[6] a) R. E. Pincock, K. R. Wilson, T. E. Kiovsky, *J. Am. Chem. Soc.* **1967**, *89*, 6890 – 6897; b) R. E. Pincock, M.-M. Tong, K. R. Wilson, *J. Am. Chem. Soc.* **1971**, *93*, 1669 – 1672; c) R. E. Pincock, K. R. Wilson, *J. Am. Chem. Soc.* **1971**, *93*, 1291 – 1292; d) D. B. Pendergrass, Jr., D. Y. Curtin, I. C. Paul, *J. Am. Chem. Soc.* **1972**, *94*, 8722 – 8730; e) D. B. Pendergrass, Jr., I. C. Paul, D. Y. Curtin, *J. Am. Chem. Soc.* **1972**, *94*, 8730 – 8737; f) T. W. Lewis, I. C. Paul, D. Y. Curtin, *Acta Crystallogr. Sect. B* **1980**, *36*, 70 – 77; g) B. J. Mann, E. N. Duesler, I. C. Paul, D. Y. Curtin, *J. Chem. Soc. Perkin Trans. 2* **1981**, 1577 – 1582; h) B. J. Mann, I. C. Paul, D. Y. Curtin, *J. Chem. Soc. Perkin Trans. 2* **1981**, 1583 – 1590; i) G. R. Desiraju, *J. Chem. Soc. Perkin Trans. 2* **1983**, 1025 – 1030; j) Q.-C. Yang, M. F. Richardson, J. D. Dunitz, *J. Am. Chem. Soc.* **1985**, *107*, 5535 – 5537; k) J. H. Matthews, I. C. Paul, D. Y. Curtin, *J. Chem. Soc. Perkin Trans. 2* **1991**, 113 – 118; l) N. Tokitoh, I. El-Tantawy El-Sayed, R. Okazaki, *Chem. Lett.* **1999**, 129 – 130; m) F. Toda, *Eur. J. Org. Chem.* **2000**, 1377 – 1386; n) S. Khatib, S. Tal, O. Godsi, U. Peskin, Y. Eichen, *Tetrahedron* **2000**, *56*, 6753 – 6771; o) E. Handelsman-Benory, M. Botoshansky, M. Greenberg, V. Shteiman, M. Kaftory, *Tetrahedron* **2000**, *56*, 6887 – 6897.

[7] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149632 (*cis*-**1a**) and CCDC-149633 (*trans*-**1a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

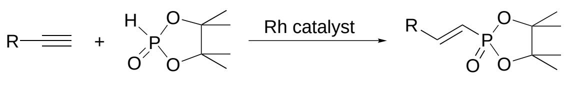
[8] *Enantiomers, Racemates and Resolutions* (Eds.: J. Jacques, A. Collet, S. H. Wilen), Wiley, New York, **1981**, pp. 104 – 131.

[9] A solid-state polymorphic transformation of racemic 1,1′-binaphthyl with spontaneous appearance of optical activity has been described. See ref. [6c]. See also: R. B. Kress, E. N. Duesler, M. C. Etter, I. C. Paul, D. Y. Curtin, *J. Am. Chem. Soc.* **1980**, *102*, 7709 – 7714. However, half-life for racemization of 1,1′-binaphthyl in solution is only about 2.5 h at 20 °C.

Rhodium-Catalyzed Hydrophosphorylation of Terminal Alkynes Leading to Highly Selective Formation of (*E*)-Alkenylphosphonates: Complete Reversal of Regioselectivity to the Palladium-Catalyzed Counterpart[**]

Chang-Qiu Zhao, Li-Biao Han,* Midori Goto, and Masato Tanaka*

Transition metal catalyzed addition reactions of heteroatom compounds across unsaturated carbon – carbon linkages are emerging rapidly as some of the most attractive, versatile, and clean methods for constructing carbon – heteroatom bonds.[1] However, similar methodologies for phosphorus compounds, which play an important role in our daily life, are limited.[1f] All of the successful metal-catalyzed additions of P^V compounds so far reported have been conducted by employing palladium catalysts, usually at elevated temperatures.[1f] Taking advantage of the exceptionally high reactivity of the five-membered cyclic hydrogen phosphonate **1**,[2] we found the first successful rhodium-catalyzed hydrophosphorylation of alkynes, which affords high yields of the corresponding (*E*)-alkenylphosphonates **2** with excellent regio- and stereoselectivities [Eq. (1)]. The reaction readily takes place even at room temperature with a complete regiochemical reversal to its palladium-catalyzed counterpart.[3] Alkenylphosphonates, which are not readily accessible by conventional methods, are key intermediates for the preparation of the commercial antibacterial agent Fosfomycin and analogues.[4] The synthetic and biological utilities of alkenylphosphonates are also well documented.[5]



1 **2** (1)

A mixture of **1** and one equivalent of phenylacetylene in toluene was stirred in the presence of $[RhCl(PPh_3)_3]$ (3 mol %) at room temperature for 2 h to give a clear yellow solution, in which the corresponding product 2-phenyl-1-ethenylphosphonate (**2a**) was formed exclusively in 31 % yield. Its yield increased to 43 % after 24 h, but further extension to 48 h resulted in only a marginal increase. However, upon heating at 80 °C, the same mixture resumed the reaction to give a quantitative yield of **2a** after 1 h.

The solvent employed significantly influenced the progress of the reaction. In THF, the reaction kept proceeding smoothly, albeit slowly, to reach 97 % yield after 48 h at room temperature. When dichloromethane, acetonitrile, and in particular, acetone were used as the solvents, great enhancement of the reaction rate was realized. Hydrophosphorylation in acetone was complete after a few hours at room temperature and gave the adduct quantitatively.

Wilkinson-type complexes $[RhX(PPh_3)_3]$ exhibited high catalytic activity. Other PPh_3-ligated Rh^I complexes such as $[RhCl(CO)(PPh_3)_2]$ also formed **2a** in moderate yields at elevated temperatures. However, the phosphane-free rhodium complexes $[\{Rh(cod)Cl\}_2]$ (cod = 1,5-cyclooctadiene) and $[\{Rh(CH_2{=}CH_2)_2Cl\}_2]$ were inactive. The cationic rhodium complex $[\{Rh(cod)_2\}]^+(OTf)^-$ ($Tf = CF_3SO_2$), used either alone or in combination with PPh_3, also did not show catalytic activity.

The rhodium-catalyzed hydrophosphorylation proved generally applicable to a variety of alkynes for synthesizing alkenylphosphonates at room temperature (Table 1).[5, 6] Thus, the $[RhBr(PPh_3)_3]$-catalyzed reaction of unsubstituted acetylene (commercial acetylene gas from a cylinder was used without purification) efficiently proceeded in acetone to form the corresponding vinylphosphonate in a high yield. Substituted terminal alkynes, both aliphatic and aromatic, reacted as efficiently to afford *trans* adducts by the regioselective attack of the phosphorus center on the terminal carbon atom of the

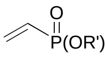
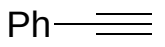
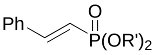
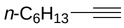
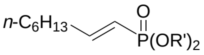
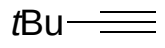
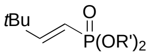
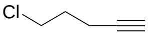
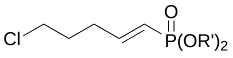
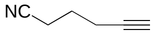
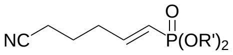
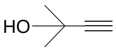
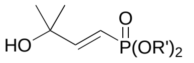
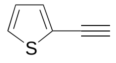
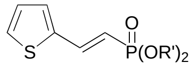
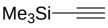
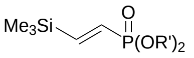
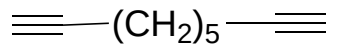
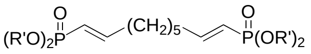
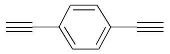
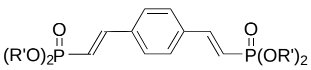
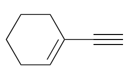
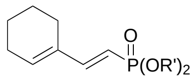
---

[*] Dr. L.-B. Han, Prof. Dr. M. Tanaka, Dr. C.-Q. Zhao, Dr. M. Goto
National Institute of Materials and Chemical Research
Tsukuba, Ibaraki 305-8565 (Japan)
Fax: (+81)298-61-4474
E-mail: han@nimc.go.jp
mtanaka@home.nimc.go.jp

[**] We are grateful to the Japan Science and Technology Corporation (JST) for financial support through the CREST (Core Research for Evolutional Science and Technology) program and for a postdoctoral fellowship to C.-Q.Z.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

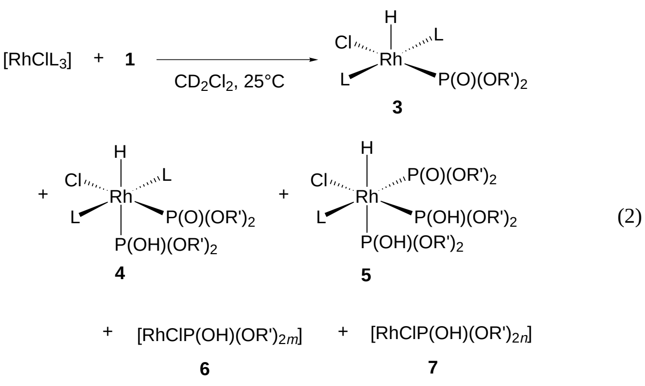
Table 1. Hydrophosphorylation of alkynes.[a]

Alkyne	Adduct[b]	Yield [%][c]
		81[d]
		93 (91)
		95 (93)
		79 (92)
		89 (96)
		95 (91)
		82 (86)
		46 (75)
		76 (98)
		93 (89)
		97 (87)
		92 (81)

[a] Run without optimization. Conditions A: an equimolar mixture of **1** and an alkyne in acetone (ca. 1 M), 1–2 mol% [$RhBr(PPh_3)_3$], 25 °C, 20 h. Conditions B: an equimolar mixture of **1** and an alkyne in toluene (0.5–1 M), 1–2 mol% [$RhCl(PPh_3)_3$], 100–110 °C, 2–6 h. ^{31}P NMR spectroscopy revealed >98% selectivity in each reaction. [b] $(OR')_2 = OCMe_2CMe_2O$. [c] Yield obtained under conditions A after isolation by column chromatography on silica gel. The yield in parentheses was obtained under conditions B. [d] Performed under 1 atm acetylene gas.

triple bond. Functional groups such as chloro, cyano, hydroxy, thienyl, and silyl all tolerated the reaction conditions. 1-Ethynylcyclohexene selectively reacted at the triple bond to give the linear adduct; this proves the inertness of the internal olefinic bond.[7]

Mechanistic studies revealed that oxidative addition of the H–P bond in **1** readily takes place.[8] Thus, when [$RhCl(PPh_3)_3$] was treated at room temperature with **1** (3 equiv) in CD_2Cl_2, new signals attributable to Rh–H (m, $\delta = -8.0$ to -10.1, -16.2 to -16.8) and Rh–P(O) ($\delta = 96$ to 135) species emerged in the ^1H and ^{31}P NMR spectra, respectively [Eq. (2)]. The starting rhodium complex disappeared after 22 h, and a yellow-orange solution formed. The ^{31}P NMR spectrum suggested the formation of three P(O)-bound Rh^{III}–PPh_3 complexes **3**–**5**. The **3**/**4**/**5** ratio varied with the reaction time, and the change from the value of 1/2.5/0.31 after 3.5 h to 1/4.82/3.36 after 22 h is indicative of an equilibrium among these species (see below). The PPh_3-free rhodium complex **6**[9] was also generated in a small amount. Since the ratio of these species depends on the conditions, elaboration of the procedure allowed successful isolation of **3**–**5**.[10] First, overnight stirring of a purple-colored suspension of [$RhCl(PPh_3)_3$] and **1** (Rh/**1** = 1/14) in acetone at room temperature resulted in a gradual color change to give a white suspension. Routine workup afforded **5** as a white solid (82% yield). Second, another reaction at room temperature starting with [$\{Rh(cod)Cl\}_2$], PPh_3, and **1** (Rh/PPh_3/**1** = 1/2/2) in dichloromethane generated **4** predominantly. Addition of pentane and refrigeration gave pale yellow crystalline **4** in 35% yield. Finally, heating a dilute solution of **4** in CH_2Cl_2 at 60 °C for 90 min resulted in dissociation of **1** to generate **3**,[11, 12] which could be readily isolated as orange solid in 52% yield.



(2)

$L = PPh_3$, $(OR')_2 = OCMe_2CMe_2O$

X-ray crystallography of **4** unambiguously confirmed the distorted octahedral structure (Figure 1).[13] The short O3–O6 distance and the P2–O3 and P4–O6 distances are between the values reported for single and double bonds and suggest strong hydrogen bonds involving the two oxygen atoms.[14, 15] The P4–Rh bond is longer than the P2–Rh bond, presumably due to the strong *trans* influence of the hydrido ligand as compared with Cl.[16]

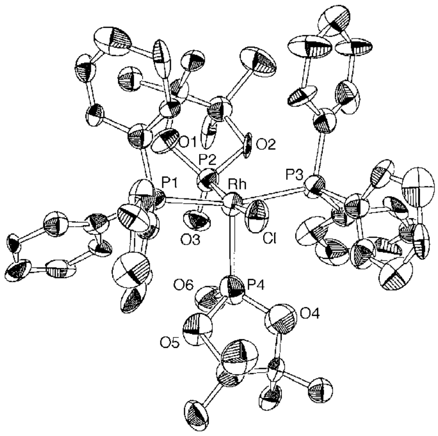


Figure 1. Molecular structure of complex **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–Rh 2.38(1), P2–Rh 2.262(9), P4–Rh 2.467(10), Cl–Rh 2.436(8), P2–O3 1.56(2), P4–O6 1.59(2), O3–O6 2.45; Cl-Rh-P2 170.5(3); P1-Rh-P3 160.9(3), Cl-Rh-P4 95.7(3), Cl-Rh-P1 85.2(3), Cl-Rh-P3 86.0(3), P1-Rh-P2 92.6(4), P1-Rh-P4 99.2(4), P2-Rh-P3 93.3(4), P3-Rh-P4 98.5(4), O1-P2-O2 96(1), O4-P4-O5 95(1).

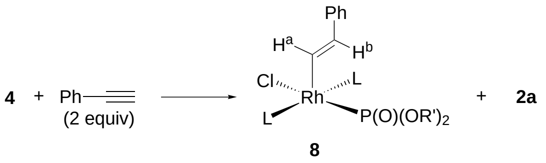
Interestingly, the distribution of rhodium species **3**–**7** generated is significantly dependent on the **1**/Rh ratio and the solvent.[17] The distribution observed in the absence of the acetylene substrate (Table 2)[18] indicates that a large excess of **1** suppresses coordination of PPh_3 and thus enhances the generation of PPh_3-free complexes **6** and **7**, which are inactive towards hydrophosphorylation. Note, however, that a considerable contribution of **5** is maintained even at higher **1**/Rh ratios (e.g., 17/1) in acetone but not in toluene. These results presumably are associated with the solvent effect observed in the catalytic reactions (see above).

Table 2. Distribution of rhodium species **3**–**7** in the reaction of $[RhCl(PPh_3)_3]$ with **1**.

$$\mathbf{1} + [RhCl(PPh_3)_3] \xrightarrow{\text{RT, 24 h}} \mathbf{3}+\mathbf{4}+\mathbf{5}+\mathbf{6}+\mathbf{7}$$

1/$[RhCl(PPh_3)_3]$	Solvent	**3**/**4**/**5**/**6**/**7**
3/1	acetone	10/57/16/17/0
17/1	acetone	0/0/40/60/0
3/1	toluene	15/28/47/10/0
17/1	toluene	0/0/7/36/57

The H–Rh bond in complex **4** was found to add across an acetylenic bond (hydrorhodation). For instance, when complex **4** (20.2 μmol) was treated with phenylacetylene (2 equiv) in $[D_2]$dichloromethane at room temperature, **4** was nearly completely consumed and about 14 μmol of alkenylrhodium complex **8**[19] and 27 μmol of **2a** (by ^1H NMR spectroscopy) were formed after 20 h [Eq. (3)]. Subsequent heating of the mixture at 50 °C for 4 h resulted in disappearance of **4** and **8** to give **2a** quantitatively. A similar but somewhat higher rate of consumption of **4** was observed in acetone. In toluene, most of **4** (ca. 93 %) remained unconverted, even after one day. Thus, the hydrorhodation process is also very much solvent-dependent, whereby acetone is far more favorable than toluene, which also conforms to the finding in the catalytic reactions.

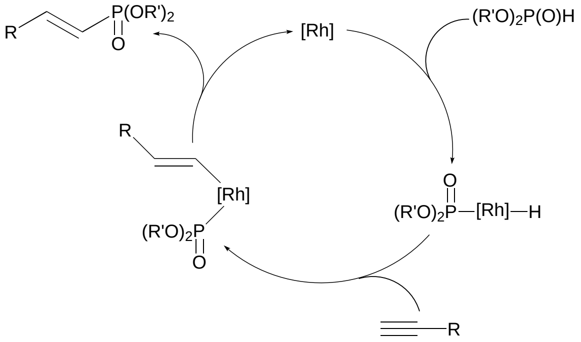


(3)

L = PPh_3, $(OR')_2 = OCMe_2CMe_2O$

Preliminary experiments revealed that **3** and **5** also react with phenylacetylene to form **8** and **2a**. On the basis of a competitive reaction with a mixture of **3**, **4**, and **5**, complex **5** appears to be most reactive.[20] In contrast, PPh_3-free complexes **6** and **7**, which could be generated in situ by addition of **1** to $[\{RhCl(cod)\}_2]$ (**1**/Rh = 3/1) in CD_2Cl_2,[8b] did not add to phenylacetylene (25 °C, 23 h).

Even though we have not studied the details of the final product-forming step, we are now able to safely propose a mechanism that accommodates the foregoing observations (Scheme 1). The significant solvent effect in the catalysis is most likely associated with the distribution and reactivity of the H–Rh species.



Scheme 1. Proposed catalytic cycle for the hydrophosphorylation of alkynes.

Experimental Section

Representative catalytic addition of **1**: Phenylacetylene (204 mg, 2.0 mmol), **1** (328 mg, 2.0 mmol), and $[RhBr(PPh_3)_3]$ (38 mg, 2 mol%) were dissolved in 3 mL of degassed dry acetone under nitrogen. The mixture was stirred at room temperature for 20 h and evaporated in vacuo to leave a pale yellow solid, which was purified by column chromatography (SiO_2, hexane/*i*PrOH 10/1) to give **2a** as white solid in 93 % yield (495 mg).

Selected data for **3**: ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.77-7.83$ (m, 12 H), 7.30–7.39 (m, 18 H), 0.82 (s, 6 H), 0.81 (s, 6 H), −16.5 (ddt, 1 H, $J = 7.3, 11.0, 18.3$ Hz); ^{31}P NMR (121.5 MHz): $\delta = 126.7$ (dt, $J(P,P) = 30.8$, $J(P,Rh) = 197.8$ Hz), 27.5 (dd, $J(P,P) = 30.8$, $J(P,Rh) = 96.7$ Hz).

Selected data for **4**: ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 16.52$ (br s, 1 H), 7.74–7.80 (m, 12 H), 7.27–7.39 (m, 18 H), 1.38 (s, 6 H), 0.76 (s, 6 H), 0.73 (s, 6 H), 0.24 (s, 6 H), −8.58 (double quintet-like, 1 H, $J(P,H) = 275.9$ Hz); ^{31}P NMR (121.5 MHz): $\delta = 132.6$ (ddt, $J(P,P) = 21.0, 37.4$, $J(P,Rh) = 91.6$ Hz), 99.5 (ddt, $J(P,P) = 21.0, 27.6$, $J(P,Rh) = 162.2$ Hz), 36.2 (ddd, $J(P,P) = 27.6, 37.4$, $J(P,Rh) = 98.4$ Hz).

Selected data for **5**: ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.28-7.68$ (m, 15 H), 3.58 (br s, 2 H), 1.52 (s, 3 H), 1.50 (s, 3 H), 1.49 (s, 6 H), 1.38 (s, 6 H), 1.16 (s, 3 H), 1.11 (s, 6 H), 1.06 (s, 3 H), 0.89 (s, 3 H), 0.24 (s, 3 H), −8.73 (ddq, 1 H, $J = 4.5, 10.1, 272.3$ Hz); ^{31}P NMR (CD_2Cl_2): $\delta = 130.7$ (dddd, $J(P,P) = 21.7, 38.2, 49.6$, $J(P,Rh) = 109.6$ Hz), 124.2 (dddd, $J(P,P) = 35.0, 49.6, 515.7$, $J(P,Rh) = 151.1$ Hz), 97.3 (dddd, $J(P,P) = 21.7, 27.0, 35.0$, $J(P,Rh) = 162.7$ Hz), 36.1 (dddd, $J(P,P) = 27.0, 38.2, 515.7$, $J(P,Rh) = 92.8$ Hz).

Received: October 30, 2000
Revised: February 14, 2001 [Z16023]

---

[1] Recent reviews: a) K. A. Horn, *Chem. Rev.* **1995**, *95*, 1317; b) H. K. Sharma, K. H. Pannell, *Chem. Rev.* **1995**, *95*, 1351; c) K. Burgess, M. J. Ohlmeyer, *Chem. Rev.* **1991**, *91*, 1179; d) I. Beletskaya, A. Pelter, *Tetrahedron* **1997**, *53*, 4957; e) I. Beletskaya, C. Moberg, *Chem. Rev.* **1999**, *99*, 3435; f) L.-B. Han, M. Tanaka, *Chem. Commun.* **1999**, 395.

[2] Acyclic hydrogen phosphonates such as $(MeO)_2P(O)H$ were unreactive under similar reaction conditions. For the exceptionally high reactivity of **1**, see L.-B. Han, F. Mirzaei, C.-Q. Zhao, M. Tanaka, *J. Am. Chem. Soc.* **2000**, *122*, 5407.

[3] Palladium-catalyzed hydrophosphorylation of terminal acetylenes forms the corresponding branched adducts predominantly: L.-B. Han, M. Tanaka, *J. Am. Chem. Soc.* **1996**, *118*, 1571, and unpublished results.

[4] S. C. Fields, *Tetrahedron* **1999**, *55*, 12237; B. Iorga, F. Eymery, P. Savignac, *Synthesis* **1999**, 207.

0044-8249/01/11310-1985 $ 17.50+.50/0

[5] For reviews, see T. Minami, J. Motoyoshiya, *Synthesis* **1992**, 333; R. Engel, *Chem. Rev.* **1977**, *77*, 349; selected recent examples: M. R. Harnden, A. Parkin, M. J. Parratt, R. M. Perkins, *J. Med. Chem.* **1993**, *36*, 1345; R. R. Breaker, G. R. Gough, P. T. Gilham, *Biochemistry* **1993**, *32*, 9125; M. J. Burk, T. A. Stammers, J. A. Straub, *Org. Lett.* **1999**, *1*, 387; J.-C. Henry, D. Lavergne, V. Ratovelomanana-Vidal, J.-P. Genêt, I. P. Beletskaya, T. M. Dolgina, *Tetrahedron Lett.* **1998**, *39*, 3473; T. Hayashi, T. Senda, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc.* **1999**, *121*, 11591; A. A. Thomas, K. B. Sharpless, *J. Org. Chem.* **1999**, *64*, 8379.

[6] The hydrolysis of the alkenylphosphonates was easy. For instance, heating a mixture of **2a**, 1 mL of 37 % HCl, and 1 mL of 1,4-dioxane at 98 °C for 2 h and removal of volatiles left a crude hydrolysis product nearly quantitatively. Recrystallization from acetone/chloroform gave an analytically pure white material, m.p. 147–149 °C (Lit.: 142–142.5 °C; C. E. Griffin, T. D. Mitchell, *J. Org. Chem.* **1965**, *30*, 1935).

[7] It is interesting to compare the regioselectivity with the palladium-catalyzed addition of H–P(O)Ph$_2$ to terminal alkynes. The reaction generally forms linear adducts. However, 1-ethynylcyclohexene was an exceptional alkyne, which did not conform to the general regiochemical trend and gave the branched adduct; see: L.-B. Han, N. Choi, M. Tanaka, *Organometallics* **1996**, *15*, 3259.

[8] Hydrogen phosphonates exist in two tautomeric forms, HP(O)(OR)$_2$ and P(OR)$_2$(OH), the former being thermodynamically more favored under ambient conditions. They coordinate, like tertiary phosphanes, to transition metals to form complexes, which have been used as catalysts in organic reactions. a) D. M. Roundhill, R. P. Sperline, W. B. Beaulieu, *Coord. Chem. Rev.* **1978**, *26*, 263. Although not known for [RhCl(PPh$_3$)$_3$], oxidative additions of H–P bonds to a few rhodium complexes have appeared in the literature. b) M. A. Bennett, T. R. B. Mitchell, *J. Organomet. Chem.* **1985**, *295*, 223; c) A. Varshney, G. M. Gray, *J. Organomet. Chem.* **1990**, *391*, 415.

[9] Although it could not be detected in this particular reaction, another PPh$_3$-free rhodium complex **7**, displaying ^{31}P NMR signals at $\delta = 126$–128, was also formed when a large excess of **1** was used. Pure **6** and **7** have not been isolated yet. However, as confirmed by ^{31}P NMR spectroscopy, a mixture of these complexes could be generated when [{RhCl(cod)}$_2$] was mixed with **1** (see ref. [8b]).

[10] The P$^{\mathrm{V}}$(O)(OR′)$_2$ and P$^{\mathrm{III}}$(OH)(OR′)$_2$ ligands in complexes **4** and **5** are not distinguishable. They are linked together by hydrogen bonds such as $\mathrm{Rh\{P(\overline{O)(OR)_2\}\{P(OH})(OR)_2\}}$, as suggested by X-ray diffraction (see below). In this context, complex **5** is envisioned on the basis of the ^{31}P NMR spectrum to adopt a pseudo-*fac* configuration. See Supporting Information for the detailed NMR data.

[11] Interestingly, the conversion of **4** to **3** in toluene was much slower than in CH$_2$Cl$_2$; **4** was still present in the solution even after 4 h of heating at 60 °C (**3**/**4** ≈ 2.8/1).

[12] Allowing the solution to stand at room temperature overnight regenerated **4** to a small extent (**4**/**3** ≈ 8/92).

[13] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150935. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[14] A. J. Carty, S. E. Jacobson, R. T. Simpson, N. J. Taylor, *J. Am. Chem. Soc.* **1975**, *97*, 7254, and references therein. Similar hydrogen bonding was also observed in other related metal complexes, see refs. [7] and [8].

[15] D. E. C. Corbridge, *Top. Phosphorus Chem.* **1966**, *3*, 57.

[16] T. G. Appleton, H. C. Clark, L. E. Manzer, *Coord. Chem. Rev.* **1973**, *10*, 335.

[17] The equilibrium between **3**, **4**, and **5** was confirmed separately. Mixing **5** (7.3 mg) with PPh$_3$ (2 equiv) in CD$_2$Cl$_2$ (0.5 mL) at room temperature generated a mixture of all three species (**3**/**4**/**5** = 1/0.38/0.29) after 20 h.

[18] Since the detailed structures of **6** and **7** are not known, the true amounts of these species in the mixture cannot be evaluated. The ratio given in Table 2 is a provisional value, calculated on the basis of an arbitrary assumption that only one molecule of **1** ligates Rh.

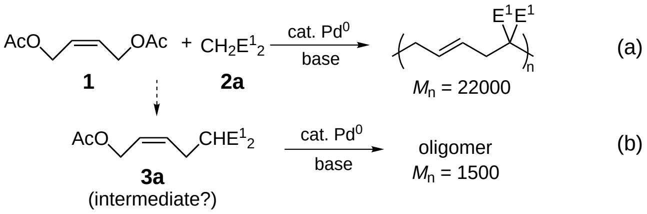
[19] Attempted isolation of **8** failed, but the structure is evidenced by its NMR spectra (CD$_2$Cl$_2$). The ^{1}H NMR spectrum displays a signal for olefinic proton H$^{\mathrm{a}}$ at $\delta = 4.63$ (dd, $J = 16.6$, J(H,Rh) = 4.6 Hz). The ^{1}H–^{1}H COSY technique confirms that another olefinic proton H$^{\mathrm{b}}$ is hidden at $\delta \sim 7.4$ in the massif of phenyl proton signals. The large coupling constant indicates an *E* configuration of the double bond. The ^{31}P NMR spectrum also conforms to the structure in showing a dd signal at $\delta = 29.0$ (J(P,P) = 25.0, J(P,Rh) = 112.0 Hz, PPh$_3$) and a dt signal at $\delta = 56.3$ (J(P,P) = 25.0, J(P,Rh) = 184 Hz, P(O)).

[20] A mixture of these complexes in CD$_2$Cl$_2$ (molar ratio **3**/**4**/**5** = 1.0/1.3/1.7), generated by the reaction of [RhCl(PPh$_3$)$_3$] with an excess of **1** (6 equiv), was allowed to react with phenylacetylene (10 equiv) at room temperature. Complex **5** was completely consumed in 26 min, and **8** and **2a** were observed (molar ratio of **3**/**4**/**5**/**8**/**2a** = 1.0/1.3/0/3.2/8.8).

Mechanistic Rationale of a Palladium-Catalyzed Allylic Substitution Polymerization—Carbon–Carbon Bond-Forming Polycondensation out of Stoichiometric Control by Cascade Bidirectional Allylation[**]

Nobuyoshi Nomura, Ko Tsurugi, and Masahiko Okada[*]

Palladium-catalyzed allylic alkylation has been the subject of intensive research in carbon–carbon bond-forming processes since its discovery,[1] and it was recently extended to an allylic substitution polymerization[2] (Scheme 1 a, E^1 = CO$_2$Et) in which the use of bis(diphenylphosphanyl)butane (dppb) was indispensable. In a survey of recent studies on palladium-catalyzed allylation reactions,[1b–f] π-allylpalladium(II) complex intermediates were extensively



Scheme 1. Palladium-catalyzed allylic substitution polymerization (E^1 = CO$_2$Et).

---

[*] Prof. M. Okada
Research Institute for Biological Functions
Chubu University
Kasugai, Aichi 487-8501 (Japan)
Fax: (+81) 568-52-6594
E-mail: okada-m@isc.chubu.ac.jp

Dr. N. Nomura, K. Tsurugi
Laboratory of Polymer Chemistry, Graduate School of Bioagricultural Sciences
Nagoya University
Nagoya 464-8601 (Japan)

[**] This work was supported by a Grant-in-Aid for Scientific Research (No. 12750778) from the Ministry of Education, Science, Sports, and Culture, Japan. A fellowship to K.T. from the Japan Society for the Promotion of Science for Young Scientists is gratefully acknowledged. In this contribution, the term “out of stoichiometric control” means that when reagent **2a** is used in excess, the polymerization is under stoichiometric control, whereas when **1** is in excess, the polymerization is not under stoichiometric control.