JOC Article

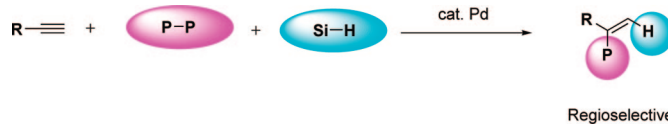
A Highly Regioselective Palladium-Catalyzed Hydrophosphination of Alkynes Using a Diphosphine−Hydrosilane Binary System

Shin-ichi Kawaguchi, Shoko Nagata, Akihiro Nomoto, Motohiro Sonoda, and Akiya Ogawa*

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan

ogawa@chem.osakafu-u.ac.jp

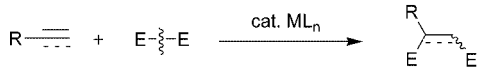
Received June 13, 2008



A novel transition-metal-catalyzed hydrophosphination of terminal alkynes using a diphosphine−hydrosilane binary system takes place regioselectively to provide vinylic phosphines, which undergo air oxidation during workup, affording the corresponding vinylphosphine oxides in good yields. In this hydrophosphination, hydrosilanes act as a useful hydrogen source, and furthermore, small amounts of oxygen is required to accomplish the reaction efficiently.

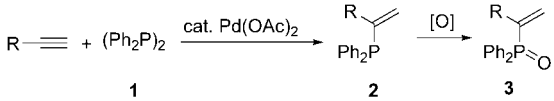
Introduction

Transition-metal-catalyzed addition of heteroatom compounds bearing heteroatom−heteroatom linkage (E−E) to carbon−carbon unsaturated bonds is one of the most straightforward and highly atom-economical methods for the synthesis of vicinally bifunctionalized heteroatom compounds[1] (eq 1).



(1)

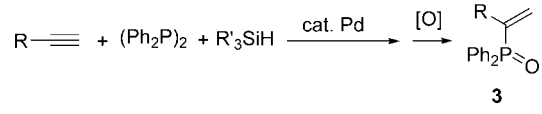
Indeed, group 13, 14, and 16[2] heteroatom compounds have been employed successfully for this purpose. In sharp contrast, however, there has been no report concerning transition-metal-catalyzed addition of group 15 heteroatom compounds bearing E−E linkage to carbon−carbon unsaturated bonds.[3−7] Very recently, we have reported the first example of transition-metal-catalyzed addition of tetraphenyldiphosphine to alkynes, which surprisingly dose not afford the expected bisphosphination products but hydrophosphination ones with excellent selectivity[8] (eq 2).



1 **2** **3**

(2)

In this reaction, it becomes apparent that the hydrogen source of the hydrophosphination product comes from alkynic hydrogen. To increase the atom-economy of alkynes, the addition of hydrogen source is attractive. In this paper, we wish to report a highly selective transition-metal-catalyzed hydrophosphination of alkynes by the novel combination of diphosphine and hydrosilane (eq 3).



3

(3)

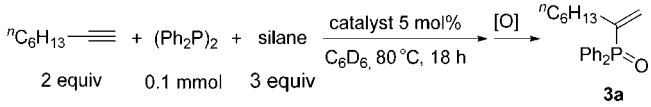
(1) (a) Beletskaya, I. P.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320. (b) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317. (c) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (d) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435. (e) Han, L.-B.; Tanaka, M. *Chem. Commun.* **1999**, 395. (f) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221. (g) Ogawa, A. *J. Organomet. Chem.* **2000**, *611*, 463.

(2) For the metal-catalyzed addition of E−E (E = group 16) to carbon−carbon unsaturated bonds, see: (a) Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796. (b) Kondo, T.; Uenoyama, S.; Fujita, K.; Mitsudo, T. *J. Am. Chem. Soc.* **1999**, *121*, 482. (c) Arisawa, M.; Yamaguchi, M. *Org. Lett.* **2001**, *3*, 763. (d) Kuniyasu, H. In *Catalytic Heterofunctionalization*; Togni, A.; Grützmacher, H., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Chapter 7. (e) Ogawa, A. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience:New York, 2002; Chapter VII.6. (f) Ananikov, V. P.; Kabeshov, M. A.; Beletskaya, I. P.; Aleksandrov, G. G.; Eremenko, I. L. *J. Organomet. Chem.* **2003**, *687*, 451. (g) Arisawa, M.; Kozuki, Y.; Yamaguchi, M. *J. Org. Chem.* **2003**, *68*, 8964. (h) Usugi, S.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2004**, *6*, 601. (i) Ananikov, V. P.; Beletskaya, I. P. *Org. Biomol. Chem.* **2004**, *2*, 284. (j) Ogawa, A. In *Main Group Metals in Organic Synthesis*; Yamamoto, H.; Oshima, K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 2, Chapter 15. (k) Moro, A. V.; Nogueira, C. W.; Barbosa, N. B. V.; Menezes, P. H.; da Rocha, J. B. T.; Zeni, G. *J. Org. Chem.* **2005**, *70*, 5257. (l) Ananikov, V. P.; Kabeshov, M. A.; Beletskaya, I. P. *Synlett* **2005**, 1012.

(3) For reviews concerning transition-metal-catalyzed hydrophosphination and hydrophosphinylation to carbon-carbon unsaturated bonds, see: Wicht, D. K.; Glueck, D. S. In *Catalytic Heterofunctionalization*; Togni, A.; Grützmacher, H., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Chapter 5.

10.1021/jo801267y CCC: $40.75
Published on Web 09/18/2008

TABLE 1. Pd-Catalyzed Hydrophosphination of 1-Octyne with $(Ph_2P)_2$ and Hydrosilanes

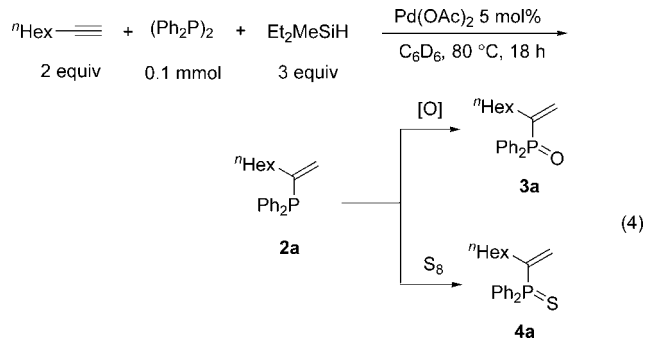


entry	catalyst	silane	yield %[a]
1	$Pd(OAc)_2$	Et_2MeSiH	84
2[b]	$Pd(OAc)_2$	Et_2MeSiH	64
3	$Pd(PPh_3)_4$	Et_2MeSiH	95
4	$Pd(PPh_3)_4$	Et_3SiH	92
5	$Pd(PPh_3)_4$	$PhSiH_3$	trace
6	$Pd(PPh_3)_4$	$(TMS)_3SiH$	7

[a] Determined by ^1H NMR. [b] The reaction condition: 1-octyne (1 equiv), Et_2MeSiH (1 equiv).

Results and Discussion

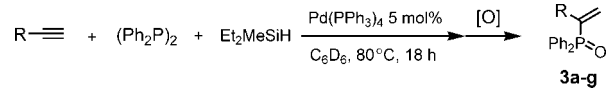
When the $Pd(OAc)_2$-catalyzed addition of tetraphenyldiphosphine (0.1 mmol) to 1-octyne (0.2 mmol) was examined in the co-presence of hydrosilane (Et_2MeSiH, 0.3 mmol) as the hydrogen source (eq 4), the hydrophosphination product was obtained in 84% yield with excellent regioselectivity. Interestingly, neither silylphosphination product of the alkynes nor hydrosilylation product of the alkynes was obtained. The hydrophosphination product provided the corresponding phosphine oxide by air oxidation during workup, whereas the treatment of S_8 before exposing to air led to the formation of the corresponding phosphine sulfide.

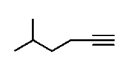
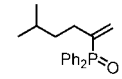
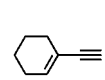
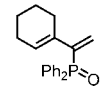


(4)

Next, to optimize the reaction conditions, the hydrophosphination using divalent or zerovalent palladium catalysts and several hydrosilanes was examined (Table 1). In the presence of 1 equiv of alkyne and 1 equiv of hydrosilane, 64% of the desired hydrophosphination product was obtained (entry 2). When $Pd(PPh_3)_4$ and Et_2MeSiH were used, the hydrophosphination product was obtained in almost quantitative yield (entry 3). Et_3SiH was also useful (entry 4), but $PhSiH_3$ and $(TMS)_3SiH$ were ineffective in the reaction (entries 5 and 6).

TABLE 2. $Pd(PPh_3)_4$-Catalyzed Hydrophosphination of Alkynes with $(Ph_2P)_2$ and Et_2MeSiH[a]



entry	alkyne	product		yield,%[b]
1	$^nC_6H_{13}$–	$^nC_6H_{13}$, Ph_2P=O	**3a**	95
2			**3b**	99
3	NC–	NC, Ph_2P=O	**3c**	86
4	Cl–	Cl, Ph_2P=O	**3d**	(75)
5	Ph–	Ph, Ph_2P=O	**3e**	(47)
6	*p*-C_5H_{11}-C_6H_4–	*p*-C_5H_{11}-C_6H_4, Ph_2P=O	**3f**	45
7	*p*-CF_3-C_6H_4–	*p*-CF_3-C_6H_4, Ph_2P=O	**3g**	46
8			**3h**	41

[a] Reaction conditions: alkyne (2 equiv), $(Ph_2P)_2$ (0.1 mmol), Et_2MeSiH (3 equiv), C_6D_6 (0.8 mL). [b] The values in parentheses are ^1H NMR yield. [c] In the case of alkynes bearing a C=O group, a complex mixture was obtained.

Table 2 represents the results of the $Pd(PPh_3)_4$-catalyzed hydrophosphination of several alkynes using the binary system of $(Ph_2P)_2$ and Et_2MeSiH. Aliphatic alkynes such as 1-octyne and 5-methyl-1-hexyne underwent the Pd(0)-catalyzed regioselective hydrophosphination, providing the corresponding vinylic phosphine oxides in excellent yields (entries 1 and 2). Cyano and chloro substituents were tolerant of the hydrophosphination (entries 3 and 4). In the cases of aromatic alkynes such as phenylacetylene, *p*-(*n*-pentyl)phenylacetylene, and *p*-trifluoromethylphenylacetylene the hydrophosphination proceeded regioselectively, but the yields were

(4) For the metal-catalyzed hydrophosphination to carbon−carbon unsaturated bonds, see: (a) Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1701. (b) Kazankova, M. A.; Efimova, I. V.; Kochetkov, A. N.; Afanas'ev, V. V.; Beletskaya, I. P.; Dixneuf, P. H. *Synlett* **2001**, 497. (c) Shulyupin, M. O.; Kazankova, M. A.; Beletskaya, I. P. *Org. Lett.* **2002**, *4*, 761. (d) Takaki, K.; Koshoji, G.; Komeyama, K.; Takeda, M.; Shishido, T.; Kitani, A.; Takehira, K. *J. Org. Chem.* **2003**, *68*, 6554. (e) Komeyama, K.; Kawabata, T.; Takehira, K.; Takaki, K. *J. Org. Chem.* **2005**, *70*, 7260. (f) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 2368. (g) Scriban, C.; Kovacik, I.; Glueck, D. S. *Organometallics* **2005**, *24*, 4871. (h) Takaki, K.; Komeyama, K.; Kobayashi, D.; Kawabata, T.; Takehira, K. *J. Alloys Compd.* **2006**, *408*, 432. (i) Hayashi, M.; Matsuura, Y.; Watanabe, Y. *J. Org. Chem.* **2006**, *71*, 9248. (j) Komeyama, K.; Kobayashi, D.; Yamamoto, Y.; Takehira, K.; Takaki, K. *Tetrahedron* **2006**, *62*, 2511. (k) Join, B.; Mimeau, D.; Delacroix, O.; Gaumont, A.-C. *Chem. Commun.* **2006**, 3249. (l) Crimmin, M. R.; Barrett, A. G. M.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A. *Organometallics* **2007**, *26*, 2953.

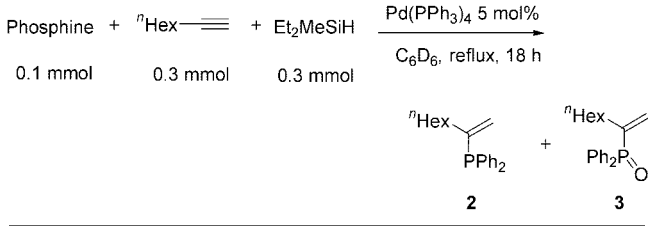
(5) For the transition-metal-catalyzed hydrophosphinylation to carbon−carbon unsaturated bonds, see: (a) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571. (b) Han, L.-B.; Choi, N.; Tanaka, M. *Organometallics* **1996**, *15*, 3259. (c) Han, L.-B.; Hua, R.; Tanaka, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 4196. (d) Zhao, C.-Q.; Han, L.-B.; Tanaka, M. *Organometallics* **2000**, *19*, 4196. (e) Han, L.-B.; Zhao, C.-Q.; Tanaka, M. *J. Org. Chem.* **2001**, *66*, 5929. (f) Deprèle, S.; Montchamp, J.-L. *J. Am. Chem. Soc.* **2002**, *124*, 9386. (g) Allen, A., Jr.; Ma, L.; Lin, W. *Tetrahedron Lett.* **2002**, *43*, 3707. (h) Milton, M. D.; Onodera, G.; Nishibayashi, Y.; Uemura, S. *Org. Lett.* **2004**, *6*, 3993. (i) Han, L.-B.; Zhang, C.; Yazawa, H.; Shimada, S. *J. Am. Chem. Soc.* **2004**, *126*, 5080. (j) Ribière, P.; Bravo-Altamirano, K.; Antczak, M. I.; Hawkins, J. D.; Montchamp, J.-L. *J. Org. Chem.* **2005**, *70*, 4064. (k) Stockland, R. A., Jr.; Lipman, A. J.; Bawiec, J. A., III.; Morrison, P. E.; Guzei, I. A.; Findeis, P. M.; Tamblin, J. F. *J. Organomet. Chem.* **2006**, *691*, 4042. (l) Dobashi, N.; Fuse, K.; Hoshino, T.; Kanada, J.; Kashiwabara, T.; Kobata, C.; Nune, S. K.; Tanaka, M. *Tetrahedron Lett.* **2007**, *48*, 4669.

(6) For the rhodium-catalyzed synthesis of 1-alkynylphosphine oxides from 1-alkynes and tetraphenyldiphosphine, see: Arisawa, M.; Onoda, M.; Hori, C.; Yamaguchi, M. *Tetrahedron Lett.* **2006**, *47*, 5211.

(7) For the Lewis acid mediated silylphosphination to substituted propiolates, see: Hayashi, M.; Matsuura, Y.; Kurihara, K.; Maeda, D.; Nishimura, Y.; Morita, E.; Okasaka, M.; Watanabe, Y. *Chem. Lett.* **2007**, *36*, 634.

(8) Nagata, S.; Kawaguchi, S.-i.; Matsumoto, M.; Kamiya, I.; Nomoto, A.; Sonoda, M.; Ogawa, A. *Tetrahedron Lett.* **2007**, *48*, 6637.

TABLE 3. Hydrophosphination to 1-Octyne with Phosphine Oxide

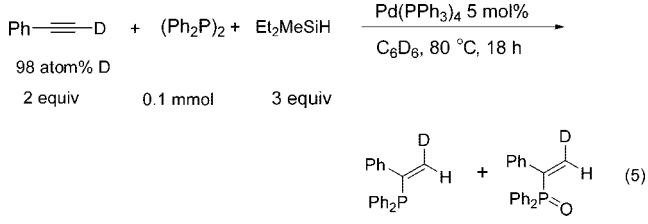


entry	phosphine	yield[a] 2	yield[a] 3
1	$Ph_2P(O)PPh_2$ (**5**)	24%	21%
2	$Ph_2P(O)H$ (**6**)	0%	0%
3	$(PPh_2)_2$ + $Ph_2P(O)PPh_2$ (1 : 1)	53%	36%
4	$(PPh_2)_2$ cat. $Ph_2P(O)PPh_2$ 11 mol%	32%	trace
5	$Ph_2P(O)PPh_2$ cat. $(PPh_2)_2$ 20 mol%	44%	23%

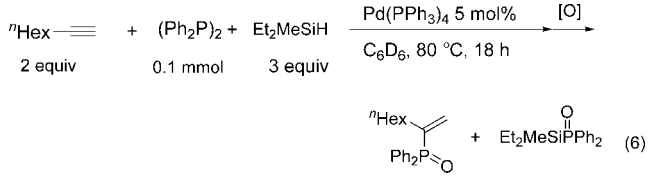
[a] ^{1}H NMR yield.

somewhat lower compared with aliphatic ones (entries 5−7). In the case of a conjugate enyne, the hydrophosphination proceeded in moderate yield (entry 8). Unfortunately, the internal alkynes such as 4-octyne and 1-phenyl-1-butyne did not afford the desired hydrophosphination product.

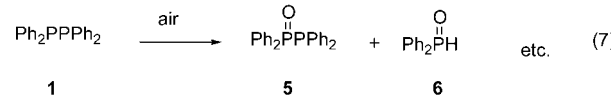
To clarify the hydrogen source of the present catalytic hydrophosphination using the diphosphine−hydrosilane binary system, we examined the hydrophosphination of phenylacetylene deuterized at the terminal acetylenic hydrogen (98 atom% D), which afforded the corresponding (*E*)-vinylphosphine and (*E*)-vinylphosphine oxide stereoselectively (eq 5). This result strongly suggests that the hydrophosphination proceeds via a *syn*-addition process using the hydrosilane as a hydrogen source.



Furthermore, the formation of silylphosphine oxide as a by-product was confirmed by ^{31}P NMR (eq 6) ($Et_2MeSiP(O)Ph_2$: ^{31}P NMR (C_6D_6) δ = 21.8 ppm, ^{29}Si NMR δ = 24.6 ppm (d, J = 8.7 Hz)).[9]

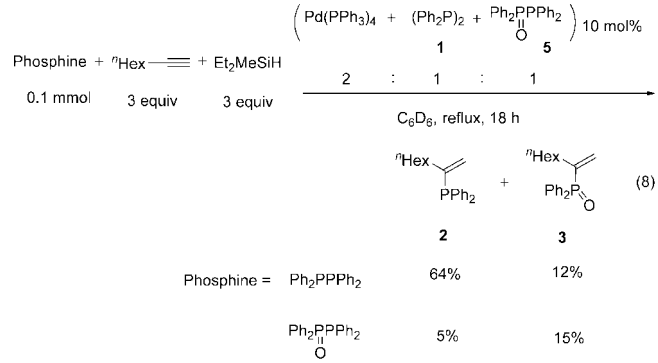


We next investigated in detail the influence of oxygen on the present hydrophosphination. When oxygen was strictly removed from this reaction system, the present hydrophosphination was dramatically suppressed (only 20% of the hydrophosphination product was obtained). This fact indicates the presence of a small amount of oxygen is essential to attain this hydrophosphination with high efficiency.[10] Although tetraphenyldiphosphine (**1**) is fairly stable in the solid state, it is extremely air-sensitive in solvent, generating immediately several oxidation products, which can be assigned unambiguously by measurement of their ^{31}P NMR spectra[11] (in C_6D_6) ($Ph_2PP(O)Ph_2$ (**5**): δ −23.1 (d, J = 218.0 Hz), 34.6 (d, J = 218.0 Hz);[12] $Ph_2P(O)H$ (**6**): δ 18.0 ppm[13]) (eq 7).



To gain insight into the role of these oxidation products (**5** and **6**) in the present hydrophosphination, we examined the hydrophosphination in the presence/absence of **5** or **6**, and the results are summarized in Table 3. When **5** was used instead of **1**, both hydrophosphination product **2** and hydrophosphinylation product **3** were obtained in low yields (entry 1). On the other hand, use of only **6** resulted in no formation of the hydrophosphinylation product (entry 2). When equimolar amounts of **1** and **5** were employed, the corresponding vinylic phosphines **2** and **3** were obtained in 53% and 36% yields, respectively (entry 3). In addition, when the proportion of **1** to **5** was altered, the yields were diminished (entries 4 and 5). These results suggest tetraphenyldiphosphine oxide (**5**) played an important role in this hydrophosphination.

In the presence of the catalyst (prepared by the reaction of $Pd(PPh_3)_4$ (0.01 mmol) with **1** (0.005 mmol) and **5** (0.005 mmol)), **1** successfully added to 1-octyne, providing the corresponding vinylic phosphine in good yield (eq 8). In contrast, when **5** was employed as the substrate in place of **1**, the hydrophosphination product was obtained in only very poor yield. These results clearly indicate that, in this hydrophosphination, tetraphenyldiphosphine (**1**), not tetraphenyldiphosphine oxide (**5**), acts as the phosphination reagent.



(9) Literature value of ^{31}P NMR of $Ph_3SiP(O)Ph_2$, which is similar compound to $Et_2MeSiP(O)Ph_2$, is δ = 28.6 ppm ($CDCl_3$). See: Ferguson, I. G. T.; Glidewell, C. *J. Chem. Soc., Dalton Trans.* **1977**, 2071.

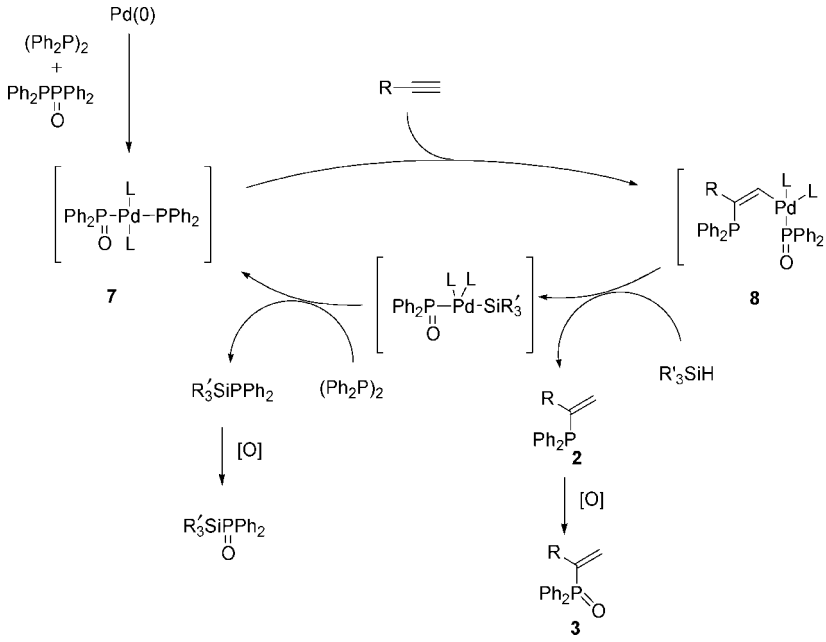
(10) To clarify the effect of oxygen on the reaction, we examined the hydrophosphination of 1-octyne (0.1 mmol) in the presence of air: (mol % of O_2, yield of **2**, yield of **3**) = (25 mol %, 30%, 6%); (50 mol %, 30%, 13 %).

(11) (a) Postigo, A.; Barata, S.; Ogawa, A.; Sonoda, M. Tetraphenyldiphosphine. In *Encycopedia of Reagent for Organic Synthesis*; John Wiley Sons, Ltd.: New York, March 14, 2008, online. (b) Kawaguchi, S.; Nagata, S.; Tsuchii, K.; Nomoto, A.; Ogawa, A. *Tetrahedron Lett.* **2006**, *47*, 3919.

(12) Irvine, D. J.; Glidewell, C.; Cole.Hamilton, D. J.; Barnes, J. C.; Howie, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1765.

(13) (a) Dabkowski, W.; Michalski, J.; Skrzypczynski, Z. *J. Chem. Soc., Chem. Commun.* **1982**, 1260. (b) Köster, R.; Schüβler, W.; Synoradzki, L. *Chem. Ber.* **1987**, *120*, 1105.

SCHEME 1. A Plausible Pathway for Hydrophosphination of Alkynes with $(Ph_2P)_2$ and R'_3SiH



A plausible catalytic pathway is shown in Scheme 1: (1) generation of the active Pd species **7**;[14] (2) the phosphinopalladation of an alkyne with this active Pd species **7**, affording a vinylpalladium intermediate **8**; (3) the exchange reaction of a vinylphosphine with the hydrosilane to afford a vinylphosphine product **2**; (4) regeneration of the active Pd species **7** by the reaction of Pd species with tetraphenyldiphosphine along with generation of silylphosphine[15] as byproduct.

Furthermore, to get some information about the mechanism for this hydrophosphination, the hydrophosphination of 1-octyne in the absence of oxygen was monitored by ^{31}P NMR. Surprisingly, ^{31}P NMR indicated the formation of the Pd complex **9**: δ 26.7−27.1 and 46.4−47.0 ppm in C_6D_6[16] (ca. 5%) (Figure 1).

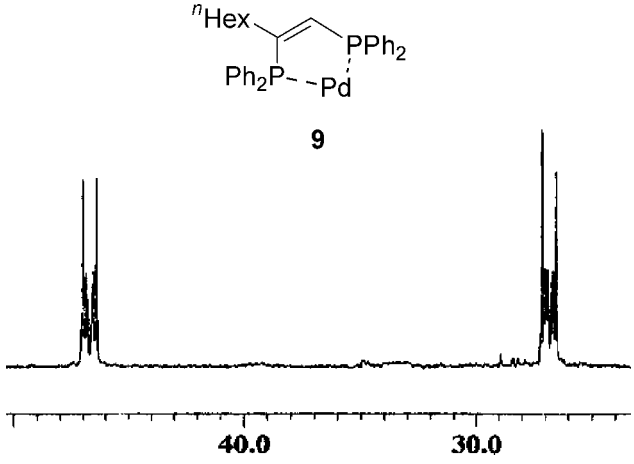
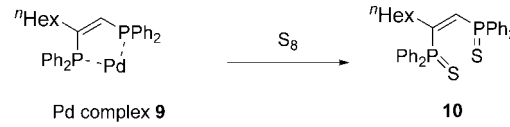


FIGURE 1. ^{31}P NMR spectrum of complex **9**.

Identification of the Pd complex **9** was performed by comparison with the authentic sample synthesized alternatively: photoinduced addition of tetraphenyldiphosphine to 1-octyne afforded (*Z*)-1,2-bis(diphenylphosphino)-1-octene,[11b] which was then treated with $Pd(PPh_3)_4$ (Scheme 2). Immediately, the signals (δ −24.5 (d, J_{P-P} = 157.0 Hz), δ −5.8 (d, J_{P-P} = 157.0 Hz), in C_6D_6) of (*Z*)-1,2-bis(diphenylphosphino)-1-octene disappeared completely, and new signals were observed at δ 26.7−27.1 and 46.4−47.0 ppm (C_6D_6) as a characteristic multiplet, which can be assigned as the signal of the Pd complex **9**.

Furthermore, when the crude solution including the Pd complex **9** was treated with S_8, (*Z*)-1,2-bis(diphenylthiophosphinyl)-1-octene (**10**) was obtained (eq 9).



(9)

Most probably, (*Z*)-1,2-bis(diphenylophosphino)-1-alkenes may work as a catalyst poison and inhibit the desired hydrophosphination reaction of alkynes and/or the bisphosphination reaction.[17] Accordingly, the existence of small amounts of oxygen in this hydrophosphination presumably leads to the formation of tetraphenyldiphosphine oxide, which may depress the formation of the Pd complex **9**.[18]

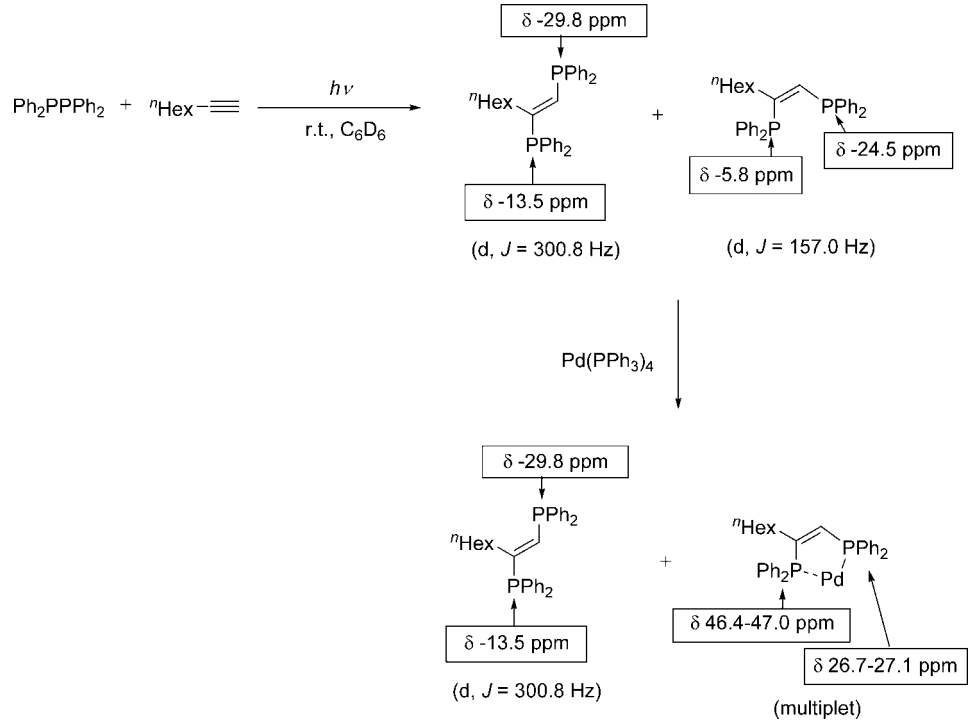
(14) We attempted the observation of Pd species **7** by ^{31}P NMR. In the literature, the chemical shift of the Pd−P(O)Ph_2 unit appears at δ 86 ppm (in benzene). When the stoichiometric reaction of $Pd(PPh_3)_4$ with $(Ph_2P)_2$ and $Ph_2PP(O)Ph_2$ (in C_6D_6, 298 K, 3 h) was conducted, we observed two signals at δ 85.8 and 86.3 ppm, which indicate the possibility of Pd−P(O)Ph_2 bond formation. See: Belntykh, L. B.; Goremyka, T. V.; Zinchenko, S. V.; Rokhin, A. V.; Ratovskii, G. V.; Shmidt, F. K. *Russ. J. Coord. Chem.* **2002**, *28*, 664.

(15) When the hydrophosphination of 1-octyne was monitored by ^{31}P NMR, three major peaks were observed at δ−2.4, 21.8, and 28.9 ppm. The two peaks (δ−2.4, 28.9 ppm) can be assigned to **2** and **3**, respectively. The other peak at δ 21.8 ppm is assumed to be $Et_2MeSiP(O)Ph_2$. However, the peak of $Et_2MeSiPPh_2$ was not observed, probably because oxygen atom exchange reaction between $Et_2MeSiPPh_2$ and other phosphine oxide products in situ may proceed immediately.

(16) (a) Carty, A. J.; Johnson, D. K. *J. Chem. Soc., Chem. Commun.* **1977**, 903. (b) Carty, A. J.; Johnson, D. K.; Jacobson, S. E. *J. Am. Chem. Soc.* **1979**, *101*, 5612. (c) Dodds, D. L.; Haddow, M. F.; Orpen, A. G.; Pringle, P. G.; Woodward, G. *Organometallics* **2006**, *25*, 5937. (d) Kondoh, A.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 4099.

(17) When 15 mol % of (*Z*)-1,2-bis(diphenylphosphino)-1-octene was added to the reaction system, no hydrophosphination product was obtained. Furthermore, when 15 mol % of *cis*-bis(diphenylphosphino)ethene was added to the reaction system, no hydrophosphination product was also obtained.

SCHEME 2. ^{31}P NMR Data Concerning the Reaction of (*Z*)-1,2-Bis(diphenylphosphino)-1-octene with $Pd(PPh_3)_4$



Conclusion

We have discovered that a novel transition-metal-catalyzed hydrophosphination of terminal alkynes using diphosphine−hydrosilane binary system, which takes place regioselectively and efficiently, provides vinylic phosphines. The present hydrophosphination of alkynes smoothly takes place in the presence of small amounts of oxygen, which leads to the tetraphenyldiphosphine oxide in situ from tetraphenyldiphosphine. It has been suggested that the presence of tetraphenyldiphosphine oxide is useful for keeping the catalytic activity forward in the hydrophosphination of alkynes. We believe this reaction opens up a new field of transition-metal-catalyzed reactions using heteroatom binary systems.

Experimental Section

General Procedure for Palladium-Catalyzed Hydrophosphination to Alkynes Using Diphosphine−Hydrosilane Binary System. $(Ph_2P)_2$ (37.6 mg, 0.1 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol), alkyne (0.3 mmol), Et_2MeSiH (43.4 μL, 0.3 mmol), and C_6D_6 (0.6 mL) were placed in a sealed Pyrex glass NMR tube under a nitrogen atmosphere. The mixture was stirred for 30 s, and the tube was covered by aluminum foil. The mixture was heated at reflux for 18 h. The reaction mixture was left under air overnight. Purification of the crude was performed by preparative TLC (silica gel, **3a**: hexane/AcOEt = 9/1, R_f = 0.04; **3b**: hexane, R_f = 0.03; **3c**: hexane/AcOEt = 3/1, R_f = 0.07; **3d**: hexane/AcOEt = 3/1, R_f = 0.09; **3e**: hexane, R_f = 0.03; **3f**: hexane/AcOEt =10/1, R_f = 0.04; **3g**: Et_2O, R_f = 0.30; **3h**: Et_2O, R_f = 0.38).

The Spectral and Analytical Data. 2-(Diphenylphosphinyl)-1-octene (3a):[5c] yellow oil; IR (NaCl) 2927, 1437, 1190, 1118, 725, 696, 540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.75 (t, J = 6.3 Hz, 3H), 1.13−1.17 (m, 6H), 1.37−1.42 (m, 2H), 2.19−2.25 (m, 2H), 5.53 (d, J = 21.4 Hz, 1H), 5.85 (d, J = 42.9 Hz, 1H), 7.36−7.47 (m, 6H), 7.60−7.64 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 28.0 (d, J_{C-P} = 5.0 Hz), 29.2 (d, J_{C-P} = 85.3 Hz), 31.49, 31.50 (d, J_{C-P} = 11.0 Hz), 128.4 (d, J_{C-P} = 12.0 Hz), 128.6, 131.4 (d, J_{C-P} = 94.4 Hz), 131.8, 131.9 (d, J_{C-P} = 10.0 Hz), 144.1 (d, J_{C-P} = 92.4 Hz); ^{31}P NMR ($CDCl_3$) δ 32.3; HRMS (EI) calcd for $C_{20}H_{25}OP$ 312.1643, found 312.1649.

2-(Diphenylphosphinyl)-5-methyl-1-hexene (3b):[8] yellow oil; IR (NaCl) 2954, 2868, 1436, 1193, 1116, 939, 725, 696, 538 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.81 (d, J = 6.4 Hz, 6H), 1.34−1.39 (m, 2H), 1.47−1.53 (m, 1H), 2.27−2.34 (m, 2H), 5.62 (d, J = 21.0 Hz, 1H), 5.94 (d, J = 42.9 Hz, 1H), 7.46−7.49 (m, 4H), 7.52−7.56 (m, 2H), 7.68−7.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 22.4, 27.7, 29.3 (d, J_{C-P} = 11.3 Hz), 37.1 (d, J_{C-P} = 4.5 Hz), 128.39, 128.42 (d, J_{C-P} = 11.3 Hz), 131.4 (d, J_{C-P} = 101.9 Hz), 131.78, 131.84 (d, J_{C-P} = 9.8 Hz), 144.3 (d, J_{C-P} = 90.5 Hz); ^{31}P NMR ($CDCl_3$) δ 32.3; HRMS (EI) calcd for $C_{19}H_{23}OP$ 298.1487, found 298.1491.

5-Cyano-2-(diphenylphosphinyl)-1-pentene (3c):[5c] yellow oil; IR (NaCl) 2358, 2341, 1437, 1182, 1119, 723, 696, 540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.83−1.99 (m, 2H), 2.25−2.37 (m, 2H), 2.46−2.53 (m, 2H), 5.58 (d, J = 19.8 Hz, 1H), 5.98 (d, J = 42.3 Hz, 1H), 7.50−7.62 (m, 6H), 7.62−7.83 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 16.6, 24.5 (d, J_{C-P} = 4.0 Hz), 31.4 (d, J_{C-P} = 10.0 Hz), 119.2, 128.7 (d, J_{C-P} = 11.0 Hz), 130.6 (d, J_{C-P} = 10.0 Hz), 130.8 (d, J_{C-P} = 102.4 Hz), 131.8 (d, J_{C-P} = 11.0 Hz), 132.2, 142.3 (d, J_{C-P} = 89.4 Hz); ^{31}P NMR (C_6D_6) δ 28.7; HRMS (EI) calcd for $C_{18}H_{18}NOP$ 295.1126, found 295.1129. Anal. Calcd for $C_{18}H_{18}NOP$: C, 73.21; H, 6.14; N, 4.74%. Found: C, 72.92; H, 6.05; N, 4.58%.

5-Chloro-2-(diphenylphosphinyl)-1-pentene (3d):[8] yellow oil; IR (NaCl) 3431, 3055, 2923, 2854, 1436, 1184, 1118, 1099, 721, 694, 540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.94−2.03 (m, 2H), 2.46−2.55 (m, 2H), 2.46−2.55 (m, 2H), 5.62 (dd, J = 20.1, 0.9 Hz, 1H), 5.98 (dd, J = 42.3, 0.9 Hz, 1H), 7.43−7.59 (m, 6H), 7.64−7.75 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 29.4 (d, J_{C-P} = 11.3 Hz), 31.2 (d, J_{C-P} = 4.5 Hz), 44.1, 128.5 (d, J_{C-P} = 12.8 Hz), 128.6 (d, J_{C-P} = 11.3 Hz), 129.8 (d, J_{C-P} = 10.6 Hz), 131.8 (d, J_{C-P} = 9.1 Hz), 132.0

(18) When the equimolar reaction of $Pd(PPh_3)_4$ (0.1 mmol) with $(Ph_2P)_2$ (0.1 mmol) was conducted in C_6D_6 at 298 K for 3 h, only 25% of $(Ph_2P)_2$ was consumed for the construction of the Pd complex by monitoring the reaction with ^{31}P NMR (75% of $(Ph_2P)_2$ was recovered). On the other hand, the equimolar reaction of $Pd(PPh_3)_4$ with $(Ph_2P)_2$ and $Ph_2PP(O)Ph_2$ at room temperature for 3 h led to a consumption of $Ph_2PP(O)Ph_2$ completely. These results suggest that $Ph_2PP(O)Ph_2$ is readily added to $Pd(PPh_3)_4$ than $(Ph_2P)_2$.

(d, J_{C-P} = 2.3 Hz), 142.7 (J_{C-P} = 92.0 Hz); ^{31}P NMR (C_6D_6) δ 28.6; HRMS (EI) calcd for $C_{17}H_{18}ClOP$ 304.0784, found 304.0787.

2-(Diphenylphosphinyl)-1-styrene (3e):[5c] yellow oil; IR (NaCl) 3060, 1436, 1180, 1116, 727, 694, 532 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.75 (d, J = 19.5 Hz, 1H), 6.24 (d, J = 40.0 Hz, 1H), 7.20−7.31 (m, 3H), 7.32−7.55 (m, 8H), 7.62−7.75 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 128.15 (d, J_{C-P} = 5.0 Hz), 128.22, 128.3, 128.4, 128.5, 131.7 (d, J_{C-P} = 104.0 Hz), 131.9 (d, J_{C-P} = 9.1 Hz), 132.0, 132.1, 144.4 (d, J_{C-P} = 93.4 Hz); ^{31}P NMR ($CDCl_3$) δ 30.8; HRMS (EI) calcd for $C_{20}H_{17}OP$ 304.1017, found 304.1021.

1-{1-(Diphenylphosphinyl)ethenyl}-4-pentylbenzene (3f): yellow oil; IR (NaCl) 2928, 2856, 1437, 1190, 1117, 748, 725, 696, 530 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 6.8 Hz 3H), 1.23−1.31 (m, 4H), 1.42−1.65 (m, 2H), 2.52 (t, J = 8.1 Hz, 2H), 5.69 (d, J = 19.8 Hz, 1H), 6.23 (d, J = 40.8 Hz, 1H), 7.05 (d, J = 8.1 Hz, 2H), 7.36−7.52 (m, 10H), 7.68−7.74 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9 (d, J = 12.5 Hz), 22.4, 30.8, 31.3, 35.5, 127.1 (d, J_{C-P} = 13.4 Hz), 127.9 (d, J_{C-P} = 21.1 Hz), 128.4 (d, J_{C-P} = 17.3 Hz), 129.4, 130.8−131.3 (m), 131.5−132.4 (m), 134.6 (d, J_{C-P} = 10.6 Hz), 143.0, 143.9 (d, J_{C-P} = 93.1 Hz), 149.4; ^{31}P NMR (C_6D_6) δ 27.9; HRMS (EI) calcd for $C_{25}H_{27}OP$ 374.1800, found 374.1775.

1-{1-(Diphenylphosphinyl)ethenyl}-4-(trifluoromethyl)benzene (3g): white yellow solid; IR (KBr) 2359, 2343, 2179, 1437, 1325, 1182, 1119, 1067, 856, 690, 538 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 5.77 (d, J = 19.6 Hz, 1H), 6.28 (d, J = 39.6 Hz, 1H), 7.44−7.92 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 125.4, 127.1 (q, J_{C-F} = 291.2 Hz), 128.5 (d, J_{C-P} = 5.0 Hz), 128.6, 128.7, 128.9, 131.0 (d, J_{C-P} = 11.0 Hz), 131.1 (d, J_{C-P} = 103.4 Hz), 132.0 (d, J_{C-P} = 10.0 Hz), 132.7 (q, J_{C-F} = 32.1 Hz), 143.7 (d, J_{C-P} = 92.4 Hz); ^{31}P NMR ($CDCl_3$) δ 30.8; HRMS (EI) calcd for $C_{21}H_{16}F_3OP$ 372.0891, found 372.0886.

1-Cyclohexen-1-yl-1-(diphenylphosphinyl)ethene (3h):[5c] yellow oil; IR (NaCl) 2927, 1431, 1180, 1115, 1070, 751, 723, 696, 536 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48−1.67 (m, 4H), 1.98−2.23 (m, 4H), 5.24 (d, J = 21.2 Hz, 1H), 5.94 (d, J = 43.0 Hz, 1H), 6.36 (s, 1H), 7.30−7.56 (m, 6H), 7.62−7.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.7, 22.6, 25.8, 27.0 (d, J_{C-P} = 5.0 Hz), 127.0 (d, J_{C-P} = 10.0 Hz), 128.3 (d, J_{C-P} = 12.0 Hz), 130.9 (d, J_{C-P} = 11.0 Hz), 131.6, 131.7 (d, J_{C-P} = 10.0 Hz), 132.3 (d, J_{C-P} = 5.0 Hz), 132.6 (d, J_{C-P} = 104.4 Hz), 144.3 (d, J_{C-P} = 91.4 Hz); ^{31}P NMR ($CDCl_3$) δ 33.4; HRMS (EI) calcd for $C_{20}H_{17}OP$ 308.1330, found 308.1334.

2-(Diphenylthiophosphinyl)-1-octene (4a): Tetraphenyldiphosphine (18.8 mg, 0.05 mmol), tetraphenyldiphosphine oxide (19.6 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (5.8 mg, 0.005 mmol), 1-octyne (44.2 μL, 0.3 mmol), diethylmethylsilane (43.4 μL, 0.3 mmol), and degassed C_6D_6 (0.6 mL) were placed in a sealed Pyrex glass NMR tube under a nitrogen atmosphere. The mixture was stirred for 30 s, and the tube was covered by aluminum foil. The mixture was heated at reflux for 18 h. The reaction mixture was added to S_8 (9.6 mg, 0.3 mmol). Purification of the crude was performed by preparative TLC (silica gel, hexane/Et_2O = 3/1, R_f = 0.47): white yellow solid; IR (KBr) 2928, 2856, 1435, 1101, 748, 713, 692, 638 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J = 6.9 Hz, 3H), 1.18−1.25 (m, 6H), 1.44−1.50 (m, 2H), 2.33−2.38 (m, 2H), 5.49 (d, J = 22.9 Hz, 1H), 5.89 (d, J = 45.9 Hz, 1H), 7.41−7.53 (m, 6H), 7.77−7.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.4 (d, J_{C-P} = 6.7 Hz), 28.9, 31.4 (d, J_{C-P} = 12.6 Hz), 31.6, 127.7, 128.6 (d, J_{C-P} = 12.6 Hz), 131.3 (d, J_{C-P} = 93.8 Hz), 131.6, 132.2 (d, J_{C-P} = 12.6 Hz), 144.1 (d, J_{C-P} = 72.9 Hz); ^{31}P NMR ($CDCl_3$) δ 47.2; HRMS (EI) calcd for $C_{20}H_{25}PS$ 328.1415, found 328.1417.

Acknowledgment. This work is supported by Grant-in-Aid for Scientific Research on Priority Areas (Area 444, No. 19020061) and Scientific Research (B, 19350095), from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Copies of ^{1}H NMR and ^{13}C NMR spectra of 2-(diphenylphosphinyl)-1-octene (**3a**), 2-(diphenylphosphinyl)-5-methyl-1-hexene (**3b**), 5-cyano-2-(diphenylphosphinyl)-1-pentene (**3c**), 2-(diphenylphosphinyl)-1-styrene (**3e**), 1-(1-diphenylphosphinylethenyl)-4-pentylbenzene (**3f**), 1-{1-(diphenylphosphinyl)ethenyl}-4-(trifluoromethyl)benzene (**3g**), 1-cyclohexen-1-yl-1-(diphenylphosphinyl)ethene (**3h**), and 2-(diphenylthiophosphinyl)-1-octene (**4a**). This material is available free of charge via the Internet at http://pubs.acs.org.

JO801267Y