Reactions of Uncoordinated Acetylenes Held Proximate to a Metal. Products from the Hydrolysis of *cis*-Dichlorobis(3,3,3-trifluoropropynyldiphenylphosphine)palladium(II)

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Abstract: The synthesis and hydrolysis of *cis*-dichlorobis(3,3,3-trifluoropropynyldiphenylphosphine)palladium(II) [$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$](I) are described. The phosphorus coordinated phosphinoacetylenes in (I) are susceptible to nucleophilic attack at both phosphorus and alkyne sites yielding a variety of new complexes. Under reflux conditions in aqueous ethanol the major products are a chloro bridged complex [$PdCl(Ph_2POHOPPh_2)$]$_2$ (IIa) containing the symmetrical hydrogen bonded anion [$Ph_2PO\cdots H\cdots OPPh_2$]$^-$, and the unsymmetrical diphosphine complex *cis*-$PdCl_2(Ph_2PCH_2C(CF_3)CHPPh_2)$ (IIIa). The infrared spectra of IIa, IIa-d_2, and bromo and thiocyanato analogues have been studied in detail to provide assignments of $O\cdots H\cdots O$ vibrational modes. Under milder conditions four other complexes have been obtained. These are the chelates $PdCl[Ph_2PCH{=}C(CF_3)O](Ph_2POEt)$ (IV), $PdCl[Ph_2PCH{=}C(CF_3)O](Ph_2POH)$ (V), and $Pd[Ph_2PCH{=}C(CF_3)O]_2$ (VI) formed via acetylene hydration, intramolecular elimination of HCl, and nucleophilic displacement at phosphorus. The β-ketophosphine complex *cis*-$PdCl_2(Ph_2PCH_2COCF_3)(Ph_2POH)$ (VII) has also been characterized. Two of these complexes (V and VII) contain stabilized diphenylphosphinous acid molecules. The compounds have been characterized by elemental analysis, infrared, ^1H, ^{19}F, and ^{31}P NMR spectroscopy and by x-ray diffraction. Mechanistic pathways for the formation of the compounds are discussed.

The activation of unsaturated molecules towards electrophilic or nucleophilic attack via coordination to a transition metal is a well-established phenomenon with considerable synthetic utility.[1] The involvement of olefin and acetylene π-complexes in many homogeneously catalyzed reaction sequences[2] and the use of acetylene complexes as precursors for carbene,[3] σ-alkenyl,[4] and π-hydrocarbon[5] derivatives has motivated numerous studies contingent on the reactivity of coordinated acetylenes, both in electron rich, low valent, metal complexes[4,6] and in divalent nickel triad derivatives.[3,7] The present work was initiated to investigate the possibility of modifying the reactivity of an acetylene *without* coordination, by holding the alkyne adjacent to the coordination sphere of a d^8 metal ion. The phosphinoacetylene complexes *cis*-$MX_2(Ph_2PC{\equiv}CR)_2$ (M = Pd, Pt; R = CF_3, CH_3, C_2H_5, *i*-Pr, *t*-Bu, Ph; X = Cl, NCS) recently described in detail elsewhere[8-10] appeared well suited to this purpose since x-ray studies[10,11] have clearly demonstrated both the noninvolvement of alkyne π-electrons in coordination and the proximity of two alkyne units to one another in these cis species. In addition the presence of good leaving groups, $-C{\equiv}CR$, attached directly to phosphorus might be expected to effect an activation of a tertiary phosphine to nucleophilic attack at phosphorus.[12] Thus in the reactions of *cis*-$MCl_2(Ph_2PC{\equiv}CR)_2$ with electrophiles and nucleophiles, products derived from the following reaction modes might be expected: (a) nucleophilic or electrophilic attack at the triple bond analogous to reactions of the "free" acetylene; (b) coupling of two adjacent acetylene moieties; (c) nucleophilic attack at phosphorus with subsequent elimination of an alkynyl anion. Investigations with a variety of electrophiles and nucleophiles have shown that all three reaction modes occur with product distributions which are a sensitive function of experimental conditions. In this paper we describe the sensitivity of the palladium complex *cis*-$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ to nucleophilic attack by water and ethanol. These reactions provide novel synthetic routes to several types of inorganic complexes including symmetrical hydrogen bonded species, unsymmetrical diphosphine complexes, chelates with P, O donor atoms, β-ketophosphine derivatives, and complexes containing stabilized diphenylphosphinous acid molecules.

Experimental Section

Palladous chloride and sodium tetrachloropalladate(II) were purchased from Johnson, Mathey and Mallory, Toronto. The palladium(II) precursors *trans*-$PdCl_2(PhCN)_2$ and $K_2Pd(SCN)_4$ were prepared by literature methods.[16,17] The phosphinoacetylene $Ph_2PC{\equiv}CCF_3$ was synthesized as previously described.[18] The solvents benzene, petroleum-ether (80–100°), diethyl ether, and *n*-hexane were routinely dried over $LiAlH_4$ in a nitrogen atmosphere and tapped from laboratory stills when needed. Other solvents were reagent grade and used as such. Deuterated solvents, including D_2O and ethanol-*d*, used in deuteration experiments, were purchased from Stohler Isotope Chemicals, Montreal.

Infrared spectra were measured on a Perkin-Elmer 180 (4000–180 cm^{-1}) spectrophotometer, using Nujol mulls on CsI plates. Where necessary spectra in the low frequency region (300–150 cm^{-1}) were measured on the same instrument using Nujol mulls on polyethylene disks. Proton NMR spectra were obtained with Varian T-60 and HA-100 spectrometers; peak positions are relative to internal tetramethylsilane. A Varian DA-60 instrument was employed to obtain 58.3-MHz ^{19}F NMR spectra, with $CFCl_3$ added as an internal standard. Proton decoupled ^{31}P NMR spectra were measured at 40.49 MHz in the FT mode on a JEOL FT100L spectrometer using trimethyl phosphite in C_6D_6 as an external standard and ^2D as a lock. X-Ray photographic measurements were made on Weissenberg and precession cameras using Cu Kα or Mo Kα radiation. Microanalyses and osmometric molecular weight determinations were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

***cis*-Dichlorobis(3,3,3-trifluoropropynyldiphenylphosphine)palladium(II) (I).** A mixture of $Ph_2PC{\equiv}CCF_3$ (5.6 g) and $PdCl_2(PhCN)_2$ (3.9 g) in 100 ml of dry benzene was stirred for 2 hr at room temperature and filtered under nitrogen. The volume of solvent was reduced to ~20 ml and a few milliliters of petroleum ether added. A 70–80% yield of yellow crystals of *cis*-$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ was generally obtained. Although this product is sufficiently pure for subsequent reactions, recrystallization from dichloromethane-ethanol affords beautiful, yellow single crystals of the analytically pure material: ir (cm^{-1}) 319 s, 301 s (ν(Pd-Cl)), 2219 m ν($C{\equiv}C$); Raman 320 s, 304 s (ν(Pd—Cl)).

Anal. Calcd for $PdCl_2(Ph_2PC{\equiv}CCF_3)_2$: C, 49.11; H, 2.75; Cl, 9.66. Found: C, 49.09; H, 2.60; Cl, 9.43.

Hydrolysis of (I) by $\mathrm{H_2O}$–EtOH under Mild Conditions. Complex I (3.2 g) was dissolved in a mixture of dichloromethane (20 ml), water (10 ml), and ethanol (30 ml). The solution was stirred for 6 hr at room temperature then taken to dryness. The residual solid was extracted with a minimum of dichloromethane, the solution dried over anhydrous magnesium sulfate, and the volume reduced to a few milliliters. Diethyl ether (10 ml) was added and the solution left to stand. Large, pale yellow needles of $\mathrm{[PdCl(Ph_2PO{\cdot}HOPPh_2)]_2}$ (IIa) crystallized (0.45 g). Recrystallization from dicloromethane–diethyl ether gave the pure product: ir ($\mathrm{cm^{-1}}$)273 m (ν(Pd–Cl)), 1040 vs (ν(P–O)), 1350 m, br, 1236 w, 773 ms (O···H···O); NMR ^{1}H ($\mathrm{CD_2Cl_2}$) δ 7.46 (m, phenyl H).

Anal. Calcd for $\mathrm{[PdCl(Ph_2POHOPPh_2)]_2}$: C, 52.87; H, 3.89; Cl, 6.50; P, 11.37. Found: C, 53.02; H, 3.89; Cl, 7.13; P, 11.70.

After removal of IIa the solution was again taken to dryness and extracted with dichloromethane (3 ml) and diethyl ether (10 ml). On standing impure $\mathrm{PdCl_2(Ph_2PCH_2C(CF_3)CHPPh_2)}$ (IIIa) (0.20 g) crystallized. Recrystallization from dichloroethane–diethyl ether gave pure IIIa: ir ($\mathrm{cm^{-1}}$) 317 s, 299 s (ν(Pd–Cl)); NMR ^{1}H ($\mathrm{CD_2Cl_2}$) δ 7.68 (m, phenyl H), 6.91 (d, vinyl H, $^2J_{\mathrm{P-H}} = 6.0$ Hz), 3.01 (dd, $\mathrm{CH_2}$, $^2J_{\mathrm{P-H}} = 11.0$ Hz, $^4J_{\mathrm{P-H}} = 4.0$ Hz); ^{19}F ($\mathrm{CD_2Cl_2}$) 69.9 (s, $\mathrm{CF_3}$).

Anal. Calcd for $\mathrm{PdCl_2(Ph_2PCHC(CF_3)CH_2PPh_2)}$: C, 51.33; H, 3.51; F, 8.70. Found: C, 51.20; H, 3.55; F, 9.03.

The residue from the remaining solution was extracted with a mixture of dichloromethane (2 ml), ethanol (3 ml), and diethyl ether (3 ml). From this solution $\mathrm{PdCl[Ph_2PCH{=}C(CF_3)O]{\cdot}(Ph_2POEt)}$ (IV) (0.10 g) contaminated with traces of IIa and IIIa was obtained. Recrystallization from dichloromethane–petroleum ether afforded yellow plates of IV: ir ($\mathrm{cm^{-1}}$) 307 s (ν(Pd–Cl)), 354 m (ν(Pd–O)), 943 m (ν(P–O)), 1559 s, 1574 m (ν(C–O) + ν(C=C)); NMR ^{1}H ($\mathrm{CD_2Cl_2}$) δ 7.55 (m, phenyl H), 4.70 (deceptively simple triplet, separation of outer components = 2.30 Hz, vinyl H), 3.32 (1:4:6:4:1 quintet, $\mathrm{CH_2}$, $^3J_{\mathrm{P-H}} = 7.0$ Hz), 0.56 (t, $\mathrm{CH_3}$, $^3J_{\mathrm{H-H}} = 7.0$ Hz); ^{19}F ($\mathrm{CD_2Cl_2}$) 73.46 (s, $\mathrm{CF_3}$).

Anal. Calcd for $\mathrm{PdCl[Ph_2PCH{=}CCF_3(O)](Ph_2POEt)CH_2Cl_2}$: C, 47.86; H, 3.49; Cl, 14.15; P, 8.23. Found: C, 47.44; H, 3.72; Cl, 14.14; P, 8.42. Mol wt Calcd for $\mathrm{PdCl[Ph_2PCH{=}CCF_3(O)](Ph_2POEt)}$ 667.3. Found: ($\mathrm{CHCl_3}$) 1240.

The residual solid was dissolved in absolute ethanol. Orange-yellow crystals of $\mathrm{Pd[Ph_2PCH{=}CCF_3(O)]_2}$ (VI) were deposited on standing in the open air for 1 day. This material was contaminated with IIa. Repeated recrystallization of the product from dichloromethane–petroleum ether yielded 0.06 g of pure complex: ir ($\mathrm{cm^{-1}}$) 362 m, 354 m (ν(Pd–O)), 1562 s, 1574 s (ν(C–O) + ν(C=C)); NMR ^{1}H ($\mathrm{CD_2Cl_2}$) δ 7.30 (m, phenyl H), 4.64 (s, vinyl H); ^{19}F ($\mathrm{CD_2Cl_2}$) 74.29 (s, $\mathrm{CF_3}$).

Anal. Calcd for $\mathrm{Pd[Ph_2PCH{=}CCF_3(O)]_2}$: C, 51.70; H, 3.19; Cl, 0.00; P, 8.88. Found: C, 51.24; H, 3.38; Cl, 0.02; P, 8.94. Mol wt Calcd 696.9. Found (x ray) 673. The same solution deposited a pale yellow precipitate on further standing. Examination under a microscope suggested that this precipitate was a mixture of two compounds. Crystallization from dichloromethane–petroleum ether yielded 0.10 g of colorless $\mathrm{PdCl_2(Ph_2PCH_2COCF_3)(Ph_2POH)}$ (VII): ir 309 s, 292 s (ν(Pd–Cl)), 965 s (ν(P–O)), 1755 s (ν(C=O)), 3310 s, br, (ν(O–H)); NMR ^{1}H ($\mathrm{CD_2Cl_2}$) 7.54 (m, phenyl H), 5.09 (AB quartet, $\mathrm{CH_2}$, $J_{\mathrm{A-B}} = 2.1$ Hz).

Anal. Calcd for $\mathrm{PdCl_2(Ph_2PCH_2COCF_3)(Ph_2POH)(CH_2Cl_2)}$: C, 44.21; H, 3.31; P, 8.14. Found: C, 44.92; H, 3.21; P, 7.84. Mol wt Calcd 760.63. Found (x ray): 767.4.

After removal of VII, crystallization from dichloromethane (2 ml) and ethanol (5 ml) gave a bright yellow sample of $\mathrm{PdCl[Ph_2PCH{=}CCF_3(O)](Ph_2POH)}$ (V) (0.06 g): ir ($\mathrm{cm^{-1}}$) 287 s (ν(Pd–Cl)), 354 s (ν(Pd–O)), 985 s, 876 m (ν(P–O)), 1568 s, 1582 s (ν(C–O) + ν(C=C)), 3150 vs, br, 3410 vs, br (ν(O–H)); NMR ^{1}H ($\mathrm{CD_2Cl_2}$) δ 7.35 (m, phenyl H), 4.63 (s, vinyl H); ^{19}F ($\mathrm{CD_2Cl_2}$) 75.34 (s, $\mathrm{CF_3}$), 75.83 (s, $\mathrm{CF_3}$).

Anal. Calcd for $\mathrm{PdCl[Ph_2PCH{=}CCF_3(O)][Ph_2POEt]}$: C, 50.72; H, 3.44; Cl, 5.54; P, 9.69. Found: C, 50.20; H, 3.95; Cl, 6.38; P, 10.36. Mol wt Calcd 639.3. Found ($\mathrm{CHCl_3}$) 1160.

Sufficient quantities of compounds IV, V, VI, and VII for complete characterization were obtained only after the reaction and fractional crystallization sequence had been repeated several times. Attempts to utilize column chromatography and preparative TLC for separation of the components were unsuccessful.

Hydrolysis of I by $\mathrm{H_2O}$–EtOH under Reflux Conditions. Complex I (3.2 g) was refluxed in dichloromethane (10 ml), water (10 ml), and ethanol (30 ml) for 72 hr. Infrared spectra of the solid residue remaining after solvent had been removed indicated that the major component was IIa with only a trace of IIIa and none of the compounds IV–VII. A substantial quantity of an unidentified red oil was formed under these conditions. Pure IIa (1.2 g) was obtained from dichloromethane–diethyl ether.

Preparation of $\mathrm{[PdX(Ph_2POHOPPh_2)]_2}$ (X = Br, SCN) (IIb, IIc). IIa (0.20 g) was dissolved in acetone (100 ml) and potassium bromide (0.30 g) added. The mixture was warmed for a few minutes, then stirred overnight. The solution was taken to dryness and the solid extracted with dichloromethane. The extracts were dried over anhydrous magnesium sulfate, the volume was reduced to ~3 ml, and diethyl ether (30 ml) was added. Bright yellow needles of IIb (0.16 g) crystallized: ir ($\mathrm{cm^{-1}}$) 182 m (ν(Pd–Br)), 1023 vs, 1035 vs (ν(P–O)), 770 s, br, 1232 w, 1350 m, br (O···H···O); NMR ^{1}H ($\mathrm{CD_2Cl_2}$) δ 7.36 (m, phenyl H), 15.3 (s, br, O···H···O).

Anal. Calcd for $\mathrm{[PdBr(Ph_2POHOPPh_2)]_2}$: C, 48.90; H, 3.40. Found: C, 48.14; H, 3.48.

The thiocyanate analogue IIc was likewise prepared by metathesis with potassium thiocyanate in acetonitrile. Pale yellow crystals were obtained from dichloromethane–diethyl ether: ir ($\mathrm{cm^{-1}}$) 1020 vs (ν(P–O)), 764 s, br, 1200 w, br, 1350 m, br (O···H···O), 2136 vs, 2087 vw (ν(C≡N)); NMR ^{1}H ($\mathrm{CD_2Cl_2}$) δ 7.40 (m, phenyl H).

Anal. Calcd for $\mathrm{[Pd(SCN)(Ph_2POHOPPh_2)]_2}$: C, 52.84; H, 3.73; P, 10.92. Found: C, 52.38; H, 3.77; P, 10.07.

Deuteration of IIa. IIa (0.21 g) was dissolved in warm deuteriochloroform (5 ml) and a mixture of ethanol-d_1 (5 ml) and $\mathrm{D_2O}$ (2 ml) added. On standing overnight crystals of $\mathrm{[PdCl(Ph_2PO{\cdot}DOPPh_2)]_2}$ grew from solution. A comparison of the infrared spectra of this complex with IIa–c indicated that only bands associated with -O-H-O- vibrations were shifted on deuteration: ir ($\mathrm{cm^{-1}}$) 273 m (ν(Pd–Cl)), 1030 vs (ν(P–O)), 575 m, br, 908 s, 1060 m, br (O···D···O).

Hydrolysis of I by $\mathrm{H_2O}$–EtOH in Presence of Added Chloride Ion. Complex I was formed in situ from $\mathrm{PdCl_2(PhCN)_2}$ (1.0 g) and $\mathrm{Ph_2PC{\equiv}CCF_3}$ (1.45 g) in dry dichloromethane (20 ml). Addition of potassium chloride (2.0 g) in water (10 ml) resulted in an immediate color change from yellow to orange. After stirring for 20 min the solvent was removed, the orange solid extracted with dichloromethane, the solution dried over anhydrous magnesium sulfate and reduced in volume, and ethanol (10 ml) added. The major product crystallizing was IIIa (0.44 g). After removal of IIIa a smaller quantity of IIa (0.05 g) was obtained. No other complexes were observed.

The above procedure was repeated under identical conditions but without the addition of potassium chloride. Infrared spectra showed the presence of ν(C≡C) at 2200 $\mathrm{cm^{-1}}$ indicating that reaction was incomplete after 20 min. Even after 1 hr the reaction had not proceeded to completion. Stirring was continued for 6 hr and the mixture worked up as before. From this reaction the following quantities of purified complexes were obtained: IIa (0.10 g), IIIa (0.04 g), IV (0.05 g), V (0.05 g).

Hydrolysis of I in Water–Acetone in the Presence of Added Thiocyanate Ion. Potassium thiocyanate (1.1 g) in acetone (20 ml) was added to I (0.77 g) in a mixture of acetone (100 ml) and water (1 ml). The solution turned instantly orange. After stirring for 1 hr at 25°C the solvent was removed and a small amount of IIc (0.06 g) crystallized from acetone–cyclohexane. The major component, IIIc (0.13 g), crystallized from an acetonitrile solution: ir ($\mathrm{cm^{-1}}$) 2121 s, sp, 2113 s, sp (ν(C≡N)); NMR ^{1}H ($\mathrm{CD_2Cl_2}$) δ 7.62 (m, phenyl H), 6.97 (d, vinyl H, $J_{\mathrm{P-H}} = 7.0$ Hz), 3.12 (dd, $\mathrm{CH_2}$, $^2J_{\mathrm{P-H}} = 10.5$ Hz, $^4J_{\mathrm{P-H}} = 3.4$ Hz).

Anal. Calcd for $\mathrm{Pd(SCN)_2(Ph_2PCH{=}CCF_3CH_2PPh_2)}$: C, 47.38; H, 3.21; N, 3.56; P, 7.88. Found: C, 47.64; H, 3.27; N, 3.48; P, 7.75. An orange, unidentified oil was also obtained in this reaction but no other palladium containing hydrolysis products were observed.

Reaction of $\mathrm{Ph_2PC{\equiv}CCF_3}$ with $\mathrm{Na_2PdCl_4}$ and $\mathrm{K_2Pd(SCN)_4}$. The ligand $\mathrm{Ph_2PC{\equiv}CCF_3}$ (1.39 g) in ethanol (20 ml) was added to sodium tetrachloropalladate(II) (0.77 g) in 50 ml of a 1:1 ethanol:water mixture at 0°. The solution turned bright yellow immediately. On work up, IIIa (0.84 g) was precipitated. No other palladium containing products were identified.

An analogous reaction of the ligand with $\mathrm{K_2Pd(SCN)_4}$ gave IIIc in 60% yield. This product was recrystallized from dichlorometh-

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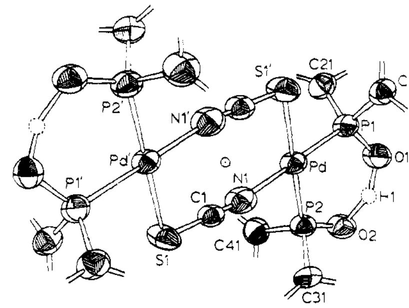

Figure 1. The molecular structure of [Pd(SCN)(Ph$_2$POHOPPh$_2$)]$_2$ (IIc) illustrating the symmetric P-O···H···O-P hydrogen bond.

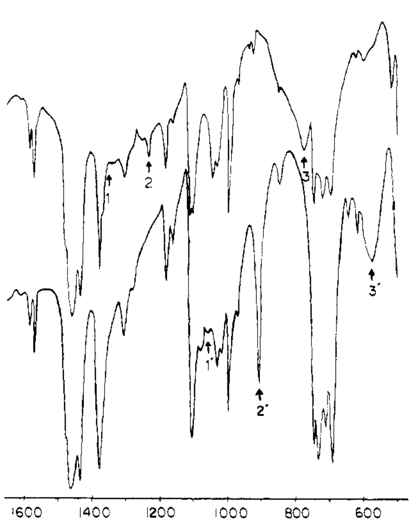

Figure 2. The infrared spectra of (a) [PdCl(Ph$_2$POHOPPh$_2$)]$_2$ (IIa) and (b) [PdCl(Ph$_2$PODOPPh$_2$)]$_2$ in the region 500-1650 cm^{-1}. Bands marked 1, 2, and 3 are due to O···H···O vibrations and have counterparts 1', 2', and 3' in the deuterated complex.

ane-ethanol as yellow prisms.

The bromide derivative IIIb was prepared from IIIa by metathesis with potassium bromide in acetone: ir (cm^{-1}) 248 m, 240 m (ν(Pd-Br)); NMR ^{1}H (CD$_2$Cl$_2$) δ 7.42 (m, phenyl H), 6.84 (d, vinyl H, $J_{\text{P-H}}$ = 6.0 Hz), 3.12 (dd, CH$_2$, $^2J_{\text{P-H}}$ = 10.5 Hz, $^4J_{\text{P-H}}$ = 4.6 Hz).

Anal. Calcd for PdBr$_2$(Ph$_2$PCH=CCF$_3$CH$_2$PPh$_2$): C, 45.16; H, 3.11; P, 8.32. Found: C, 45.54; H, 3.30; P, 8.59.

Results

Reaction of Ph$_2$PC≡CCF$_3$ (2 mol/g-atom of Pd) with *trans*-PdCl$_2$(PhCN)$_2$ in benzene (or dry dichloromethane-ethanol mixtures) gives a yellow, air-stable complex of formula PdCl$_2$(Ph$_2$PC≡CCF$_3$)$_2$ (I). This complex shows a ν(C≡C) band of an uncomplexed alkyne triple bond at 2219 cm^{-1} [18,19] and two strong ν(Pd-Cl) bands at 319 and 301 cm^{-1} with Raman counterparts at 320 and 304 cm^{-1}. There is no band between 330 and 360 cm^{-1} due to ν(Pd-Cl) of a trans square-planar phosphine complex.[20] Thus I has a cis configration in the solid state. In dichloromethane, chloroform, and carbon tetrachloride solution the analogous complexes *cis*-PdCl$_2$(PhMePC≡CR)$_2$ (R = CH$_3$, Ph, CF$_3$) retain their cis stereochemistry as demonstrated by ^{1}H NMR studies.[8] A thiocyanate derivative Pd(NCS)(SCN)(Ph$_2$PC≡C-*t*-Bu)$_2$, which can be prepared from *cis*-PdCl$_2$(Ph$_2$PC≡C-*t*-Bu)$_2$, has been shown to have a cis square-planar structure by x ray diffraction.[11]

Compounds with Hydrogen Bis(diphenylphosphinate) Anions (IIa-c). When I is refluxed in a dichloromethane-ethanol-water mixture for 72 hr the major product isolated is an air stable, crystalline complex, IIa, showing no ν(C≡C) or ν(C-F) vibrations in the infrared spectrum and no ^{19}F NMR resonances. However, the infrared spectrum exhibited a strong band at 1040 cm^{-1} in the P-O stretching region and a medium intensity far-infrared band (273 cm^{-1}) attributable to ν(Pd-Cl)$_{\text{br}}$. Metathesis of IIa with potassium bromide or thiocyanate yielded corresponding derivatives IIb and IIc. The latter showed a strong, slightly broadened ν(C≡N) band (half-width 42 cm^{-1}) at a frequency (2136 cm^{-1}) characteristic of bridging thiocyanate groups in square planar complexes[21] while the bromide had ν(Pd-Br)$_{\text{br}}$ at 182 cm^{-1}. Neither IIb or IIc contained fluorine but ν(P-O) absorptions were again evident. The appearance of three additional, unusual spectral features, namely a broad band envelope centered near 1300 cm^{-1}, a broad strong absorption near 773 cm^{-1}, and a weak band in the 1200-1240 cm^{-1} region prompted a single-crystal x ray structural study of IIc. The molecular structure[22] (Figure 1) consists of a centrosymmetric, thiocyanate bridged dimer in which each palladium atom is coordinated in square-planar fashion by a nitrogen atom of one thiocyanate, a sulfur of the other and two phosphorus atoms of a symmetrically hydrogen bonded hydrogen bis(diphenylphosphinate) anion. The oxygen-oxygen distance in the symmetrical anion is 2.421 (7) Å which compares favorably with the corresponding distances in CsH(CF$_3$COO)$_2$ (2.38 (5) Å[23]), KH(CF$_3$COO)$_2$ (2.434 (7) Å[23]), and KH(CH$_2$COO)$_2$ (2.446 Å[24]) where symmetrical O-H-O bonds are known to be present. An O-O distance of ≤2.5Å is thought to be indicative of strong, symmetrical hydrogen bonds.[25] Despite the fact that the phosphorus atoms of the anion are trans to groups of different trans influence,[9] the P-O···H···O-P unit shows no significant asymmetry.[26] This fact may be of relevance in the context of the possible presence of symmetrical hydrogen bonds in related but ostensibly unsymmetrical phosphinate and phosphonate complexes (vide infra). Subsequent to the x ray analysis, the infrared spectra of IIa-c were examined in more detail. The absence of any bands in the normal ν(O-H) region of the spectrum is entirely consistent with symmetrical hydrogen bond formation as it is characteristic of such bonding that O···H···O vibrations occur below 2000 cm^{-1}.[25] It was apparent from a comparison of the spectra of IIa-c with I and IIIa that the three bands mentioned previously arose from vibrations of the O···H···O bonds. To confirm this, IIa was deuterated in ethanol-d_1-D$_2$O mixtures. The spectra of IIa and IIa-d_2 in the spectral region 500-1600 cm^{-1} are shown in Figure 2. For IIa the broad band envelope centered approximately at 1350 cm^{-1} moves to 1060 cm^{-1} on deuteration while bands at 1236 and 773 cm^{-1} move to 915 and 575 cm^{-1}, respectively giving ratios $\nu_{\text{H}}/\nu_{\text{D}}$ of 1.27, 1.34, and 1.35, close to the theoretical value of 1.35. A definitive assignment of each of these bands to a different vibrational mode is more difficult, due in part to a considerable controversy in the literature concerning vibrational assignments for symmetrically hydrogen bonded species.[28,29] For example Hadzi and Novak[28] assign ν_{as}(O-H-O) at 800 cm^{-1} and δ(O-H-O) at 1480 cm^{-1} for KH(CF$_3$COO)$_2$ whereas Lippincott et al[29] assign the same vibrations to bands at 1838 and 1041 cm^{-1}. The latter authors also attributed a band at 960 cm^{-1} to γ(O-H-O). In the spectra of IIa-c there are weak bands in the region of 1600-2000 cm^{-1} but these are also present in I and IIIa-c and appear to be characteristic of phenylphosphorus compounds. Thus there are definitely no bands in this region attributable to vibrations of the P-O···H···O-P moiety. Our data for IIa-c thus lend some credence to the assignments of Hadzi and Novak[28] for short hydrogen bonds. Tentative assignments for IIa are then as follows: 773 cm^{-1} ν_{as}(O···H···O); 1236 γ(O···H···O); 1350 δ(O···H···O).

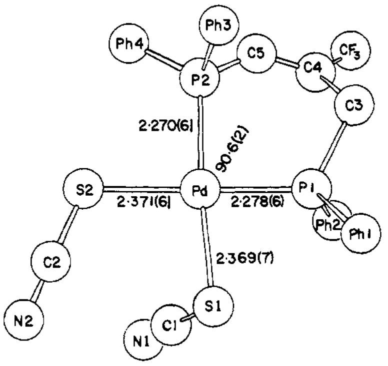

Figure 3. The molecular structure and atomic numbering for *cis*-$Pd(SCN)_2(Ph_2PCH_2C(CF_3)CHPPh_2)$ (IIIc).

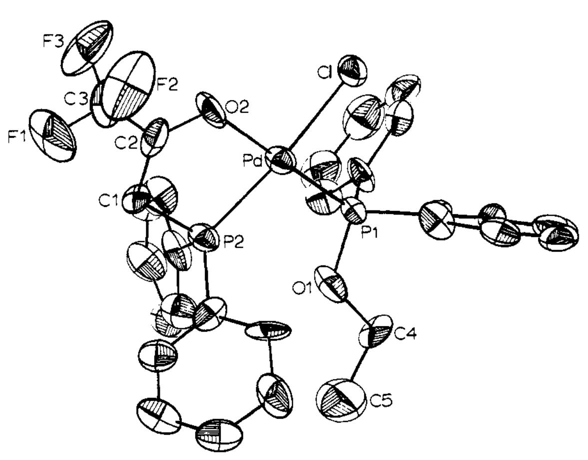

Figure 4. The molecular structure of *cis*-$PdCl[Ph_2PCH{=}C(CF_3)O](PPh_2OEt)$ (IV).

The 100-MHz nmr spectrum of IIb in CD_2Cl_2 exhibits, in addition to a multiplet phenyl resonance (δ 7.36; 20 H), a broad single line at very low field (δ 15.3 s, br, 2 H) due to the hydrogen bonded hydrogen nuclei, which disappears on deuteration. The latter resonance could not be detected for IIa and IIc owing to poor solubility in CD_2Cl_2.

The formation of complexes IIa–c in good yields requires vigorous conditions and is not dependent on the presence of ethanol since a similar hydrolysis of I to IIa occurs in acetone–water mixtures. Smaller quantities of IIa are, however, isolated when I is hydrolyzed at room temperature and when Na_2PdCl_4 is treated with ligand in the presence of water. Analogously, traces of IIc can be obtained from mixtures of $K_2Pd(SCN)_4$, $Ph_2PC{\equiv}CCF_3$, and H_2O-EtOH. The cleavage of both alkynyl groups from the phosphorus ligands in I via nucleophilic attack by water at a coordinated phosphorus atom appears to compete with reactions which involve attack at the triple bonds and is favored by more drastic conditions and low halide ion (or thiocyanate) concentrations.

Compounds with Unsymmetrical Diphosphine Ligands (IIIa–c). Complex IIIa can be isolated from the hydrolysis of I at room temperature and also as a contaminant to IIa when vigorous conditions are employed. However, the most efficient syntheses (60–75% yields) utilize the reaction of sodium tetrachloropalladate(II) with ligand in aqueous ethanol or the in situ generation of I followed by hydrolysis in the presence of excess chloride ion. IIIc can be generated in analogous fashion.

The infrared spectrum of IIIa indicates the absence of alkynyl groups and the presence of cis chloride ligands (ν(Pd–Cl) 317 s, 299 s).[8,20] Strong bands due to ν(C–F) appear in the region 1100–1250 cm^{-1} as for I but additional strong absorptions at 1345, 1404 cm^{-1}, absent in I, were considered evidence for C=C or $-CH_2-$ groups in IIIa. Complexes IIIb and IIIc have similar spectral features. In addition the appearance of two sharp ν(C≡N) bands at 2121, 2113 cm^{-1} in IIIc is consistent with S bonding of both thiocyanate groups to palladium(II)[9,21] in the solid state. The ^1H NMR spectrum of IIIa shows a double doublet resonance with a chemical shift characteristic of a $-CH_2-$ group attached directly to phosphorus, a doublet in the vinyl proton region, and a complex phenyl proton resonance. The corresponding thiocyanate has a similar spectrum. Complex IIIa gave a single resonance in an ^{19}F NMR spectrum. An x ray structural study of the dichloromethane solvate of IIIc has revealed[30] (Figure 3) that the ligand in IIIa–c is an unsymmetrical diphosphine formed by α–β coupling of the two alkynes in I and loss of a CF_3C moiety. In the light of this structure the NMR spectra of IIIa–c can be rationalized. The $-CH_2-$ protons are coupled to both phosphorus atoms while the vinyl proton is coupled to only one phosphorus, there being no observable ^1H–^1H, ^{19}F–^1H, or ^{31}P–^{19}F coupling. Referring to Figure 3 where C(3) is the methylene carbon atom, it can be seen that the coupling constant assignments (A), $^2J_{P(1)-H}$ = 11 Hz, $^4J_{P(2)-H}$ = 4 Hz, or alternatively (B), $^4J_{P(2)-H}$ = 11 Hz, $^2J_{P(1)-H}$ = 4 Hz, are possible. If the assumption is made that the long range coupling is smaller than $^2J_{P(1)-H}$, assignment A is correct. However, assignment B derives support from the following facts: (a) $^2J_{P-H}$ in tertiary phosphines and their complexes is generally small (cf. Ph_2PCH_3, $^2J_{P-H}$ = 6 Hz;[31] $Ph_2POCH_2CH_2PPh_2$, $^2J_{P-H}$ = 5 Hz; $M(CO)_4(Ph_2POCH_2PPh_2)$ (M = Cr, Mo, W), $^2J_{P-H} \sim$ 0–1 Hz[32]) (b) in propadienylphosphines $R_2PCH{=}C{=}CH_2$, $^2J_{P-H}$ values vary from 8.7 to 17.7 Hz and $^4J_{P-H}$ from 0.5 to 5.0 Hz. In the phosphine oxides, however, where phosphorus is tetracoordinated $^2J_{P-H}$ magnitudes are considerably less (0–4 Hz) whereas $^4J_{P-H}$ varies between 10 and 18 Hz.[33] A definitive choice between these two assignments will require heteronuclear double resonance experiments. The long range coupling $^4J_{P(2)-H}$ may be transmitted either through the metal atom or via the σ and π bonds of the diphosphine skeleton. In view of the fact that cis metal-phosphorus bonds transmit coupling effects relatively weakly,[34] the latter explanation seems more likely. The thiocyanate analogue IIIc has a very similar spectrum, and the same arguments are relevant.

Complexes with Chelating 1-Diphenylphosphino-3,3,3-trifluoropropene-2-olato Ligands (IV–VI). When the hydrolysis of I is conducted under mild conditions several other complexes, in addition to IIa and IIIa can be isolated but only after a tedious procedure of fractional crystallization. Yellow crystals of a dichloromethane solvate of IV which have been characterized by analysis, infrared, and NMR spectroscopy and single-crystal x ray diffraction[35] were crystallized from dichloromethane–ethanol–ether mixtures in small yield (23%). The structural study[35] (Figure 4) has revealed the expected square planar stereochemistry of the palladium atom with the phosphorus atoms of two new ligands, a diphenylethoxyphosphine and a deprotonated 1-diphenylphosphino-3,3,3-trifluoropropene-2-ol, occupying cis positions, the phosphorus atom of the latter being trans to the one remaining chloride. Thus one alkynyl group in I has been replaced by an ethoxy group derived from ethanol, whereas the second acetylene moiety appears to have added the elements of water, deprotonated and simultaneously coordinated as an anionic ligand to palladium, forming a novel chelate. When this work was completed to our knowledge, no other complexes of anionic chelating ligands with P, O donor sets had been described. However, recently,

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Shaw and co-workers[36] have characterized rhodium and platinum metal derivatives via demethylation of *o*-methoxyphenylphosphines. Ligands of this type might, by analogy with acetylacetone, be of considerable utility in coordination chemistry.

The cis stereochemistry of IV is notable since palladium(II) phosphine complexes are more commonly trans. Two factors of relevance in the present context are the weak trans directing influence of the chelate oxygen donor and the small O(2)-Pd-P(2) angle. The latter allows the strongly trans directing phosphorus ligands to adopt positions trans to the poor trans ligands Cl and O, without unfavorable steric interaction between bulky cis phosphines.

The chelate ligand in IV can be very readily recognized by the appearance of strong bands in the region 1500–1600 cm^{-1}. We attribute these to mixed $\nu(C{=}C)$ and $\nu(C{-}O)$ vibrations. The x ray determination of IV supports this assignment in that the C(1)-C(2)(1.45 (3) Å) and C(2)-O(2) (1.29 (2) Å) distances suggest multiple bond character in both of these bonds, reminiscent of the delocalization in β-ketoenolates.[37] The ^{19}F NMR spectrum of IV consists of a single sharp resonance, there being, surprisingly, no resolvable $^{19}F-^{31}P$ or $^{19}F-^{1}H$ coupling. In the ^{1}H NMR spectrum, typical methyl and methylene resonances of a coordinated ethoxyphosphine are evident. The vinyl proton appears as a deceptively simple triplet, with the central line broader and less than twice the intensity of the outer lines. Triplets of this type are frequently found for the proton resonances of virtually coupled trans phosphines[34] but instances of cis virtual coupling are relatively rare.[38] A molecular weight determination of IV in chloroform solution gave a measured value of 1240 (calcd 668) indicating dimer formation. One possible mode of association for this highly polar species is via hydrogen bonding of the acidic vinyl hydrogen to an oxygen atom (from either the chelate ring or the ethoxyphosphine) of a second molecule. The chemical shift of the vinyl proton is solvent sensitive. We were not, however, able to confirm the proposition by infrared studies owing to our failure to positively identify $\nu(C-H)$ of the vinyl group.

The last compound V obtained on fractional crystallization of the reaction mixture from the mild hydrolysis of I, crystallizes as air-stable yellow plates. Microanalytical, infrared and NMR data are consistent with a structure analogous to that of IV, but with a diphenylphosphinous acid ligand replacing the diphenylethoxyphosphine of IV. Infrared spectra of V exhibit the characteristic, strong $\nu(C{=}C)$ and $\nu(C{-}O)$ bands at 1569 s and 1582 s, of the chelate ligand. The frequency of the single $\nu(Pd-Cl)$ band (288 cm^{-1}) indicates that the chloride ligand is trans to a phosphine. The stabilized diphenylphosphinous acid ligand is readily identified by the presence of strong, broad $\nu(O-H)$ absorptions in the region 3100-3400 cm^{-1} together with $\nu(P-O)$ bands at 985 and 876 cm^{-1}. These frequencies compare favorably with values for the complexes *cis*-$[PtX_2(MR_2OH)(M'R_3')]$[14] and $Mo(CO)_5(R_2POH)$ (R = Me, Ph)[39] thought to contain hydrogen bonded diphenylphosphinous acid molecules. By contrast "free" OH groups would be expected to absorb in the 3600-cm^{-1} region. Indeed Kraihanzel[39] has shown that the hydrogen bonds present in $Mo(CO)_5(R_2POH)$ in the solid state are absent in dilute carbon tetrachloride solutions, where sharp $\nu(O-H)$ bands near 3600 cm^{-1} can be identified. Complex V, however, is dimeric in chloroform, and broad $\nu(O-H)$ bands are retained in solution indicating the persistence of strong intermolecular hydrogen bonding in this solvent. Strong hydrogen bonding is an important structural feature of P-OH groups whether present in free or complex stabilized molecules.[14,40,41]

Good quality NMR spectra of V were difficult to obtain owing to insolubility in suitable solvents. The ^{1}H spectrum showed a multiplet phenyl resonance (20 protons) and a singlet, which by analogy with the chemical shifts of the vinyl protons in IV and VI is assigned to the C-H resonance. Unresolved ^{31}P coupling to both phosphorus atoms presumably accounts for the broadness of the resonance. We were unable to unequivocally identify the hydroxylic resonance although a broad doublet (δ 4.18; peak separation = 5.5 Hz) observable at high amplitudes may be the expected resonance of this proton coupled to ^{31}P. An ^{19}F NMR spectrum shows two singlets with relative intensities of ca. 1:3, which we assign to a mixture of trans and cis isomers in solution with the latter predominating.

The infrared spectrum of complex VI is characterized by the strong absorptions of the chelate ligand $Ph_2PCH{=}C(CF_3)O$ and the ^{1}H NMR spectrum exhibits a single broadened line at δ 4.64 integrating for two protons. Analytical data are consistent with the formulation $\overline{Pd[Ph_2PCH{=}C(CF_3)O]_2}$. A ^{31}P NMR spectrum in CH_2Cl_2 shows two narrow resonances of almost equal heights at δ +62.35 ppm and δ +102.38 ppm upfield from $(MeO)_3P$. The two resonances are undoubtedly due to the two equivalent phosphorus atoms in the cis and trans bis chelates although these isomers cannot be differentiated on the basis of chemical shifts alone. Crystals of VI are triclinic, space group $P\bar{1}$ or $P1$; a = 9.80, b = 15.36, c = 10.14 Å; α = 98.2, β = 95.5, γ = 98.3°; Z = 2, ρ_m = 1.58, ρ_c = 1.56 g cm^{-3} for a molecular weight of 696.9. The x ray data confirm the molecular formula of VI. Moreover the molecule does not lie on a crystallographic center of symmetry. The cis structure thus seems likely for the solid with some isomerization to the trans species occurring in solution.

***cis*-Dichloro(diphenylphosphinous acid)(1-diphenylphosphino-3,3,3-trifluoroacetone)palladium(II) (VII).** The formulation of compound VII as a β-ketophosphine derivative is supported by microanalysis, infrared NMR, and x ray data. The infrared spectrum has two strong $\nu(Pd-Cl)$ bands typical of a cis complex with both chlorides trans to phosphorus. A single broad, hydrogen bonded $\nu(O-H)$ band (cf. V) appears at 3300 cm^{-1} and a strong band is present in the $\nu(C{=}O)$ region (1755 cm^{-1}). The frequency of the latter band is in excellent agreement with a value of 1749 cm^{-1} in the related complex *cis*-$PdCl_2[Ph_2PCH_2OCOMe]_2$[42] and in a variety of other complexes with R_2PCH_2OCOMe complexes. In the ^{1}H NMR spectrum the P-CH_2- proton resonance is an AB quartet with J_{AB} = 2.1 Hz. Owing to solubility problems we were unable to positively identify the resonance of the hydroxylic proton. Studies of acetoxymethylphosphine complexes of palladium and platinum have revealed that $^{2}J_{P-H}$ is small, as also is $^{4}J_{P-H}$.[42] For instance the methylene resonance of *trans*-$PdCl_2[PMe(CH_2OCOMe)_2]_2$ is an AB quartet, with no resolvable $^{31}P-CH_2$ coupling.[42] Colorless needles of VII are monoclinic, space group $P2_1/c$, a = 11.25 Å, b = 19.24 Å, c = 15.42 Å, and β = 107.4°. Systematic absences for $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$. With four molecules per unit cell and a measured density of 1.60 g cm^{-3} the molecular weight is 767.4 ($PdCl_4P_2F_3O_2C_{28}H_{25}$ mol wt = 760.67, ρ_c = 1.59).

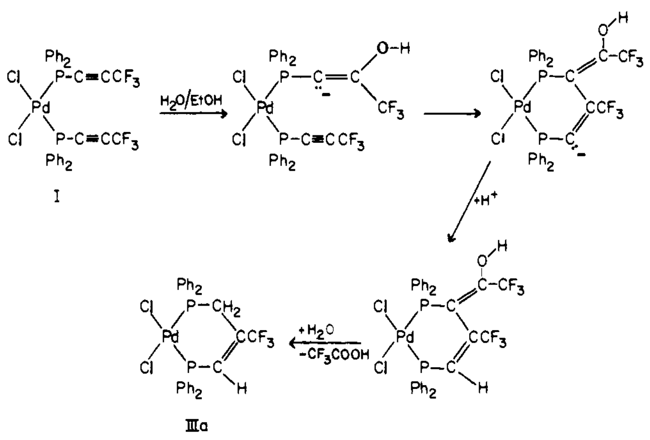
Discussion

The hydration of alkynes has been extensively studied as a result of the former commercial importance of the acetylene to acetaldehyde process.[43] Although highly activated acetylenes add water in the presence of aqueous acid alone, more generally a catalyst, typically mercuric perchlorate[44] or $RuCl_3$ in 4 *M* HCl,[45] is required. Hydration generally gives ketones with the structure of the acetylene determining which carbon adds OH to form the intermediate vinyl alcohol. Acetylenic ethers, thioethers, and amines add OH to the carbon attached to the heteroatom.[43]

The results of the present study indicate that coordinated phosphinoacetylenes are susceptible to attack by water at the triple bond and at phosphorus. From product distributions, more vigorous conditions appear to favor complete cleavage of alkynyl groups from the coordinated phosphines. The hydrogen bonded anion $Ph_2PO\cdots H\cdots OPPh_2$ present in complex IIa can be considered as derived from two molecules of coordinated diphenylphosphinous acid Ph_2POH. Formation of II can be envisaged in terms of nucleophilic attack by H_2O at two cis tetracoordinate phosphorus atoms of I, expulsion of two molecules of trifluoropropyne, intramolecular elimination of one molecule of HCl with generation of a coordinated diphenylphosphinate (Ph_2PO^-) anion, and subsequent symmetrization of the *cis*-Ph_2PO^- and Ph_2POH moieties. Although the susceptibility of a phosphine to nucleophilic attack at phosphorus should be enhanced by coordination, the facile displacement of $-C\equiv CCF_3$ from I contrasts sharply with the normally encountered resistance of tertiary alkyl or aryl phosphine complexes to hydrolysis.[14] Indeed we know of no analogous examples of facile hydrolytic cleavage of an organic group from a coordinated phosphine although the hydrolysis of $[PtCl_2(PCl_3)_2]$ was recognized in 1872[46] and the hydrolytic behavior of other chlorophosphine complexes of platinum has since been investigated in detail.[14] Two factors relevant in the present instance are the character of the alkynyl anion as a good leaving group and a substituent of small steric bulk, the latter facilitating approach of the nucleophile and the former further reaction of the intermediate 5-coordinate phosphorus atom. The cleavage of $P-C_{(sp)}$ bonds of phosphinoacetylenes has been noted previously in reactions with metal carbonyls[47] but in these cases strain resulting from simultaneous coordination of alkyne and phosphorus may promote bond scission. The apparent similarity of complexes containing Ph_2PCl[14] and $Ph_2PC\equiv CCF_3$ ligands to hydrolysis, specifically with respect to the formation of diphenylphosphinous acid and its anions, suggests the possible use of $PhP(C\equiv CCF_3)_2$ and $P(C\equiv CCF_3)_3$ precursors for the synthesis of coordinatively stabilized phenyldihydroxyphosphine and phosphorous acid molecules.

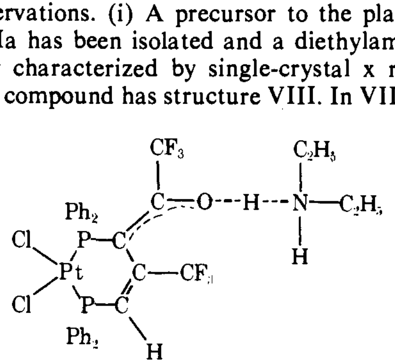
The identification of symmetrical hydrogen bonds in IIa–c and the recognition of the characteristic spectroscopic features of these bonds prompted a literature search for compounds purported to contain groups of the types R_2PO^-, R_2POH, $(RO)_2PO^-$, and $(RO)_2POH$ which might also contain strong hydrogen bonds. Several direct analogues of IIa apparently exist. The compound $[PdCl(EtO)_2PO(EtO)_2POH]$ has been described by Russian workers[48] but not structurally characterized. Pidcock and Waterhouse[49] prepared $[PdCl\{(PhO)_2PO\}\{(PhO)_2POH\}]$ and recognized this compound as a chloro-bridged dimer. The terminal phosphorus ligands were thought to be discrete diphenylphosphonate anions and diphenylphosphonous acid molecules. Both of the above compounds are undoubtedly further examples of hydrogen bonded complexes analogous to IIa. Likewise the compounds *cis*-$[L(Cl)Pt\{P(OR)_2O\}\{P(OR)_2OH\}]$ (L = Et_3P, Et_3As; R = Me, Ph) may contain symmetrical hydrogen bis(dimethyl(phenyl)phosphonate) anions despite their unsymmetrical nature (cf. IIc).[49] The structures of $[M\{(PhO)_2PO\}_2\{(PhO)_2POH\}_2]$ (M = Pd, Pt)[48,49] may also involve similar $P-O\cdots H\cdots O-P$ bridges. Chatt and Heaton[14] have characterized several complexes of platinum containing Ph_2POH groups. It appears that these compounds are strongly hydrogen bonded intermolecularly; the nature of the $P-O\cdots H\cdots O-P$ interactions in these derivatives merits x ray study.

Scheme I



After completion of this work we became aware of studies on diphenylphosphinate and diphenylphosphinous acid complexes of palladium and platinum.[50] Dixon and Rattray utilized the reactions of K_2MX_4 with diphenylphosphine oxide or diphenylchlorophosphine in acetone–water to prepare IIa, IIb, platinum analogues thereof and other derivatives with stoichiometries $[MX(Ph_2PO)(Ph_2POH)_2]$ and $[MX(Ph_2PO)(Ph_2POH)(PEt_3)]$ (M = Pd, Pt; X = Cl, Br).[50a] On the basis of unusual infrared spectra, symmetrical (or slightly asymmetrical) hydrogen bonds linking phosphinate and phosphinous acid moieties were postulated. Our x ray results for IIc confirm the basic deductions of Dixon and Rattray.[50] We have also confirmed their suggestion that broad bands in the 1200–1600 cm^{-1} region are associated with the $O\cdots H\cdots O$ system. However, the lack of ν(O–H) bands in the normal spectral region is a major characteristic of strong $O\cdots H\cdots O$ bonds and not simply due to broadening as implied previously. Indeed our assignments should serve as a basis for the recognition of $P-O\cdots H\cdots O-P$ bonding in coordination complexes.

The second major product from the hydrolysis of I is the unsymmetrical diphosphine complex IIIa. Formation of IIIa must involve coupling of two alkynyl moieties with expulsion of a molecule containing a CF_3C fragment. The mechanism of acetylene coupling probably proceeds as shown in Scheme I with initial nucleophilic attack by H_2O at a β-carbon of the activated acetylene, followed by intramolecular attack of the generated carbanion on the second alkyne moiety. This mechanism is supported by the following observations. (i) A precursor to the platinum analogue of IIIa has been isolated and a diethylamine adduct structurally characterized by single-crystal x ray diffraction.[51] This compound has structure VIII. In VIII, α–β coupling of the alkyne moieties in the platinum analogue of IIIa has already occurred but the intermediate vinyl alcohol is stabilized by hydrogen bonding to a diethylamine molecule. Vinyl alcohols are of course unstable with respect to their ketone counterparts[52] and in the absence of hydrogen bond stabilization, decomposition of the intermediate vinyl



VIII

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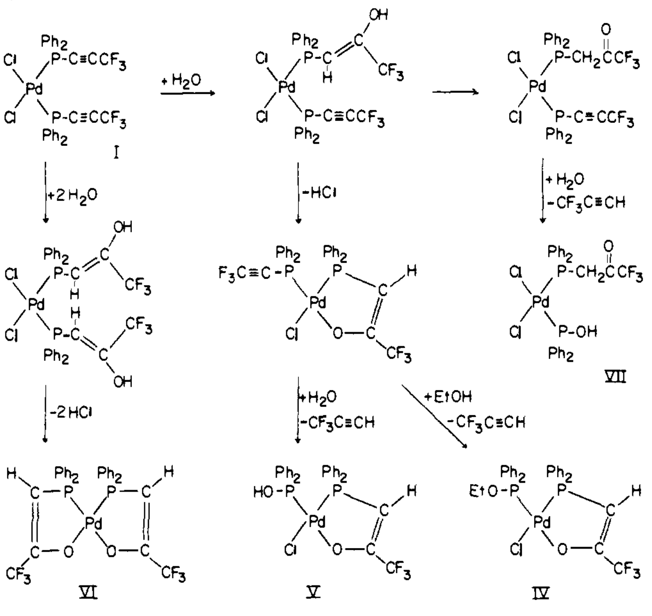
Scheme II



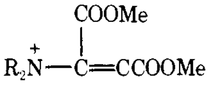
alcohol via addition of water, liberation of CF_3COOH, and generation of IIIa can be readily envisaged. (ii) The formation of IIIa is favored by the presence of Cl^- ion. Similarly IIIc is best prepared from solutions containing an excess of SCN^- ions. These results indicate the possibility that acetylene coupling may also be triggered by nucleophilic attack of Cl^- or SCN^- on a β-carbon. The same final products would of course be produced since generated CF_3COCl (or CF_3COSCN) would be hydrolyzed under the reaction conditions. A further reason for the higher yields of IIIa in the presence of added Cl^- is that formation of IIa, IV, V, and VI requires intramolecular HCl elimination, a process disfavored by high Cl^- concentrations. Hence poorer yields of the other complexes are expected, as is observed.

The coupling of the acetylenes in II bears some similarities to the synthesis of five-membered rings from *o*-bis(phenylethynyl)benzene via electrophilic or nucleophilic attack.[53] The facility with which coupling occurs in *o*-bis(phenylethynyl)benzene has been ascribed in part to an interaction between the triple bonds in the bis(acetylene).[53] It is of interest that x ray structure determinations of *cis*-$Pd(NCS)(SCN)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$[11] and *cis*-$Pt(NCS)(SCN)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$[9] have revealed interligand C(alkyne)-C(alkyne) distances of 3.5-4.0 Å, thus suggesting a favorable geometry for coupling. The utilization of cis phosphinoacetylene complexes corresponding to I as a novel route to unsymmetrical diphosphine complexes via acetylene coupling may, in some instances have advantages over other recently developed methods[32,54] of synthesis since the phosphinoacetylenes can be prepared with facility in high yields.

The presence of two S-bonded thiocyanate groups in IIIc appears at first sight somewhat surprising in view of the antisymbiotic behavior often exhibited by Pd(II) towards thiocyanate ion in phosphine complexes.[55,57] However, it has recently been amply demonstrated[9,10,58,59] that in the absence of steric inhibition of S bonding, the Pd(II) ion frequently favors Pd-SCN bonding. In IIIc therefore the occurrence of Pd-SCN bonding can be attributed to the higher affinity of Pd(II) for "soft" donor sites, together with the absence of any steric restrictions to S bonding. The mode of bonding of thiocyanate ion in other Pd(II) diphosphine derivatives has been rationalized elsewhere.[58]

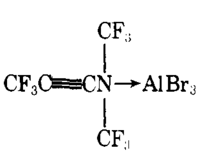
Likely reaction sequences for the formation of compounds IV-VII from I are shown in Scheme II. The relatively lower yields of these compounds can be rationalized on the basis that the reactions compete unfavorably with nucleophilic attack at phosphorus to give IIa at higher temperatures and with acetylene coupling to give IIIa in the presence of chloride ion. At room temperature in the absence of added Cl^- the sum total quantity of IV-VII is ca. 50% of that of IIa and IIIa.

On account of the highly polarized nature of the triple bonds in I we propose that formation of the intermediate vinyl alcohol from addition of H_2O to I involves initial nucleophilic attack at a β-carbon of the alkyne followed by protonation of the resulting anion. In support of this, it has been conclusively demonstrated that although acetylenes are susceptible to both electrophilic and nucleophilic attack, the latter is preferred, especially for dipolar acetylenes.[43] For instance Huisgen[60] has clearly shown the intermediacy of a zwitterion



$$R_2\overset{+}{N}-\overset{\displaystyle COOMe}{\overset{|}{C}}=CCOOMe$$

in the reactions of secondary amines with acetylene carboxylic esters. In considering the role of the metal atom in activating the acetylene towards hydration and determining the course of these reactions several other points can be made. Firstly, it is apparent from the work of others[61-63] that group 5 heteroatom substituted acetylenes are resistant to hydration in the absence of catalysts. For example Borkent and Drenth[61] failed in attempts to add water to a variety of phosphinoacetylenes $R_2PC{\equiv}CCH_3$ (R = n-C_4H_9, i-C_3H_7, t-C_4H_9) and $(n\text{-}C_4H_9)_2PC{\equiv}CR$ (R = CH_3, C_2H_5, i-C_3H_7, i-C_4H_9) while bis(diphenylphosphino)acetylene, $Ph_2PC{\equiv}CPPh_2$ cannot be cleaved by dilute alkali, silver nitrate, or cuprammonium solution.[63] Likewise the acid-catalyzed hydration of $(CF_3)_2NC{\equiv}CCF_3$ proceeds only slowly at 55° in the presence of mercuric sulfate.[62] Secondly, the free phosphinoacetylene $Ph_2PC{\equiv}CCF_3$, being polarized in the sense $Ph_2PC^{\delta+}{\equiv}^{\delta-}CCF_3$, would, by analogy with $(CF_3)_2NC{\equiv}CCF_3$[62] be expected to yield products derived from carbanions $Ph_2PC(B){=}CCF_3^-$ (B^- = base) resulting from nucleophilic attack at the carbon atom adjacent to phosphorus. The nature of the products III-VI demonstrates that in the *coordinated* phosphinoacetylene the normal acetylene polarization is reversed, probably as a result of strong phosphorus σ-donation to palladium.[64] It is of interest that formation of a Lewis acid-base complex



$$CF_3C{\equiv}C\underset{\underset{\displaystyle CF_3}{|}}{\overset{\overset{\displaystyle CF_3}{|}}{N}}\rightarrow AlBr_3$$

has been postulated to account for the unexpected mode of ionic addition of HBr to $(CF_3)_2NC{\equiv}CCF_3$ in the presence of aluminium tribromide catalyst. Coordinative modification of the polarization of acetylenes in this fashion may have important consequences in organic synthesis, when it is desired to reverse the normal mode of addition to an acetylene.

The chelate ligands in IV and V (Scheme II) can be readily formed from the vinyl alcohol intermediate via intramolecular HCl elimination, a process facilitated by a mutual cis configuration for Cl and vinyl phosphine in the intermediate. The phosphine ligand in IV and V is presumably formed via displacement of $CF_3C{\equiv}C^-$ anion (as $CF_3C{\equiv}CH$) from the second phosphinoacetylene in I, by OEt^- and OH^-, respectively. It is worth noting that in all of these reactions a certain amount of unidentified red polymer is formed. Infrared spectra of thin films of this material showed strong ν(C-F) bands in the 1000-1250 cm^{-1} region, hence the oil is probably a fluorine containing polymer derived from $CF_3C{\equiv}CH$. A very similar reaction sequence effectively explains the synthesis of the bis chelate VI in this reaction. The elements of two water molecules are added across the triple bonds of I giving a cis (diphenylphosphinovinyl alcohol) intermediate which yields IV on elimination of two molecules of HCl. Finally the scheme readily accommodates the formation of the β-ketophosphine complex VII from I. The β-ketophosphine ligand in this complex is the expected product from the "normal" hydration of a phosphinoacetylene molecule in I, with the vinyl alcohol species being an intermediate in the hydration.

The appearance of coordinated diphenylphosphinous acid in V and VII deserves comment. This molecule in the free state in aqueous solution exists almost entirely in the phosphine oxide form $Ph_2P(O)H$.[14] Only when highly electronegative substituents such as CF_3 or C_6F_5 are present on phosphorus, do R_2POH species, exist in the tautomeric hydroxyphosphine form. Compounds V and VII join a growing list of derivatives having phosphinous (or phosphonous) acids in the phosphine form coordinated to transition metals. Presumably $RP(OH)_2$ and $P(OH)_3$ may also be capable of existence as hydroxyphosphine complexes although to our knowledge there are as yet no well-established examples of the stabilization of these molecules.

It is clear from the complexes described in this paper that the palladium atom plays a highly significant role in dictating the nature of the products formed in the hydrolysis of I even though the acetylenic triple bonds are not coordinated to the metal in the starting complex. This conclusion is reinforced by the synthesis of a bis chelate with Pt-C and Pt-P bonds via the reaction of the prop-2-ynyl-phosphine complex *cis*-$PtCl_2(Ph_2PCH_2C{\equiv}CH)_2$ with methanol.[66] Further studies are in progress to utilize these ideas in both inorganic and organic synthesis.

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Carty et al. / Hydrolysis of cis-[$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$]

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Mechanistic Studies of Nickel Catalysis in the Cross Coupling of Aryl Halides with Alkylmetals. The Role of Arylalkylnickel(II) Species as Intermediates

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Abstract: The cross coupling of bromobenzene and *o*-bromotoluene with methyllithium and methylmagnesium bromide to produce toluene and *o*-xylene, respectively, is used for the mechanistic study of nickel catalysis. The synthesis, characterization, and reactions of arylmethylnickel(II) compounds (I) as reaction intermediates provide a rational basis for examining individual steps in the catalytic cycle. It is shown that I is formed rapidly under reaction conditions from either nickel(II) or nickel(0) as potential precursors. The subsequent reductive elimination of I does afford the requisite arene products by an intramolecular route, but it proceeds too slowly for the catalytic process to be effective. The rate is enhanced by aryl bromide and by methyllithium or methylmagnesium bromide and even more strikingly by molecular oxygen. A mechanism is proposed in which reductive elimination is promoted by prior electron transfer from I and the corresponding nickelate species to the aryl bromide. The stereochemical features inherent in reductive eliminations of *trans*-arylmethylnickel(II) compounds are discussed.

The formation of carbon-carbon bonds is one of the most important operations in organic synthesis, and it is represented by the coupling of organometallic reagents R-m including alkyllithium and Grignard reagents, with organic derivatives R-X such as alkyl halides among others.

$$R{-}m + R'{-}X \xrightarrow{[M]} R{-}R' + m{-}X \qquad (1)$$

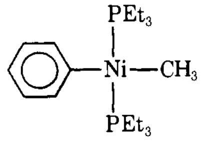
Transition metal complexes are particularly effective catalysts in the cross coupling reaction depicted in eq 1.[1-4] However, the role played by the metal has not been clearly delineated in most cases. It has been generally and presumptively assumed that the catalyst undergoes a series of two-electron oxidation and reduction cycles via a dialkylmetal intermediate.[5] Thus, a species such as I has been presented without direct proof as an intermediate in the nickel catalyzed coupling of Grignard reagents and aryl halides as outlined in eq 2 and 3.[1,7]

$$\underset{\text{I}}{L_2Ni(Ar)R} + Ar{-}X \longrightarrow \underset{\text{II}}{L_2Ni(Ar)X} + Ar{-}R \qquad (2)$$

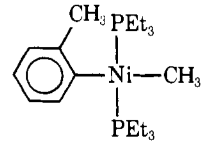
$$\text{II} + R{-}MgX \longrightarrow MgX_2 + \text{I, etc.} \qquad (3)$$

Indeed, recent studies by Parshall have shown that nickel(0) complexes can be used in the synthesis of I via a two-step sequence involving oxidative addition of aryl halide followed by metathesis with methyllithium.[8] He also observed qualitatively the reductive elimination of the fluorophenylmethylnickel species I (L = triethylphosphine) to fluorotoluene.

The sequence of reactions 2 and 3 constitutes a potentially attractive catalytic scheme for the cross coupling process and obviously merits further attention. We feel that the mechanism of the formation and decomposition of the arylmethylnickel species I is central to the understanding of the catalytic cycle. In this report we describe the isolation and decomposition of two series of arylnickel complexes using the phenyl and *o*-tolyl moieties. The *o*-tolyl group allowed the relevant arylnickel complexes to be isolated and well characterized due to the stabilization known to be imparted by the presence of *o*-methyl groups.[6,9] Factors involved in the reductive elimination of methyl and aryl ligands from I have provided interesting insight into the mechanism of the nickel catalyzed cross coupling reaction.



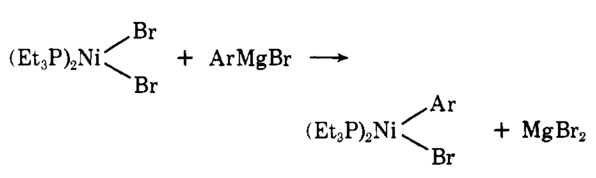
Ia



Ib

Results

Synthesis and Characterization of Arylmethylbis(triethylphosphine)nickel(II) Complexes. The nickel(II) complexes II, *trans*-arylbromobis(triethylphosphine)nickel, were synthesized by the reaction of dibromobis(triethylphosphine)nickel with the aryl Grignard reagent according to eq 3



$$(Et_3P)_2NiBr_2 + ArMgBr \longrightarrow (Et_3P)_2Ni(Ar)Br + MgBr_2 \qquad (3)$$

IIa, Ar = C_6H_5
b, Ar = *o*-$C_6H_4CH_3$