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Article

Coordination Chemistry of the Water-Soluble Ligand TPPTP and Formation of a $[Mo(CO)_5(m\text{-}TPPTP)]$ Monolayer on an Alumina Surface

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Phosphonate and phosphonic acid functionalized phosphine complexes of platinum(II) were prepared via direct reaction of the ligands with K_2PtCl_4 in water. Either *cis* or *trans* geometries were found depending on the nature of the ligand. The crystal structure of $P(3\text{-}C_6H_4PO_3H_2)_3\cdot 2H_2O$ (**6b**) (triclinic, $P\bar{1}$, $a = 8.3501(6)$ Å, $b = 10.1907(6)$ Å, $c = 14.6529(14)$ Å, $\alpha = 94.177(6)°$, $\beta = 105.885(6)°$, $\gamma = 108.784(5)°$, $Z = 2$) shows a layered arrangement of the phosphonic acid. The phosphonodiamide complex *cis*-$[PtCl_2(P[4\text{-}C_6H_4PO\{N(CH_3\}_2\}]_3)_2]\cdot 3H_2O$ (**10**) was synthesized in 89% yield and hydrolyzed to the phosphonic acid complex using dilute HCl. Aqueous phase and silica gel supported catalytic phosphonylation of phenyl triflate using palladium phosphine complexes was achieved. A molybdenum complex, $Mo(CO)_5\{P(3\text{-}C_6H_4PO_3H_2)_3\}$ (**11**), was synthesized in situ and grafted to an alumina surface. XPS, RBS, and AFM studies confirm the formation of a monolayer of **11** on the alumina surface.

Introduction

Phosphonic acid functionalized phosphine complexes of transition metals are of general interest for a number of reasons. First, the presence of the phosphonic acid group renders the complexes water-soluble. This has allowed the application of these, and related hydrophilic complexes, to aqueous or biphasic homogeneous catalysis where separation of catalyst from the reaction mixture is an issue, or where the need for removal of an organic solvent from a chemical process is desired.[1] The water solubility is increased when the phosphonic acid is in the anionic phosphonate form, as present in compound **1** (Chart 1). This rhodium complex was derived from the phosphine *p*-TPPMP ($Na_2[Ph_2P(4\text{-}C_6H_4\text{-}PO_3)]\cdot 1.5H_2O$) and was successfully applied in the biphasic catalytic carbonylation of benzyl bromide.[2] The presence of the dianionic phosphonate moiety not only increases the relative aqueous solubility, compared with sulfonate analogues, but also increases the relative *organophobicity*. This property can be exploited if leaching of the phosphine, or phosphine–metal complex, into the organic phase of an aqueous/organic biphasic solvent combination is undesirable. A number of water-soluble phosphine–phosphonate ligands have recently appeared in the literature.[3]

In addition to desirable solubility characteristics, organophosphonic acids are known to form layered di- and trivalent metal phosphonates.[4] If the phosphonic acid is derived from a catalytically active metal complex, then an ordered, supported catalyst may be formed which is expected to have enhanced selectivity over the homogeneous form of the

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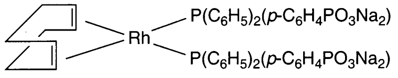
Chart 1. Examples of Phosphine−Phosphonate Complexes as Supported or Aqueous Phase Catalysts



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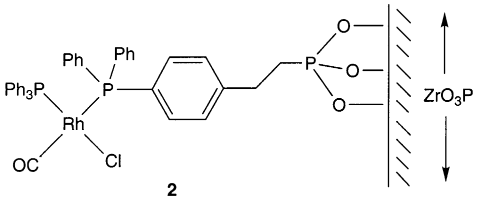

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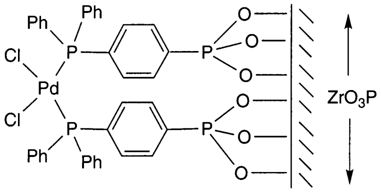

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catalyst, as well as to allow separation of catalyst from organic reaction mixture, and subsequent recycle. The concept itself is not particularly novel. In 1982, Dines and co-workers at Occidental Research Corporation first reported the in situ preparation of a layered material in which rhodium complex **2** containing a coordinated phosphonate-functionalized phosphine ligand was supported within a zirconium phosphonate matrix.[5] The supported catalyst was catalytically active for the hydroformylation of propene to *n*- and *i*-butanal without loss of activity when compared to $RhCl(CO)(PPh)_3$, although no modification of selectivity was achieved. More recently, Villemin described the formation of a layered zirconium phosphonate/phosphite containing a *p*-TPPMP palladium complex **3** which is both active and *selective* in the Heck reaction between methyl acrylate and aryl iodides, with no leaching of palladium from the phosphonate support.[6] The use of catalytically active supported complexes has not been restricted to phosphonate-functionalized phosphines; for example, Bujoli prepared a zirconium phosphonate-supported manganese porphyrin complex which was active for olefin epoxidation, although X-ray powder diffraction revealed the absence of layering within the structure.[7]

The phosphonic acid group is particularly useful for immobilizing molecules to oxide surfaces. Thus, monolayers of redox-active ruthenium complexes functionalized with $-PO_3H_2$ have been adsorbed to nanocrystalline TiO_2 [8] and TiO_2 modified ITO.[9] Electronic coupling with the surface is achieved allowing efficient light-induced charge separation, and such systems show promise in the fabrication of devices for the conversion of light to electricity. The clear advantage of the phosphonic acid group over sulfonic and carboxylic acids is the lack of desorption of the acid from the TiO_2 surface over a wide pH range. Bujoli, Odobel, and Talham recently reported the formation of organized monolayers of phosphonic acid functionalized manganese porphyrins on zirconium phosphonate Langmuir−Blodgett films.[10] Silane functionalized phosphines have been used to build up thin films of organometallic complexes on surfaces such as silica, glass, and quartz.[11] To the best of our knowledge, phosphine−phosphonic acids have not been utilized for the monolayer deposition of transition metal complexes onto alumina surfaces.

Recently, we described the preparation of a variety of tris-substituted triphenylphosphine ligands bearing phosphonic acid, phosphonate, or phosphonodiamide substituents on each aromatic ring.[3e] We address here some of the key issues associated with the use of these new ligands for catalytic applications and as structural units for the fabrication of 2D/3D surface-bound supramolecular architectures. In particular, we demonstrate the ability to form phosphine coordinated Pt or Mo complexes containing these ligands and confirm the structure of the *meta* isomer of the free *m*-TPPTP ligand by X-ray crystallography. Analogous palladium complexes, prepared in situ, are shown to be effective catalysts for the formation of C−P bonds in both homogeneous solution and as heterogeneous species adsorbed to silica particles. In addition, the ability to form monolayer films of complexes, required for future studies of these species as heterogeneous catalysts and building blocks for the formation of 2D/3D supramolecular structures, is illustrated by the stepwise synthesis and characterization of a molybdenum based mono-$TPPTP(H)_6$ complex monolayer on an Al_2O_3 surface.

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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 Mattson and Nicolet FT spectrometers. All ^1H and ^{31}P NMR spectra were recorded on Varian Inova 400, Bruker DRX 400, or Bruker AM-300 spectrometers and referenced to internal or external tetramethylsilane (^1H) and external H_3PO_4 (^{31}P). GC/MS analyses were performed on a Hewlett-Packard 6890 equipped with an HP-5 (5%)-diphenyl-(95%)-dimethylpolysiloxane capillary column (30 m, 0.25 mm). The mass spectra under electron impact conditions (EI) were recorded at 70 eV ionizing potential. High resolution ESI-MS performed with an ABI QSTAR Pulsar QTOF mass spectrometer. TGA was performed on a TA Instruments Hi-Res TGA 2950 under N_2 atmosphere.

Solvents were purified as follows: toluene (EM Science or Aldrich), distilled from Na/benzophenone; acetonitrile (Baker), distilled from CaH_2; ether (Fisher), xylene (Aldrich), $CDCl_3$ (Cambridge Isotope Laboratories), used as received. Silica gel (Scientific Products, 230−400 mesh) was used as received.

Reagents and chemicals were obtained as follows: diethyl phosphite (Strem), molybdenum hexacarbonyl (Strem), phenyl triflate (Aldrich), sodium borohydride (W. H. Curtin), used as received; potassium tetrachloroplatinate and sodium tetrachloropalladate (Johnson Matthey), used as received; triethylamine, distilled from CaH_2; *cis*-$[PtCl_2(PPh_3)]_2$,[12] $P(4\text{-}C_6H_4PO_3Na_2)_3$ (*p*-TPPTP, **4**),[3e] $P(3\text{-}C_6H_4PO_3H_2)_3$ (*m*-TPPTP(H)$_2$, **6b**),[13] and $P[4\text{-}C_6H_4\text{-}PO\{N(CH_3)_2\}]_3$ (*p*-TPPTA, **8**)[3e] were prepared according to the literature procedures. $P(4\text{-}C_6H_4PO_3H_2)_3$ (*p*-TPPTP(H)$_2$, **6a**) was prepared according to the literature procedure[3e] and isolated as the heptahydrate (determined from TGA analysis). Microanalyses are not reported for metal complexes of ligands **4**, **6a**, and **6b** because of variable degrees of hydration or mixed counterions, and thus, purity cannot be assessed. ^{31}P NMR spectra for compounds **5**, **7a**, and **7b** are included in the Supporting Information.

***trans*-[PtCl$_2$(*p*-TPPTP)$_2$] (5).** A Schlenk flask was charged with K_2PtCl_4 (0.18 g, 0.43 mmol), water (15 mL), and a stir bar. Compound **4** (0.545 g, 0.859 mmol) was added as a solid in a single portion with stirring. The solution turned yellow and was stirred for 5 h. The solvent was concentrated under oil-pump vacuum and ethanol added. A yellow solid formed which was collected by filtration and dried under a stream of nitrogen to give **5** as a pale yellow amorphous solid contaminated with approximately 5% of phosphine oxide. Crude yield 0.61 g. IR (KBr pellet): ν (P−O) 1081, 999 cm^{-1}. $^{31}P\{^1H\}$ NMR (D_2O): δ 20.2 (t, $J_{PtP} = 2519$ Hz, P), 10.9 (s, PO). ^1H NMR (D_2O): δ 7.91−6.99 (m, 24H, C_6H_4).

***cis*-[PtCl$_2$\{*p*-TPPTP(H)$_6$\}$_2$] (7a).** A Schlenk flask was charged with K_2PtCl_4 (0.20 g, 0.48 mmol), water (15 mL), and a stir bar. Compound **6a** (0.48 g, 0.76 mmol, 1.6 equiv) was added as a solid in a single portion with stirring. The reaction was stirred for 3 h, and the solution was concentrated under oil-pump vacuum and ethanol added. A solid formed which was collected by filtration and dried under a stream of nitrogen to give **7a** as a cream powder. Yield 0.42 g. IR (KBr pellet): ν(P−OH) 2900 cm^{-1}. $^{31}P\{^1H\}$ NMR (H_2O): δ 14.8 (t, $J_{PtP} = 3720$ Hz, P), 14.0 (s, PO(OH)$_2$). ^1H NMR (D_2O): δ 7.83−7.21 (m, 24H, br, C_6H_4).

***cis*-[PtCl$_2$\{*m*-TPPTP(H)$_6$\}$_2$] (7b).** A Schlenk flask was charged with K_2PtCl_4 (0.33 g, 0.79 mmol), water (20 mL), and a stir bar. Compound **6b** (0.844 g, 1.57 mmol) was added as a solid in a single portion with stirring. The reaction was stirred for 1 h, and the solution was concentrated under oil-pump vacuum and ethanol added. A solid formed which was collected by filtration and dried under a stream of nitrogen to give **7b** as a pure cream powder. Yield 0.51 g. IR (KBr pellet): ν(P−OH) 2875 cm^{-1}. $^{31}P\{^1H\}$ NMR (H_2O): δ 14.0 (t, $J_{PtP} = 3740$ Hz, P), 16.1 (s, br, PO(OH)$_2$). ^1H NMR (D_2O): δ 7.73−7.01 (m, 24H, br, C_6H_4).

***cis*-[PtCl$_2$(*p*-TPPTA)$_2$]·3H$_2$O (9).** A Schlenk flask was charged with K_2PtCl_4 (0.50 g, 1.2 mmol), xylene (50 mL), and *p*-TPPTA (**8**) (2.30 g, 3.46 mmol). The mixture was refluxed for 3 days and then allowed to cool to room temperature. Then, an off-white solid formed which was collected by filtration, washed with ether, and dried under oil-pump vacuum to give **9** (1.76 g, 89%). Concentration of the filtrate gave a small number of white crystals which have been identified by single-crystal X-ray analysis as the phosphonium salt $HP[4\text{-}C_6H_4PO\{N(CH_3)_2\}]_3OH$.[14] Anal. Calcd for $C_{60}H_{102}\text{-}Cl_2N_{12}O_9P_8Pt$: C, 43.69; H, 6.18. Found: C, 43.59; H, 6.13. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 15.6 (t, $J_{PtP} = 3626$ Hz, P), 29.0 (s, P(O)(NMe$_2$)$_2$). ^1H NMR ($CDCl_3$): δ 7.70-7.29 (m, 24H, C_6H_4), 2.61 (d, $J_{PH} = 10.1$ Hz, CH_3).

Aqueous Phase Palladium Catalyzed Coupling Reaction. The following procedure is typical: A Schlenk tube was charged with Na_2PdCl_4 (0.050 g, 0.170 mmol), **4** (0.500 g, 0.800 mmol), and water (20 mL). The solution was sparged for 5 min with nitrogen. Then, a solution of sodium borohydride (0.016 g, 0.423 mmol, 2.5 equiv) in water (2 mL) was added dropwise with stirring over a period of 3 min. Once H_2 evolution had ceased, the solution was sparged with nitrogen for 3 min. A solution of phenyl triflate (0.769 g, 3.40 mmol), diethyl phosphite (0.563 g, 4.08 mmol), and triethylamine (0.57 mL, 4.1 mmol) in degassed acetonitrile (2 mL) was added to the reaction mixture. The solution was refluxed overnight, allowed to cool to room temperature, and extracted with ether (4 × 10 mL). The organic layer was washed with brine (4 × 10 mL), dried over anhydrous sodium sulfate and the solvent removed by evaporation to give crude diethyl phenylphosphonate. Yield 0.565 g, 78%.

Synthesis of Mo(CO)$_5$(*m*-TPPTP(H)$_6$) (11). A Schlenk flask was charged with a mixture of *m*-TPPTP(H$_6$) (0.140 g, 0.260 mmol) in ethanol (15 mL) and Mo(CO)$_6$ (0.343 g, 0.130 mmol) in toluene (15 mL). The reaction mixture was heated to approximately 100 °C in an oil bath. After 30 min, a golden yellow solution was obtained. A check of the reaction mixture by ^{31}P NMR showed no free phosphine remaining, and nearly exclusive conversion to the desired product. A small impurity peak was seen at 30.9 ppm (ca. 6%), along with a corresponding phosphonate peak at 13.2 ppm. The solvent was removed under oil-pump vacuum to give an orange-brown solid, which was used without further purification. ^{31}P NMR: δ 40.7 (P), 13.8 (PO). ESI mass spectrum *m*/*z*: 738.8623 [M − H], calcd 738.8622.

Silica Gel Supported Palladium Catalyzed Coupling Reaction. A Schlenk flask was charged with Na_2PdCl_4, **6a**, water (20 mL), and sodium borohydride using the same procedure described previously for the aqueous phase catalytic reaction using identical amounts of reagents. The water was removed in vacuo, and then, methanol (15 mL) was added. Silica gel (∼2 g) was added in a single portion, and the mixture was refluxed for 30 min. The resulting yellow solid was collected using filtration and washed with ether. The solid was then dried in vacuo at 40 °C for 1 h. To the dry solid was then added phenyl triflate (0.769 g, 3.40 mmol), diethyl phosphite (0.563 g, 4.08 mmol), triethylamine (0.57 mL,

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4.1 mmol), and toluene (30 mL). The reaction mixture was refluxed overnight, allowed to cool to room temperature, and then analyzed by GC. GC yield (diethyl phenylphosphonate) 84%.

Preparation of Aluminized Glass Substrate. A standard glass microscope slide (1 in. × 3 in.) was prepared for deposition using the RCA method:[15] the substrate was immersed in a solution of $H_2O/H_2O_2/NH_4OH$ (5.0/2.0/1.0 by volume) at 75 °C for 10−15 min (to remove any organic contaminants). The substrate was then rinsed with deionized water, immersed in $H_2O/H_2O_2/HCl$ (6.0/1.0/1.0 by volume) at 75 °C for 10−15 min (to remove any heavy metals), rinsed again with deionized water, and then dried under a stream of N_2. Then, a 150−200 nm thick layer of aluminum was thermally evaporated onto the glass surface. Substrates not used immediately upon removal from the evaporator were air plasma cleaned (20 min, 200 mTorr, 100 W RF) before use.

Reflection−Absorption Infrared (RAIR).[16] Analysis was performed on a Nicolet Magna-IR System 750 Series II spectrometer equipped with a liquid nitrogen-cooled MCT-A detector. The aluminum-coated glass slides were taken directly from the thermal evaporator and placed on a fixed 80° grazing angle sample holder in the sample chamber. The sample chamber was purged with nitrogen overnight. For each slide, a background spectrum was collected (2000 scans, 2 cm^{-1} resolution). Once the background spectrum was acquired, each slide was transported directly to a nitrogen-purged trap and dip-coated with the desired solution. Following immersion for the specified time, each slide was removed, blown dry with filtered nitrogen, and carefully placed back on the grazing angle stage in exactly the same position. The sample chamber was again purged overnight, and the spectrum was acquired (2000 scans, 2 cm^{-1} resolution). The background was subtracted from the sample spectrum, using a multiplicative constant to match the intensity of the water absorptions as closely as possible. The resulting difference spectrum was then truncated to highlight the 2200−750 cm^{-1} region, and automatic baseline correction was applied.

IR Sample Preparation. The aluminized glass slide was immersed in a methanolic solution of **11** (ca. 1 mM) for 4 h at room temperature. The slide was removed and washed thoroughly with methanol and dried under a stream of N_2. Once the RAIR spectra were acquired, the slides were stored in Fluoroware containers under ambient conditions. As needed, the slides were cut into sections approximately 1 cm^2 for further analysis. This was done on the benchtop under ambient conditions. Samples were stored in glass vials under air.

X-ray Photoelectron Spectroscopy. Experiments were performed on a Surface Science Instruments SSX-100 surface analysis system, equipped with a monochromatic Al Kα (1486.6 eV) source, a hemispherical analyzer, and a position-sensitive detector. All samples were analyzed at a 35° takeoff angle. The pressure in the analysis chamber was typically between 1×10^{-9} and 5×10^{-9} Torr. Survey scans were taken to identify major elements present on the surface. Chemical state information and surface concentrations were derived from high-resolution scans of individual elements measured with a pass energy of 100 eV. Measurements were calibrated by assigning the C 1s binding energy as 284.5 eV. Relative abundances were determined using the instrument background subtraction and peak-fitting software.

AFM Analysis. AFM tapping mode images were acquired under air ambient conditions with a Nanoscope III AFM with a cantilever tip radii of approximately 40 nm. Data processing consisted of a correction to account for sample tilt followed by the application of a median filter.

Rutherford Backscattering Spectroscopy. RBS was conducted at 2.000 MeV using the Naval Research Laboratory's 3 MeV Pelletron on the 55° beamline. The experiments were performed using a scattering angle of 165° and sample angles of both 15° and 30°. In total, six measurements were made, a blank and sample at 30° and two blanks and two samples at 15°. All the blanks and samples gave reproducible results within experimental error.

X-ray Data Collection and Structure Refinement for $P(3\text{-}C_6H_4PO_3H_2)_3 \cdot 2H_2O$ (6b). A clear ($0.41 \times 0.17 \times 0.05$ mm^3) crystal was mounted on a thin glass rod for data collection on a Bruker P4 automated four circle diffractometer using an incident beam monochromator ($\lambda = 1.54178$ Å). The unit cell parameters were determined from 40 centered reflections in the range $9.3° \leq 2\theta \leq 54.9°$. A total of 3123 reflections were measured in the $\theta/2\theta$ mode to $2\theta_{\max} = 115°$, $-8 \leq h \leq 8$, $-10 \leq k \leq 10$, $-4 \leq l \leq 14$, of which 2641 were observed with $F_o > 4\sigma(F_o)$, $R_{int} = 0.015$. Three standards monitored every 100 reflections showed no decay during data collection. Corrections were applied for Lorentz and polarization effects. A face-indexed absorption correction was applied, and max and min transmissions were 0.813 and 0.348, respectively. The structure was solved by direct methods with the aid of the program SHELXTL[17] and refined with a full-matrix least-squares[17] on F^2. The 322 parameters refined include the coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Hydrogens were included using a riding model in which the coordinate shifts of the carbons were applied to the attached hydrogens, C−H = 0.96 Å, and H angles idealized. One of the PO_3 groups was disordered, and the oxygens were refined in two orientations with the occupancy required to sum to 1.0. The occupancy ratio was ca. 9:1, and the lower occupancy oxygens were refined with fixed isotropic thermal parameters. The final *R* values were R1 = 0.044, and wR2 = 0.120 for $I > 2\sigma(I)$, and R1 = 0.048, and wR2 = 0.129 for all data; the goodness of fit parameter was 1.08. Final difference Fourier excursions were 0.42 and −0.48 e $Å^{-3}$. Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles are available as Supporting Information.

Results and Discussion

Synthesis of Platinum Complexes. A variety of water-soluble phosphine complexes of Pt(II) have been previously prepared using a number of different methods. The direct reaction of water-soluble phosphines with K_2PtCl_4 in water has been used for the synthesis of *cis*-$[PtCl_2(PTA)_2]$ (PTA = 1,3,5-triaza-7-phosphaadamantane),[18] *cis*- and *trans*-$[PtCl_2\{Ph_2P(CH_2)_nSO_3M\}_2]$[19] ($n$ = 2, 3, 4; M = Na, K), and *cis*-$[PtCl_2(m\text{-TPPTS})_2]$.[20] Addition of K_2PtCl_4 to aqueous solutions of $[PtCl_2(PTA)_2]$ or $[PtCl_2\{Ph_2P(CH_2)_nSO_3M\}_2]$ resulted in the formation of $[PtL_3Cl]^+$, that is, platinum analogues of Wilkinson's catalyst, presumably via a chloride−phosphine exchange mechanism.[18b] An alternative procedure using a

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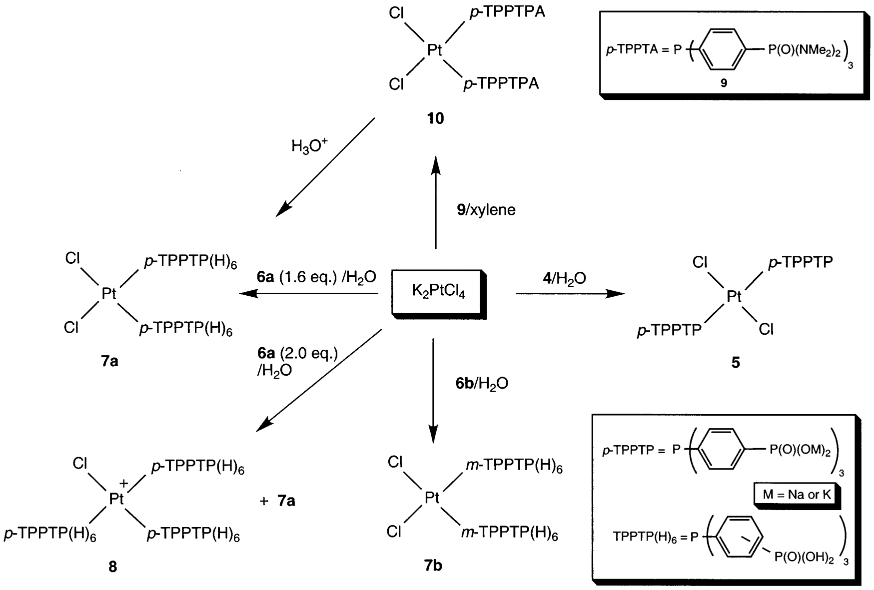
Scheme 1. Synthesis of Phosponate, Phosphonic Acid, and Phosphonodiamide Functionalized Phosphine Complexes of Platinum



biphasic ligand exchange reaction of [Pt(cod)$_2$Cl$_2$] with Ph$_2$P(CH$_2$)$_n$SO$_3$M resulted in the formation of the tris(phosphine) platinum cation,[19] which slowly converts to *cis*-[PtCl$_2${Ph$_2$P(CH$_2$)$_n$SO$_3$M}$_2$] in solution.

We suspected that the lack of solubility of *p*-TPPTP (**4**) in organic solvents would preclude any biphasic ligand exchange reaction. When an aqueous solution of **4** was rapidly stirred for 3 days, with either benzene or dichloromethane solutions of *cis*-[PtCl$_2$(PPh$_3$)]$_2$, no platinum phosphine species in the aqueous phase were observed by NMR. This is in contrast to the biphasic exchange reaction of triphenylphosphine metal complexes with *m*-TPPTS[19] or *p*-TPPMP[2] (TPPTS = tris(sodium sulfonatophenyl)phosphane, TPPMP = sodium phosphonatophenylphosphane), which readily takes place under ambient conditions. Combining a stoichiometric amount of **4** and K$_2$PtCl$_4$ in water and monitoring the reaction by ^{31}P NMR revealed that the *trans* complex, *trans*-[PtCl$_2$(*p*-TPPTP)$_2$] (**5**), was formed (Scheme 1).[21] This was indicated by a peak in the spectrum at 20.2 with corresponding ^{195}Pt satellites (J_{PtP} = 2519 Hz). A broad peak at 10.9 ppm is due to the uncoordinated phosphonate group. No peaks corresponding to the presence of a *cis* isomer or a tris(phosphine) species were present. This behavior is quite different from the reaction of K$_2$PtCl$_4$ and *m*-TPPTS where the *cis* isomer is the sole product[20] and the recently described reaction of the ester phosphonate ligand Ph$_2$PC$_6$H$_4$P(O)(OEt)$_2$ with PtCl$_2$(PhCN)$_2$ which gives a 57/43 ratio of *trans*/*cis* PtCl$_2$L$_2$ isomers.[22]

Contrasting this behavior, a 2:1 mixture of *cis*- and *trans*-[PtCl$_2$(*m*-TPPTS)$_2$] is formed when *m*-TPPTS is allowed to react with Ziese's salt, K[PtCl$_3$(η^2-C$_2$H$_4$)]H$_2$O.[20] We as yet do not understand the anomalous behavior of *p*-TPPTP although we speculate that the high anionic charge on the phosphine ligand and associated Coulombic repulsion may account for the preferred geometry in solution. These results prompted us to return to the reaction of *p*-TPPMP with *cis*-[PtCl$_2$(PPh$_3$)]$_2$ under biphasic conditions (H$_2$O/CH$_2$Cl$_2$), and close inspection of the ^{31}P NMR spectrum of the product in CD$_3$OD contained a doublet and triplet at 27.9 and 17.0 ppm, respectively, (J_{PP} = 18.8 and 18.6, 3.6 Hz) with associated ^{195}Pt satellites (J_{PtP} = 3620 and 2472 Hz), indicating formation of [PtCl(*p*-TPPMP)$_3$]Cl and the misassignment of the resonances to *cis* and *trans* isomers of [PtCl$_2$(*p*-TPPMP)$_2$] in the original report.[2]

The direct reaction of 1.6 equiv of phosphonic acid functionalized phosphine ligand **6a** and 1.6 equiv of **6b** with K$_2$PtCl$_4$ in water resulted in the formation of the new *cis* complexes *cis*-[PtCl$_2$(*p*-TPPTP(H)$_6$)$_2$] (**7a**) and *cis*-[PtCl$_2$(*m*-TPPTP(H)$_6$)$_2$] (**7b**), respectively (Scheme 1). No evidence for coordination or reaction of the phosphonic acid group was observed, and both complexes have the expected shifts and coupling constants in the ^{31}P NMR spectra (see Experimental Section). In addition, a broad band due to the free phosphonic acid OH groups was observed at approximately 2900 cm^{-1} in the IR spectra. Both complexes are water soluble. When exactly 2 equiv of **6a** was used, a doublet and triplet in a 2:1 ratio, corresponding to the tris(phosphine) cation [PtCl(*p*-TPPTP(H)$_6$)$_3$]$^+$ (**8**), appeared in the ^{31}P NMR spectrum at 22.7 and 12.2 ppm, respectively ($J_{P_AP_B}$ = 15 Hz, J_{P_APt} = 2462 Hz, J_{P_BPt} = 3629 Hz). Complex **7a** was also present in the solution, and no attempts were made to separate these two species from the mixture. Similar observations on the reaction of *m*-TPPTS with K$_2$PtCl$_4$ in water at room temperature have recently been published by Atwood.[23] In this report, 1.5 equiv of phosphine ligand to Pt gives exclusively the *cis* complex *cis*-[PtCl$_2$(*m*-TPPTS)$_2$], and 2.0 equiv of ligand gives a 3/1 mixture of both *cis*-[PtCl$_2$(*m*-TPPTS)$_2$] and the tris complex [PtCl(*p*-TPPTS)$_3$]Cl. In

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[21] Minor impurities (<10%) were also observed which were attributed to phosphine oxide (37 ppm) or unidentified species which could not be assigned to simple PtCl$_2$L$_2$ or [PtClL$_3$] complexes.

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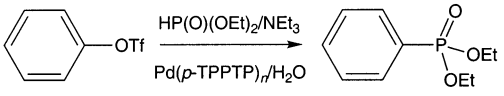
Scheme 2. Aqueous Phase Coupling of Phenyl Triflate with Diethylphosphite



the case of our phosphonic acid ligand **6a**, the ratio of *cis* bis(phosphine) complex to tris(phosphine) complex is reversed (1/3).

An alternative route to platinum complexes of TPPTP involves coordination of triarylphosphine−phosphonodiamide ligand *p*-TPPTA (**9**) to platinum and subsequent post-complexation ligand hydrolysis to give the desired *p*-TPPTP-$(H)_6$ complex **7a** (Scheme 1). *p*-TPPTA was prepared from red phosphorus, lithium, and *N*,*N*,*N′*,*N′*-tetramethyl-4-fluorophenylphosphonodiamide according to the literature procedure[3e] and reacted with K_2PtCl_4 in refluxing xylene for 3 days. On cooling of the xylene solution, *cis*-$[PtCl_2(p\text{-}TPPTA)_2]\cdot 3H_2O$ (**9**) precipitated as a white solid which was collected by filtration and characterized using NMR, IR, and elemental analysis (see Experimental Section). The ^{31}P NMR spectrum of **10** shows the expected triplet at 15.6 with ^{195}Pt satellites ($J_{PtP} = 3620$ Hz). After concentration of the filtrate following the isolation of **10**, a very small amount of a colorless, crystalline compound was collected and subsequently identified, using single-crystal X-ray crystallography, as the phosphonium salt $HP[4\text{-}C_6H_4PO\{N(CH_3\}_2\}]_3OH$, which presumably results from phosphine protonation due to adventitious water.[14]

Aqueous Phase and Supported Catalysis. Water-soluble palladium phosphine complexes are known to catalyze a wide variety of coupling reactions in aqueous solution.[1e] We chose the palladium(0) coupling of diethyl phosphite and phenyl triflate to give diethyl phosphonate as a test case for *p*-TPPTP under homogeneous and heterogeneous catalytic conditions. While aryl iodides have previously been used as substrates for the aqueous phase phosphonylation reaction,[24] aryl triflates have not been explored.[25] The addition of 5 equiv of **4** to a solution of sodium tetrachloropalladate in water at room temperature resulted in the formation of a bright yellow solution. To this was added sodium borohydride, triethylamine, diethyl phosphite, and phenyl triflate. The mixture was refluxed for 24 h, and following workup (see Experimental Section), diethyl phenylphosphonate was obtained in 78% yield (Scheme 2). A notable increase in catalytic activity was observed when a small amount of acetonitrile (∼10%) was added as co-solvent. The role of the co-solvent is unknown, but we suggest that it improves the solubility of the substrate in the aqueous phase. Under biphasic conditions using a 50/50 water/toluene or water/dichloromethane mixture, no activity was observed. This is not too surprising as *p*-TPPTP is particularly organophobic.

The grafting of phosphonic acids onto silica gel[26] and metal oxide[27] surfaces has been previously reported; for example, phenylphosphonic acid reacts covalently with the surface hydroxy groups of silica gel to give a surface-bonded mono ester. The general procedure involves stirring a slurry of silica gel with the desired phosphonic acid in a polar solvent such as 2-propanol, followed by collection of the supported silica, with washing and drying. We were interested in assessing the catalytic activity of a supported phosphine−phosphonic acid complex of palladium in the C−P coupling reaction. Thus, the catalyst was prepared in the manner described previously, and to a methanolic solution of Pd(0) complex containing **6a** as the ligand was added silica gel in a single portion with stirring. The mixture was rapidly stirred for 1 h, and the bright yellow silica gel was collected, washed with ether, and dried in vacuo at 60 °C. Although detailed measurements of palladium loading were not made, the presence of the coordinated phosphonate ligand was confirmed by direct observation of the characteristic PO_3 bands in the IR spectrum at 1000−1080 cm^{-1}. The supported palladium complex is an effective catalyst for the coupling of phenyl triflate with diethyl phosphite. Using toluene as a solvent, a GC yield of 84% diethyl phenylphosphonate was obtained from the reaction mixture (see Experimental Section).

Crystal Structure Analysis of $P(3\text{-}C_6H_4PO_3H_2)_3\cdot 2H_2O$ (6b). Given our successful demonstration of heterogeneous catalysis using the silica supported catalyst, we examined the interaction of the *m*-TPPTP$(H)_6$ ligand **6b** with solid supports further. Molecular modeling studies indicated that the ideal arrangement of metal complexes of TPPTP in a layered fashion on a planar surface would require the *meta* isomer of the ligand to achieve optimum geometry. To confirm this, we analyzed the structure of **6b** in the solid state using X-ray crystallography. Recrystallization of a sample of **6b** from HCl acidified water yielded single colorless crystals of the phosphine dihydrate. The ORTEP representation is shown in Figure 1, and crystallographic data and selected bond distances and angles are listed in Tables 1 and 2. A comparison of the metric parameters of the triarylphosphine subunit with those of triphenylphosphine[28] revealed no remarkable or unexpected bond lengths or angles, the phosphine phosphorus atom P(2) has a trigonal pyramidal geometry, the P(2)−C distances are all virtually identical, the mean P(2)−C distance is 1.832 Å, and the mean C−P(2)−C angle is 102.4°. Very few crystal structures of arylphosphonic acids have been reported in the literature although, notably, the crystal structure of phenylphosphonic acid was reported by Weakley in 1976.[29] The structure of $PhP(O)(OH)_2$ is held together by a combination of both a centrosymmetric dimer and continuous chain hydrogen bonded motifs incorporating four carbon chains which result in the formation of layered structure. The mean P(1)−C bond

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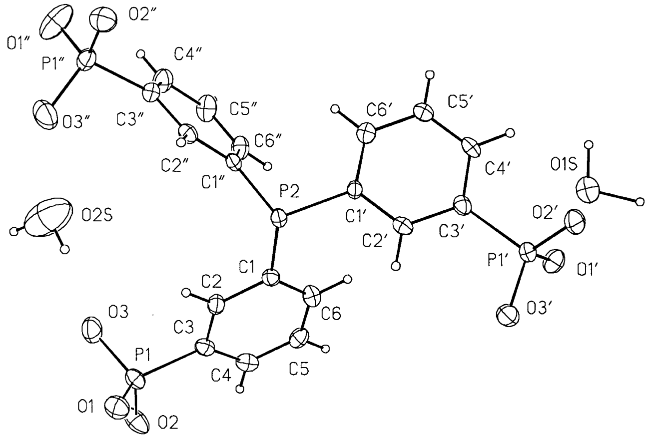

Figure 1. Structure of **6b** drawn from experimental coordinates. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30% probability level. The lower occupancy disorder of the PO_3 group on C3″ is not shown for clarity.

Table 1. Summary of Crystallographic Data for **6b**

empirical formula	$C_{22}H_{12}O_{11}P_4$
fw	532.19
temp, K	213(2)
wavelength, Å	1.54178
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimensions	
a, Å	8.3501(6)
b, Å	10.1907(6)
c, Å	14.6529(14)
α, deg	94.177(6)
β, deg	105.885(6)
γ, deg	108.784(5)
V, Å^3	1117.50(15) Å^3
Z	2
d_{calcd}, g/cm^3	1.582
abs coeff, mm^{-1}	3.668
F(000)	544
cryst size, mm^3	0.41 × 0.17 × 0.05
θ	3.19−57.49
index ranges	$-8 \le h \le 8$, $-10 \le k \le 10$, $-4 \le l \le 14$
reflns collected	3123
indep reflns	2884 [*R*(int) = 0.0146]
completeness to *θ* = 57.49°	94.2%
abs correction	integration
max and min transm	0.8126 and 0.3840
refinement method	full-matrix least-squares on F^2
data/restraints/params	2884/13/322
GOF on F^2	1.079
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0441, wR2 = 0.1201
R indices (all data)	R1 = 0.0484, wR2 = 0.1295
largest diff peak and hole, e Å^{-3}	0.424 and −0.479

length of 1.785 Å in $P(3\text{-}C_6H_4PO_3H_2)_3 \cdot 2H_2O$ is slightly longer than 1.773(5) Å found in phenylphosphonic acid. The two long P(1)−O bonds (mean value 1.543 Å) and one short P(1)−O bond (mean value 1.503 Å) fall into the expected range. The phosphonic acid phosphorus atom, P(1), is tetrahedral with a mean X−P−X angle of 109.4°. Two water molecules of solvation are present in the unit cell which are hydrogen bonded to the PO_3H_2 groups. Hydrogen bond distances are listed in Table 3.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **6b**

P(2)−C(1″)	1.827(4)	O(1′)−P(1′)−O(2′)	112.51(16)
P(2)−C(1)	1.835(4)	O(1′)−P(1′)−O(3′)	111.06(16)
P(2)−C(1′)	1.835(3)	O(2′)−P(1′)−O(3′)	106.76(15)
P(1)−O(2)	1.484(3)	O(1′)−P(1′)−C(3′)	107.91(16)
P(1)−O(3)	1.552(3)	O(2′)−P(1′)−C(3′)	109.68(16)
P(1)−O(1)	1.554(3)	O(3′)−P(1′)−C(3′)	108.88(16)
P(1)−C(3)	1.790(4)	O(2")−P(1″)−O(3″)	110.17(16)
P(1′)−O(1′)	1.512(3)	O(2″)−P(1″)−O(1″)	112.30(18)
P(1′)−O(2′)	1.524(3)	O(3″)−P(1″)−O(1″)	111.3(2)
P(1′)−O(3′)	1.558(3)	O(2″)−P(1″)−C(3″)	112.72(16)
P(1′)−C(3′)	1.780(4)	O(3″)−P(1″)−C(3″)	105.18(17)
P(1″)−O(2″)	1.514(3)	O(1″)−P(1″)−C(3″)	104.84(17)
P(1″)−O(3″)	1.533(3)	C(6)−C(1)−P(2)	127.3(3)
P(1″)−O(1″)	1.536(3)	C(2)−C(1)−P(2)	114.2(3)
P(1″)−C(3″)	1.784(4)	C(4)−C(3)−P(1)	121.9(3)
C(1″)−P(2)−C(1)	99.48(15)	C(2)−C(3)−P(1)	119.2(3)
C(1″)−P(2)−C(1′)	103.18(16)	C(6′)−C(1′)−P(2)	123.2(3)
C(1)−P(2)−C(1′)	104.66(15)	C(2′)−C(1′)−P(2)	117.8(3)
O(2)−P(1)−O(3)	115.50(17)	C(4′)−C(3′)−P(1′)	118.4(3)
O(2)−P(1)−O(1)	112.22(16)	C(2′)−C(3′)−P(1′)	123.0(3)
O(3)−P(1)−O(1)	104.02(15)	C(2″)−C(1″)−P(2)	117.6(3)
O(2)−P(1)−C(3)	108.84(16)	C(6″)−C(1″)−P(2)	124.6(3)
O(3)−P(1)−C(3)	107.69(16)	C(4″)−C(3″)−P(1″)	122.3(3)
O(1)−P(1)−C(3)	108.24(15)	C(2″)−C(3″)−P(1″)	118.5(3)

Table 3. Hydrogen Bonds for **6b** [Å and deg]

D−H····A	D−H (Å)	H····A (Å)	D····A (Å)	D−H····A (deg)
O(1S)−H(1SA)···O(2″)#1[a]	0.985(10)	1.653(13)	2.632(4)	172(4)
O(1S)−H(1SB)···O(2′)#2	0.991(10)	1.580(14)	2.561(4)	170(5)
O(1S)−H(1SB)···O(1′A)#2	0.991(10)	1.74(5)	2.49(3)	130(4)
O(2S)−H(2SB)···O(2′A)#3	0.980(11)	1.74(3)	2.72(3)	173(7)
O(2S)−H(2SB)···O(3′)#3	0.980(11)	2.12(5)	2.931(6)	139(6)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, -z + 1$; #2 $-x, -y + 1, -z$; #3 $-x + 1, -y + 2, -z + 1$.

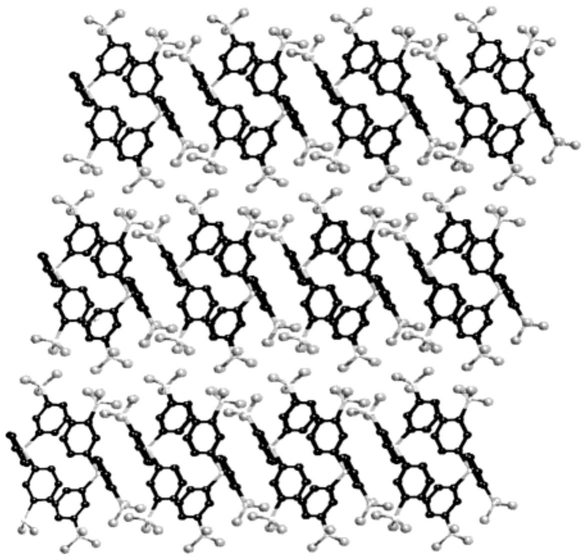

Figure 2. Molecular drawing of **6b** showing layered structure of crystal lattice. View is approximately along the *a* axis.

It is clear that $P(3\text{-}C_6H_4PO_3H_2)_3 \cdot 2H_2O$ also has a layered structure in the solid state, as shown in Figure 2, with the organic triphenylphosphine groups forming one layer, and the phosphonic acid groups forming a second layer. The water molecules form a hydrogen bonded network within the phosphonic acid layer. Presumably, weak van der Waals' forces are responsible for holding the organic layers together, similar to those proposed for layered metal organophosphonates.[4]

Formation of $Mo(CO)_5\{P(3\text{-}C_6H_4PO_3H_2)_3\}$ and Surface Grafting to Alumina. To further study the nature of the supported phosphonate ligand, we investigated the attachment of phosphonate functionalized phosphine complexes to planar Al_2O_3 by IR. The careful choice of a molybdenum carbonyl derivative was made because of the intense and characteristic CO stretching frequencies which are sensitive to the metal complex environment and the well-known ability of metal carbonyls to undergo ligand substitution reactions. In addition, the stepwise formation of group VI metal carbonyl phosphine complexes is well-known, and the molybdenum phosphine stoichiometry is more readily controlled and easier to study than that of platinum and palladium derivatives. The reaction of **6b** with an excess of $Mo(CO)_6$ in refluxing ethanol/toluene resulted in the formation of yellow $Mo(CO)_5\{P(3\text{-}C_6H_4PO_3H_2)_3\}$ (**11**) as shown by IR and ^{31}P NMR spectroscopies. Analogous sulfonated phosphine complexes $[M(CO)_5(m\text{-TPPTS})]$ (M = Mo, W) have been previously studied by Darensbourg and also provided us with useful spectral data for comparison.[30,31] The IR spectrum of **11**, recorded as a KBr pellet, contained the expected A_1^2, E, and A_1^1 bands in the carbonyl region at 2074, 1990, and 1935 cm^{-1}, consistent with the formation of a monophosphine adduct (cf. $Mo(CO)_5(PPh_3)$,[32] 2073, 1984, 1952 cm^{-1}; and $Mo(CO)_5(m\text{-TPPTS})$,[30] 2075, 1955, 1941 cm^{-1}). Although water is clearly present in the spectrum, the degree of hydration remains unknown. The phosphonic acid P−OH absorption was observed as a broad band at 3412 cm^{-1}. The ^{31}P NMR spectrum of **11** recorded in methanol showed peaks at 41.1 and 14.2 ppm corresponding to coordinated phosphine and uncoordinated phosphonic acid groups, respectively. No evidence for the formation of a bis(phosphine) complex was observed in solution by ^{31}P NMR. We were interested to know whether complex **11** could be deposited as a monolayer onto the surface of an oxide such as alumina via direct attachment of the phosphonic acid group. Because alumina is transparent in the carbonyl region of the IR spectrum, it proved to be a useful substrate for binding the phosphonic acid complex and observing any possible chemical changes occurring at the molybdenum center. A glass 3 in. × 1 in. microscope slide was vapor deposited with 150−200 nm of aluminum substrate, plasma cleaned, and air oxidized. The slide was subsequently immersed in a 1 mM methanolic solution of **11** for 4 h, washed exhaustively with methanol, and dried under a stream of filtered nitrogen. A reflection−absorption infrared (RAIR) spectrum of the surface-grafted phosphine complex was recorded, and the spectrum indicated little change in the metal carbonyl absorption frequencies compared to the spectrum recorded as a KBr disk, suggesting that the carbonyl groups are not interacting with the alumina surface (Figure 3).

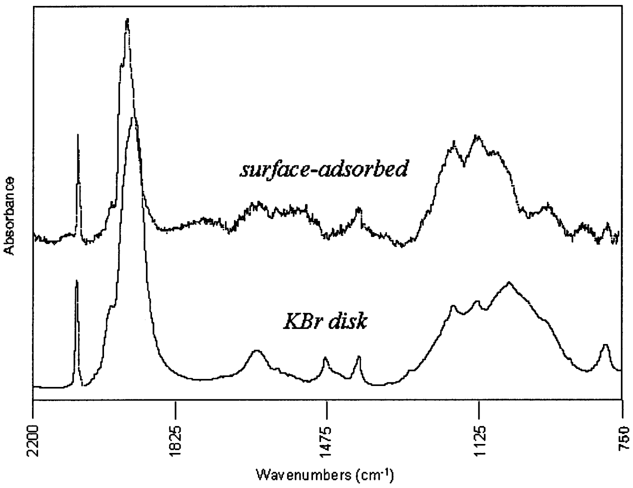

Figure 3. Comparison of the RAIR spectrum of surface-adsorbed $Mo(CO)_5\{P(3\text{-}C_6H_4PO_3H_2)_3\}$ on alumina with the transmission IR spectrum of the complex prepared as a KBr pellet. Absorbances are normalized for comparison purposes.

Previous workers have observed substantial differences in the IR carbonyl stretching frequencies of the solid state molecular species compared to alumina supported complexes. The adsorption of $Mo(CO)_6$ onto partially de-hydroxylated γ-alumina resulted in significant spectral changes in the carbonyl region of the IR spectrum compared to the gas phase spectrum of the complex[33] The single strong absorption at 1998 cm^{-1} is gradually transformed to a pair of superimposable quartets centered at 2031 cm^{-1}. The shift is ascribed to the interaction of the carbonyl oxygen atoms with Lewis acidic sites on the alumina surface. The absence of such interactions for **11** adsorbed to alumina indicates that the $Mo(CO)_5$ kernal is well separated from the alumina surface by the m-TPPTP(H)$_6$ spacer ligand. Such behavior is consistent with the crystal structure of **6b** and a surface binding model involving interaction of each of the three PO_3^{2-} groups with the alumina in a tripodal binding configuration.[34]

Surface Analysis of $Mo(CO)_5\{P(3\text{-}C_6H_4PO_3H_2)_3\}$ on Alumina. To further understand the nature of the molybdenum phosphine complex on the surface of alumina and to unambiguously show the presence of monolayers of **11**, XPS, Rutherford backscattering spectrometry (RBS), and AFM measurements were made. A survey scan of a 600 μm^2 area of the samples by XPS showed that carbon, phosphorus, and molybdenum were present on the aluminum/aluminum oxide surface. Integration of the C 1s and P 2p peaks gave a C/P ratio of 4.7/1. The calculated C/P ratio for $Mo(CO)_5\{P(3\text{-}C_6H_4PO_3H_2)_3\}$ is 5.75/1. However, analysis at the Mo 3d energy level showed two molybdenum containing species present on the surface, with an approximate ratio of 70/30, thought to be $Mo(CO)_5\{P(3\text{-}C_6H_4PO_3H_2)_3\}$ and molybdenum oxide resulting from oxidative degradation of the Mo(0) complex. If 30% of the CO ligands were lost due to decomposition, the expected C/P ratio would be closer to 4. Thus, a C/P ratio between 4 and 5.75 is in reasonable agreement with the expected results.

The major fraction of molybdenum species had binding energies of 233.8 eV ($3d_{3/2}$) and 230.7 eV ($3d_{5/2}$). This can be compared with $[Mo(CO)_5(PPh_3)]$ which is reported to have

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(31) Darensbourg, D. J.; Bischoff, C. J.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 1144.
(32) Poilblanc, R.; Bigorgne, M. *Bull. Soc. Chim. Fr.* **1962**, 1301.
(33) Reddy, K. P.; Brown, T. L. *J. Am. Chem. Soc.* **1995**, *117*, 2845.
(34) Similar observations were made when using the para isomer. Control experiments involving immersion of aluminized slides into ethanolic solutions of $Mo(CO)_5(PPh_3)$ and $Mo(CO)_5$(solvate) and recording RAIR spectra show no adsorption of these species to the surface and clearly implicate the phosphonic acid group in surface adsorption.

$3d_{3/2}$ and $3d_{5/2}$ binding energies of 230.8 and 227.6 eV[35] and for elemental molybdenum (231.1 and 227.8 eV).[36] The minor fraction had $3d_{3/2}$ and $3d_{5/2}$ binding energies at 235.4 and 238.4 eV, respectively, as compared to the values reported for native films of molybdenum oxide (232.7 eV, 235.8 eV, presumably as MoO_2/MoO_3).[36] It is not clear why the binding energies are consistently high for the molybdenum 3d spectrum although it does not appear to be related to sample charging, as the C 1s binding energy was actually 1 eV too low, and the adjusted binding energies for Al/Al_2O_3 2p electrons (72.1 and 74.6 eV) are in reasonable agreement with the expected values (72.7 and 74.7 eV).[3b]

To calculate the estimated density of a monolayer of $Mo(CO)_5\{P(3\text{-}C_6H_4PO_3H_2)_3\}$, a molecular model was constructed[37] in which the phosphonate groups were assumed to be oriented toward the surface. In this configuration, the molecule was projected on the surface as a circle approximately 9 Å in diameter, and from this estimate, a molecular area of 2.03×10^{-15} cm^2 was calculated, giving a maximum surface coverage for a monolayer on a flat surface of approximately 4.93×10^{14} molecules/cm^2. The actual surface coverage was determined by Rutherford backscattering spectrometry. The integrated area under the Mo edge was 448 counts, corresponding to approximately 5.0×10^{14} atoms/cm^2 ±5%. This value is consistent with full monolayer coverage by the molybdenum complex but does not rule out the formation of crystallites or patches of multilayer coverage.

To address this issue, atomic force microscopy of the surface was carried out. AFM images of aluminum coated control samples showed a homogeneous pebble-grained morphology with an average surface roughness (rms) of 12.7 nm over a 25 μm^2 area (5 μm × 5 μm scan area). The deviation in surface area from an atomically flat surface was calculated to be 2.65%. This is less than the experimental error for RBS measurements, so surface roughness was ignored when estimating the RBS value expected for monolayer coverage.

Surfaces exposed to a solution of $Mo(CO)_5\{P(3\text{-}C_6H_4\text{-}PO_3H_2)_3\}$ exhibited no significant morphological differences from the control sample over scan areas ranging from 1 to 100 μm^2. High-resolution scans exhibited no evidence of crystalline deposition on the substrate surface, and there was no evidence of multilayer domains. This further supports the RBS measurements indicating that monolayer coverage of the molybdenum complex exists.

In conclusion, new water-soluble complexes of phosphonic acid substituted phosphines have been prepared and characterized, and we have demonstrated application of a palladium complex in aqueous phase and supported C−P bond formation. A crystal structure of *m*-TPPTP(H)$_6$ revealed the presence of a layered structure in the solid state and an ideal molecular geometry for building a monolayer of a metal phosphine complex on a planar surface. We have also shown that a phosphonic acid functionalized phosphine can act as suitable supporting ligand for a metal carbonyl monolayer on the surface of alumina.

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Supporting Information Available: ^{31}P NMR spectra for complexes **5**, **7a**, **7b**, and **8**. XPS and RBS data for **11** on alumina. X-ray crystal files for **6b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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