Oxidative Addition of $HP(O)Ph_2$ to Platinum(0) and Palladium(0) Complexes and Palladium-Catalyzed Regio- and Stereoselective Hydrophosphinylation of Alkynes

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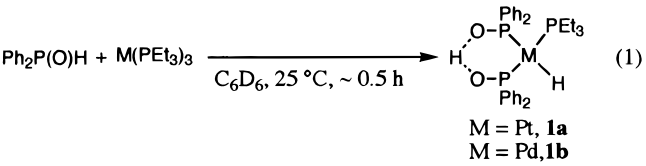
Summary: Oxidative addition of $Ph_2P(O)H$ to $M(PEt_3)_3$ ($M = Pd, Pt$) readily took place at room temperature in benzene to afford cis-$MH[P(O)Ph_2][PPh_2(OH)](PEt_3)$ complexes. The structure of the platinum complex was determined by X-ray crystallography. The palladium complex was found to undergo an insertion reaction with oct-1-yne to give 1- and 2-(diphenylphosphinyl)oct-1-enes. $Pd(PPh_3)_4$ catalyzed regio- and stereoselective synthesis of alkenyldiphenylphosphine oxides (hydrophosphinylation) from alkynes and $Ph_2P(O)H$.

Alkenylphosphine oxides are a useful class of compounds that undergo numerous synthetic transformations. For example, a number of heteroatom nucleophiles, such as alcohols,[1] thiols,[2] and primary and secondary amines[3] and phosphines,[4] readily add to the olefinic bond to provide bifunctional adducts, which allow further synthetic elaboration. Carbon−carbon bond formation is also easily achieved by the reactions with carbanion species[5] or carbon-centered radicals.[6] Accordingly, a wide spectrum of practical applications are possible as such or as their derivatives, inclusive of biologically active compounds,[7] fire retardants,[8] ligands for homogeneous catalysts,[3d,4b] etc. Despite these diverse practical applications, however, synthetic methods available are quite limited.[9] Our continued effort to manipulate the H−P bond by means of transition metal complexes[10] has uncovered (1) the facile oxidative addition of the P−H bond of diphenylphosphine oxide[11] to Pd and Pt complexes[12] and (2) the first efficient Pd-catalyzed regio- and stereoselective hydrophosphinylation of alkynes affording alkenylphosphine oxides. Although $Ph_2P(O)H$ has been used as a ligand for transition metal complexes,[13] metal complex-catalyzed addition reactions to unsaturated compounds have never been reported.[14]

When $Ph_2P(O)H$ (0.520 mmol in 0.8 mL of C_6D_6) was added to a solution of $Pt(PEt_3)_3$ (0.234 mmol) in 0.5 mL of C_6D_6 at room temperature, the color of the solution immediately turned from orange to pale yellow (eq 1).



(1)

^1H NMR spectroscopy revealed that most of the starting $Ph_2P(O)H$ was consumed within 0.5 h while a new broad signal centered at −4.3 ppm developed, indicative of the conversion to **1a**.[15] Removal of the solvent *in vacuo* afforded a pale yellow solid, which was recrystallized from a toluene−hexane mixture at −30 °C to provide an analytically pure sample as white crystals (126 mg, 0.175 mmol, 75%). In the ^1H NMR spectrum, a broad signal, assignable to the hydrogen interacting with the two oxygens, was found at 13.2 ppm. In agreement with the proposed structure, the ^1H resonance for H−Pt

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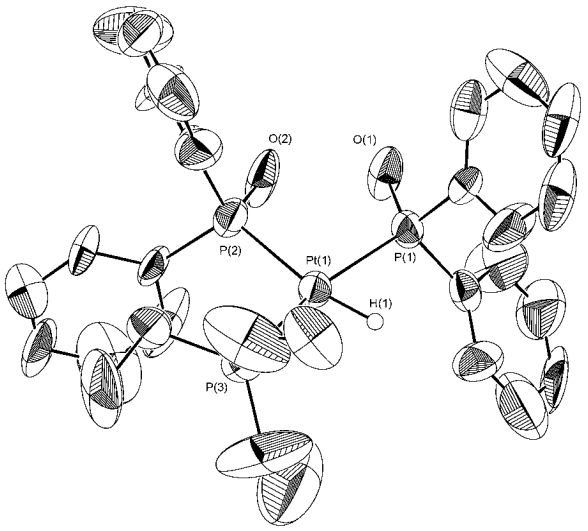
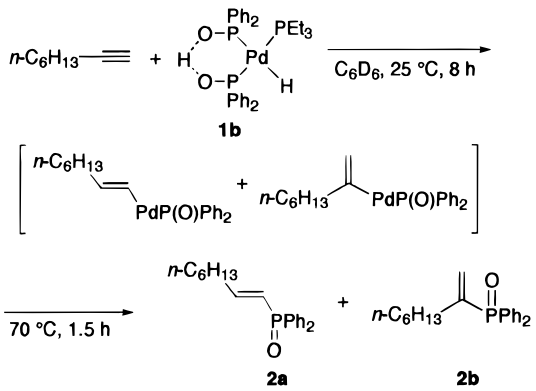


Figure 1. Molecular structure of *cis*-PtH[P(O)Ph_2][PPh_2-(OH)](PEt_3) (**1a**). For clarity, hydrogen atoms except that bound to Pt were omitted. Selected bond lengths (Å) and angles (deg): Pt(1)−P(1) = 2.280(4), Pt(1)−P(2) = 2.313(5), Pt(1)−P(3) = 2.301(4), P(1)−O(1) = 1.532(1), P(2)−O(2) = 1.569(1); P(1)−Pt(1)−P(2) = 92.5(2), P(2)−Pt(1)−P(3) = 100.7(2), P(1)−Pt(1)−P(3) = 166.6(2), O(1)−P(1)−Pt(1) = 114.9(5), O(2)−P(2)−Pt(1) = 111.4(6).

centered at −3.94 ppm exhibited a *ddd* coupling pattern due to three nonequivalent phosphorus nuclei, and the three ^{31}P NMR signals coupled with each other were observed at 13.8, 79.1, and 90.1 ppm.[16] The structure was finally determined by X-ray crystallography unambiguously to confirm that two $Ph_2P(O)H$ molecules reacted with the metal, one as such to undergo oxidative addition and the other to coordinate in the $Ph_2P(OH)$ tautomeric form. As shown in Figure 1, the complex has a slightly distorted square-planar geometry in which the $P(O)Ph_2$ and $PPh_2(OH)$ ligands are accommodated at the mutually *cis* positions with bond lengths being 2.280 and 2.313 Å. The O1−O2 distance is 2.317 Å, which is shorter than the sum of the van der Waals radii, indicative of strong hydrogen bonding with the two oxygens.[17] In further support of this conclusion is the observation that bond lengths of the two P−O bonds (P1−O1, P2−O2) have values between those reported for single and double P−O bonds.[18] The P(2)−Pt bond is longer than P(1)−Pt, presumably due to the hydrido ligand having a stronger *trans* influence than PEt_3.[19]

Scheme 1[a]



[a] Only actively reacting ligands are illustrated for the reacting intermediates, with disregard of other incidental ligands that may be bound to palladium.

A similar oxidative addition of the H−P bond to Pd also proceeded readily. Thus, upon mixing $Ph_2P(O)H$ and $Pd(PEt_3)_3$ in C_6D_6 at room temperature, broad signals centered at δ −5.6, assignable to H−Pd, emerged in the ^1H NMR spectrum. Addition of hexane to the solution resulted in the precipitation of a yellow solid **1b**, which displayed ^1H and ^{31}P NMR spectra similar to those of the Pt analogue **1a**.[16,20]

The H−Pd bond of hydrido complex **1b** smoothly added across the triple bonds of alkynes in C_6D_6 at room temperature (Scheme 1). Monitoring the reaction of **1b** with oct-1-yne (5 equiv) by NMR clearly revealed that, at the expense of the signals due to **1b**, several new ^1H signals were emerging over 8 h at 4.8−6.3 ppm, assignable to vinylic protons, and there were ^{31}P signals at 86−108 ppm, assignable to $P(O)Ph_2$ bound to Pd; note that a $P(O)Ph_2$ moiety bound to an alkenyl carbon usually displays a ^{31}P signal in 15−35 ppm range. Accordingly, these NMR data appear to strongly suggest that oct-1-yne was inserting into the H−Pd bond (hydropalladation) rather than the Pd−$P(O)Ph_2$ bond (phosphinylpalladation). At this stage, only trace amounts of (*E*)-1-(diphenylphosphinyl)oct-1-ene (**2a**) and 2-(diphenylphosphinyl)oct-1-ene (**2b**) were found in the mixture. However, when the resulting orange transparent solution was subsequently heated at 70 °C for 1.5 h, the color changed to brown and **2a**,**b** were formed in ∼65% total yield (^1H NMR yield based on **1b**; **2a**/**2b** = 54/48).[21]

With the foregoing observations in mind, we could design a new catalysis of the Pd-catalyzed regio- and stereoselective addition of $Ph_2P(O)H$ to alkynes, namely hydrophosphinylation. As shown in Table 1, $Pd(OAc)_2$ that might be reluctant to be reduced under the conditions was totally ineffective toward the addition reaction with oct-1-yne, while $Pd(PPh_3)_4$ and $PdMe_2(PR_3)_2$ did catalyze the reaction to yield **2a**,**b**. Unidentified byproducts were also formed,[22] in particular when less basic phosphines (PPh_2Me, PPh_3) were used. Lowering the reaction temperature to room temperature could substantially suppress the byproduct formation, and a

(15) The broad ^1H signals observed with the *reaction mixture* are presumably due to an equilibrium among **1a**, PEt_3, and $Ph_2P(O)H$. After isolation, a C_6D_6 solution of **1a**, in the absence of free PEt_3, displayed sharp ^1H and ^{31}P signals with distinct couplings. Upon an addition of PEt_3 (1 equiv), significant broadening resulted and signals due to free $Ph_2P(O)H$ developed to become evident. When a 10-fold excess of PEt_3 was added, signals due to H−Pt and P(O)−Pt moieties disappeared and $Ph_2P(O)H$ and $Pt(PEt_3)_4$ were the only recognizable species in ^{31}P NMR, suggesting the reversibility of the reaction of eq 1.

(16) **1a**: Mp 162−163 °C; ^1H (300 MHz, C_6D_6) δ 13.2 (bs, 1H), 8.21−8.27 (m, 4H), 7.71−7.85 (m, 4H), 6.85−7.01 (m, 12H), 1.10−1.36 (m, 6H), 0.58−0.66 (m, 9H), −3.94 (ddd, 1H, J_{H-P} = 10.2, 23.1, 162.8 Hz, J_{H-Pt} = 882.2 Hz); ^{31}P NMR (121.5 MHz, C_6D_6) δ 90.1 (dd, $J_{P-P(O)}$ = 17.5 Hz, $J_{P(O)-P(O)}$ = 30.1 Hz, $J_{P(O)-Pt}$ = 2295.1 Hz), 79.1 (dd, $J_{P(O)-P(O)}$ = 30.1 Hz, $J_{P-P(O)}$ = 361.1 Hz, $J_{P(O)-Pt}$ = 2789.6 Hz), 13.8 (dd, $J_{P-P(O)}$ = 17.5 Hz, $J_{P-P(O)}$ = 361.1 Hz, $J_{P(O)-Pt}$ = 2178.5 Hz). Anal. Calcd for $C_{30}H_{37}O_2P_3Pt$: C, 50.21; H, 5.20. Found: C, 50.48; H, 5.22. **1b**: ^1H (300 MHz, C_6D_6) δ 16.9 (bs, 1H), 8.15−8.31 (m, 4H), 7.61−7.92 (m, 4H), 6.95−7.08 (m, 12H), 1.00−1.08 (m, 6H), 0.60−0.71 (m, 9H), −5.36 (d, 1H, J_{H-P} = 197.5 Hz); ^{31}P NMR (121.5 MHz, C_6D_6) δ 95.5 (d, $J_{P(O)-P(O)}$ = 37.6 Hz), 89.3 (broad d, $J_{P-P(O)}$ = 305.9 Hz), 16.4 (broad d, $J_{P-P(O)}$ = 305.9 Hz).

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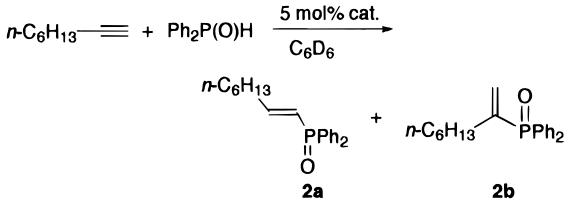
(20) As compared with **1a**, Pd complex **1b** was somewhat thermally unstable; ^{31}P NMR revealed only about a half of **1b** in C_6D_6, on standing at room temperature, remained unchanged. Diphenylphosphine oxide was extruded as the decomposition progressed.

(21) In a sharp contrast, the H−Pt bond of **1a** was inert toward alkynes. No reaction was observed even when a mixture of **1a** and oct-1-yne in C_6D_6 was heated at 70 °C for 5 h.

Table 1. Hydrophosphinylation of Oct-1-yne



2a **2b**

catalyst	conditions[a]	% NMR yield (**2a**/**2b**)
$Pd(PPh_3)_4$	35 °C, 20 h	82 (96/4)[b]
	50 °C, 4 h	65 (93/7)[c]
	70 °C, 3 h	54 (92/8)[c]
cis-$PdMe_2(PPh_3)_2$	3 h	43 (91/9)[c]
cis-$PdMe_2(PPh_2Me)_2$	3 h	56 (90/10)[c]
cis-$PdMe_2(PPhMe_2)_2$	2 h	75 (88/12)
$PdMe_2(PMe_3)_2$[d]	4 h	41 (92/8)[e]
$PdMe_2(PEt_3)_2$[f]	4 h	51 (87/13)[g]
$Pd(OAc)_2$	4 h	none

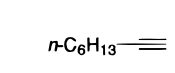
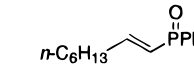
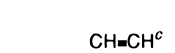
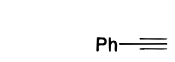
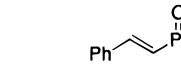
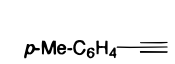
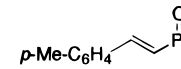
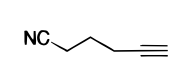
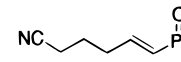
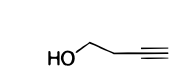
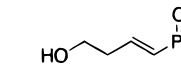
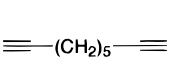
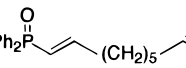
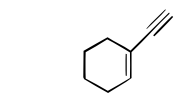
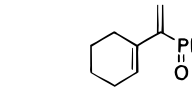
[a] An equimolar mixture of $Ph_2P(O)H$ and 1-octyne in C_6D_6 (0.3 ~ 0.5 M). [b] About 10% $Ph_2P(O)H$ remained. [c] > 90% of $Ph_2P(O)H$ was consumed. [d] *cis*/*trans* = 69/31. [e] (*Z*)-**2a**/(*E*)-**2a** = 10/90. [f] *cis*/*trans* = 1/1. [g] (*Z*)-**2a**/(*E*)-**2a** = 11/89.

Slight increase in the selectivity for *anti*-Markovnikov adduct **2a** (*vs* **2b**) also resulted. The nature of the phosphine ligand only marginally affected the regio- and stereoselectivities of the catalysis; less basic phosphines were favorable for the regioselective formation of **2a** (*vs* **2b**), while more basic phosphines (PMe_3, PEt_3) not only formed **2b** in slightly larger quantities but afforded **2a** as *E*/*Z* mixtures. On the basis of the foregoing brief optimization, a high-yield synthesis of **2a** (96% regioselectivity, ~100% stereoselectivity) could be achieved by the use of $Pd(PPh_3)_4$ at room temperature.[23]

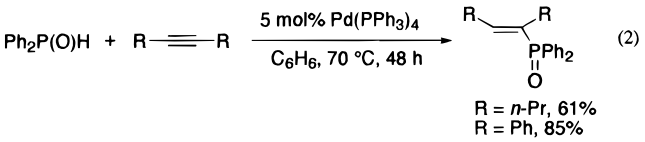
The hydrophosphinylation reaction could be readily applied to other alkynes. Selected preliminary examples were collected in Table 2. A moderate yield of dinylphosphine oxide was obtained by using acetylene gas under 1 atm. Aromatic alkynes such as phenylacetylene and 4-ethynyltoluene also served as good substrates to give the corresponding (*E*)-adducts in high yields regio- and stereoselectively. Functionalities such as cyano and hydroxy groups were tolerant toward the reaction, and satisfactory results were obtained as well. As exemplified by run 7, two phosphinyl groups could be easily introduced to diyne compounds such as nona-1,8-diyne. Exceptional regioselectivity was found with 1-ethynylcyclohexene (run 8), which formed only the Markovnikov product in a high yield, indicative of the olefinic bond directing the course of the reaction.[24]

Finally, internal alkynes are also successfully hydrophosphinylated (eq 2). Both oct-4-yne and diphenylacetylene gave good yields of the addition products at 70 °C. Note that only the (*E*)-adducts could be detected by NMR.

Table 2. Hydrophosphinylation of Terminal Alkynes[a]

run	alkyne	adduct	% yield[b]
1			81
2			51
3			79[d]
4			83[d]
5			73
6			86
7			61[e]
8			91

[a] Conditions: equimolar $Ph_2P(O)H$ and an alkyne in benzene (0.5 ~0.8 M), 5 mol% $Pd(PPh_3)_4$, 35 °C, 20 ~ 22 h. [b] Yields refer to isolated yields after PTLC or HPLC isolation. Regioselectivity to the product > 95% as determined by ^1H NMR of the crude reaction mixture. [c] 1 atm CH≡CH, 40 h. [d] 70 °C, 12 h. [e] 2.2 equiv of $Ph_2P(O)H$ were used.



(2)

R = *n*-Pr, 61%
R = Ph, 85%

In summary, transition metal complexes are demonstrated to be useful tools to cleave the H−P bond of the phosphine oxide and to design new catalysis involving the cleavage. Extensions to other H−heteroatom bonds and interheteroatom bonds will be the subjects of forthcoming papers.

Acknowledgment. L.-B.H. and N.C. are postdoctoral fellowship awardees from the Research Development Corp. of Japan.

Supporting Information Available: Text describing experimental details and spectral and/or analytical data for alkenylphosphine oxides and complexes **1a**,**b**, a perspective view of **1a**, and tables of crystallographic data, atomic coordinates and thermal parameters, and bond lengths and angles for **1a** (14 pages). Ordering information is given on any current masthead page.

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(22) In the reactions run in the presence of $Pd(PPh_3)_4$ as catalyst, neither the use of an excess of $Ph_2P(O)H$ (2 equiv) nor the use of other solvents such as THF and MeCN suppressed the formation of the byproducts.

(23) Typical reaction procedure: To a mixture of $Ph_2P(O)H$ (51 mg, 0.25 mmol) and oct-1-yne (28 mg, 0.25 mmol) in benzene (0.4 mL) was added $Pd(PPh_3)_4$ (15 mg, 5 mol %). The solution was stirred at 35 °C for 20 h and was evaporated *in vacuo* to leave an orange semisolid, which was subjected to HPLC isolation using $CHCl_3$ as eluent to yield a mixture of adducts **2** as a white solid (63 mg, 0.201 mmol, **2a**/**2b** = 96/4). These two regioisomers (**2a**,**b**) were separated by preparative TLC (silica gel, hexane/EtOAc = 2/3).

(24) ^1H NMR confirmed that the regioselectivity was nearly constant throughout the reaction. Accordingly, the unusual selectivity is not due to an isomerization of an initially formed isomer.