1990; Vol. XXI.

(40) Yalkowsky, S. H.; Banerjee, S. *Aqueous Solubility, Methods of Estimation for Organic Compounds*; Marcel Dekker, Inc.: New York, 1992.

Scheme 2. Proposed Mechanism for the Formation of Phosphine Oxide **3**



Scheme 3. Synthesis of $Na_2[Ph_2P(4\text{-}C_6H_4PO_3)]\cdot 1.5H_2O$ (**4a**)



are apparently held together via two bridging water molecules and four sodium ions. The molecular structure also contains a unique eight-membered P−O−Na−O−P−O−Na−O ring which is fused to two four-membered O−Na−O−Na rings. An inversion point is located at the center of the eight-membered ring.

The structure contains the sodium ions in two different coordination geometries. Na2 is tricoordinate, and bridges two independent phosphonate oxygens [O1 and O2′]. A water molecule oxygen O4 occupies the third site which in turn bridges the two sodium ions Na2 and Na1′. Sodium ion Na1 is coordinated to one phosphonate oxygen atom O(2), three water molecules O4′, O5, and O6, and a methanol molecule in a distorted trigonal bipyramidal geometry. The equatorial plane is bound by phosphonate, water, and methanol oxygens respectively, while the oxygens of two further water molecules are located on the axis [O5−Na1−O6 = 169.7(2)°]. The closest cation−cation contact [Na1−Na2] is 3.470 Å. A comparison of the metric parameters of the triarylphosphine subunit with those of a representative monosubstituted triphenylphosphine, (*p*-bromophenyl)diphenylphosphine[41] revealed no unusual or unexpected bond lengths or angles. The phosphonate phosphorus atom P2 has a distorted tetrahedral geometry [O3−P2−C16 = 105.7(2)°, O3−P2−O1 = 111.2(2)°, O3−P2−O2 = 112.0(2)°], and the three phosphonate P−O bond lengths [P2−O1 = 1.520(3) Å, P2−O2 = 1.523(3) Å, P2−O3 = 1.540(3) Å] are typical.[42] The unit cell also contains two uncoordinated methanol molecules.

Synthesis of Complexes. The mixed phosphine−phosphonate ligands have the potential to coordinate to a transition metal via two bonding modes: (i) through the anionic phosphonate moiety or (ii) via the phosphine phosphorus atom. Organophosphonate complexes of high-valent early transition metals, e.g. molybdenum,[43] zirconium,[44] and vanadium,[45] have been investigated, and solid state studies have revealed that such complexes can form inorganic polymer-like materials in which layering of the inorganic−organic hybrid is often observed. Triarylphosphine complexes of late transition metals have also been extensively studied. To asses the binding properties of a mixed phosphine−phosphonate ligand to a late transition metal, the reaction of **4c** with $PtCl_2(PPh_3)_2$ using a biphasic phosphine transfer method was studied. Thus, the addition of an aqueous solution of **4c** to a solution of $PtCl_2(PPh_3)_2$ in dichloromethane, followed by stirring overnight, resulted in the transfer of yellow color from the organic phase to the aqueous phase. Following workup (Experimental Section), the new platinum complexes *cis*- and *trans*-$Na_4[PtCl_2\{Ph_2P(4\text{-}C_6H_4PO_3)\}_2]\cdot 3H_2O$ (**5**) were obtained as a 64/36 mixture of isomers. All attempts to separate the two isomers using crystallization from various polar solvents (H_2O, MeOH, acetone, EtOH) were unsuccessful.

The ^{31}P NMR spectrum of **5** was recorded in CD_3OD and contained two singlets at 12.7 and 12.0 ppm which have been assigned to the unbound phosphonate group (*cf* 12.9 ppm, **4a**). The spectrum also contains two triplets at 25.7 (J_{PtP} = 3630 Hz) and 14.8 (J_{PtP} = 2486 Hz) with a ratio of intensities of 64/36. These resonances and coupling constants are characteristic of *cis* and *trans* isomers of PtX_2L_2 (L = triarylphosphine; X = halide).[46] The ^{31}P spectrum remained unchanged when the NMR sample was heated to 80 °C indicating that the isomers could not be thermally interconverted. These spectral observations provide compelling evidence that at least for the phosphine **4a**, that the platinum binds exclusively through the phosphine moiety, and there is no coordination of the phosphonate group to the metal as seen, for example, in $[Pt(NH_3)_2(ampH_2\text{-}O)(H_2O)]^{2+}$ (amp = (aminomethyl)phosphonic acid).[47]

Catalysis. The palladium-catalyzed carbonylation of aryl and alkyl halides in the presence of a suitable stabilizing triarylphosphine ligand such as triphenylphosphine is a well-studied reaction.[48] Under phase-transfer conditions in the presence of a base (e.g. sodium hydroxide), $PdCl_2$, triphenylphosphine, and

(41) Kuhn, H.-J.; Plieth, K. *Naturwissenschaften* **1966**, *53*, 359.
(42) (a) Cao, G.; Lynch, V. M.; Swinnea, J. S.; Mallouk, T. E. *Inorg. Chem.* **1990**, *29*, 2112. (b) Bhardwaj, C.; Hu, H.; Clearfield, A. *Inorg. Chem.* **1993**, *32*, 4294.
(43) Cao, G.; Haushalter, R. C.; Strohmaier, K. G. *Inorg. Chem.* **1993**, *32*, 127.
(44) Dines, M. B.; DiGiacomo P., M.; *Inorg. Chem.* **1981**, *20*, 92.
(45) Soghomonian, V.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1995**, *7*, 1648.
(46) Hartley, F. R. *The Chemistry of Platinum and Palladium*, Wiley: New York, 1973.
(47) Appleton, T. G.; Hall, J. R.; McMahon, I. J. *Inorg. Chem.* **1986**, *25*, 720.

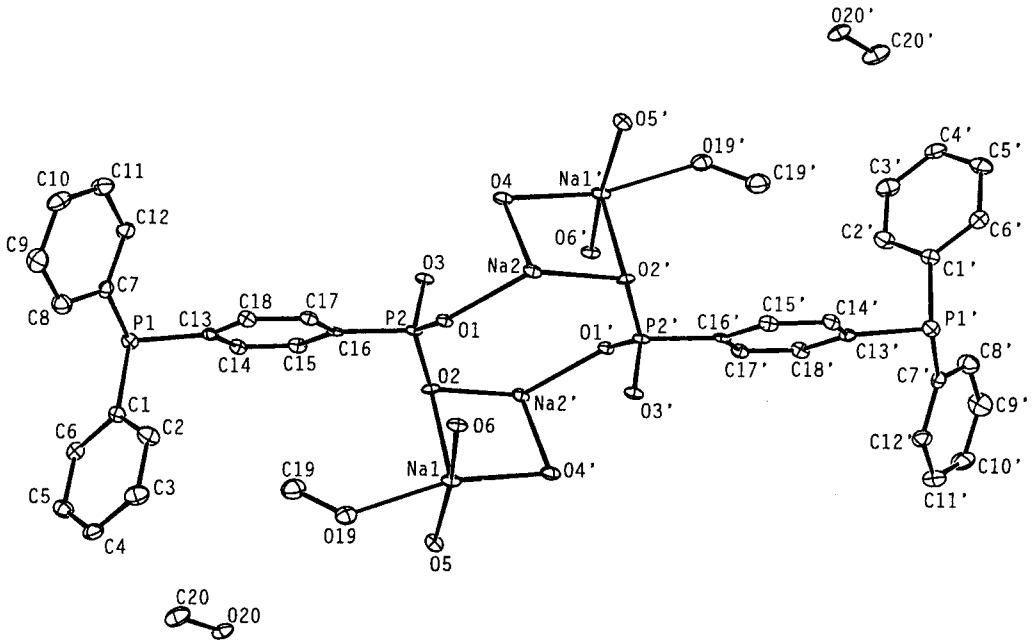


Figure 1. ORTEP diagram of the structure of $Na_2[Ph_2P(4\text{-}C_6H_4PO_3)(H_2O)_3(CH_3OH)]\cdot CH_3OH$. Hydrogen atoms have been omitted for clarity.

Table 1. Crystallographic Data for $Na_2[Ph_2P(4\text{-}C_6H_4PO_3)(H_2O)_3(CH_3OH)]\cdot CH_3OH$

chem formula	$C_{20}H_{28}Na_2O_8P_2$	V, Å^3	2423.6(4)
fw	504.34	Z	4
space group	$P2_1/n$ (No. 14)	ρ_{calc}, g/cm^3	1.382
a, Å	6.4457(8)	λ, Å	0.710 73
b, Å	8.1226(8)	abs coeff, mm^{-1}	0.257
c, Å	46.351(3)	temp, K	153(2)
α, deg	90	R^a	0.0505
β, deg	92.902(8)	$R_w{}^b$	0.1157
γ, deg	90		

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

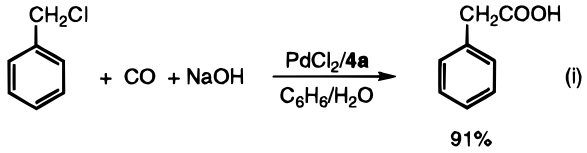
Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Na_2[Ph_2P(4\text{-}C_6H_4PO_3)(H_2O)_3(CH_3OH)]\cdot CH_3OH$

P1−C7	1.827(5)	C3−C4	1.380(8)
P1−C13	1.838(5)	C4−C5	1.371(7)
P1−C1	1.841(5)	C5−C6	1.392(7)
P2−O1	1.520(3)	C7−C12	1.393(7)
P2−O2	1.523(3)	C7−C8	1.398(7)
P2−O3	1.540(3)	C8−C9	1.390(7)
P2−C16	1.818(5)	C9−C10	1.384(8)
Na1−O5	2.300(4)	C10−C11	1.369(8)
Na1−O6	2.335(4)	C11−C12	1.394(7)
Na1−O2	2.448(3)	C13−C18	1.396(6)
Na1−O19	2.545(4)	C13−C14	1.402(7)
Na2−O1	2.249(3)	C14−C15	1.378(7)
Na2−O4	2.390(4)	C15−C16	1.394(6)
C1−C6	1.379(7)	C16−C17	1.402(6)
C1−C2	1.402(7)	C17−C18	1.379(7)
C2−C3	1.390(7)	O19−C19	1.420(7)
C7−P1−C13	102.9(2)	C5−C4−C3	119.8(5)
C7−P1−C1	102.2(2)	C4−C5−C6	120.3(5)
C13−P1−C1	102.4(2)	C1−C6−C5	120.9(5)
O1−P2−O2	113.3(2)	C12−C7−C8	117.6(5)
O1−P2−O3	111.2(2)	C12−C7−P1	119.6(4)
O2−P2−O3	112.0(2)	C8−C7−P1	122.2(4)
O1−P2−C16	107.0(2)	C9−C8−C7	121.3(5)
O2−P2−C16	107.1(2)	C10−C9−C8	119.6(5)
O3−P2−C16	105.7(2)	C11−C10−C9	120.3(5)
O2−P2−Na2	112.09(13)	C10−C11−C12	120.0(5)
O3−P2−Na2	84.34(12)	C7−C12−C11	121.1(5)
C16−P2−Na2	132.03(14)	C18−C13−C14	117.7(4)
O5−Na1−O6	169.7(2)	C18−C13−P1	126.1(4)
O1−Na2−O4	90.59(14)	C14−C13−P1	116.2(3)
O4−Na2−P2	75.07(11)	C15−C14−C13	121.4(4)
P2−O1−Na2	128.2(2)	C14−C15−C16	120.9(4)
C6−C1−C2	118.4(5)	C15−C16−C17	117.9(4)
C6−C1−P1	118.0(4)	C15−C16−P2	120.8(3)
C2−C1−P1	123.6(4)	C17−C16−P2	121.3(3)
C3−C2−C1	20.4(5)	C18−C17−C16	121.3(4)
C4−C3−C2	120.1(5)	C17−C18−C13	120.9(4)

tetrabutylammonium iodide, the carbonylation of benzyl chloride can be achieved to give phenylacetic acid in high yield.[49] This catalytic system is ideally suited to assess the performance of a hydrophilic phosphonate functionalized phosphine ligand such as **4** in biphasic carbonylation catalysis. The addition of three equivalents of **4a** to an aqueous solution of palladium dichloride resulted in the formation of a bright yellow solution. ^{31}P NMR analysis of the solution indicated several new resonances including a triplet at 34.1 ppm and a doublet at 29.5 ppm ($^2J_{PP}$ = 14.4 Hz) which have been assigned to the new palladium species $[PdCl(p\text{-TPPMP})_3]^+$. A singlet at 37.6 ppm was also observed and has been assigned to *p*-TPPMP oxide; this was later verified by preparing an independent sample via oxidation of *p*-TPPMP with hydrogen peroxide. No new resonances corresponding to a phosphonate bound palladium complex or a pendant uncoordinated phosphine were observed. Sheldon recently reported similar species on the addition of TPPTS to palladium dichloride in water and confirmed using labeling studies that the phosphine oxide formed results from oxygen atom transfer from water to the phosphine.[50] The flask containing palladium chloride and *p*-TPPMP was pressurized to 8 psi with carbon monoxide, which resulted in an immediate color change from yellow to red, presumably resulting from the reduction of $[PdCl(p\text{-TPPMP})_3]^+$ to a zerovalent palladium phosphine complex.[50] Our attempts to isolate $[PdCl(p\text{-TPPMP})_3]^+$ using chromatography on silica gel and various crystallization techniques all resulted in extensive decomposition of the palladium-containing species. After the addition of sodium hydroxide and benzyl chloride, the mixture was heated for 12 h at 55 °C. Following separation of the two-phases and

(48) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1985.
(49) Cassar, L.; Foà, M.; Gardano, A. *J. Organomet. Chem.* **1976**, *121*, C55.
(50) Papagogianakis, G.; Peters, J. A.; Maat, L.; Sheldon, R. A. *J. Chem. Soc., Chem. Commun.* **1995**, 1105.

work-up of the organic phase, ^{1}H NMR analysis indicated that phenylacetic acid had been formed in 91% yield (eq i). No



catalytic activity was observed in the absence of $PdCl_2$ or *p*-TPPMP. Furthermore, the same carbonylation reaction containing catalytic amounts of palladium dichloride and *p*-TPPMP oxide gave no appreciable yield of phenylacetic acid.

In summary, we have prepared and fully characterized new highly water-soluble phosphonate-functionalized triarylphosphines and representative platinum(II) complexes; the spectral data clearly indicating that the hybrid hard−soft donor ligand binds exclusively to the platinum(II) center via the phosphine phosphorus atom. We have also demonstrated that one of the phosphonated phosphine ligands in combination with palladium dichloride is a catalyst for the carbonylation of benzyl chloride under biphasic conditions.

Acknowledgment. We are grateful for support from The George Washington University in the form of startup funds (to D.A.K). We also acknowledge a gift of precious metal salts from the Johnson-Matthey Aesar/Alfa metal loan program.

Supporting Information Available: Complete tables of bond distances, bond angles, atomic coordinates, and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

IC960506B