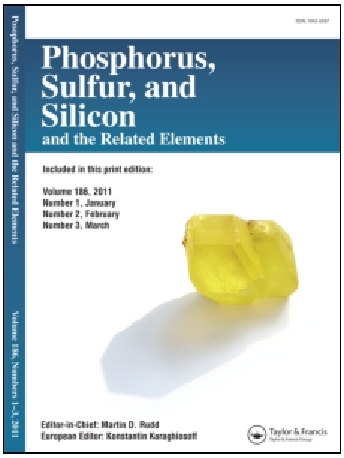

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Rhodium-Catalyzed *Anti*-Markovnikov-Type Hydrophosphination of Terminal Alkynes with Diphosphines and Hydrosilanes in the Presence of Oxygen

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RHODIUM-CATALYZED *ANTI*-MARKOVNIKOV–TYPE HYDROPHOSPHINATION OF TERMINAL ALKYNES WITH DIPHOSPHINES AND HYDROSILANES IN THE PRESENCE OF OXYGEN

Shin-ichi Kawaguchi, Mao Kotani, Takashi Ohe, Shoko Nagata, Akihiro Nomoto, Motohiro Sonoda, and Akiya Ogawa
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A novel rhodium(I)-catalyzed hydrophosphination of terminal alkynes with diphosphines and hydrosilanes takes place regioselectively in the presence of small amounts of oxygen. After air-oxidation during workups, the corresponding* anti-*Markovnikov–type vinylic phosphine oxides were obtained in good yields.

Keywords Alkyne; *anti*-Markovnikov; diphosphine; hydrophosphination; hydrosilane; rhodium catalyst

INTRODUCTION

Numerous studies of the additions of heteroatom compounds bearing a heteroatom–heteroatom linkage such as B–B,[1] Si–Si,[2] Ge–Ge,[3] Sn–Sn,[4] S–S,[5] and Se–Se[5] to alkynes catalyzed by transition metal catalysts have been reported.[6] These addition reactions provide useful tools to vicinally bifunctionalized vinylic compounds. Recently, we reported the addition of tetraphenyldiphosphine as heteroatom compounds bearing a P–P linkage, to terminal alkynes in the presence of palladium catalyst.[7] Surprisingly, this reaction afforded not the corresponding bisphosphination[8] product but a Markovnikov-type hydrophosphination[9–12] product (**3**), regioselectively, in the co-presence of oxygen (Scheme 1).

Based on the result of the hydrophosphination using deuterized alkyne, it has been apparent that the substrate alkynes also act as a hydrogen source in this hydrophosphination.[7] Furthermore, we found that this hydrophosphination of alkynes proceeded efficiently by the addition of hydrosilane as a hydrogen source in the presence of small amounts of

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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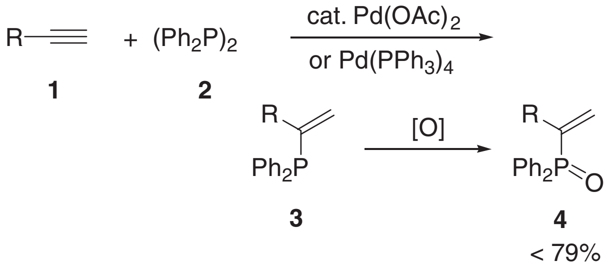
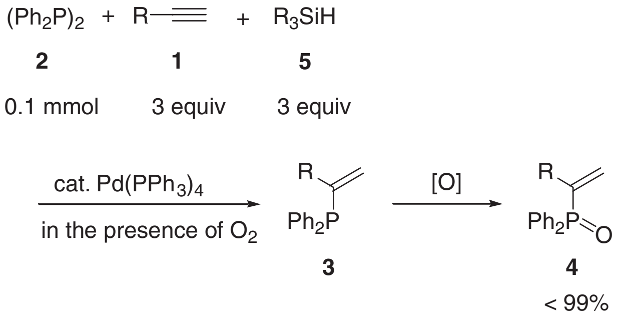


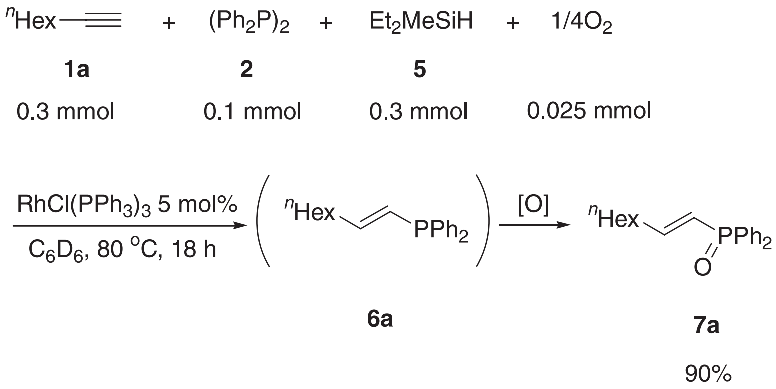
Scheme 1

oxygen (Scheme 2).[13] Oxygen seems to oxidize appropriate amounts of tetraphenyldiphosphine to tetraphenyldiphosphine oxide, which inhibits the deactivation of the catalyst in this hydrophosphination reaction.



Scheme 2

By switching the catalyst simply from palladium(0) to rhodium(I), *anti*-Markovnikov–type hydrophosphination of terminal alkynes has been found to take place regioselectively (Scheme 3). In this article, we report a novel rhodium-catalyzed *anti*-Markovnikov–type hydrophosphination of terminal alkynes using a diphosphine–hydrosilane binary system in the presence of oxygen.



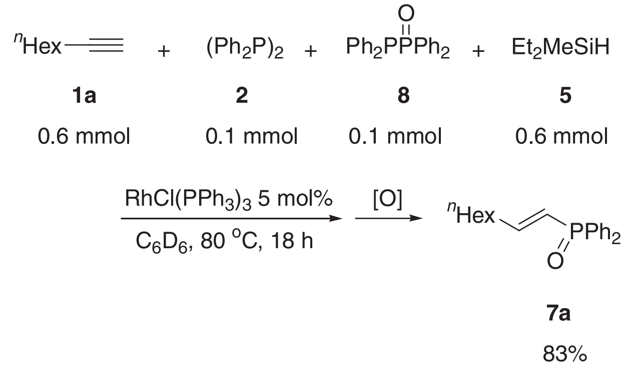
Scheme 3

RESULTS AND DISCUSSION

In a sealed NMR tube under N_2 atmosphere, 1-octyne (**1a**) (0.3 mmol), tetraphenyldiphosphine (**2**) (0.1 mmol), diethylmethylsilane (**5**) (0.3 mmol), tris(triphenylphosphine) rhodium(I) chloride (0.005 mmol), and C_6D_6 (600 μl) were placed, and then a quarter equivalent of oxygen (0.025 mmol) was introduced into the tube. Heating the resulting mixture at 80°C for 18 h, and the subsequent air-oxidation during workups, afforded the corresponding *anti*-Markovnikov–type hydrophosphination product, (*E*)-1-diphenylphosphinyl-1-octene (**7a**), in 90% yield (Scheme 3).

In addition, the formation of silylphosphine oxide as a byproduct was observed by ^{31}P NMR ($Et_2MeSiP(O)Ph_2$: ^{31}P NMR (C_6D_6) δ 21.8 ppm).[13]

Since tetraphenyldiphosphine (**2**) may be oxidized by oxygen to the corresponding oxide **8**, we next examined this hydrophosphination of 1-octyne (**1a**) by adding tetraphenyldiphosphine oxide (**8**) in the absence of oxygen. When a mixture of 1-octyne (**1a**) (0.6 mmol), tetraphenyldiphosphine (**2**) (0.1 mmol), tetraphenyldiphosphine oxide (**8**) (0.1 mmol), diethylmethylsilane (**5**) (0.6 mmol), and C_6D_6 (600 μl) in the presence of tris(triphenylphosphine)rhodium(I) chloride (0.025 mmol) was heated under the same conditions, the corresponding vinylphosphine as the hydrophosphination product and its oxide **7a** were formed. After air-oxidation during workups, vinylphosphine oxide **7a** was obtained in 83% yield (Scheme 4). (The yield was based on the sum of the mole numbers of tetraphenyldiphosphine and tetraphenyldiphosphine oxide.)

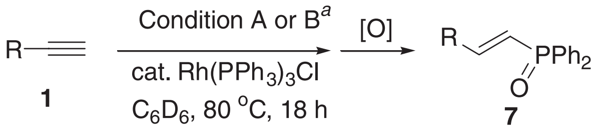


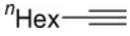
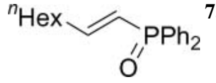
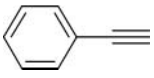
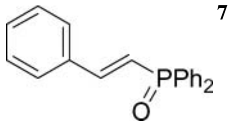
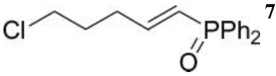
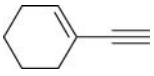
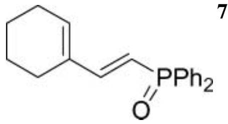
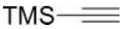
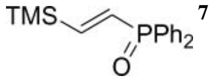
Scheme 4

We next examined the hydrophosphination of several alkynes by using the methods shown in Schemes 3 and 4 (Table I). Aromatic alkynes such as phenylacetylene underwent the Rh(I)-catalyzed regioselective hydrophosphination, providing the corresponding (*E*)-vinylic phosphine oxide (**7b**) in good yield (Table I, entry 3). Chloro and silyl substituents are tolerant of the reaction (Table I, entries 4, 5, and 7). In the case of a conjugate enyne, the corresponding phosphinyl diene (**7d**) was obtained in good yield (Table I, entry 6).

Although additional detailed experiments are required in order to clarify the reaction mechanism of this rhodium(I)-catalyzed hydrophosphination, possible pathways[13] are shown in Scheme 5: (i) at first, oxidative addition of diphosphine oxide to rhodium(I) to generate active species (**9**); (ii) regioselective phosphinorhodation of alkyne, to form vinylrhodium intermediate (**10**); two possible pathways (path A and B) are considered: path A: (iii) the reaction of vinylrhodium **10** with the hydrosilane to form vinylphosphine (**6**) and

Table I Rhodium(I)-catalyzed hydrophosphination of alkynes using diphosphine-hydrosilane binary systems



Entry	Alkyne	Condition	Product	Yield%[b]
1		A	 **7a**	90%
2		B		83%
3		A	 **7b**	82%[d]
4		A	 **7c**	80%
5		B		63%
6		A	 **7d**	90%[d]
7[c]		A	 **7e**	71%

[a] Reaction condition A: alkyne (0.3 mmol), $(Ph_2P)_2$ (0.1 mmol), Et_2MeSiH (0.3 mmol), oxygen (0.025 mmol), $RhCl(PPh_3)_3$ (0.005 mmol). Reaction condition B: alkyne (0.6 mmol), $(Ph_2P)_2$ (0.1 mmol), $Ph_2PP(O)Ph_2$ (0.1 mmol), Et_2MeSiH (0.6 mmol), $RhCl(PPh_3)_3$ (0.01 mmol).

[b] Determined by ^1H NMR.

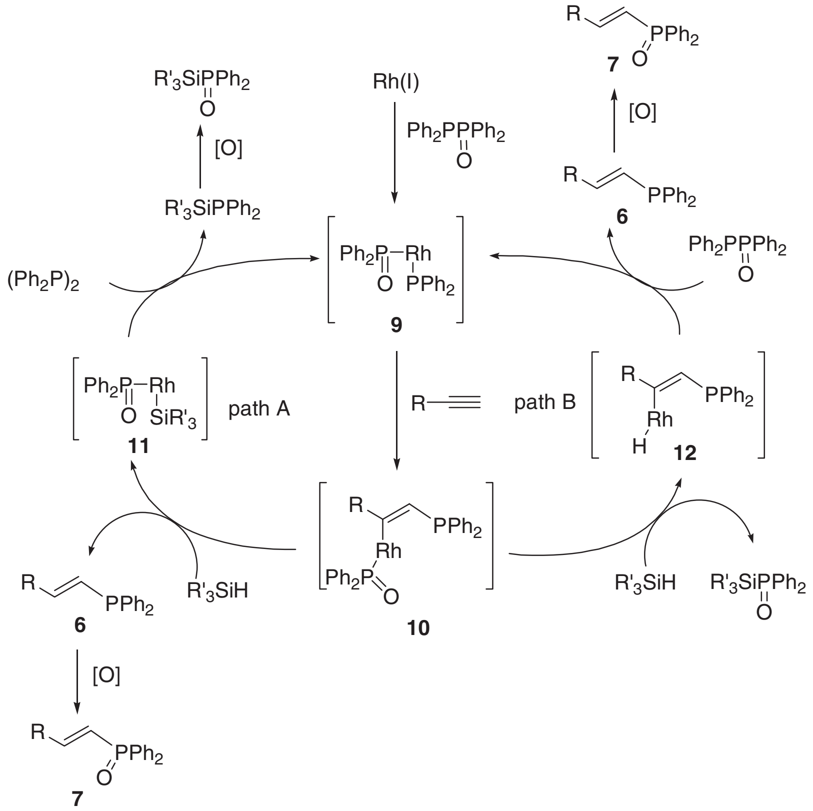
[c] $RhCl(PPh_3)_3$ (10 mol%, 0.02 mmol) was used.

[d] The yield of this Rh-catalyzed reaction was higher compared with that of the $Pd(PPh_3)_4$-catalyzed hydrophosphination,[13] in which some minor byproducts were formed concomitantly.

silylphosphinylrhodium species (**11**) and (iv) exchange reaction of the silyl group of **11** with the phosphino group of tetraphenyldiphosphine to regenerate Rh species **9** with the concomitant formation of silylphosphine as a byproduct; path B: (iii) exchange of phophinyl group with hydride group to form vinylrhodium hydride species (**12**) and silylphosphine oxide and (iv) reductive elimination to give vinylphosphine **6** and addition of diphosphine oxide to regenerate **9**.

An alternative pathway may involve the formation of phosphinylrhodium hydride (**13**) (Scheme 6): (i) the reaction of rhodium species **9** with the hydrosilane to generate phosphinylrhodium hydride **13**[14]; (ii) hydrorhodation of alkyne to generate vinylrhodium hydride (**14**); (iii) the reaction of **14** with the diphosphine to give vinylphosphine **6** along with the regeneration of **9**.

In summary, rhodium-catalyzed highly regioselective hydrophosphination of terminal alkynes has been developed by using diphosphine-hydrosilane binary systems, which affords the *anti*-Markovnikov–type addition products. This reaction is regiocomplementary with the palladium-catalyzed Markovnikov-type hydrophosphination reported previously.



Scheme 5

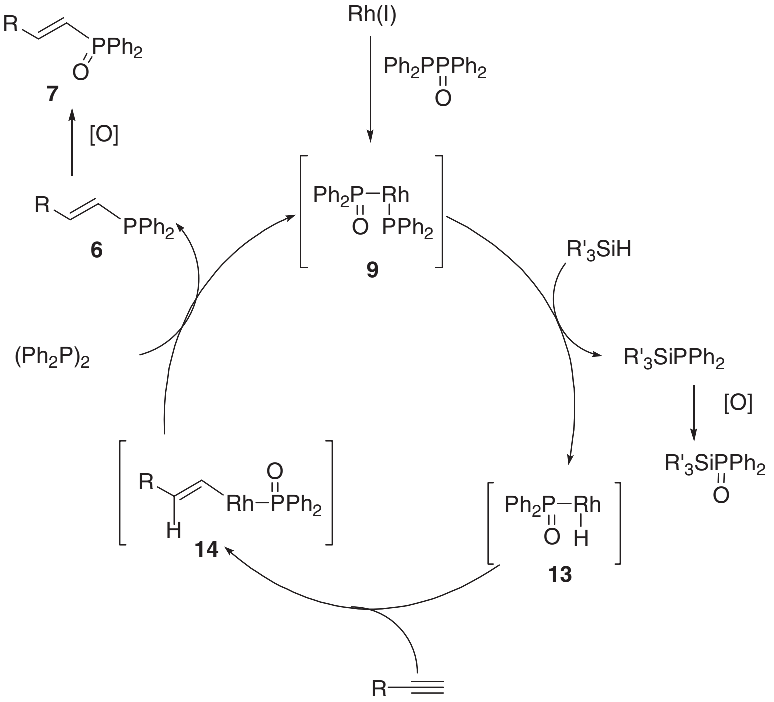
EXPERIMENTAL

General Procedure for Rhodium-Catalyzed Hydrophosphination of Alkynes Using Diphosphine-Hydrosilane Binary Systems

Condition A. $(Ph_2P)_2$ (37.0 mg, 0.1 mmol), $Ph_2PP(O)Ph_2$ (38.6 mg, 0.1 mmol), $RhCl(PPh_3)_3$ (9.3 mg, 0.01 mmol), alkyne (0.6 mmol), Et_2MeSiH (87 μl, 0.6 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 sec, and the tube was covered with aluminum foil. The mixture was heated under reflux for 18 h, and then was left under air overnight. Purification of the crude materials was performed by preparative TLC.

Condition B. $(Ph_2P)_2$ (37.0 mg, 0.1 mmol), $RhCl(PPh_3)_3$ (4.6 mg, 0.005 mmol), alkyne (0.3 mmol), Et_2MeSiH (43 μl, 0.3 mmol), and C_6D_6 (0.6 mL) were placed in a sealed Pyrex glass NMR tube. Next, oxygen (0.6 mL, 0.025 mmol) was introduced into the tube. The mixture was stirred for 30 sec, and the tube was covered with aluminum foil. The mixture was heated under reflux for 18 h, and was left under air overnight. Purification of the crude products was performed by preparative TLC.

(*E*)-1-(Diphenylphosphinyl)-1-octene (7a). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.72 (m, 10H), 6.73 (ddt, $J = 6.5, 16.9$, $J_{HP} = 19.4$ Hz, 1H), 6.22 (dd, $J = 17.0$, $J_{HP} = 24.7$ Hz, 1H), 2.30 (q, 2H), 1.28–1.50 (m, 8H), 0.86 (t, 3H); ^{13}C NMR (100



Scheme 6

MHz, $CDCl_3$) δ 153.0, 133.2 ($J_{CP} = 104.5$ Hz), 131.6 ($J_{CP} = 2.5$ Hz), 131.3 ($J_{CP} = 9.9$ Hz), 128.5 ($J_{CP} = 12.3$ Hz), 121.5 ($J_{CP} = 102.8$ Hz), 34.5 ($J_{CP} = 16.5$ Hz), 31.5, 28.8, 27.8, 22.5, 14.0; ^{31}P NMR (200 MHz, $CDCl_3$) δ 24.2.

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