JOC Article

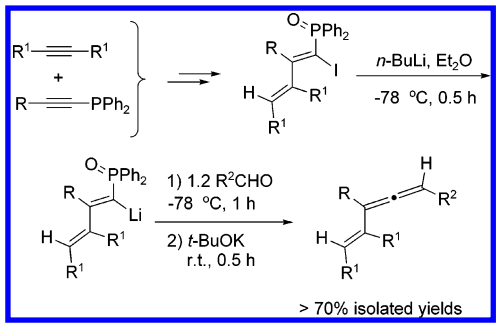
Preparation of Vinyl Allenes from 1-Lithio-1,3-dienyl Phosphine Oxides and Aldehydes by the Wittig−Horner Reaction

Zhenfeng Xi,*,† Wen-Xiong Zhang,† Zhiyi Song,† Weixin Zheng,† Fanzhi Kong,† and Tamotsu Takahashi*,‡

Peking University-Hokkaido University Joint Lab, College of Chemistry, Peking University, Beijing 100871, China, and Catalysis Research Center, Graduate School of Pharmaceutical Sciences, Hokkaido University and SORST, Japan Science and Technology Agency (JST), Kita-Ku, Sapporo 001-0021, Japan

zfxi@pku.edu.cn

Received June 11, 2005



Vinyl allenes were prepared in high yields by the Wittig−Horner reaction of 1-lithio-1,3-dienyl phosphine oxides with aldehydes. 1-Lithio-1,3-dienyl phosphine oxides were generated in situ from lithiation of 1-iodo-1,3-dienyl phosphine oxides, which were obtained by iodination of α-phosphinozirconacyclopentadienes. As a whole, a vinyl allene is synthesized from two different alkynes and one aldehyde.

Introduction

Development of synthetic methods for vinyl allenes has attracted much attention,[1−15] since vinyl allenes, which bear a cumulenic and conjugated vinyl functionality, are useful and unique precursors or intermediates in organic synthesis.[1−15] Several useful methods have been reported, mainly based on reactions of organometallic reagents with suitably functionalized propargyl derivatives.[2−14]

We have recently investigated reactions of 1-lithio-1,3-dienes **1** with unsaturated substrates.[16] Treatment of 1-lithio-1,3-dienes **1** (X = alkyl, aryl or $SiMe_3$) with aldehydes or ketones afforded stereodefined dienols or

† Peking University.
‡ Hokkaido University.

(1) (a) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes, Cumulenes, A Laboratory Manual*; Elsevier: Amsterdam, 1981. (b) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; John Wiley and Sons: New York, 1984. (c) Bruneau, C.; Dixneuf, P. H. Allenes and Cumulenes. In *Comprehensive Organic Functional Group Transformations*; Elsevier: Oxford, 1995; Vol. 1, p 966 and references therein. (d) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31. (e) Murakami, M.; Itami, K.; Ubukata, M.; Tsuji, I.; Ito, Y. *J. Synth. Org. Chem. Jpn*. **1998**, *56*, 406. (f) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 3590. (g) Huang, W. W.; Tidwell, T. T. *Synthesis* **2000**, 457. (h) Hoffmann-Roder, A.; Krauce, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 2933. (i) Sydnes, L. K. *Chem. Rev.* **2003**, *103*, 1133. (j) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701. (k) Hoffmann-Roder, A.; Norbert, K. *Tetrahedron* **2004**, *60*, 11671. (l) Ma, S. *Eur. J. Org. Chem*. **2004**, 1175. (m) Ma, S. *Chem. Rev*. **2005**, *105*, 2829.

(2) (a) Lopez, S.; Rey, J. G.; Rodríguez, J.; de Lera, A. R. *Tetrahedron Lett*. **1995**, *36*, 4669. (b) Lopez, S.; Rodríguez, J.; Rey, J. G.; de Lera, A. R. *J. Am. Chem. Soc.* **1996**, *118*, 1881. (c) de Lera, A. R.; Torrado, A.; Rey, J. G.; Lopez, S. *Tetrahedron Lett*. **1997**, *38*, 7421. (d) de Lera, A. R.; Rey, J. G.; Hrovat, D.; Iglesias, B.; Lopez, S. *Tetrahedron Lett.* **1997**, *38*, 7425. (e) Iglesias, B.; de Lera, A. R.; Rodriguez-Otero, J.; Lopez, S. *Chem. Eur. J*. **2000**, *6*, 4021. (f) Souta, J. A.; Lopez, S.; Faza, O. N.; Alvarez, R.; de Lera, A. R. *Org. Lett*. **2005**, *7*, 1565.

(3) (a) Regas, D.; Afonso, M. M.; Galindo, A.; Palenzuela, J. A. *Tetrahedron Lett.* **2000**, *41*, 6781. (b) Regas, D.; Ruiz, J. M.; Afonso, M. M.; Galindo, A.; Palenzuela, J. A. *Tetrahedron Lett.* **2003**, *44*, 8471. (c) Regas, D.; Afonso, M. M.; Rodriguez, M. L.; Palenzula, J. A. *J. Org. Chem*. **2003**, *68*, 7845. (d) Regas, D.; Afonso, M. M.; Palenzuela, J. A. *Synthesis* **2004**, 757.

(4) (a) Murakami, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl*. **1996**, *34*, 2691. (b) Murakami, M.; Itami, K.; Ito, Y. *Synlett* **1999**, 951. (c) Murakami, M.; Itami, K.; Ito, Y. *Organometallics* **1999**, *18*, 1326. (d) Murakami, M.; Ashida, S.; Matsuda, T. *J. Am. Chem. Soc.* **2004**, *126*, 10838.

(5) (a) Okamoto, S.; Takayama, Y.; Gao, Y.; Sato, F. *Synthesis* **2000**, 975. (b) Delas, C.; Urabe, H.; Sato, F. *J. Am. Chem. Soc*. **2001**, *123*, 7937. (c) Tanaka, R.; Sasaki, M.; Sato, F.; Urabe, H. *Tetrahedron Lett*. **2005**, *46*, 329.

(6) Descoins, C.; Henrick, C. A.; Siddall, J. B. *Tetrahedron Lett.* **1972**, 3777.

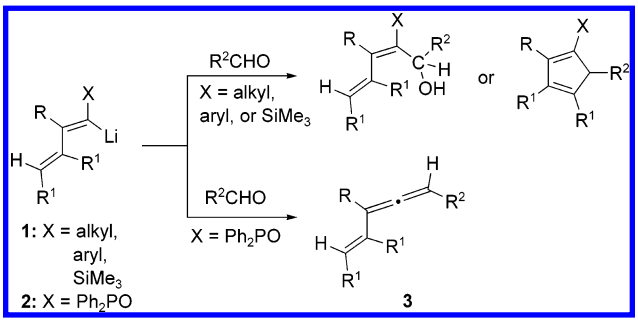
(7) (a) Spino, C.; Thibault, C.; Gingras, S. *J. Org. Chem*. **1998**, *63*, 5283. (b) Spino, C.; Frechette, S. *Tetrahedron Lett*. **2000**, *41*, 8033.

(8) Nakamura, H.; Onagi, S.; Kamakura, T. *J. Org. Chem*. **2005**, *70*, 2357.

(9) Yoshikawa, E.; Kasahara, M.; Asao, N.; Yamamoto, Y. *Tetrahedron Lett*. **2000**, *41*, 4499.

10.1021/jo051178c CCC: $30.25
Published on Web 10/04/2005

SCHEME 1

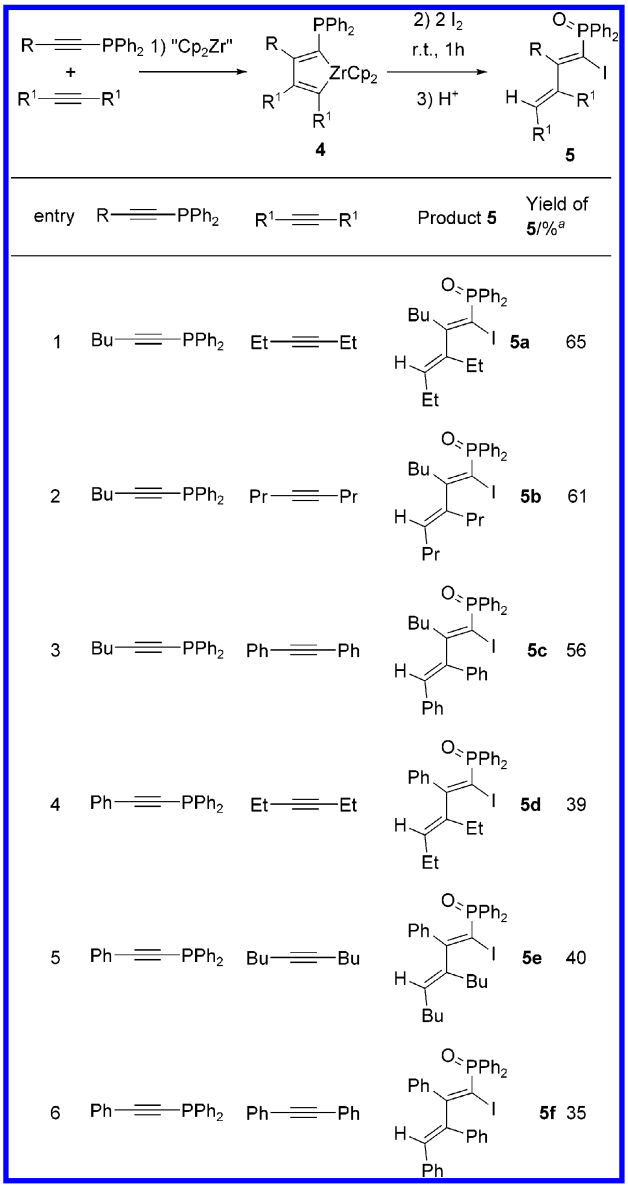


cyclopentadienes (Scheme 1).[17] However, reactions of 1-lithio-1,3-dienyl phosphine oxides **2** (X = Ph_2PO) with aldehydes afforded stereodefined vinyl allenes **3** via the Wittig−Horner reaction.[18,19] In this paper, we report the preparation of vinyl allenes by the Wittig−Horner reaction from 1-lithio-1,3-dienyl phosphine oxides **2** with aldehydes. We also report the scope and limitations of iodination reactions of α-phosphinozirconacyclopentadienes that produce the starting materials 1-iodo-1,3-dienyl phosphine oxides.[20]

Results and Discussion

Preparation of 1-Iodo-1,3-dienyl Phosphine Oxides from Iodination of α-Phosphinozirconacyclopentadienes. Cross-coupling of an alkynylphosphine with a different alkyne took place highly selectively on a low valent zirconocene to afford α-phosphinozirconacyclopentadienes **4**.[20,11] Treatment of **4** with 2 equiv of I_2 afforded 1-iodo-1,3-dienyl phosphine oxides **5** as the only product in moderate isolated yields with high selectivity (Table 1).

TABLE 1. Preparation of 1-Iodo-1,3-dienyl Phosphine Oxides from Two Different Alkynes via α-Phosphinozirconacyclopentadienes



entry	$R-\equiv-PPh_2$	$R^1-\equiv-R^1$	Product **5**	Yield of **5**/%[a]
1	Bu—≡—PPh_2	Et—≡—Et	**5a**	65
2	Bu—≡—PPh_2	Pr—≡—Pr	**5b**	61
3	Bu—≡—PPh_2	Ph—≡—Ph	**5c**	56
4	Ph—≡—PPh_2	Et—≡—Et	**5d**	39
5	Ph—≡—PPh_2	Bu—≡—Bu	**5e**	40
6	Ph—≡—PPh_2	Ph—≡—Ph	**5f**	35

[a] Isolated yields.

Similarly, one Ph_2P- or two Ph_2P-substituted diynes **6** could also be applied to the above reaction. Treatment of a THF solution of Cp_2ZrEt_2 or Cp_2ZrBu_2 with diynes **6** resulted in the formation of the α-phosphinobicyclozirconacyclopentadienes **7**. Hydrolysis with 3 N HCl afforded products **8** in more than 80% isolated yields. As in the case for iodination of the in situ generated intermediate **4**, treatment of **7a** with 2 equiv of I_2 gave the monoiodination product **9a**. The diiodo compound **10a** was formed in good isolated yield when **7a** was first treated with 2 equiv of I_2 and followed by further treatment with 1 equiv of CuCl and 1 equiv of I_2.[21]

(10) (a) Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J. P.; Dupuis, L.; Pirio, N.; Meunier, P. *Chem. Commun*. **1997**, 279. (b) Zablocka, M.; Miquel, Y.; Igau, A.; Majoral, J. P.; Skowronska, A. *Chem. Commun*. **1998**, 1177. (c) Quntar, A. A. A.; Srebnik, M. *Org. Lett*. **2004**, *6*, 4243. (d) Ben-Valid, S.; Quntar, A. A. A.; Srebnik, M. *J. Org. Chem*. **2005**, *70*, 3554.

(11) Huang, W. W.; Fang, D.; Temple, K.; Tidwell, T. T. *J. Am. Chem. Soc*. **1997**, *119*, 2832.

(12) Morwick, T. M.; Paquette, L. A. *J. Org. Chem*. **1997**, *62*, 627.

(13) (a) Koop, U.; Handke, G.; Krause, N. *Liebigs Ann*. **1996**, 1487. (b) Purpura, M.; Krause, N. *Eur. J. Org. Chem*. **1999**, 267. (c) Krause, N.; Purpura, M. *Angew. Chem., Int. Ed*. **2000**, *39*, 4355.

(14) Werner, H. *Chem. Commun*. **1997**, 903.

(15) (a) Jones, E. R. H.; Lee, H. H.; Whitting, M. C. *J. Chem. Soc*. **1960**, 341. (b) Dulcere, J. P.; Roumestant, M. L.; Gore, J. *Tetrahedron Lett*. **1972**, 4465. (c) Gore, J.; Dulcere, J. P. *J. Chem. Soc., Chem. Commun*. **1972**, 866. (d) Baudouy, R.; Gore, J. *J. Chem. Res*. **1981**, 278.

(16) (a) Chen, J.; Song, Q.; Wang, C.; Xi, Z. *J. Am. Chem. Soc*. **2002**, *124*, 6238. (b) Wang, C.; Chen, J.; Song, Q.; Li, Z.; Xi, Z. *Arkivoc* **2003**, Part ii, 155. (c) Song, Q.; Li, Z.; Chen, J.; Wang, C.; Xi, Z. *Org. Lett*. **2002**, *4*, 4627. (d) Xi, Z. *Eur. J. Org. Chem*. **2004**, 2773. (e) Wang, C.; Lu, J.; Mao, G.; Xi, Z. *J. Org. Chem*. **2005**, *70*, 5150.

(17) Fang, H.; Song, Q.; Wang, Z.; Xi, Z. *Tetrahedron Lett*. **2004**, *45*, 5159.

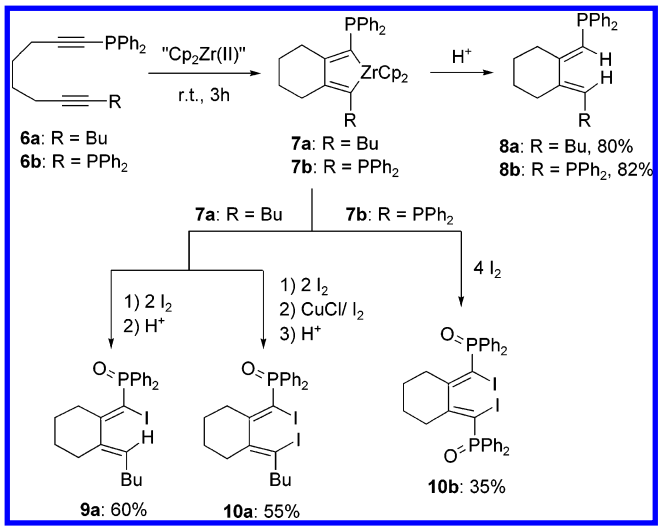
(18) (a) Pelter, A.; Smith, K.; Jones, K. D. *J. Chem. Soc., Perkin Trans. 1* **1992**, 747. (b) Reynolds, K. A.; Dopico, P. G.; Sundermann, M. J.; Hughes, K. A.; Finn, M. G. *J. Org. Chem*. **1993**, *58*, 1298. (c) Reynolds, K. A.; Dopico, P. G.; Brody, M. S.; Finn, M. G. *J. Org. Chem*. **1997**, *62*, 2564. (d) Fox, D. J.; Medlock, J. A.; Vosser, R.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2240. (e) Inoue, H.; Tsubouchi, H.; Nagaoka, Y.; Tomioka, K. *Tetrahedron* **2002**, *58*, 83. (f) Liu, B.; Wang, K. K.; Petersen, J. L. *J. Org. Chem*. **1996**, *61*, 8503. (g) Wang, K. K.; Zhang, H. R.; Petersen, J. L. *J. Org. Chem*. **1999**, *64*, 1650. (h) Huang, X.; Xiong, Z. *Chem. Commun*. **2003**, 1714. (i) Huang, X.; Xiong, Z. *Tetrahedron Lett*. **2003**, *44*, 5913.

(19) Johnson, A. W.; Kaska, W. C.; Starzewski, K. A. O.; Dixon, D. A. *Ylides and Imines of Phosphorus*; Wiley-Interscience: New York, 1993; p 314.

(20) Xi, Z.; Zhang, W.; Takahashi, T. *Tetrahedron Lett*. **2004**, *45*, 2427.

(21) Xi, C.; Huo, S.; Afifi, T. H.; Hara, R.; Takahashi, T. *Tetrahedron Lett*. **1997**, *38*, 4099.

SCHEME 2



However, when **7b** was treated with 2 equiv of I_2, it afforded a mixture of mono- and diiodide products. Treatment of **7b** with 4 equiv of I_2 afforded the diiodo compound **10b** (Scheme 2).

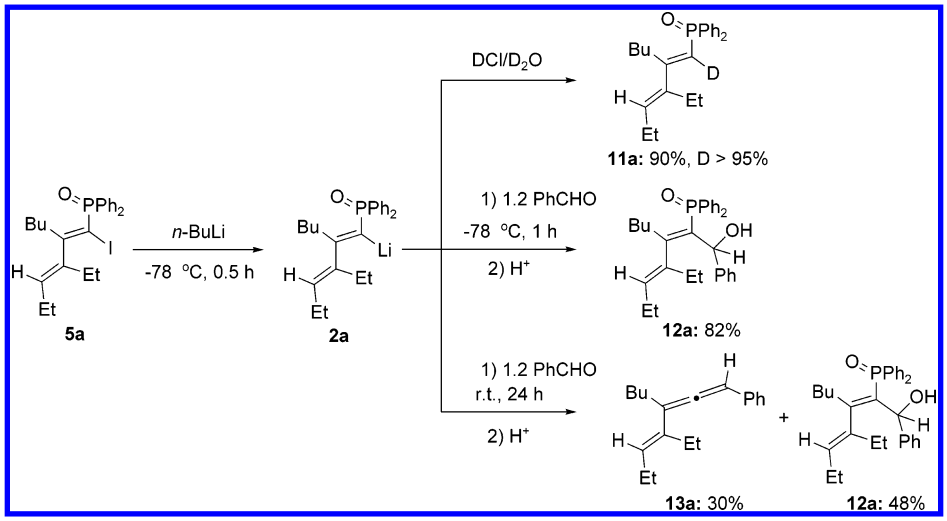
Preparation of Vinyl Allenes from 1-Lithio-1,3-dienyl Phosphine Oxides and Aldehydes. Lithiation of 1-iodo-1,3-dienes with 2 equiv of *t*-BuLi at −78 °C gave their corresponding 1-lithio-1,3-dienes in quantitative yields, as we have already reported.[16,17] Treatment of 1-lithio-1,3-dienes with aldehydes afforded dienols or cyclopentadienes depending on the nature of substituents and hydrolysis conditions.[17] Similarly, 1-lithio-1,3-dienyl phosphine oxide **2a** was prepared by treatment of 1-iodo-1,3-dienyl phosphine oxide **5a** with 1 equiv of *n*-BuLi in Et_2O at −78 °C for 0.5 h. After deuterolysis with 20% DCl in D_2O, **11a** was obtained in 99% GC yield with >95% deuterium incorporation (90% isolated yield). Reaction of **2a** with benzaldehyde at −78 °C for 1 h produced **12a** as a single product in 82% isolated yields after quenching with saturated $NaHCO_3$. When the reaction mixture of **2a** with benzaldehyde was allowed to warm to room temperature for 24 h and quenched with saturated $NaHCO_3$, in addition to **12a**, a vinyl allene **13a** was also obtained in 30% isolated yield (Scheme 3).

These results suggested dienols **12** that came from hydrolysis of intermediate lithium alkoxides **14** and vinyl allenes **13** were formed by spontaneous Wittig−Horner elimination of lithium diphenylphosphinate from **14**.[19] A proposed mechanism for the formation of **12** and **13** is given in Scheme 4. To confirm the formation of intermediate **14**, we treated the isolated alcohol **12a** with *n*-BuLi and *t*-BuOK, and the vinyl allene **13a** was formed in a quantitative yield.

To obtain the vinyl allenes **13** selectively and in high yields, we applied the model reaction of **2a** with benzaldehyde to optimize elimination conditions of lithium diphenylphosphinate from **14**. These results are summarized in Table 2. In the absence of *t*-BuOK, vinyl allene **13a** was formed in 5% isolated yield at room temperature and 76% of **12a** was obtained after hydrolysis (Entry 1). When the reaction time was prolonged, the yield of **13a** increased to 30%. However, when the reaction time was increased to 12 or 24 h, no improvement of the yield of **13a** was observed. These results indicated that the direct conversion of lithium alkoxides **14** to vinyl allenes **13** was not efficient. At the same time, when reaction temperature increased, the reaction was not clean. Therefore, promotion of elimination of lithium alkoxides from **14** was critical for successful preparation of vinyl allenes **13**. Tomioka and co-workers have reported that *t*-BuOK, as a co-base, can work effectively for the activation of lithium alkoxides to afford alkenes.[18e] Therefore, we chose *t*-BuOK as an activating co-base of **14**. When 1 equiv of *t*-BuOK was added to the reaction mixture and the mixture was sirred for 0.5 h at room temperature, the isolated yield of vinyl allene **13a** increased up to 85% as a single product and **12a** was not observed (entry 9). These results indicate that *t*-BuOK, as a strong co-base, can also promote the Wittig−Horner elimination of diphenylphosphinate derivatives from **14**. Use of **9a** and **10a,b** for the Wittig−Horner reaction generated a mixture of products.

Results for the formation of vinyl allenes from 1-lithio-1,3-dienyl phosphine oxides **2** and aldehydes are given in Table 3. The reaction conditions are given in Scheme 5. As shown in Table 3, all aromatic, aliphatic and α,β-unsaturated aldehydes were suitable for the formation of vinyl allenes in more than 70% isolated yields under

SCHEME 3



SCHEME 4

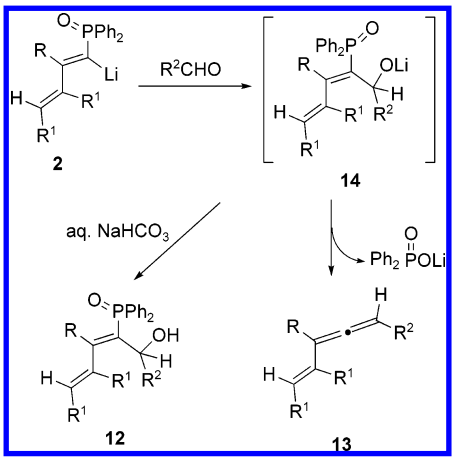
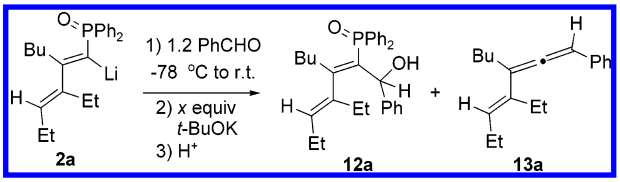


TABLE 2. Elimination Conditions for Formation of Vinyl Allenes



			yields (%)[a]	
entry	equiv of *t*-BuOK	time (h)	**12a**	**13a**
1	0	1	76	5
2	0	2	70	10
3	0	3	60	18
4	0	6	50	25
5	0	12	48	30
6	0	24	48	30
7	0.5	1	25	55
8	0.5	2	0	82
9	1	0.5	0	85

[a] Isolated yields.

the present reaction conditions. At the same time, the substituent R could be an aromatic or aliphatic group. Obviously, this method provides a convenient way to obtain multisubstituted vinyl allenes in high yields by tuning the substituents R and R^1.

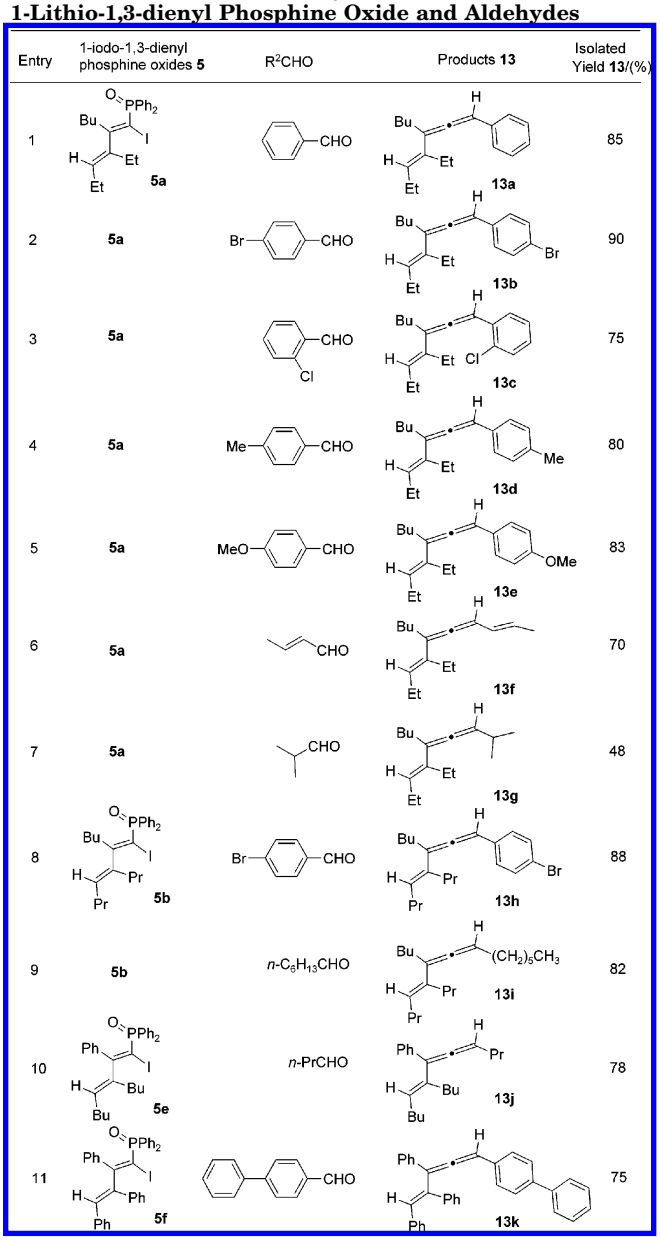
In summary, we have reported a new and convenient method for the preparation of multisubstituted vinyl allenes from 1-lithio-1,3-dienyl phosphine oxides and aldehydes in excellent yields by the Wittig−Horner reaction and widened the scope of iodination reactions of α-phosphinozirconacyclopentadienes. As a whole, the vinyl allene is composed of three molecules including two different alkynes and one aldehyde.

Experimental Section

Typical Procedure for Preparation of 1-Iodo-dienyl Phosphine Oxides. To a solution of Cp_2ZrCl_2 (365 mg, 1.25 mmol) in THF (10 mL) was added EtMgBr (2.5 mmol) at −78 °C. After the mixture was stirred for 1 h at the same temperature, the alkynylphosphine (1.0 mmol) was added and the reaction mixture was allowed to warm to 0 °C for 3 h. The second alkyne (1.0 mmol) was added and stirring was continued at 50 °C for 3 h. After cooling to 0 °C, I_2 (2.0 mmol) was added and stirring was continued at room temperature for 1 h. Then the reaction mixture was quenched with 3 N HCl and extracted with ether. Column chromatography on silica gel afforded 1-iodo-dienyl phosphine oxides.

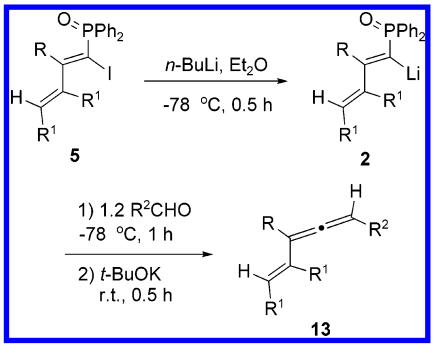
(1*Z*,3*E*)-2-Butyl-3-ethyl-1-iodo-1,3-hexadienyl(diphenyl)-phosphine Oxide (5a). Light red liquid, isolated yield 65%

TABLE 3. Formation of Vinyl Allenes from 1-Lithio-1,3-dienyl Phosphine Oxide and Aldehydes



Entry	1-iodo-1,3-dienyl phosphine oxides **5**	R^2CHO	Products **13**	Isolated Yield **13**/(%)
1	**5a**	CHO	**13a**	85
2	**5a**	Br-CHO	**13b**	90
3	**5a**	CHO, Cl	**13c**	75
4	**5a**	Me-CHO	**13d**	80
5	**5a**	MeO-CHO	**13e**	83
6	**5a**	CHO	**13f**	70
7	**5a**	CHO	**13g**	48
8	**5b**	Br-CHO	**13h**	88
9	**5b**	n-$C_6H_{13}CHO$	**13i**	82
10	**5e**	n-PrCHO	**13j**	78
11	**5f**	CHO	**13k**	75

SCHEME 5



(320 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.76 (t, J = 7.2 Hz, 3H), 1.01−1.30 (m, 12H), 2.09−2.18 (m, 2H), 2.26 (q, J = 7.2 Hz, 2H), 5.16 (t, J = 7.2 Hz, 1H), 7.44−7.85 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.7, 13.7, 13.8, 20.9, 22.3, 22.4, 30.7, 34.6 (d, $^3J_{PC}$ = 5.6 Hz), 91.8 (d, $^1J_{PC}$ = 87.8 Hz), 128.2 (d, $^2J_{PC}$ = 12.4 Hz), 131.5 (d, $^4J_{PC}$ = 1.2 Hz), 131.8 (d, $^4J_{PC}$ = 2.5 Hz), 132.3 (d, $^3J_{PC}$ = 9.3 Hz), 133.5 (d, $^1J_{PC}$ = 108.8 Hz), 144.9 (d, $^3J_{PC}$ = 14.4 Hz), 173.2 (d, $^2J_{PC}$ = 6.8 Hz); HRMS calcd for $C_{24}H_{30}OPI$ 492.1079, found 492.1084.

Typical Procedure for Preparation of 8a and 8b. To a solution of Cp_2ZrCl_2 (365 mg, 1.25 mmol) in THF (10 mL) was added EtMgBr (2.5 mmol) or *n*-BuLi (2.5 mmol) at −78 °C. After the mixture was stirred for 1 h at the same temperature, the diynes (1.0 mmol) was added and the reaction mixture was allowed to warm to room temperature for 3 h to give the α-phosphinobicyclozirconacyclopentadienes **7**. Then the reaction mixture was quenched with 3 N HCl and extracted with ether followed by normal workup to afford crude products, which were purified by column chromatography on silica gel.

(2-Pentylidene-cyclohexylidenemethyl)-diphenyl-phosphane (8a). Colorless viscous liquid, isolated yield 80% (279 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 7.2 Hz, 3H), 1.31−1.65 (m, 8H), 2.04 (q, J = 7.2 Hz, 2H), 2.28−2.60 (m, 4H), 5.54 (t, J = 7.2 Hz, 1H), 6.03 (s, 1H), 7.26−7.42 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.0, 22.4, 26.2, 26.6 (d, $^4J_{PC}$ = 1.2 Hz), 27.3, 28.7, 31.9, 32.6 (d, $^3J_{PC}$ = 24.1 Hz), 119.4 (d, $^1J_{PC}$ = 6.8 Hz), 125.1, 128.1, 128.3 (d, $^3J_{PC}$ = 6.8 Hz), 132.6 (d, $^2J_{PC}$ = 18.5 Hz), 140.0 (d, $^1J_{PC}$ = 9.3 Hz), 141.9 (d, $^3J_{PC}$ = 6.8 Hz), 159.1 (d, $^2J_{PC}$ = 24.1 Hz); HRMS calcd for $C_{24}H_{29}P$ 348.2007, found 348.2009.

Preparation of 9a, 10a, and 10b. The α-phosphinobicyclozirconacyclopentadienes **7a** or **7b** were prepared according to the above-mentioned procedure. **7a** was treated with I_2 (2 mmol) for 1 h at room temperature to give **9a**. **7b** was treated with I_2 (4 mmol) for 1 h at room temperature to give **10b**. When **7a** was first treated with I_2 (2 mmol) for 1 h, followed by addition of CuCl (1 mmol) and I_2 (1 mmol) with stirring for 1 h, **10a** was obtained by the normal purification processes.

Iodo-(2-pentylidene-cyclohexylidene)-methyl(diphenyl)phosphine Oxide (9a). Light red viscous liquid, isolated yield 60% (294 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, J = 6.9 Hz, 3H), 1.37−1.59 (m, 8H), 2.11 (q, J = 6.9 Hz, 2H), 2.33 (t, J = 5.7 Hz, 2H), 3.00−3.04 (m, 2H), 5.35 (t, J = 7.5 Hz, 1H), 7.44−7.84 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.0, 22.5, 27.0, 27.1, 28.0, 29.5, 31.4, 36.9 (d, $^3J_{PC}$ = 6.2 Hz), 85.5 (d, $^1J_{PC}$ = 89.6 Hz), 128.1 (d, $^4J_{PC}$ = 1.9 Hz), 128.3 (d, $^3J_{PC}$ = 12.4 Hz), 131.9 (d, $^4J_{PC}$ = 3.1 Hz), 132.2 (d, $^2J_{PC}$ = 46.4 Hz), 133.6 (d, $^1J_{PC}$ = 108.2 Hz), 144.9 (d, $^3J_{PC}$ = 12.4 Hz), 171.9 (d, $^2J_{PC}$ = 7.4 Hz); HRMS calcd for $C_{24}H_{28}OPI$ 490.0923, found 490.0916.

Iodo-[2-(1-iodopentylidene)cyclohexylidene]methyl-(diphenyl)phosphine oxide (10a). Light red viscous liquid, isolated yield 55% (339 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J = 7.2 Hz, 3H), 1.33−1.63 (br, 6H), 1.82−1.90 (m, 2H), 2.00−3.88 (br, 6H), 7.44−7.98 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.9, 21.8, 28.2, 29.5, 31.3, 33.5, 36.6 (d, $^3J_{PC}$ = 5.6 Hz), 39.8, 89.7 (d, $^1J_{PC}$ = 87.8 Hz), 100.7 (d, $^4J_{PC}$ = 1.9 Hz), 128.1, 128.2, 128.4, 131.9, 132.3 (d, $^2J_{PC}$ = 9.8 Hz), 132.5 (d, $^2J_{PC}$ = 9.3 Hz), 133.6 (d, $^1J_{PC}$ = 5.3 Hz), 151.3 (d, $^3J_{PC}$ = 12.1 Hz), 173.4 (d, $^2J_{PC}$ = 8.7 Hz); HRMS calcd for $C_{24}H_{27}OPI_2$ 615.9889, found 615.9873.

1,2-Bis(1-iodo-1-(diphenylphosphinoyl)methylene)-cyclohexane (10b). Light red solid, isolated yield 35% (266 mg). Mp 152−154 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.58 (t, J = 9 Hz,2H), 1.87−2.22 (m, 4H), 4.06 (d, J = 12 Hz, 2H), 5.29 (s, 2H), 7.41−7.91 (m, 20H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 29.1, 37.3 (d, $^3J_{PC}$ = 4.9 Hz), 53.5, 88.6 (dd, $^1J_{PC}$ = 85.9 Hz, $^4J_{PC}$ = 1.9 Hz), 128.4 (d, $^3J_{PC}$ = 13.0 Hz), 131.0 (d, $^1J_{PC}$ = 109.4 Hz), 132.1 (d, $^1J_{PC}$ = 109.4 Hz), 132.2 132.3 (d, $^3J_{PC}$ = 12.4 Hz), 132.5 (d, $^3J_{PC}$ = 12.4 Hz), 173.4−173.7 (m). Anal. Calcd for $C_{33}H_{30}Cl_2O_2P_2I_2$: C, 46.89; H, 3.58. Found: C, 46.58; H, 3.70. HRMS calcd for $M^+ - CH_2Cl_2$, $C_{32}H_{28}O_2P_2I_2$ 759.9654, found 759.9653.

Typical Procedure for Preparation of 11a and 12a. To an Et_2O (10 mL) solution of **5a** (1.0 mmol) at −78 °C was added *n*-BuLi (1.0 mmol). After this reaction mixture was stirred at −78 °C for 0.5 h and quenched with 20% DCl in D_2O, **11a** was obtained. If a benzaldehyde (1.2 mmol) was added to the above reaction mixture and stirred for 1 h at −78 °C, **12a** was formed after quenching with saturated $NaHCO_3$. Column chromatography on silica gel afforded pure **11a** and **12a**.

(2-Butyl-3-ethyl-1-D-hexa-1,3-dienyl)-diphenyl-phosphine Oxide (11a). Coloress liquid, GC yield 99%, isolated yield 90% (331 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.74 (t, J = 7.2 Hz, 3H), 0.96−1.05 (m, 6H), 1.11−1.24 (br, 4H), 2.12 (q, J = 7.8 Hz, 2H), 2.19−2.29 (m, 2H), 2.63−2.68 (m, 2H), 5.67 (t, J = 7.2 Hz, 1H), 7.40−7.81 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.7, 13.8, 14.2, 21.2, 21.6, 22.7, 31.1, 31.2, 115.7 (d, $^1J_{PC}$ = 104.5 Hz), 128.5 (d, $^2J_{PC}$ = 11.7 Hz), 130.9 (d, $^3J_{PC}$ = 9.9 Hz), 131.2 (d, $^4J_{PC}$ = 3.1 Hz), 132.4, 135.5 (d, $^1J_{PC}$ = 103.2 Hz), 141.7 (d, $^3J_{PC}$ = 16.7 Hz), 166.2 (d, $^2J_{PC}$ = 2.5 Hz); HRMS calcd for $C_{24}H_{30}ODP$ 367.2175, found 367.2177.

3-Butyl-2-(diphenyl-phosphinoyl)-4-ethyl-1-phenyl-hepta-2,4-dien-1-ol (12a). White solid, isolated yield 82% (387 mg). Mp 162−164 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.54−1.14 (br, 13H), 2.06−2.29 (br, 6H), 5.43 (s, 1H), 5.57(s, 1H), 5.93−6.04 (br, 1H), 7.03−7.64 (m, 15H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ13.3, 13.6, 14.1, 21.1, 22.6, 23.3, 29.3, 30.9 (d, $^3J_{PC}$ = 9.3 Hz), 75.4 (d, $^2J_{PC}$ = 7.4 Hz), 126.1, 126.3, 127.6, 128.1 (d, $^2J_{PC}$ = 12.4 Hz), 128.4 (d, $^2J_{PC}$ = 12.4 Hz), 129.7 (d, $^1J_{PC}$ = 93.3 Hz), 131.4 (d, $^3J_{PC}$ = 10.5 Hz), 131.5, 131.8 (d, $^3J_{PC}$ = 10.5 Hz), 132.2, 132.8, 135.7 (d, $^1J_{PC}$ = 100.1 Hz), 138.7 (d, $^2J_{PC}$ = 13.0 Hz), 143.5. Anal. Calcd for $C_{31}H_{37}O_2P$: C, 78.78; H, 7.89. Found: C, 78.62; H, 8.01. HRMS calcd for $C_{31}H_{37}O_2P$ 472.2531, found 472.2546.

Typical Procedure for Preparation of Vinyl Allenes. To an Et_2O (10 mL) solution of 1-iodo-1,3-dienyl phosphine oxide (1.0 mmol) at −78 °C was added *n*-BuLi (1.0 mmol). After this reaction mixture was stirred at −78 °C for 0.5 h, an aldehyde (1.2 mmol) was added and stirred for 1 h at this temperature. Then *t*-BuOK (1 mmol) was added at −78 °C and stirred for 0.5 h at room temperature. The reaction mixture was quenched with saturated $NaHCO_3$ and extracted with ether. Column chromatography on silica gel afforded vinyl allenes.

(3-Butyl-4-ethyl-hepta-1,2,4-trienyl)-benzene (13a). Colorless liquid, isolated yield 85% (216 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H), 1.03 (t, J = 7.5 Hz, 3H), 1.31−1.52 (m, 4H), 2.12−2.32 (m, 6H), 5.47 (t, J = 7.2 Hz, 1H), 6.33 (s, 1H), 7.13−7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.0, 14.4, 14.5, 21.6, 22.8, 23.1, 29.2, 30.3, 96.8, 111.4, 126.5, 126.6, 127.5, 128.6, 135.5, 136.3, 206.5; HRMS calcd for $C_{19}H_{26}$ 254.2035, found 254.2023.

Acknowledgment. This work was partially supported by National Natural Science Foundation of China (20172003, 20232010, 20328201), the Major State Basic Research Development Program (G2000077502-D), and Dow Corning Corporation. Cheung Kong Scholars Program, Qiu Shi Science & Technologies Foundation, and BASF are gratefully acknowledged.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all new products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO051178C