Pergamon

Tetrahedron Letters 39 (1998) 7529–7532

TETRAHEDRON
LETTERS

Phosphine Sulfides: Novel Effective Ligands for the Palladium-Catalyzed Bisalkoxycarbonylation of Olefins

Minoru Hayashi, Hiroshi Takezaki, Yukihiko Hashimoto,* Kazuo Takaoki, and Kazuhiko Saigo*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Received 26 June 1998; accepted 31 July 1998

Abstract:

Phosphine sulfides were found to be effective as a ligand in the palladium(II)-catalyzed bisalkoxycarbonylation of olefins. Aromatic olefins and vinylsilanes were converted into the corresponding succinates in high yields under mild conditions. Enantioselection was observed when chiral bisphosphine sulfides were used as ligands.

© 1998 Elsevier Science Ltd. All rights reserved.

Keywords: phosphine sulfides; palladium and compounds; carbonylation; olefins; silicon and compounds

A wide variety of transition metal catalysts involve phosphines as ligands; trialkyl- and triarylphosphines are especially versatile and indispensable as ligands in many transition metal-catalyzed reactions such as reductions and carbon-carbon bond forming reactions. Phosphine oxides have been also reported to be suitable ligands for transition metal catalysts, [1,2] and some of the complexes have shown superior reactivity to the corresponding phosphine complexes. However, only few reports appear in patents dealing with the application of other phosphine chalcogenides [1,3] as the ligands of transition metal catalysts, for example, the hydroformylation of olefins using the complexes of cobalt and rhodium with phosphine chalcogenides, [4] despite the fact that the isolation and characterization of the transition metal complexes of phosphine chalcogenides have been achieved through intensive studies in coordination chemistry. [1,3,5] The electronic features of phosphine chalcogenides and their complexes will provide new reactions, especially under oxidative conditions, since phosphine chalcogenides would be stable and survive in the presence of oxidants. We report herein a successful application of phosphine chalcogenides as ligands to the palladium-catalyzed bisalkoxycarbonylation of olefins.

---

*Corresponding author. Phone: (+)81-3-5689-8306; fax: (+)81-3-5802-3348; e-mail: saigo@chiral.t.u-tokyo.ac.jp

0040-4039/98/$ - see front matter © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)01637-2

In our search for a suitable reaction catalyzed by the transition metal complexes of phosphine chalcogenides, triphenylphosphine chalcogenides were used, since they are commercially available and/or are easily prepared from the parent triphenylphosphine by treating with hydrogen peroxide, or atomic sulfur or selenium. The palladium-catalyzed bisalkoxycarbonylation of olefins in the presence of a copper co-catalyst and oxygen as an oxidant proved to be the reaction of choice. [6,7] Although it has been reported that the bisalkoxycarbonylation of aliphatic terminal olefins proceeded smoothly without any ligand, [6,8-10] the use of aromatic olefins such as styrene as substrates was limited; moreover, the chemoselection was far from satisfactory. [11-13]

Since almost no information was available on the catalytic activity of phosphine chalcogenide-palladium catalysts, the effect of ligands in the bisalkoxycarbonylation of styrene was examined at first (Table 1). The reactions were carried out in the presence of 10 mol% of $PdCl_2$, 20 mol% of a ligand, and 1 equivalent of CuCl in MeOH under atmospheric pressure of a ca. 1/1 (v/v) mixture of carbon monoxide and oxygen at rt for 3 days. The reaction proceeded even in the absence of any ligand to give the desired product (entry 1). A clear contrast was observed between trivalent triphenylphosphine and pentavalent triphenylphosphine chalcogenides; triphenylphosphine strongly inhibited the reaction (entry 2), whereas the reactions using triphenylphosphine oxide (entry 3) and triphenylphosphine sulfide (entry 4) as ligands gave the product in highly improved yields. The results shown in Table 1 clearly demonstrate that triphenylphosphine sulfide is the most suitable ligand for the palladium-catalyzed bisalkoxycarbonylation.

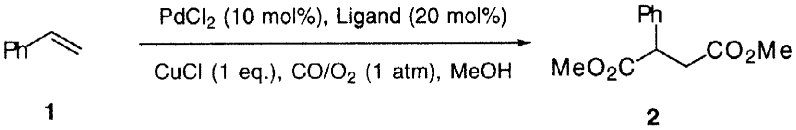


Table 1. Effect of additives in bisalkoxycarbonylation.[a]

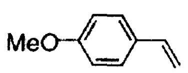
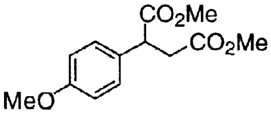
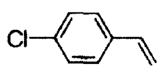
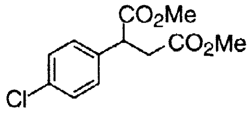
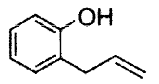
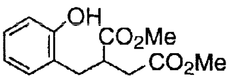
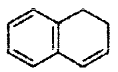
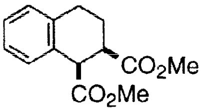
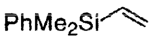
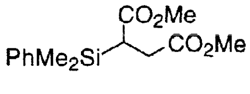
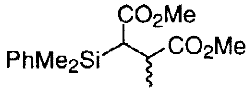
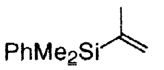
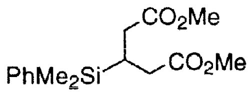
Entry	Ligand	Yield (%)[b]
1	none	36
2	Ph_3P	0
3	$Ph_3P=O$	60
4	$Ph_3P=S$	80
5	$Ph_3P=Se$	16

[a] Reactions were carried out in a 1-mmol scale by using 10 mol% of $PdCl_2$ and 20 mol% of the additive for 3 days at rt. [b] GC yields of phenylsuccinate. Diphenyl ether was used as an internal standard.

Although the mechanism of the present reaction is not clear, it is evident that the inhibition of the reaction by the use of triphenylphosphine does not arise from the oxidation of the phosphine but from its fundamental characteristics, since phosphine oxide did not inhibit the reaction. The lability of triphenylphosphine sulfide in the ligand exchange might play a central role.

The bisalkoxycarbonylation of other olefins also proceeded smoothly in the presence of triphenylphosphine sulfide (Table 2). The reactions of aromatic olefins gave the desired bisalkoxycarbonylated products in good to moderate yields (entries 1–2), and the reactions of aliphatic terminal olefins also gave the products in moderate yields (entry 3). Although the reactions of trans- and cis-stilbene did not proceed at all, the reactions of a cyclic olefin conjugated with an aromatic ring afforded exclusively the cis isomer of the diester (entry 4). [14,15] Noteworthy is that vinylsilanes are suitable substrates in the present reaction system (entries 5–7). The 1,3-bisalkoxycarbonylated product in entry 7 may be obtained through a β-hydride elimination and a re-insertion. [14,15] Although a few research groups have reported the alkoxycarbonylation of vinylsilanes, including hydroesterification, [16-18] no report has been published dealing with bisalkoxycarbonylation; the present reaction is the first example of the bisalkoxycarbonylation of vinylsilanes to afford α-silylsuccinates.

Table 2. Bisalkoxycarbonylation of olefins using Pd-Ph_3PS system.

Entry	Substrate	Product	Yield (%)[a]
1			82
2			59
3			68
4			35
5			90
6[b]			66
7			61

[a] All reactions were carried out in a 1-mmol scale by using $PdCl_2$ (10 mol%), Ph_3PS (20 mol%), CuCl (1 equiv.), CO/O_2 (ca. 1/1 v/v, 1 atm), in MeOH (10 ml) for 3 days at rt. [b] A mixture of the isomers (*E*/*Z* = 63/37) was used as the substrate, and a mixture of the diastereomers (dr = 77/23) was obtained. The stereochemistry of the product was not determined.

Since the present reaction gave the products with chirality, phosphine sulfides, derived from enantiopure phosphines, would be applicable to an asymmetric version of the present reaction. Enantiopure phosphine sulfides, $DIOPS_2$, $BINAPS_2$, and $ChiraphosS_2$, [19] were prepared from commercially available, enantiopure bisphosphines, DIOP, BINAP, and Chiraphos, respectively. In the presence of these chiral phosphine sulfides the reactions also proceeded enantioselectively, affording phenyl succinate, even though the enantioselectivity was low (Table 3).

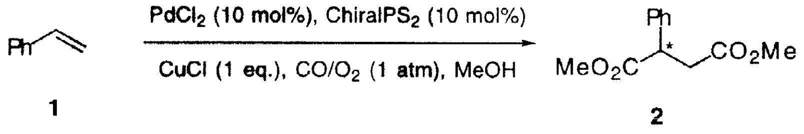


Table 3. Enantioselective bisalkoxycarbonylation of styrene by Pd-ChiralPS$_2$-system.[a]

Entry	ChiralPS$_2$	Yield (%)	E.e.(%)[b]
1	BINAPS$_2$	48	8
2	DIOPS$_2$	41	24
3	ChiraphosS$_2$	68	30

[a] All reactions were carried out in a 1-mmol scale by using $PdCl_2$ (10 mol%), chiral bisphosphine sulfide (10 mol%), CuCl (1 equiv.), CO/O_2 (ca 1/1 v/v, 1 atm), in MeOH (10 ml) for 3 days at rt. [b] Determined by HPLC (Daicel Chiralcel OD, hexane/2-propanol (15/1)).

In conclusion, we have found that phosphine sulfides can be applied as ligands to the palladium-catalyzed bisalkoxycarbonylation reaction of olefins; phosphine sulfides are a new class of ligands applicable to transition metal-catalyzed reactions under oxidative conditions. Further applications of phosphine chalcogenides are now under investigation.

References and Notes

[1] Lobana, T. S. Coordination Chemistry of phosphine chalcogenides and their analytical and catalytic applications. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R. Ed.; Wiley: NewYork, 1992; Vol. 2; pp. 521-525.

[2] For a recent example: see, Mikami, K.; Yamaoka, M. *Tetrahedron Lett.* **1998**, *39*, 4501-4504.

[3] Lobana, T. S. *Prog. Inorg. Chem.* **1989**, *37*, 495-581.

[4] Gipson, R. M. Hydroformylation of Olefins. In *3,954,877*: US, 1976; pp. 9.

[5] Reactions by palladium-thiourea catalyst have been reported; J. R. Norton, K. E. Shenton, J. Schwartz, *Tetrahedron Lett.*, **1975**, *16*, 51-54.; B. Gabriele, G. Salerno, M. Costa, G. P. Chiusoli, *J. Organomet. Chem.*, **1995**, *503*, 21-28.

[6] Toda, S.; Miyamoto, M.; Kinoshita, H.; Inomata, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3600-3606.

[7] Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: NewYork, 1995.

[8] Fenton, D. M.; Steinward, P. J. *J. Org. Chem.* **1972**, *37*, 2034-2035.

[9] Tamaru, Y.; Hojo, M.; Yoshida, Z.-i. *Tetrahedron Lett.* **1987**, *28*, 325-328.

[10] Ukaji, Y.; Miyamoto, M.; Mikuni, M.; Takeuchi, S.; Inomata, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 735-742.

[11] Nefkens, S. C. A.; Sperrle, M.; Consiglio, G. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1719-1720.

[12] Pennequin, P.; Fontaine, M.; Castanet, Y.; André Mortreux; Petit, F. *Applied Catalysis* **1996**, *A: General 135*, 329-339.

[13] Pisano, C.; Neflins, S. C. A.; Consiglio, G. *Organometallics* **1992**, *11*, 1975-1978.

[14] James, D. E.; Stille, K. J. *J. Am. Chem. Soc.* **1976**, *98*, 1810-1823.

[15] James, D. E.; Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1806-1809.

[16] Lee, B.; Alper, H. *J. Mol. Cat.* **1996**, *A: Chemical 111*, L3-L6.

[17] Takeuchi, R.; Ishii, N.; Sugiura, M.; Sato, N. *J. Org. Chem.* **1992**, *57*, 4189-4194.

[18] Takeuchi, R.; Sugiura, M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1031-1037.

[19] Bisphosphine sulfides, derived from bisphosphines XP, are abbreviated as XPS$_2$.