Metallophosphination of Alkynes: Efficient Synthesis of β-Functionalized Alkenylphosphines

Chanjuan Xi,*[,†,‡] Xiaoyu Yan,[†] and Chunbo Lai[†]

Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China, and State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

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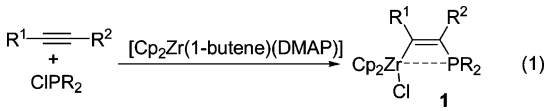
Reactions of alkynes with [Cp_2Zr(1-butene)(DMAP)] (DMAP = 4-(dimethylamino)pyridine) and chlorophosphines afforded zirconoalkenylphosphines in good to high yields, and their molecular structures were determined by single-crystal X-ray diffraction. The zirconoalkenylphosphines could be transformed into β-functionalized alkenylphosphines through coupling reactions with various electrophiles in the presence of CuCl.

Introduction

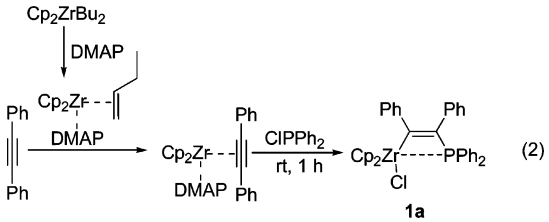
Alkenylphosphines have been attracting interest because they serve not only as starting materials in organic synthesis[1] but also as useful ligand precursors in organometallic chemistry.[2] A number of synthetic methods affording alkenylphosphines have been reported.[3,4] Among them, metal-catalyzed hydrophosphination of alkynes, the addition of phosphines to carbon−carbon triple bonds, provided a straightforward method for the synthesis of alkenylphosphines.[5,6] Nonetheless, it is often difficult to prepare β-functionalized alkenylphosphines by these methods. Consequently, development of a versatile and general method for the preparation of β-functionalized alkenylphosphines is a necessity. Herein we report the metallophosphination of alkynes based on the reaction of alkynes with [Cp_2Zr(1-butene)(DMAP)] (DMAP = 4-(dimethylamino)pyridine) and chlorophosphines (eq 1). Moreover, the resulting zirconophosphination products **1** can be converted into β-functionalized alkenylphosphines.



(1)

Results and Discussion

We have previously reported that the reaction of alkynes with Cp_2Zr species and chlorophosphates (P(V) compounds) afforded β-zirconoalkenylphosphonates.[7] To achieve the zirconophosphination of alkynes, we chose chlorophosphines (P(III) compounds) as reagents. At the outset, to a solution of [Cp_2Zr(1-butene)(DMAP)][8] (1 mmol, generated via Cp_2ZrBu_2[9] with DMAP in THF at room temperature) was added 1 equiv of diphenylacetylene at room temperature. The resulting mixture was stirred for 1 h. Chlorodiphenylphosphine (1 mmol) then was added, and stirring was continued for an additional 1 h. The zirconoalkenylphosphine **1a** was mainly observed (eq 2).



(2)

The ^{1}H NMR spectrum of **1a** showed a singlet at 5.91 ppm assigned to the Cp protons. In its ^{13}C NMR spectrum, the Cp carbon signals appeared at 111.2 ppm and two sp^2 carbon signals at 215.0 and 137.8 ppm, assigned to Zr−*C*(Ph)═ and −C(Ph)═*C*(Ph)P, respectively. Its ^{31}P NMR spectrum showed a strong signal at −38.8 ppm, assigned to ═C(Ph)*P*Ph$_2$. Treatment of the reaction mixture with 3 N HCl and extraction of the product with CH_2Cl_2 followed by removal of the solvent afforded **1a** as a yellow solid in 90% yield. Further purification was performed by column chromatography on silica gel (1/1 petroleum ether/THF) to obtain a white powder in 75% isolated

* To whom correspondence should be addressed. E-mail: cjxi@tsinghua.edu.cn.

† Tsinghua University.

‡ Nankai University.

(1) (a) Gilheany, D. G.; Mitchell, C. M. In *The Chemistry of Organophosphorus Compounds*; Hartley, J. F., Ed.; Wiley: Chichester, U.K., 1990; Vol. 1, p 151. (b) Brunner, H.; Furst, J. *Tetrahedron* **1994**, *50*, 4293.

(2) (a) Adams, H.; Bailey, N. A.; Blenkiron, P.; Morris, M. J. *J. Organomet. Chem.* **1993**, *460*, 73. (b) Hansen, H. D.; Nelson, J. H. *Organometallics* **2000**, *19*, 4740. (c) Glaser, P. B.; Tilley, T. D. *Organometallics* **2004**, *23*, 5799. (d) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 2030. (e) Braunstein, P. *Chem. Rev.* **2006**, *106*, 134.

(3) (a) Hudson, H. R. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: Chichester, U.K., 1990; Vol. 1, pp 309−401. (b) Heesche-Wagner, K.; Mitchell, T. N. *J. Organomet. Chem.* **1994**, *468*, 99.

(4) (a) Goldwhite, H. *Introduction to Phosphorus Chemistry*, Cambridge University Press: Cambridge, U.K., 1981. (b) Mitchell, T. N.; Heesche, K. *J. Organomet. Chem.* **1991**, *409*, 163.

(5) (a) Douglass, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 1824. (b) Takaki, K.; Koshoji, G.; Komeyama, K.; Takeda, M.; Shishido, T.; Kitani, A.; Takehira, K. *J. Org. Chem.* **2003**, *68*, 6554. (c) Takaki, K.; Komeyama, K.; Takehira, K. *Tetrahedron* **2003**, *59*, 10381.

(6) (a) Arisawa, M.; Yamaguchi, M. *J. Am. Chem. Soc.* **2000**, *122*, 2387. (b) Jérôme, F.; Monnier, F.; Lawicka, H.; Dérien, S.; Dixneuf, P. H. *Chem. Commun.* **2003**, 696. (c) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 2368. (d) Alonso, F.; P. Beletskaya, I.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079. (e) Sato, A.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 1694.

(7) Lai, C.; Xi, C.; Chen, C.; Ma, M.; Hong, X. *Chem. Commun.* **2003**, 2736.

(8) Wagenen, B. C. V.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495.

(9) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

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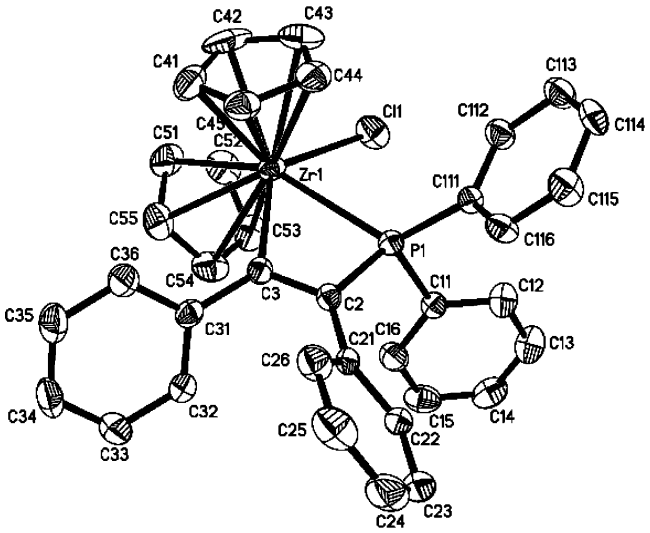


Figure 1. Molecular structure of **1a**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr(1)−C(3), 2.410(3); Zr(1)−Cl(1), 2.5583(10); Zr(1)−P(1), 2.7458(9); P(1)−C(2), 1.795(3); C(2)−C(3), 1.364(4); C(3)−Zr(1)−P(1), 57.22(8); C(2)−C(3)−Zr(1), 112.6(2); C(3)−C(2)−P(1), 103.0(2); C(2)−P(1)−Zr(1), 86.72(11); C(3)−Zr(1)−Cl(1), 130.42(8).

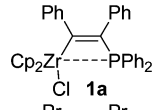
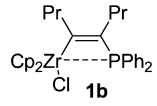
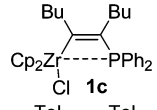
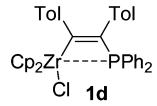
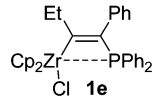
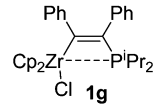
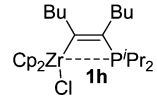
yield. Remarkably, the zirconoalkenylphosphine **1a** proved to be stable to air and water as well as in 3 N HCl solution. It is worth noting that air- and water-stable C−Zr σ-bond-containing complexes are rare.[10]

To confirm the structure of the product, colorless crystals of **1a** suitable for X-ray analysis were obtained from its solution of petroleum ether and THF (15:1) at room temperature. The structure of **1a** in Figure 1 clearly shows the formation of the zirconophosphination product of diphenylacetylene. The coordination of the phosphorus atom to the zirconium metal center gives the zirconium atom an 18e electron configuration which involves two cyclopentadienyl rings, one chlorine atom, one σ-organyl, and one phosphine. Thus, the air and water stability may be explained by an electronically saturated (18e) zirconium center.

A variety of alkynes were subjected to metallophosphination, and all reactions afforded analogous products in good to high yield. The results are summarized in Table 1. When chlorodiisopropylphosphine was used instead of chlorodiphenylphosphine as phosphination reagent, similar products were obtained (Table 1, entries 6 and 7). Colorless crystals of **1g** suitable for X-ray analysis were obtained in a manner similar to that for its analogue **1a**, and the structure of **1g** is identical with that of **1a**, except for the different substituents on the phosphorus atom. An ORTEP plot of **1g** appears in the Supporting Information.

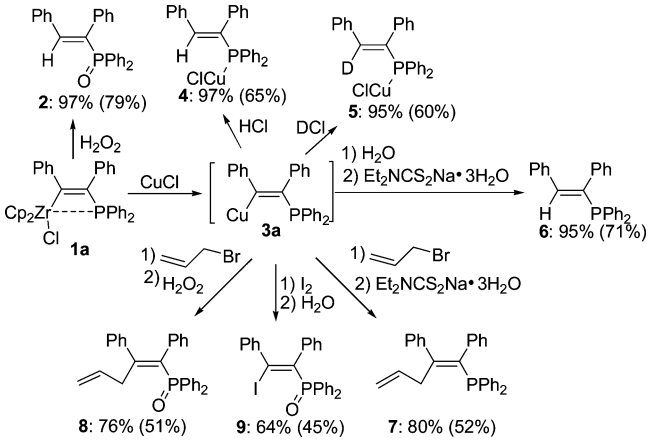
The zirconophosphination products of alkynes are stable in air, water, and dilute HCl solution. Some of their reactions are shown in Scheme 1. When 30% H_2O_2 was added to the THF solution of complex **1a**, compound **2** was produced quantitatively. Zr−C to Cu−C transmetalation has been shown to be an effective method for the activation of Zr−C bonds.[11] Thus,

Table 1. Metallophosphination of Alkynes via the Reaction of Alkynes with [Cp_2Zr(1-butene)(DMAP)] and Chlorophosphines

entry	R^1—≡—R^2	$ClPR_2$	Temp.(°C)	product	yield[a]
1	Ph—≡—Ph	$ClPPh_2$	rt	 **1a**	95(75)
2	Pr—≡—Pr	$ClPPh_2$	35	 **1b**	80(63)
3	Bu—≡—Bu	$ClPPh_2$	35	 **1c**	85(65)
4	Tol—≡—Tol	$ClPPh_2$	rt	 **1d**	90(73)
5	Et—≡—Ph	$ClPPh_2$	35	 **1e**	60(40)[b]
6	Ph—≡—Ph	ClP^iPr_2	rt	 **1g**	92(71)
7	Bu—≡—Bu	ClP^iPr_2	35	 **1h**	95(69)

[a] NMR yields were obtained in proportion to the integral area of all the ^{31}P signals; isolated yields are given in parentheses. [b] A mixture of two regioisomers with a ratio of 2:1; the major isomer is shown.

Scheme 1

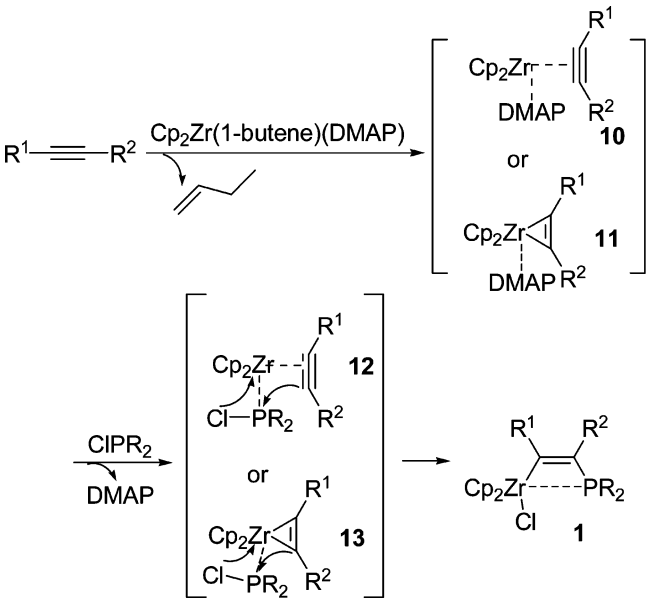


addition of 1 equiv of CuCl to THF solutions of compounds of type **1** afforded the copper(I) intermediates **3**. The intermediates **3** could be converted to β-functionalized, stereodefined alkenylphosphines by coupling with electrophiles. Such reactions of **3a** are summarized in Scheme 1. Hydrolysis of **3a** with 3 N HCl gave **4** in 97% NMR yield. Deuteriolysis instead of hydrolysis of **3a** afforded the monodeuterated compound **5** in 95% yield with 93% deuterium incorporation. It is noteworthy that in compounds **4** and **5** phosphine−CuCl complexes are formed. The formation of **5** provides good proof that the Zr−C bond has been replaced by the more active Cu−C bond. It is well-known that the diethyldithiocarbamate ligand possesses the unsuspected capacity of effectively stabilizing transition metals.[12] To remove Cu(I) from the products, **3a** was treated with water followed by 2.2 equiv of sodium diethyldithiocarbamate;

(10) (a) Luker, T.; Whitby, R. J.; Webster, M. *J. Organomet. Chem.* **1995**, *492*, 53. (b) Mohamadi, F.; Spees, M. M. *Organometallics* **1992**, *11*, 1398. (c) Takahashi, T.; Xi, C.; Xi, Z.; Kageyama, M.; Fischer, R.; Nakajima, K.; Negishi, E. *J. Org. Chem.* **1998**, *63*, 6802. (d) Zhou, S.; Liu, D.; Liu, Y. *Organometallics* **2004**, *23*, 5900.

(11) (a) Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N.; Nakajima, N. *Organometallics* **1994**, *13*, 4183. (b) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154. (c) Xi, C.; Kotora, M.; Nakajima, K.; Takahashi, T. *J. Org. Chem.* **2000**, *65*, 945.

Scheme 2



compound **6** was formed in 95% NMR yield and in 71% isolated yield after purification by short-column chloromatography. The reaction of **3a** with allyl bromide gave the corresponding products **7** and **8** after treatment with $Et_2NCS_2Na{\cdot}3H_2O$ and H_2O_2, respectively. Treatment of **3a** with 3 equiv of iodine gave the product **9** after hydrolysis. It is worth noting that direct iodination of **1a** led to the formation of a complex mixture. Only a trace amount of **9** was detected by GC-MS after hydrolysis.

Coupling reactions of zirconocene alkyne complexes with various unsaturated compounds such as alkynes, alkenes, and ketones have been reported.[8,9,13] Although the mechanism of reaction presented here is not yet clear, one possible reaction pathway is shown in Scheme 2. Reaction of [Cp_2Zr(1-butene)(DMAP)] with alkynes gives the zircono-alkyne complex **10** or the zirconacyclopropene **11**.[8,9,13] Complex **10** or **11** reacts with $ClPR_2$ to give product **1** via complex **12** or **13**. An alternative reaction pathway involving oxidative addition of $ClPR_2$ to the complex [$Cp_2Zr(R^1CCR^2)$(DMAP)], giving [$Cp_2ClZrPR_2(R^1CCR^2)$(DMAP)], and subsequent insertion of alkynes into the Zr−PR_2 moiety to afford **1** cannot be ruled out.[14]

In conclusion, zirconophosphination of alkynes to produce air- and water-stable phosphazirconacyclobutene has been described. The resulting zirconoalkenylphosphines, as characterized by X-ray crystal analysis, can act as useful intermediates for the construction of various β-functionalized alkenylphosphine derivatives.

Experimental Section

General Comments. All manipulations were conducted in predried Schlenk tubes and under nitrogen with a slightly positive pressure. The reaction progress was monitored by ^{31}P NMR. The ^{31}P NMR yields were obtained in proportion to the integral area of all the ^{31}P signals determined by integration of all the ^{31}P signals. Zirconocene dichloride, *n*-BuLi (1.6 M solution in hexane), and DMAP were purchased from Aldrich Chemical Co. Inc. Chlorodiphenylphosphine, chlorodiisopropylphosphine, and alkynes were purchased from Fluka Co. Inc. Unless otherwise noted, all starting materials were used without further purification. Tetrahydrofuran (THF) was refluxed and freshly distilled from dark purple solutions of sodium and benzophenone under a nitrogen atmosphere. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL 300 NMR spectrometer with TMS as internal standard. ^{31}P NMR spectra were recorded on a Bruker AC 200 NMR spectrometer at 81 MHz using 85% H_3PO_4 (δ_P 0) as an external standard. Mass spectra were obtained using a Bruker Esquire ion trap mass spectrometer in the positive ion mode. Elemental analyses were performed on a Flash EA 1112 instrument.

Typical Procedure for the Reaction of [$Cp_2Zr(R^1C{\equiv}CR^2)$(DMAP)] with Chlorodiphenylphosphine: Preparation of (*Z*)-[2-(Dicyclopentadienylchlorozircono)-1,2-diphenylvinyl]diphenylphosphine (1a). To a solution of Cp_2ZrCl_2 (1.2 mmol, 351 mg) in 5 mL of THF was added *n*-BuLi (2.4 mmol, 1.5 mL, 1.6 M in hexane) at −78 °C, and the mixture was stirred for 1 h at the same temperature. To this solution was added 366 mg of 4-(dimethylamino)pyridine (DMAP, 3.0 mmol). The resulting mixture was warmed to room temperature and stirred for 1 h. Diphenylacetylene (1.0 mmol, 178 mg) was added, and the mixture was stirred for 1 h at the same temperature. Subsequently PPh_2Cl (184 μL, 1.0 mmol) was added, and the solution was stirred for 1 h at room temperature. ^{31}P NMR (81 MHz, THF, 85% H_3PO_4): δ −38.8. The NMR yield is 95%. The solvents were evaporated under reduced pressure. The resulting residue was washed with 3 N HCl. Extraction of the product with CH_2Cl_2 and removal of the solvent afforded **1a** as a yellow solid in 90% yield. Further purification was performed by column chromatography on silica gel (1/1 petroleum ether/THF) to obtain a white powder (464 mg, 75% isolated yield). Mp: 227−228 °C. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 5.91 (s, 10H), 6.81−6.84 (m, 2H), 6.96−7.12 (m, 6H), 7.26−7.31 (m, 2H),7.40−7.42 (m, 6H), 7.73−7.79 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 111.2, 124.9, 125.0, 126.3, 127.8, 128.5, 128.7 (d, $^3J_{PC}$ = 7.5 Hz), 129.1 (d, $^3J_{PC}$ = 3.0 Hz), 129.7, 132.8 (d, $^2J_{PC}$ = 9.8 Hz), 133.2 (d, $^1J_{PC}$ = 18.6 Hz), 137.8 (d, $^1J_{PC}$ = 38.7 Hz), 138.0 (d, $^2J_{PC}$ = 2.9 Hz), 150.4 (d, $^3J_{PC}$ = 38.7 Hz), 215.0 (d, $^2J_{PC}$ = 21.5 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ −40.0. Positive ion ESI-MS: 583.0 (M − Cl). Anal. Calcd for $C_{36}H_{30}ClPZr$: C, 69.71; H, 4.87. Found: C, 69.66; H, 4.79.

(*Z*)-[2-(Dicyclopentadienylchlorozircono)-1,2-dipropylvinyl]diphenylphosphine (1b). White solid (326 mg, 63%). Mp: 167−168 °C. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.73 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 0. 85 (m, 2H), 1.07 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 1.66−1.74 (m, 2H), 2.26−2.40 (m, 4H), 5.90 (s, 10H), 7.37 (m, 6H), 7.56−7.62 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 14.5, 15.7, 22.4, 24.0, 34.0 (d, $^2J_{PC}$ = 3.6 Hz), 42.4 (d, $^3J_{PC}$ = 37.3 Hz), 110.1, 128.5 (d, $^3J_{PC}$ = 7.9 Hz), 129.4, 133.3 (d, $^2J_{PC}$ = 10.5 Hz), 135.0 (d, $^1J_{PC}$ = 18.6 Hz), 138.8 (d, $^1J_{PC}$ = 40.2 Hz), 214.1 (d, $^2J_{PC}$ = 15.1 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ −44.2. Positive ion ESI-MS: 515.0 (M − Cl). Anal. Calcd for $C_{30}H_{34}ClPZr$: C, 65.25; H, 6.21. Found: C, 65.35; H, 6.24.

(*Z*)-[2-(Dicyclopentadienylchlorozircono)-1,2-di-*n*-butylvinyl]diphenylphosphine (1c). White solid (377 mg, 65%). Mp: 183−184 °C. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.72 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.03 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.11−1.18 (m, 2H), 1.28−1.35 (m, 2H), 1.43−1.51 (m, 2H), 1.62−1.72 (m, 2H), 2.28−2.42 (m, 4H), 5.90 (s, 10H), 7.37 (m, 6H), 7.56−7.62 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 13.8, 14.2, 23.0, 24.2, 31.1, 31.4 (d, $^2J_{PC}$ = 3.6 Hz), 32.8, 39.6 (d, $^3J_{PC}$ = 37.3 Hz), 110.1, 128.4 (d, $^3J_{PC}$ = 7.9 Hz), 129.4, 133.3 (d, $^2J_{PC}$ = 10.8 Hz), 135.0 (d, $^1J_{PC}$ =

(12) (a) Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1974**, *13*, 1933. (b) Chant, R.; Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1975**, *14*, 1894. (c) Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1975**, *14*. 2980. (d) Brinkhoff, H. C.; Cras, J. A.; Steggerda, J. J.; Willemse, J. *Recl. Trau. Chim. Pays-Bas* **1969**, *88*, 633.

(13) (a) Erker, G.; Dorf, U.; Mynott. R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 584. (b) Buchwald, S. L.; Watson, B. T. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (c) Takahashi, T.; Suzuki, N.; Kaheyama, M.; Kondakov. D. Y.; Hara, R. *Tetrahedron Lett.* **1993**, *34*, 4811.

(14) (a) Hey-Hawkins, E.; Lindenberg, F. *Chem. Ber.* **1992**, *125*, 1815. (b) Matthias, W.; Matthias, H. D.; Heinrich, N.; Thomas, S.; Arno, P. *J. Am. Chem. Soc.* **1998**, *120*, 6722.

17.9 Hz), 138.8 (d, $^1J_{PC}$ = 38.7 Hz), 214.1 (d, $^2J_{PC}$ = 15.1 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ −44.2. Positive ion ESI-MS: 543.0 (M − Cl). Anal. Calcd for $C_{32}H_{38}ClPZr$: C, 66.23; H, 6.60. Found: C, 66.23; H, 6.66.

(*Z*)-[2-(Dicyclopentadienylchlorozircono)-1,2-bis(4-methylphenyl)vinyl]diphenylphosphine (1d). White solid (473 mg, 73%). Mp: 230−231 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 2.18 (s, 3H), 2.34 (s, 3H), 5.89 (s, 10H), 6.73−6.79 (m, 4H), 6.92−6.95 (m, 2H), 7.09−7.11 (m, 2H),7.40−7.42 (m, 6H), 7.76−7.78 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 21.2, 111.1, 124.9, 128.5, 128.6 (d, $^3J_{PC}$ = 7.9 Hz), 129.0 (d, $^3J_{PC}$ = 2.9 Hz), 129.2, 129.60 (d, $^4J_{PC}$ = 1.4 Hz), 132.7 (d, $^2J_{PC}$ = 10.0 Hz), 133.2 (d, $^1J_{PC}$ = 17.9 Hz), 134.2, 135.1 (d, $^2J_{PC}$ = 2.9 Hz), 135.8, 137.3 (d, $^1J_{PC}$ = 40.2 Hz), 147.6 (d, $^3J_{PC}$ = 40.2 Hz), 214.5 (d, $^2J_{PC}$ = 20.1 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ −41.0. Positive ion ESI-MS: 611.0 (M − Cl). Anal. Calcd for $C_{38}H_{34}ClPZr$: C, 70.40; H, 5.29. Found: C, 70.51; H, 5.30.

(*Z*)-[2-(Dicyclopentadienylchlorozircono)-2-ethyl-1-phenylvinyl]diphenylphosphine (1e). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.98 (t, J = 7.2 Hz, 3H), 2.60 (m, J = 3.78 Hz, $^4J_{PH}$ = 15.1 Hz, 2H), 6.00 (s, 10H), 7.08−7.11 (m, 2H), 7.20−7.23 (m, 3H), 7.32−7.34 (m, 6H), 7.57−7.62 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 14.4, 32.4 (d, $^3J_{PC}$ = 35.9 Hz), 110.1, 126.5, 128.0 (d, $^3J_{PC}$ = 2.2 Hz), 128.4 (d, $^3J_{PC}$ = 7.9 Hz), 128.4, 129.5, 133.3 (d, $^2J_{PC}$ = 10.0 Hz, 4C), 134.2 (d, $^1J_{PC}$ = 17.9 Hz), 138.3 (d, $^1J_{PC}$ = 39.4 Hz), 139.9 (d, $^2J_{PC}$ = 3.6 Hz), 220.3 (d, $^2J_{PC}$ = 16.5 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ −39.4. Positive ion ESI-MS: 535.0 (M − Cl). Anal. Calcd for $C_{32}H_{30}ClPZr$: C, 67.17; H, 5.28. Found: C, 67.01; H, 5.15.

(*Z*)-[2-(Dicyclopentadienylchlorozircono)-1-ethyl-2-phenylvinyl]diphenylphosphine (1e′). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.63 (t, J = 7.5 Hz, 3H), 2.22−2.29 (m, J = 7.5 Hz, $^3J_{PH}$ = 2.4 Hz, 2H), 5.91 (s, 10H), 7.16−7.26 (m, 2H), 7.34−7.38 (m, 3H), 7.41−7.45 (m, 6H), 7.69−7.75 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 14.8, 25.7 (d, $^2J_{PC}$ = 4.3 Hz), 111.1, 123.9, 124.5, 125.6, 128.7 (d, $^3J_{PC}$ = 8.6 Hz), 129.7, 133.1 (d, $^2J_{PC}$ = 10.8 Hz), 134.1 (d, $^1J_{PC}$ = 18.6 Hz), 141.2 (d, $^1J_{PC}$ = 37.3 Hz), 150.5 (d, $^3J_{PC}$ = 39.4 Hz), 221.2 (d, $^2J_{PC}$ = 24.4 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ −40.2. Positive ion ESI-MS: 535.0 (M −Cl).

(*Z*)-[2-(Dicyclopentadienylchlorozircono)-1,2-diphenylvinyl]-diisopropylphosphine (1g). White solid (392 mg, 71%). Mp: 226−227 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.25 (dd, J = 7.2 Hz, $^3J_{PH}$ = 12.4 Hz, 6H), 1.48 (dd, J = 7.2 Hz, $^3J_{PH}$ = 14.8 Hz, 6H), 2.51 (m, J = 7.2 Hz, $^2J_{PH}$ = 3.1 Hz, 2H), 6.08 (s, 10H), 6.85−7.13 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.9, 20.8 (d, $^2J_{PC}$ = 5.7 Hz), 26.7 (d, $^1J_{PC}$ = 2.9 Hz), 110.5, 124.2, 125.2, 125.9, 127.9, 128.3, 140.8 (d, $^2J_{PC}$ = 2.2 Hz), 140.9 (d, $^1J_{PC}$ = 33.0 Hz), 150.6 (d, $^3J_{PC}$ = 34.4 Hz, 1C), 209.6 (d, $^2J_{PC}$ = 23.7 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ −24.6. Positive ion ESI-MS: 515.1 (M − Cl). Anal. Calcd for $C_{30}H_{34}ClPZr$: C, 65.25; H, 6.21. Found: C, 65.15; H, 6.33.

(*Z*)-[2-(Dicyclopentadienylchlorozircono)-1,2-dibutylvinyl]diisopropylphosphine (1h). Oily liquid (353 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.93 (t, J = 6.8 Hz, 3H), 0. 96 (t, J = 7.2 Hz, 3H), 1.14−1.50 (m, 20H), 2.01−2.10 (m, 2H), 2.14−2.33 (m, 4H), 6.00 (s, 10H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 14.0, 14.2, 20.4, 20.8 (d, $^2J_{PC}$ = 5.7 Hz), 23.6, 24.2, 25.9 (d, $^1J_{PC}$ = 2.2 Hz), 31.5, 32.0 (d, $^4J_{PC}$ = 3.6 Hz), 32.4 (d, $^3J_{PC}$ = 5.0 Hz), 38.9 (d, $^3J_{PC}$ = 33.0 Hz), 109.6 (10C), 140.5 (d, $^1J_{PC}$ = 34.4 Hz), 209.4 (d, $^2J_{PC}$ = 14.1 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ −30.9. Positive ion ESI-MS: 475.0 (M − Cl). Anal. Calcd for $C_{26}H_{42}ClPZr$: C, 60.90; H, 8.26. Found: C, 60.98; H, 8.35.

Reaction of [(*Z*)-2-(Dicyclopentadienylchlorozircono)-1,2-diphenylvinyl]diphenylphosphine (1a). (*E*)-(1,2-Diphenylvinyl)-diphenylphosphine Oxide (2). White solid, 79% isolated yield. ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ 29.9. Positive ion ESI-MS: 381.1 (M + H^+), 403.1 (M + Na^+). ^{1}H and ^{13}C NMR data are consistent with the published data.[5c]

{**[(*E*)-(1,2-Diphenylvinyl)diphenylphosphine)]CuCl**} **(4).** To a solution of **1a** (0.4 mmol, 248 mg) in 5 mL of THF were added 40 mg of CuCl (0.4 mmol) and 5 μL of H_2O, and the solution was stirred for 2 h at 50 °C. ^{31}P NMR (81 MHz, THF, 85% H_3PO_4): δ 13.2. The NMR yield was 97%. Removal of the solvent and subsequent purification by column chromatography on silica gel (1/1 ethyl acetate/ petroleum ether) afforded 126 mg of the title compound as a yellow solid (isolated yield 65%). Mp: 89−90 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 4.1 (br, H_2O), 6.94−7.66 (m, 21H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 127.6, 128.2, 128.3, 128.8 (d, $^3J_{PC}$ = 9.3 Hz), 128.8, 130.2 (d, $^4J_{PC}$ = 4.3 Hz), 130.2, 130.4, 131.9 (d, $^1J_{PC}$ = 33.0 Hz), 135.0 (d, $^2J_{PC}$ = 15.8 Hz), 136.5 (d, $^1J_{PC}$ = 26.3 Hz), 136.6 (d, $^3J_{PC}$ = 15.8 Hz), 138.6 (d, $^2J_{PC}$ = 8.6 Hz), 143.0 (d, $^2J_{PC}$ = 22.9 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ 12.5. Positive ion ESI-MS: 427.1 (M − Cl). Anal. Calcd for $C_{26}H_{21}ClCuP\cdot H_2O$: C, 64.86; H, 4.82. Found: C, 64.51; H, 4.61.

{**[(*E*)-(2-Deuterio-1,2-diphenylvinyl)diphenylphosphine]-CuCl**} **(5).** ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 4.4 (br, H_2O) 6.87−7.55 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 127.4, 128.1, 128.2, 128.6 (d, $^3J_{PC}$ = 12.9 Hz), 128.7, 129.6, 129.9, 130.0, 130.8 (d, $^1J_{PC}$ = 34.4 Hz), 134.5 (d, $^2J_{PC}$ = 14.3 Hz), 135.3 (d, $^1J_{PC}$ = 26.5 Hz), 135.9 (d, $^3J_{PC}$ = 13.6 Hz), 138.2 (d, $^2J_{PC}$ = 8.6 Hz), 142.9 (m). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ 13.0. Positive ion ESI-MS: 427.9 (M − Cl). Anal. Calcd for $C_{26}H_{20}DClCuP\cdot H_2O$: C, 64.73; H, 5.01. Found: C, 64.49; H, 4.98.

(*E*)-(1,2-Diphenylvinyl)diphenylphosphine (6). To a solution of **3a** prepared in situ by **1a** (0.1 mmol, 62 mg) and CuCl (0.1 mmol, 10 mg) in 1 mL of THF was added 2 μL of H_2O, followed by addition of sodium diethyldithiocarbamate trihydrate (50 mg, 0.22 mmol). After the mixture had been stirred for 2 h at room temperature, removal of the solvent and subsequent purification by column chromatography on silica gel (1/25 ethyl acetate/ petroleum ether) afforded 26 mg of the title compound as a white solid (isolated yield 71%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 6.57 (d, $^3J_{PH}$ = 9.2 Hz, 1H), 6.93−7.00 (m, 2H), 7.09−7.25 (m, 8H), 7.33−7.40 (m, 6H), 7.48−7.52 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 127.1, 127.4, 128.1, 128.5, 128.6 (d, $^3J_{PC}$ = 5.0 Hz), 129.1, 129.3 (d, $^4J_{PC}$ = 6.5 Hz), 129.5, 134.4 (d, $^2J_{PC}$ = 19.4 Hz), 135.5 (d, $^1J_{PC}$ = 11.5 Hz), 137.0 (d, $^2J_{PC}$ = 6.5 Hz), 138.2 (d, $^2J_{PC}$ = 18.6 Hz), 140.1 (d, $^1J_{PC}$ = 16.5 Hz), 141.6 (d, $^3J_{PC}$ = 18.6 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ 9.1. Positive ion ESI-MS: 365.2 (M + H^+), 387.1 (M + Na^+). Spectroscopic characterization data for compound **6** are consistent with the published data.[5b]

Preparation of (*E*)-(1,2-Diphenylpenta-1,4-dienyl)diphenylphosphine (7). To a solution of **1a** (0.4 mmol, 248 mg) in 5 mL of THF were added 40 mg of CuCl (0.4 mmol) and 35 μL of allyl bromide (0.4 mmol), and the solution was stirred for 2 h at 50 °C. Sodium diethyldithiocarbamate trihydrate (200 mg, 0.88 mmol) was added. After the mixture had been stirred for 2 h at room temperature, removal of the solvent and subsequent purification by column chromatography on silica gel (1/25 ethyl acetate/ petroleum ether) afforded the title compound (210 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 3.98 (d, $^3J_{HH}$ = 6.2 Hz, 2H), 5.04 (d, $^3J_{HH}$(cis) = 11.3 Hz, 1H), 5.09 (d, $^3J_{HH}$(trans) = 17.2 Hz, 1H), 5.85 (m), 6.75−7.78 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 41.3 (d, $^3J_{PC}$ = 30.1 Hz), 117.0, 125.3, 126.5, 126.9 (2C), 127.6 (2C), 128.2 (d, $^3J_{PC}$ = 5.7 Hz, 4C), 128.3 (2C), 128.8 (d, $^4J_{PC}$ = 5.0 Hz, 2C), 129.1 (2C), 129.9, 133.8 (d, $^2J_{PC}$ = 20.1 Hz, 4C), 135.2, 136.4 (d, $^2J_{PC}$ = 20.1 Hz), 136.8 (d, $^1J_{PC}$ = 12.2 Hz, 2C), 137.2 (d, $^1J_{PC}$ = 22.2 Hz), 140.2 (d, $^2J_{PC}$ = 5.0 Hz), 142.3 (d, $^3J_{PC}$ = 6.5 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ −4.8. Positive ion ESI-MS: 405.2 (M + H^+). HRMS: calcd for

Table 2. Crystal Data

	1a	1g
empirical formula	$C_{36}H_{30}ClPZr$	$C_{30}H_{34}ClPZr$
formula wt	620.24	552.21
cryst color	colorless	colorless
temp (K)	293(2)	298(2)
Crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	19.0266(9)	13.8113(1)
b (Å)	8.3521(4)	12.0911(9)
c (Å)	19.7203(9)	16.0607(1)
β (deg)	110.936(3)	91.971(3)
V (Å^3)	2926.9(2)	2680.5(4)
Z	4	4
D_{calcd} (g cm^{-3})	1.408	1.368
μ (mm^{-1})	0.545	0.586
F(000)	1272	1144
cryst size (mm)	0.24 × 0.18 × 0.12	0.43 × 0.22 × 0.20
θ range (deg)	2.10−28.31	2.11−28.30
limiting indices	$-25 \le h \le 25$, $-8 \le k \le 11$, $-26 \le l \le 21$	$-18 \le h \le 15$, $-16 \le k \le 16$, $-21 \le l \le 16$
no. of rflns collected	26 546	24 933
no. of unique rflns	7227	6614
completeness to θ (%)	99.3 (θ = 28.31°)	99.4 (θ = 28.30°)
abs cor	empirical	empirical
no. of params	352	302
goodness of fit on F^2	0.919	0.812
final R indices ($I > 2\sigma(I)$)	R1 = 0.0479, wR2 = 0.0606	R1 = 0.0486, wR2 = 0.0769
R indices (all data)	R1 = 0.1681, wR2 = 0.0730	R1 = 0.1997, wR2 = 0.0978
largest diff peak, hole (e Å^{-3})	0.437, −0.823	0.374, −0.802

$C_{29}H_{25}P$, 404.1694, found 404.1699. Anal. Calcd for $C_{29}H_{25}P$: C, 86.11; H, 6.23. Found: C, 86.01; H, 6.33.

(*E*)-(1,2-Diphenylpenta-1,4-dienyl)diphenylphosphine Oxide (8). To a solution of **1a** (0.4 mmol, 248 mg) in 5 mL of THF were added 40 mg of CuCl (0.4 mmol) and 35 μL of allyl bromide (0.4 mmol), and the solution was stirred for 2 h at 50 °C. Then 30% H_2O_2 (2 mL) was added dropwise and the mixture was stirred for 24 h. ^{31}P NMR (81 MHz, THF, 85% H_3PO_4): δ 26.9. The NMR yield was 76%. Removal of the solvent and subsequent purification by column chromatography on silica gel (2/1 ethyl acetate/petroleum ether) afforded the title compound as an oil (214 mg, 51%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 3.76 (d, J = 6.5 Hz, 2H), 4.70 (d, $^3J_{HH}$(trans) = 16.8 Hz, 1H), 4.74 (d, $^3J_{HH}$(cis) = 10.3 Hz, 1H), 5.49 (dd, $^3J_{HH}$(trans) = 16.8 Hz, $^3J_{HH}$(cis) = 10.3 Hz, 1H), 6.90−7.05 (m, 6H), 7.22−7.39 (m, 10H), 7.54−7.77 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 41.5 (d, $^3J_{PC}$ = 7.9 Hz), 117.6, 126.1, 127.0, 127.6 (d, $^3J_{PC}$ = 15.8 Hz), 128.2, 128.4, 128.4, 131.0 (d, $^3J_{PC}$ = 3.6 Hz), 131.4 (d, $^4J_{PC}$ = 2.2 Hz), 131.9 (d, $^2J_{PC}$ = 9.3 Hz), 132.9 (d, $^1J_{PC}$ = 50.2 Hz), 133.9 (d, $^1J_{PC}$ = 101.8 Hz), 134.0, 134.6 (d, $^3J_{PC}$ = 11.5 Hz), 138.5 (d, $^2J_{PC}$ = 11.5 Hz), 143.3 (d, $^2J_{PC}$ = 14.3 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ 26.2. Positive ion ESI-MS: 421.2 (M + H$^+$), 443.1 (M + Na$^+$). HRMS: calcd for $C_{29}H_{25}OP$, 420.1643; found, 420.1650. Anal. Calcd for $C_{29}H_{25}OP$: C, 82.84; H, 5.99. Found: C, 82.69; H, 6.08.

Preparation of (*Z*)-(2-Iodo-1,2-diphenylvinyl)diphenylphosphine Oxide (9). To a solution of **1a** (0.1 mmol, 62 mg) in 2 mL of THF were added 38 mg of CuI (0.2 mmol) and 76 mg of I_2 (0.3 mmol), and the solution was stirred for 2 h at 50 °C. ^{31}P NMR (81 MHz, THF, 85% H_3PO_4): δ 54.8. The reaction mixture was treated with $Na_2S_2O_3$. Removal of the solvent and subsequent purification by column chromatography on silica gel (2/1 ethyl acetate/petroleum ether) afforded the title compound (23 mg, 45%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 6.71−7.73 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 117.2 (d, $^2J_{PC}$ = 4.3 Hz), 126.7, 127.7, 128.0, 128.3 (4C), 128.3 (d, $^3J_{PC}$ = 12.2 Hz, 4C), 128.4 (2C), 139.8 (d, $^3J_{PC}$ = 3.6 Hz, 2C), 131.5 (d, $^4J_{PC}$ = 2.5 Hz, 2C), 132.0 (d, $^2J_{PC}$ = 9.3 Hz, 4C), 132.3 (d, $^1J_{PC}$ = 107.5 Hz, 2C), 138.7 (d, $^3J_{PC}$ = 10.8 Hz), 145.2 (d, $^2J_{PC}$ = 38.06 Hz), 145.3 (d, $^1J_{PC}$ = 53.1 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4): δ 30.9. Positive ion ESI-MS: 507.0 (M + H$^+$). HRMS: calcd for $C_{26}H_{20}IOP$, 506.0296; found, 506.0290. Anal. Calcd for $C_{26}H_{20}IOP$: C, 61.68; H,3.98. Found: C, 61.59; H, 4.09.

X-ray Crystallographic Studies. Single-crystal X-ray diffraction studies for **1a** and **1g** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.[15] Crystal data and processing parameters for **1a** and **1g** are summarized in Table 2.

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Supporting Information Available: X-ray crystallography data as CIF files for complexes **1a** and **1g** and an ORTEP plot of **1g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Sheldrick, G. M. SHELXTL-97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.