Facile Oxidative Addition of the Phosphorous−Selenium Bond to Pd(0) and Pt(0) Complexes and Development of Pd-Catalyzed Regio- and Stereoselective Selenophosphorylation of Alkynes

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Received March 19, 1996

Transition metal complex-catalyzed addition of E−E (E = a heteroatom) bonds to carbon−carbon unsaturated bonds, as exemplified by the Pd- and Pt-catalyzed double silylations and related reactions,[1] is generally characterized by its high product yield and selectivity under mild reaction conditions and hence is particularly attractive from the synthetic viewpoint. Although mechanistic details are variant depending on the identity of E, most of these additions may be overall envisioned to proceed *via* a simple sequence of oxidative addition of the E−E bond to the transition metal complex, insertion of an alkene or alkyne, and reductive elimination. Heteroatom compounds having B−B,[2] Si−Si,[1] Sn−Sn,[3] S−S,[4] and Se−Se[4] bonds undergo such reactions, and some of them are now widely used in organic synthesis. However, similar reactions for organophosphorous compounds have never been documented.[5] Now we wish to disclose herein (1) the facile oxidative addition of a phosphorous-selenium bond to Pd(0) and Pt(0) complexes which represents the first example of phosphorous−heteroatom bond additions to transition metal complexes and (2) the first palladium-catalyzed regio- and stereoselective selenophosphorylation of alkynes with selenophosphates[6,7] affording synthetically versatile (*Z*)-1-(diphenoxyphosphinyl)-2-(phenylseleno)alkenes.[8]

When 1 equiv of $PhSeP(O)(OPh)_2$ was added to $Pd(PEt_3)_3$ in C_6D_6 at room temperature, the color of the solution immediately turned from pale-orange to brown (eq 1). Monitoring of the reaction by NMR spectroscopy indicated that both of the starting materials disappeared completely within 0.5 h, while two new signals centered at 68.0 and 16.8 ppm appeared in ^{31}P NMR. The former was a triplet having a coupling constant of 14.1 Hz, assignable to $P(O)(OPh)_2$, and the latter was a doublet with the same coupling constant, assignable to PEt_3 ligating to Pd. Evaporating the solvent afforded a brown oil. Upon addition of hexane to the oil followed by slow cooling from room temperature to −30 °C overnight, orange crystals precipitated out. Both its NMR and analytical data were in good agreement with the structure of *trans*-$Pd(PhSe)[P(O)(OPh)_2][PEt_3]_2$ (**1a**),[9] which was unambiguously confirmed by the X-ray crystallographic analysis (Figure 1). The complex has a slightly distorted square-planar geometry with bond distances of Se−Pd and Pd−P(3) being 2.518 and 2.275 Å, respectively. The two PEt_3 ligands (PhSe and $P(O)(OPh)_2$ groups) are bound to the palladium center in the positions *trans* to each other. Very similarly, the reaction of $PhSeP(O)(OEt)_2$ with $Pd(PEt_3)_3$ afforded *trans*-$Pd(PhSe)[P(O)(OEt)_2][PEt_3]_2$ (**1b**) in 87% yield as a yellow solid.[9] Platinum(0) complexes were also as reactive as their palladium(0) analogues. For example, when $Pt(PEt_3)_3$ was allowed to react with $PhSeP(O)(OPh)_2$ at room temperature, the color of the solution immediately changed from orange to pale yellow, and *trans*-$Pt(PhSe)[P(O)(OPh)_2][PEt_3]_2$ (**1c**) was obtained in 95% yield as an off-white solid.[9]

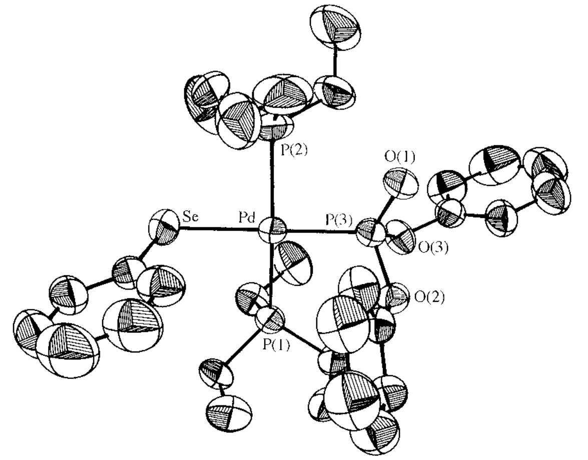
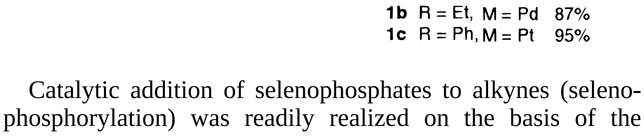


Figure 1. Molecular structure of *trans*-$Pd(PhSe)[P(O)(OPh)_2][PEt_3]_2$ (**1a**). Selected bond lengths (Å) and angles (deg): Pd−Se = 2.518(9), Pd−P(1) = 2.351(2), Pd−P(2) = 2.351(3), Pd−P(3) = 2.275(2), Se−Pd−P(1) = 86.90(5), Se−Pd−P(2) = 89.58(6), Se−Pd−P(3) = 174.01(6), P(1)−Pd−P(2) = 164.02(9), P(1)−Pd−P(3) = 95.72(7), P(2)−Pd−P(3) = 89.33(7).



$$PhSeP(O)(OR)_2 + M(PEt_3)_3 \xrightarrow[C_6D_6,\ 25\ ^\circ C]{} PhSe{-}\underset{PEt_3}{\overset{PEt_3}{M}}{-}P(O)(OR)_2 \quad (1)$$

1a R = Ph, M = Pd 93%
1b R = Et, M = Pd 87%
1c R = Ph, M = Pt 95%

Catalytic addition of selenophosphates to alkynes (selenophosphorylation) was readily realized on the basis of the foregoing findings. Thus, when $Pd(PPh_3)_4$ (35 mg, 3 mol %)

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[1] For recent reviews, see: (a) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317. (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. See also: (c) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16. (d) Finckh, W.; Tang, B.-Z.; Lough, A.; Manners, I. *Organometallics* **1992**, *11*, 2904.

[2] (a) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018. (b) Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **1995**, *117*, 4403.

[3] (a) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1983**, *241*, C45. (b) Killing, H.; Mitchel, T. N. *Organometallics* **1984**, *3*, 1318. (c) Piers, E.; Skerlj, R. T. *J. Chem. Soc., Chem. Commun.* **1986**, 626.

[4] Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796.

[5] We have recently reported the activation of P−H bonds by transition metal complexes: Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571.

[6] (Phenylseleno)phosphates $PhSeP(O)(OR)_2$ (R = Et, Ph) used in this study were readily prepared by adding corresponding $(RO)_2P(O)Cl$ at −78 °C to a THF solution of PhSeLi which was *in situ* generated by the reaction of PhLi with Se and purified by column chromatography on silica gel (Et_2O/hexane = 1/5−1/1). The yields were acceptable (55−63%). These selenophosphates were colorless in their pure forms. However, they were occasionally contaminated by a trace of $(PhSe)_2$ and could become pale yellow.

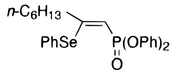
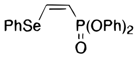
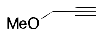
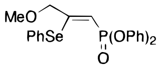
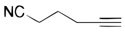
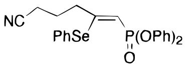
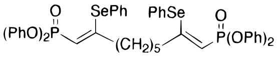
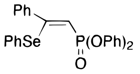
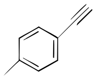
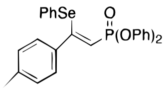
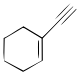
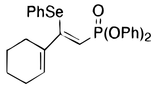
[7] Only very limited studies have been documented on these compounds. For preparations of (alkylseleno)phosphates, see: (a) Melnik, Y. G. *Ukr. Khim. Zh. (Russ. Ed.)* **1993**, *59*, 654. (b) Dybowski, P.; Krawczyk, E.; Skowronska, A. *Synthesis* **1992**, 601. (c) Markowka, A.; Buchowiecki, W. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1973**, *21*, 455. (d) Kataev, E. G.; Mannafov, T. G.; Kostina, G. I. *Zh. Obshch. Khim.* **1968**, *38*, 363. For their reactivities, halogenlysis: (e) Krawiecka, B. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1991**, *62*, 199. (f) Markowska, A. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1967**, *15*, 153. Alcolysis: (g) Wozniak, L. A.; Krzyzanowska, B.; Stec, W. J. *J. Org. Chem.* **1992**, *57*, 6057.

[8] Reviews on the synthetic utility of vinylselenides and vinylphosphonates: (a) Comasseto, J. V. *J. Organomet. Chem.* **1983**, *253*, 131. (b) Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 333.

[9] ^1H (300 MHz) and ^{31}P (121.5 MHz) NMR spectral data of **1** in C_6D_6. **1a**: ^1H NMR δ 7.88−7.91 (m, 2H), 7.50−7.54 (m, 4H), 6.87−7.16 (m, 9H), 2.08−2.18 (m, 12H), 0.92 (dt, 18H, $J = 7.6$ Hz, $J_{H-P} = 16.6$ Hz); ^{31}P NMR δ 68.0 (t, $J_{P-P(O)} = 14.1$ Hz, $J_{P(O)-Se} = 108.4$ Hz), 16.8 (d, $J_{P-P(O)} = 14.1$ Hz). **1b**: ^1H NMR δ 7.92−7.95 (m, 2H), 6.89−7.02 (m, 3H), 4.04−4.30 (m, 4H), 2.10−2.20 (m, 12H), 1.21 (t, 6H, $J = 7.1$ Hz), 0.98 (dt, 18H, $J = 7.1$ Hz, $J_{H-P} = 16.5$ Hz); ^{31}P NMR δ 66.9 (t, $J_{P-P(O)} = 4.7$ Hz, $J_{P(O)-Se} = 120.3$ Hz), 16.8 (d, $J_{P-P(O)} = 4.7$ Hz). **1c**: ^1H NMR δ 7.85−7.88 (m, 2H), 7.50−7.54 (m, 4H), 6.87−7.16 (m, 9H), 2.18−2.28 (m, 12H), 0.84−0.99 (m, 18H); ^{31}P NMR δ 51.8 (t, $J_{P-P(O)} = 25.4$ Hz, $J_{P(O)-Se} = 87.2$ Hz, $J_{P(O)-Pt} = 4669.3$ Hz), 12.5 (d, $J_{P-P(O)} = 25.4$ Hz, $J_{P(O)-Pt} = 2477.0$ Hz).

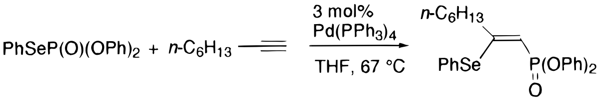
S0002-7863(96)00886-4 CCC: $12.00

Table 1. Pd-Catalyzed Selenophosphorylation of Terminal Alkynes[a]

run	alkyne	adduct	% yield[b]
1	$n\text{-}C_6H_{13}-\equiv$		95
2	CH≡CH[c]		68
3			87
4			91
5	$\equiv-(CH_2)_5-\equiv$		97[d]
6	$Ph-\equiv$		65
7			87
8			79

[a] Conditions: equimolar $PhSeP(O)(OPh)_2$ and an alkyne in THF (1 M), 3 mol % $Pd(PPh_3)_4$, 67 °C, 15−20 h. [b] Yields refer to isolated yields after PTLC isolation on silica gel. [c] 1 atm CH≡CH. [d] 2.2 equiv of $PhSeP(O)(OPh)_2$ were employed.

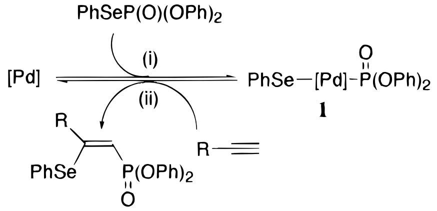
was added to a mixture of $PhSeP(O)(OPh)_2$ (389 mg, 1 mmol) and 1-octyne (110 mg, 1 mmol) in dry THF (1 mL) under argon, the color of the solution immediately turned from colorless to reddish brown.[10] Heating the mixture at 67 °C overnight resulted in a complete consumption of the starting materials, yielding (*Z*)-1-(diphenoxyphosphinyl)-2-(phenylseleno)-1-octene (**2a**) as the sole product (eq 2).[11] Evaporation of the solvent followed by PTLC purification (EtOAc/hexane = 1/1) afforded pure **2a** in 95% yield as a pale yellow oil. A 5 mmol scale experiment also gave a similar result (89% isolated yield after column chromatography; see the supporting information).



2a, 95% (2)

The Pd catalyst is essential for this addition reaction. In the absence of the catalyst, no adduct could be obtained under similar reaction conditions. Besides $Pd(PPh_3)_4$, *cis*-$PdMe_2(PPh_2Me)_2$ (76% yield) and *cis*-$PdEt_2(PPh_2Me)_2$ (82% yield) also catalyzed the reaction under identical conditions. In contrast, Pt complexes such as $Pt(PPh_3)_4$, $Pt(PEt_3)_3$, and $Pt(CH_2{=}CH_2)(PPh_3)_2$ did not show any catalytic activity under similar reaction conditions despite the ready oxidative addition of P−Se bonds to the complexes. Benzene and toluene could also be used as solvents for the reaction, and good yields of the adduct (87−91%) were obtained as long as reactions were run at 67 °C as in the case of THF. Conducting the reaction at higher temperatures was not beneficial since side reactions such as oligomerization of the alkyne took place. For example, yields of the adduct dropped to 86% and 65%, respectively, when the reactions were run at 80 °C (benzene) and 110 °C (toluene). Similar temperature dependence was also observed when THF-d_8 was used as the solvent in a sealed NMR tube.

Scheme 1[a]



[a] Only actively reacting ligands are illustrated in the Scheme, disregarding other incidental ligands that may be bound to palladium.

As demonstrated in Table 1, the Pd-catalyzed selenophosphorylation could be readily applied to other terminal alkynes, yielding the corresponding 1-(diphenoxyphosphinyl)-2-(phenylseleno)alkenes in good yields with excellent regio- and stereoselectivities.[12,13] Besides the reaction of 1-octyne, the reaction of acetylene under atmospheric pressure as well as functionalized aliphatic alkynes such as those having methoxy and cyano groups also proceeded efficiently, affording the adducts in high yields. Multiple PhSe and $(PhO)_2(O)P$ groups could be easily introduced regio- and stereoselectively to acetylenes having more than one C−C triple bond. For example, the selenophosphorylation reaction of 1,8-nonadiyne using 2.2 equiv of $PhSeP(O)(OPh)_2$ afforded the corresponding product nearly quantitatively. Aromatic alkynes like phenylacetylene and 4-ethynyltoluene also reacted efficiently, and good yields of the selenophosphorylation products were obtained in both cases. In contrast to alkynes, alkenes were inert toward the reaction under the present reaction conditions. Consequently, only the adduct formed by the addition of $PhSeP(O)(OPh)_2$ to the triple bond was obtained from 1-ethynylcyclohexene.

On the basis of the results described above, the catalytic reaction is very likely to proceed *via* the oxidative addition of the P−Se bond of selenophosphates followed by insertion[14] of an alkyne to the resulting species **1** (Scheme 1). However details, including the preference of the two possible insertion processes (i.e. selenopalladation *vs* phosphinylpalladation) as well as the regioselectivity, still remain to be clarified in the forthcoming papers.

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

Supporting Information Available: Text describing experimental details and spectral and/or analytical data of (*Z*)-1-(diphenoxyphosphinyl)-2-(phenylseleno)alkenes and complexes **1a**−**c**; a perspective view and tables of crystallographic data, atomic coordinates and thermal parameters, and bond lengths and angles for **1a** (24 pages). See any current masthead page for ordering and Internet access instructions.

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[10] When an equimolar mixture of $Pd(PPh_3)_4$ and $PhSeP(O)(OPh)_2$ in C_6D_6 was stirred at 25 °C, a facile oxidative addition of the P−Se bond of $PhSeP(O)(OPh)_2$ to $Pd(PPh_3)_4$ also took place, as evidenced by the appearance of three ^{31}P NMR signals centered at 56, 30, and −5 ppm. Unfortunately, however, we have not succeeded in the isolation of the resulting complexes; see the supporting information for more details.

[11] Other isomers of **2a** could not be detected by ^1H NMR. Although a small amount (< 3%) of an adduct formed by the addition of $(PhSe)_2$ to the alkyne was also obtained when a $(PhSe)_2$-contaminated selenophosphate was used, its formation could not be confirmed when carefully purified $PhSeP(O)(OPh)_2$ was employed.

[12] As compared to $PhSeP(O)(OPh)_2$, the addition of $PhSeP(O)(OEt)_2$ to alkynes proceeded slower under the same reaction conditions. Thus, after the THF solution of $PhSeP(O)(OEt)_2$ and 1-octyne was refluxed in the presence of 3 mol % of $Pd(PPh_3)_4$, only 15% of the corresponding adduct was obtained. Most of the starting materials remained unreacted.

[13] Internal alkynes were unreactive under the present conditions.

[14] Though very sluggish, formation of **2a** could be observed by NMR spectroscopy when **1a** was allowed to react in a sealed NMR tube with an excess of 1-octyne in C_6D_6 at 100 °C.