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Unprecedented Insertion of Alkynes into a Palladium−Phosphine Bond. A Facile Route to Palladium-Bound Alkenyl Phosphorus Ylides

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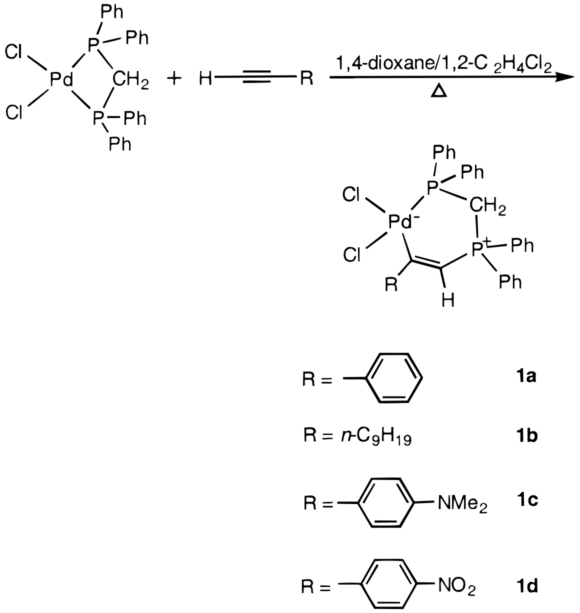
Summary: Refluxing a mixture of (dppm)palladium(II) dichloride (where dppm is bis(diphenylphosphino)methane) and various alkynes in the 1,2-dichloroethane/1,4-dioxane mixed solvents affords a variety of Pd-bound alkenyl phosphorus ylides in modest to good yields. Detailed spectroscopic data for these Pd-bound alkenyl phosphorus ylides along with the X-ray single-crystal structure of ***1c*** *are reported. The mechanism and implications for such an unprecedented apparent insertion of alkynes into the Pd−phosphine bond are also discussed.*

Phosphines are among the most important ancillary ligands for transition-metal catalysts. In particular, palladium phosphine complexes have been widely used to catalyze many organic transformations that utilize unsaturated hydrocarbon substrates.[1] For example, additions of HX to unsaturated hydrocarbons (e.g., hydrogenation[2] and hydrosilation[3] reactions) and carbon−carbon bond forming reactions[4] (e.g., Heck and Stille reactions) are readily catalyzed by palladium phosphine complexes. Under these often forcing conditions, orthometalation and carbon−phosphorus bond cleavage of arylphosphines represent common catalyst deactivation pathways.[5] Herein we wish to report an unprecedented apparent insertion of alkynes into palladium−phosphine bonds to result in the first examples of alkenyl phosphorus ylides of palladium. Such a phosphorus−carbon bond forming process will lead to thermodynamically stable, catalytically inactive alkenyl phosphorus ylides and thus presents a potential catalyst deactivation pathway for palladium-catalyzed organic transformations with unsaturated hydrocarbon substrates.

Refluxing a mixture of (dppm)palladium(II) dichloride[6] (where dppm is bis(diphenylphosphino)methane) and excess phenylacetylene in the 1,2-dichloroethane/1,4-dioxane mixed solvents results in the Pd-bound alkenyl phosphorus ylide **1a** in 49% yield after purification by column chromatography (eq 1). The ^{1}H NMR spectrum of **1a** exhibits a characteristic doublet of doublet for the alkenyl proton at δ 5.88; the alkenyl proton is coupled to two inequivalent phosphorus nuclei with $^2J_{H-P}$ = 47.7 Hz and $^4J_{H-P}$ = 10.3 Hz. The methylene protons of the Pd-bound alkenyl phosphorus ylide ligand also appear as a doublet of doublet at δ 3.69 due to the coupling to two inequivalent phosphorus nuclei. Consistent with the formation of the phosphorus ylide, the $^{31}P\{^1H\}$ NMR spectrum of **1a** shows two downfield doublets at δ 50.1 and 47.1. The characteristic C≡C stretch at ~2106 cm^{-1} for phenylacetylene has also disappeared in the IR spectrum of **1a**.



(1)

Other alkynes with either electron-donating or electron-withdrawing substituents can be used in place of phenylacetylene in this insertion reaction to result in a variety of Pd-bound alkenyl phosphorus ylides. Compounds **1b−d** were synthesized by refluxing a mixture of (dppm)palladium dichloride and *n*-undecyne, (*p*-(dimethylamino)phenyl)acetylene,[7] and (*p*-nitrophenyl)acetylene[7] in the 1,2-dichloroethane/1,4-dioxane mixed solvents, respectively. These Pd-bound alkenyl phosphorus ylides all exhibit characteristic doublets of

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Table 1. Data for the X-ray Diffraction of 1c

chem formula	$C_{35}H_{33}Cl_2NP_2Pd{\cdot}CH_2Cl_2$
cryst size, mm	0.04 × 0.05 × 0.14
a, Å	16.7972(5)
b, Å	14.7025(5)
c, Å	14.5388(5)
β, deg	104.167(1)
V, Å^3	3481.3(2)
Z	4
fw	791.86
space group	$P2_1/c$ (No. 14)
T, °C	−75(1)
λ(Mo Kα), Å	0.71073
ρ_{calcd}, g/cm^3	1.51
μ(Mo Kα), cm^{-1}	13.5
min and max residual density, e/Å^3	−0.58, 0.56
no. of rflns	2184 ($I > 2\sigma$)
no. of params	276
R	0.049
R_w	0.078
goodness of fit	0.71

doublets for the alkenyl proton in the ^1H NMR spectra and two downfield doublets for the two inequivalent phosphorus nuclei in the $^{31}P\{^1H\}$ NMR spectra. All these alkenyl phosphorus ylides are extremely thermally stable. They are also air- and moisture-stable and have in fact all been purified by silica column chromatography with a mixture of chloroform and methanol as eluents without any sign of decomposition. Compounds **1a**−**d** represent the first examples of alkenyl phosphorus ylides of palladium.

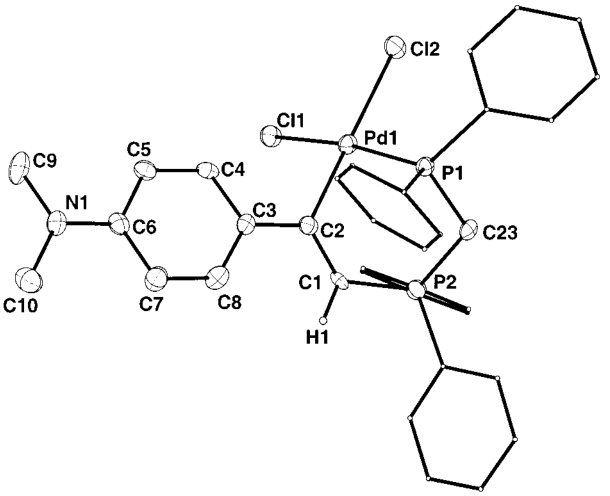

Figure 1. ORTEP drawing of **1c** with 30% probability ellipsoids. The phenyl groups on the phosphorus centers have been refined isotropically and represented with small circles. Hydrogen atoms (except H1) have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 1c

Pd1−C2	2.017(7)	Pd1−P1	2.215(2)
Pd1−Cl1	2.378(2)	Pd1−Cl2	2.394(2)
P1−C23	1.823(6)	C1−C2	1.350(8)
C1−P2	1.757(7)	N1−C6	1.399(8)
N1−C9	1.425(8)	N1−C10	1.463(8)
P2−C23	1.815(6)	C2−C3	1.451(9)
C3−C4	1.402(9)	C3−C8	1.405(8)
C4−C5	1.391(8)	C5−C6	1.371(8)
C6−C7	1.415(9)	C7−C8	1.373(9)
C1−H1	0.96(5)		
C2−Pd1−P1	85.5(2)	C2−Pd1−Cl1	90.6(2)
P1−Pd1−Cl1	169.83(7)	C2−Pd1−Cl2	178.5(2)
P1−Pd1−Cl2	93.38(7)	Cl1−Pd1−Cl2	90.69(7)
C23−P1−Pd1	104.2(2)	C1−C2−C3	120.3(6)
C2−C1−P2	126.0(6)	C1−P2−C11	108.1(3)
C1−P2−C23	110.5(3)	C11−P2−C23	110.5(3)
C1−C2−Pd1	120.1(6)	C3−C2−Pd1	119.5(5)
C11−P2−C17	105.1(3)	C2−C1−H1	124(3)

Because no coordinated alkenyl phosphorus ylides of palladium are known in the literature, we undertook an X-ray single-crystal structural determination on the representative compound **1c** (Table 1). Dark red crystals of **1c** were obtained by slow diffusion of diethyl ether into a concentrated solution of **1c** in dichloromethane. An X-ray single-crystal diffraction study of **1c** establishes the phosphonium alkenyl ylide structure (Figure 1). Pd1 coordinates to C2 and P1 of the alkenyl phosphorus ylide and to two chloride atoms in a slightly distorted square planar fashion (Table 2). Pd1 is 0.08 Å out of the plane defined by C2, P1, Cl1, and Cl2 atoms. The Pd1−P2 distance is very long at 3.42 Å, indicating that no interaction exists between the Pd1 center and the ylide phosphorus. The palladium−phosphorus and palladium−chloride distances are all normal, while the Pd1−C2 distance of 2.022(6) Å is very close to the sum of covalent radii of Pd(II) and sp^2-hydridized carbon (1.97 Å) and comparable to other known Pd−alkenyl bonds.[8] The C1−C2 distance of 1.349(8) Å indicates the double-bond nature, which has been further supported by the bond angles of near 120° surrounding the C1 and C2 atoms. These structural data indicate that compounds **1a**−**d** can be described as phosphonium alkenyl ylides[9−11] (i.e., the zwitterionic structure as shown in eq 1) with the Pd center coordinated to one phosphine ligand, one alkenyl group, and two chloride atoms. The P2−C1 distance is not significantly different from the average of P2−C11 and P2−C17 distances. It is also noteworthy that the insertion of alkynes is highly regiospecific: only the alkenyl ylides with the terminal alkyne carbon bonded to the phosphorus center are formed. This regiospecificity is undoubtedly a consequence of the steric crowdedness of the phosphorus center in dppm (vs the palladium center).

The description of **1a**−**d** as phosphonium alkenyl ylides is further supported by the chemical reactivity of the ylide carbon center (C1). Earlier reports indicated that ylide carbon centers in rhenium alkenyl phosphorus ylides were susceptible to electrophilic attack as a result of the partial negative charge on ylide carbon centers (facile deuterium incorporation from methanol-d_4 into the ylide carbons was observed).[11] In contrast, no deuterium incorporation was observed when complexes **1a**−**d** were treated with methanol-d_4. This result strongly supports the phosphonium alkenyl ylide structure of **1a**−**d**, and the different behavior between palladium and rhenium alkenyl phosphorus ylides can

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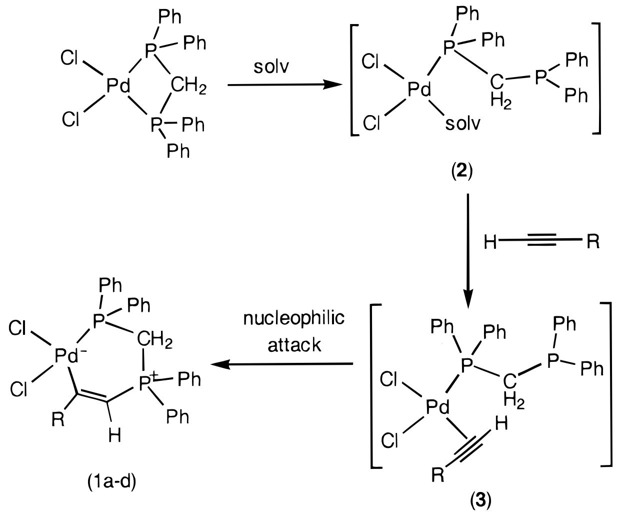
Scheme 1



be attributed to the different electronegativity of palladium vs rhenium.

Insertion of in situ generated carbenes into metal−phosphine bonds represents an important pathway for the synthesis of metal-bound phosphorus ylides.[12] However, the insertion of an alkyne molecule into the Pd−phosphine bond is unprecedented.[13] We speculate that compounds **1a**−**d** may have formed via the nucleophilic attack on the palladium-coordinated alkynes by the dangling phosphine moiety of the dppm ligand (Scheme 1). Several lines of evidence support this nucleophilic attack pathway. First, the insertion reaction critically depends on the coordinating capability of the solvent. When only a noncoordinating polar solvent such as 1,2-dichloroethane or chlorobenzene is used, no reaction is observed. The strongly coordinating solvent *p*-dioxane is needed to generate intermediates **2** and **3**. Second, the insertion reaction only occurred when (dppm)PdCl$_2$ was used. When (dppe)PdCl$_2$ (dppe represents 1,2-bis(diphenylphosphino)ethane) was used, no reaction was observed. The large strain in the four-membered chelate ring presumably facilitates the formation of intermediates **2** and **3**. Third, the Pd^{II} center renders the coordinated alkynes in **3** susceptible to nucleophilic attack by the dangling phosphine. For example, Pd^{II}-promoted ethylene oxidation is a key step in the Wacker process, which converts ethylene into acetaldehyde.[1] Moreover, nucleophilic attack of phosphines on coordinated alkynes has been used to synthesize alkenyl phosphorus ylides of manganese and is proposed to be the pathway for the formation of alkenyl phosphorus ylides of rhenium. Although we have not yet carried out kinetic studies with different alkynes, the isolated yields for **1a**−**d** are consistent with the proposed mechanism. The isolated yield under comparable conditions increases in the order **1c** < **1b** < **1a** < **1d**; this order of isolated yields correlates well with the electron-withdrawing capability of the substituents on the phenyl groups in **1a**−**d**. Finally, insertion of internal alkynes does not occur under similar conditions, apparently as a consequence of the steric hindrance of the dangling phosphine moiety.

In summary, we have discovered an unprecedented apparent insertion of alkynes into the Pd−phosphine bond to result in the first examples of palladium alkenyl phosphorus ylides. The formation of thermodynamically stable alkenyl phosphorus ylides could present a potential catalyst deactivation pathway for palladium-catalyzed organic transformations using unsaturated hydrocarbons.

Experimental Section

All reactions were performed under an argon atmosphere using standard Schlenk techniques. 1,4-Dioxane and 1,2-dichloroethane were dried over molecular sieve (4 Å). (*p*-(dimethylamino)phenyl)acetylene,[8] (*p*-nitrophenyl)acetylene,[8] and (dppm)PdCl$_2$ were prepared according to literature procedures. The IR spectra were recorded as Nujol mulls on a Paragon 1000 FT-IR spectrometer. ^{1}H, ^{13}C{^{1}H}, and ^{13}P{^{1}H} NMR spectra were taken on a Varian Unity 400 Plus spectrometer at 399.7, 100.5, and 161.8 MHz, respectively. Elemental analyses were done at the Microanalytical Laboratory of University of Illinois at Urbana-Champaign.

Synthesis of 1a. Pd(dppm)Cl$_2$ (250 mg, 0.46 mmol) and phenylacetylene (70 mg, 0.69 mmol) were dissolved in a mixture of dry 1,4-dioxane (10 mL) and 1,2-dichloroethane (10 mL) under argon. The solution was heated with stirring at 110 °C for 90 h and evaporated in vacuo to leave a pale orange solid. The solid was purified by column chromatography (SiO$_2$, CHCl$_3$/MeOH, 6/1) to afford 150 mg (49%) of pure **1a** as a bright orange solid. Mp: 218−220 °C. ^{1}H NMR (CDCl$_3$): δ 8.61−6.98 (25 H, aromatic H), 5.88 (dd, 1H, $^2J_{\mathrm{H-P}} = 47.7$ Hz, $^4J_{\mathrm{H-P}} = 10.3$ Hz), 3.69 (dd, 2H, $^2J_{\mathrm{H-P}} = 17.1$ Hz). ^{13}C NMR (CDCl$_3$): δ 134.1, 133.9, 133.6, 133.4, 130.8, 129.9, 129.5, 128.4, 128.3, 128.1, 127.5, 121.9, 121.0, 102.9, 101.9, 22.1. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 50.1 (d, $^2J_{\mathrm{P-P}} = 40.3$ Hz), 47.1 (d, $^2J_{\mathrm{P-P}} = 40.3$ Hz). IR (Nujol, cm^{-1}): 3050.4, 1508.1, 1481.0, 1435.9, 1111.1, 739.2, 689.7. Anal. Calcd for $C_{33}H_{28}Cl_2P_2Pd{\cdot}0.5CH_2Cl_2$: C, 57.0; H, 4.11. Found: C, 56.5; H, 4.16.

Synthesis of 1b. A mixture of (dppm)PdCl$_2$ (100 mg, 0.18 mmol) and 1-undecyne (100 mg, 0.72 mmol) in dry 1,4-dioxane (10 mL) and 1,2-dichloroethane (10 mL) was heated with stirring at 110 °C for 100 h and evaporated in vacuo to leave a pale orange solid. The solid was purified by column chromatography (SiO$_2$, CHCl$_3$/MeOH, 15/1) to afford 60 mg (48%) of pure **1b** as a pale orange solid. Mp: 195−200 °C. ^{1}H NMR (CDCl$_3$): δ 8.29−7.02 (20 H, aromatic H), 5.54 (dd, 1H, $^2J_{\mathrm{H-P}} = 50.7$, 1H, $^4J_{\mathrm{H-P}} = 11.6$ Hz), 4.45 (dd, 2H, $^2J_{\mathrm{H-P}} = 22.6$ Hz), 3.43 (s, 2H), 1.61−1.59 (m, 2H), 1.37−1.10 (m, 9H), 0.92 (t, 3H, $J = 14.1$ Hz). ^{13}C NMR (CDCl$_3$): δ 134.3, 133.6, 133.4, 133.3, 131.0, 130.2, 130.0, 128.6, 128.5, 31.9, 29.7, 29.5, 29.4, 29.3, 22.7. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 51.7 (d, $^2J_{\mathrm{P-P}} = 44.5$ Hz), 47.7 (d, $^2J_{\mathrm{P-P}} = 44.5$ Hz). IR (Nujol, cm^{-1}): 3050.9, 2916.0, 2843.4, 1518.9, 1430.7, 1098.6, 787.3, 735.4, 683.5, 507.1. Anal. Calcd for $C_{36}H_{42}Cl_2P_2Pd{\cdot}CH_2Cl_2$: C, 55.6; H, 5.51. Found: C, 56.0; H, 5.99.

Synthesis of 1c. (dppm)PdCl$_2$ (100 mg, 0.18 mmol) and 4-ethynyl-*N*,*N*-dimethylaniline (40 mg, 0.27 mmol) were dissolved in a mixture of dry 1,4-dioxane (10 mL) and 1,2-dichloroethane (10 mL) under argon. The solution was heated with stirring at 105 °C for 72 h and evaporated in vacuo to leave a brown solid. The solid was purified by column chromatography (SiO$_2$, CHCl$_3$/MeOH, 11/1) to afford orange **1c**. Yield: 40 mg (31%). Mp: 229−232 °C. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.83 (d, 2H, $J = 8.9$ Hz), 7.73−7.24 (20 H, aromatic H), 6.56 (d, 2H, $J = 8.9$ Hz), 5.76 (dd, 1H, $^2J_{\mathrm{H-P}} = 49.5$ Hz, $^4J_{\mathrm{H-P}} =$

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12.2 Hz), 3.48 (dd, 2H, $^2J_{H-P} = 20.1$ Hz), 2.99 (s, 6H). ^{13}C NMR (CD_2Cl_2): δ 151.9, 134.8, 133.4, 131.6, 130.0, 128.7, 110.6, 40.3. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 49.8 (d, $^2J_{P-P} = 43.3$ Hz), 48.1 (d, $^2J_{P-P} = 43.3$ Hz). IR (Nujol, cm^{-1}): 3050.9, 2884.9, 1596.7, 1477.4, 1430.7, 1358.0.

Synthesis of 1d. A mixture of (dppm)PdCl (200 mg, 0.36 mmol) and 4-ethynylnitrobenzene (60 mg, 0.41 mmol) in dry 1,4-dioxane (10 mL) and 1,2-dichloroethane (10 mL) was heated with stirring at 105 °C for 48 h and evaporated in vacuo to leave a dark brown solid. The solid was purified by column chromatography (SiO_2, $CHCl_3$/MeOH, 15/1) to afford **1d**. Yield: 185 mg (73%). Mp: 265−270 °C. ^{1}H NMR (DMSO-d_6): δ 7.89−7.20 (24 H, aromatic H), 5.98 (dd, 1H, $^2J_{H-P} = 46.5$ Hz, $^4J_{H-P} = 9.78$ Hz), 3.41 (dd, 2H, $^2J_{H-P} = 13.6$ Hz). ^{13}C NMR (DMSO-d_6): 146.3, 134.5, 134.0, 133.9, 133.6, 133.5, 131.1, 130.2, 130.0, 128.6, 128.5, 127.9, 122.6, 120.8, 119.9. ^{31}P{^{1}H} NMR (DMSO-d_6): δ 50.5 (d, $^2J_{P-P} = 39.1$ Hz), 45.8 (d, $^2J_{P-P} =$ 39.1 Hz). IR (Nujol, cm^{-1}): 3050.9, 1518.9, 1503.3, 1430.7, 1342.5, 1109.0, 854.7, 740.6, 693.9, 501.9. Anal. Calcd for $C_{33}H_{27}Cl_2NO_2P_2Pd\cdot0.5CH_2Cl_2$: C, 53.5; H, 3.73; N, 1.86. Found: C, 54.0; H, 4.20; N, 1.59.

X-ray Structure Determination of 1c. Data collection for **1c** was carried out with an orange crystal of dimensions of 0.04 × 0.05 × 0.14 mm on a Siemens SMART system equipped with a CCD detector using Mo Kα radiation. Of the 6129 reflections measured, 2184 reflections with $I > 2\sigma(I)$ were used in structure solution and refinement. The structure was solved by direct methods using SHELX-TL[14] and refined by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms except the phenyl groups on the phosphorus centers. The carbon atoms of the phenyl groups were refined isotropically because of insufficient data points. H1 was located in an electron density difference map and refined isotropically, while all the other hydrogen atoms were located by geometric placing. Final refinement gave $R = 0.049$, $R_w = 0.078$, and goodness of fit = 0.71. Experimental details for the X-ray data collection of **1c** are tabulated in Table 1. Selected bond distances and angles for **1c** are listed in Table 2.

Acknowledgment. We are indebted to Dr. Scott R. Wilson and the Materials Chemistry Laboratory at University of Illinois at Urbana-Champaign for X-ray data collection and to Dr. Zhiyong Wang for help with the synthesis of alkynes. We acknowledge the NSF (Grant No. CHE-9727900) and ACS-PRF for financial support.

Supporting Information Available: Tables giving positional and thermal parameters and bond distances and angles for **1c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] SHELX-TL Version 5.1; Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.