A New Route to Vinyl Phosphorus Derivatives by Formal Insertion of Phosphinidenes into the Carbon−Chlorine Bond of Chloroalkenes

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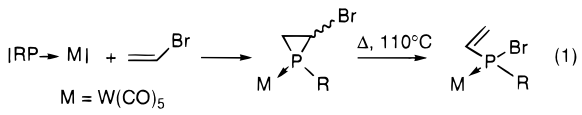
The reaction of a transient terminal phosphinidene complex such as [PhP−$W(CO)_5$] with chloroalkenes yields (phenyl)(vinyl)chlorophosphine complexes formally resulting from an insertion of the phosphorus unit into the C−Cl bond with retention of the alkene stereochemistry. The mechanism involves intermediate phosphirane complexes in which a concerted migration of chlorine takes place from carbon to phosphorus. Oxidative decomplexation yields the corresponding (phenyl)-(vinyl)phosphinates.

Introduction

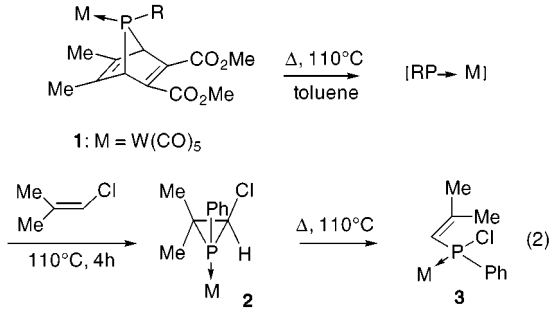
Vinylphosphorus derivatives play an important role in organic synthesis (vinyl phosphonates,[1] vinylphosphonium salts[2]), organophosphorus synthesis (preparation of polyphosphines[3]), and coordination chemistry.[4] Recently, we have observed that a 2-bromophosphirane complex obtained by [2 + 1] cycloaddition of vinyl bromide with a terminal phosphinidene complex cleanly rearranges to give a vinylbromophosphine complex[5] (eq 1).



On this basis, it was conceivable to devise a synthetic scheme allowing the preparation of vinylphosphorus compounds via a formal insertion of a phosphinidene unit into a vinyl−halogen bond. With that idea in mind, we decided to check the following points: (1) Is it possible to insert a phosphinidene into the less reactive but more common vinyl−chlorine bond? (2) Does this formal insertion take place with retention of the alkene stereochemistry? (3) Is it possible to break the phosphorus−metal bond to get the free vinyl phosphorus derivatives? The answers of these questions are the subject of the following paper.

Results and Discussion

All our experiments were performed with the readily available phenylphosphinidene−pentacarbonyltungsten complex as prepared by thermal decomposition of the appropriate 7-phosphanorbornadiene complex **1**.[6] To answer the first question, we allowed complex **1** to react with 1-chloro-2-methylpropene (eq 2).



The phosphirane **2** is essentially produced as a single isomer. The presence of the three-membered ring was ascertained by the ^{31}P resonance at δ −110 ($CDCl_3$). The stereochemistry was established by the $^2J(H-P)$ coupling of the ring α-proton (2.7 Hz).This low value means that H is cis to the tungsten atom.[7] Note that the opposite stereochemistry was found for the major isomer of the 2-bromophosphirane of eq 1.[5] When monitoring the reaction by ^{31}P NMR, the phosphirane **2** appeared as the major product after heating the reaction mixture at 110 °C for 2.5 h. But after 4 h at 110 °C, **2** was isolated in only 13% yield. The major part of it was already transformed into the vinylchlorophosphine complex **3** isolated in 39% yield. The rearrangement of **2** into **3** is accompanied by a downfield shift of the ^{31}P resonance that appears at δ 80 ($CDCl_3$). The olefinic proton resonates at 6.24, $^2J(H-P)$ =32.7 Hz.[8] The answer to the first question is thus positive.

To answer the second question, we decided to investigate the reaction of the phenyl phosphinidene complex with *cis*- and *trans*-1,2-dichloroethene. The reaction of **1** with *cis*-1,2-dichloroethene under the same conditions as above yields exclusively the *cis*-phosphirane **5** in 57% isolated yield (eq 3).

(1) Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 333.
(2) Johnson, A. W. *Ylides and Imines of Phosphorus;* Wiley: New York, 1993; p 112.
(3) Stelzer, O.; Langhans, K.-P. In *The Chemistry of Organophosphorus Compounds*, Hartley, F. R., Ed.; Wiley: Chichester, 1990; Vol. 1, p 191.
(4) Some recent references: Ji, H.-L.; Nelson, J. H.; DeCian, A.; Fischer, J.; Solujic, L.; Milosavljevic, E. B. *Organometallics* **1992**, *11*, 401. Alcock, N. W.; Wilson, W. L.; Nelson, J. H. *Inorg. Chem.* **1993**, *32*, 3193. Barthel-Rosa, L. P.; Maitra, K.; Fischer, J.; Nelson, J. H. *Organometallics* **1997**, *16*, 1714.
(5) Tran Huy, N. H.; Mathey, F. *Synlett* **1995,** 353.
(6) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982,** 667.
(7) Marinetti, A.; Mathey, F. *Tetrahedron* **1989**, *45*, 3061.
(8) Related data on [$Ph_2P-CH=CH_2$]Mo($CO)_5$: Maitra, K.; Nelson, J. H. *Polyhedron* **1998**, *18*, 203.

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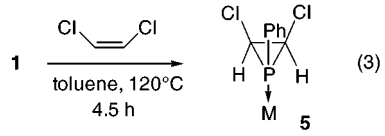
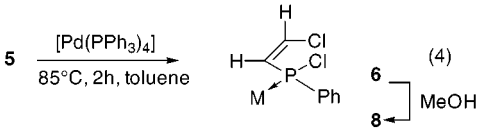
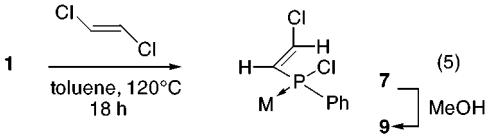


The cis disposition of the two chlorine substituents is indicated by the presence of a single resonance for the ring CH units in both the ^{1}H and ^{13}C NMR spectra. The ^2J(H−P) coupling of 1.4 Hz implies that the ring hydrogens are cis to tungsten. The retention of alkene stereochemistry during the [C═C + P] cycloadditions of that type is well established.[9] The ring opening of **5** needs 8 h at 110 °C in toluene but is more readily achieved at 85 °C when a Pd(0) catalyst is added (eq 4).

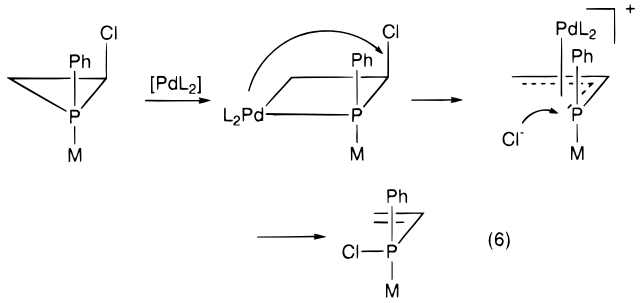


It is important to notice that the stereochemistry of the ring opening is not modified by the catalyst. We shall come back to this problem later. Compound **6** is very sensitive toward hydrolysis and needs special care for its purification by chromatography. The vinylic protons of **6** appear as an ABX system (X = P) with a ^3J(A−B) coupling of 8.45 Hz.

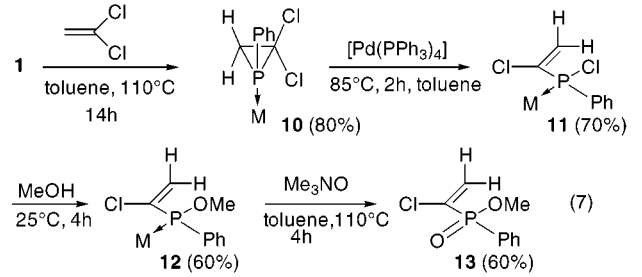
The reaction of **1** with *trans*-1,2-dichloroethene at 120 °C overnight directly affords the less sensitive *trans*-vinylchlorophosphine complex **7** in 35% isolated yield (eq 5).



The vinylic protons of **7** display a ^3J(H−H) coupling of 14 Hz. Thus, the stereochemistry is necessarily cis for **6** and trans for **7** ($J_{trans} > J_{cis}$). Compounds **6** and **7** were allowed to react with methanol to give **8** and **9**. The phosphinite complex **8** displays a ^{31}P resonance at δ 112.5 ($CDCl_3$). The olefinic protons appear as an ABX system (X = P) with ^3J(A−B) = 8.7 Hz. The data for **9** are as follows: δ^{31}P 113.4 ($CDCl_3$); ^3J(A−B) = 14.3 Hz. These results confirm the stereochemical assignments for **6** and **7**. The answer to the second question is thus that the overall insertion process takes place with retention of the alkene stereochemistry. This observation in turn suggests that the ring opening of the intermediate 2-chlorophosphirane complexes is a concerted process. A favorable overlap between a lone pair orbital of chlorine and a low-lying empty orbital of phosphorus[10] could explain this migration of chlorine. The complexation of phosphorus by [$W(CO)_5$] probably lowers the energy of these accepting orbitals and prevents the repulsion between the lone pairs at P and Cl. The catalytic process probably involves an insertion of [PdL_2] into the P−C ring bond opposite to the CCl unit as a first step. Such insertions are known to occur with retention of the ring stereochemistry.[11] The nucleophilic palladium then favors the departure of Cl^- to give a η^3-1-phosphaallyl cationic complex. Such η^3-complexes have been described in the literature.[12] The proposed mechanism is summarized in eq 6.



To answer the third question, we decided to test the decomplexation step on the products resulting from the reaction of the phenylphosphinidene complex with 1,1-dichloroethene. The condensation of **1** with 1,1-dichloroethene proved to be rather sluggish (14 h at 110 °C). The phosphirane complex **10** was subjected to a palladium-catalyzed ring opening. The resulting chlorovinyl−chlorophosphine complex **11** was then allowed to react with methanol, and the phosphinite complex thus formed **12** was subjected to an oxidative decomplexation with trimethylamine oxide (eq 7).



According to phosphorus NMR, all the steps were close to quantitative, and the quoted yields corresponds to the isolated products after chromatographic purification on small-scale reactions. Taking into account the variety of the available phosphinidene complexes (alkoxy,[13] amino,[14] alkyl, ...) and the possibility to recover the uncomplexed phosphorus compound also as a vinylchlorophosphine,[15] it appears that this method is highly versatile. Its sophistication of course restricts its use to complex halogenoalkenes. In such a case, the high tolerance of the condensation of alkenes with phosphinidenes toward functional groups is an additional advantage.[16]

Experimental Section

All reactions were performed under nitrogen. The solvents were purified, dried, and degassed by standard techniques.^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13, 50.32, and 81.01 MHz,

(9) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.
(10) On the nature of these vacant accepting orbitals, see: Pacchioni, G.; Bagus, P. S. *Inorg. Chem.* **1992**, *31*, 4391.
(11) Carmichael, D.; Hitchcock, P. B.; Nixon, J. F.; Mathey, F.; Ricard, L. *J. Chem. Soc., Dalton Trans.* **1993**, 1811.
(12) Mercier, F.; Fischer, J.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 357. For a recent review, see: Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998; p 259.
(13) Holand, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796.
(14) Mercier, F.; Deschamps, B.; Mathey, F. *J. Am. Chem. Soc.* **1989**, *111*, 9098.
(15) Deschamps, B.; Mathey, F. *Synthesis* **1995,** 941.
(16) For a recent review on the chemistry of electrophilic terminal phosphinidene complexes, see: Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998; p 20.

respectively, unless stated otherwise. All chemical shifts are reported in ppm downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra (EI) were obtained at 70 eV by the direct inlet method. Elemental analysis were performed by Service de Microanalyze ICSN, CNRS, Gif Sur Yvette.

(1-Phenyl-2-chloro-3,3-dimethylphosphirane)pentacarbonyltungsten 2 and [(2-Methylpropenyl)phenylchlorophosphine]pentacarbonyltungsten 3. A solution of **1** (1.9 g, 3 mmol) and an excess of 1-chloro-2-methylpropene in 10 mL of toluene were heated in a sealed tube at 110−120 °C for 4 h. The two products **2** and **3** were separated by chromatography on silica gel with hexane/dichloromethane 20/1 as the eluent.

3: yield 0.6 g (39%) of white crystals; ^{31}P NMR ($CDCl_3$) δ 80.2 $^1J(^{31}P-^{183}W) = 273.6$ Hz; ^{1}H NMR ($CDCl_3$) δ 1.70 (d, 3H, Me), 2.04 (s, 3H, Me), 6.24 (dd, 1H, ^2J(H−P) = 32.7 Hz, =CHP), 7.23−7.81 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 22.49 (d, ^3J(C−P) = 9 Hz, Me), 28.36 (d, ^3J(C−P) = 13.7 Hz, Me), 124.71 (d,^1J(C−P) = 30.8 Hz, =CHP), 156.72 (s, =*C*Me$_2$), 196.39 (d, ^2J(C−P) = 6.7 Hz, cis CO), 199.68 (d, ^2J(C−P) = 29.2 Hz, trans CO); MS (^{184}W,^{35}Cl) *m*/*z* 522 (M, 11), 348 (M − 5 CO − Cl + H, 100).

2: yield 0.2 g (13%) of white powder; ^{31}P NMR ($CDCl_3$) δ −109.7 $^1J(^{31}P-^{183}W) = 263.5$ Hz; ^{1}H NMR ($CDCl_3$) δ 1.24 (d, 3H, ^3J(H−P) = 12.15 Hz, Me), 1.52 (d, 3H, ^3J(H−P) = 18.23 Hz, Me), 3.97 (d, 1H, ^2J(H−P) = 2.70 Hz, ring H), 7.39 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 22.01 (d, ^2J(C−P) = 9.1 Hz, Me), 24.64 (s, Me), 32.73 (d, ^1J(C−P) = 13.7 Hz, *C*Me$_2$), 51.45 (d, ^1J(C−P) = 11.8 Hz, CHCl), 195.29 (d, ^2J(C−P) = 7.6 Hz, cis CO), 197.61 (d, ^2J(C−P) = 32.1 Hz, trans CO); MS (^{184}W, ^{35}Cl) *m*/*z* 522 (M, 49), 382 (M − 5 CO, 100). Anal. Calcd for $C_{15}H_{12}ClO_5PW$: C, 34.48; H, 2.31. Found: C, 34.41; H, 2.21

(*cis*-1-Phenyl-2,3-dichlorophosphirane)pentacarbonyltungsten 5. From **1** (0.65 g, 1 mmol) and *cis*-1,2-dichloroethene (0.5 mL), phosphirane **5** was obtained as a white powder (0.3 g, 57%) using the same conditions as above: ^{31}P NMR ($CDCl_3$) δ −110.6 $^1J(^{31}P-^{183}W) = 282.4$ Hz; ^{1}H NMR ($CDCl_3$) δ 4.22 (d, 2H, ^2J(H−P) = 1.4 Hz, 2H, ring CH), 7.44 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 43.88 (d, ^1J(C−P) = 8.9 Hz, ring CH), 194.00 (d, ^2J(C−P) = 7.6 Hz, cis CO); MS (^{184}W,^{35}Cl) *m*/*z* 528 (M , 5), 350 (M − 5 CO − HCl, 100). Anal. Calcd for $C_{13}H_7Cl_2O_5PW$: C, 29.52; H, 1.33. Found: C, 29.31; H, 1.26.

[(*cis*-2-Chlorovinyl)phenylchlorophosphine]pentacarbonyltungsten 6. A solution of **5** (0.53 g, 1 mmol) in toluene (5 mL) was heated at 85 °C for 2 h in the presence of [$Pd(PPh_3)_4$] (20 mg). Purification on Florisil with hexane as the eluent gave **6** (0.2 g, 38%): ^{31}P NMR ($CDCl_3$) δ 79.8, $^1J(^{31}P-^{183}W) = 286.4$ Hz; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.83 (*A*BX, ^3J(A−B) = 8.45 Hz, J(A−X) = 10.8 Hz, =CH), 6.88 (A*B*X, J(B−X) = 21.6 Hz, =CH); MS (^{184}W,^{35}Cl) *m*/*z* 528 (M, 11), 352 (M − 5 CO − HCl, 100).

[Methyl (*cis*-2-chlorovinyl)phenylphosphinite]pentacarbonyltungsten 8. The chloro complex **6** (0.2 g, 0.38 mmol) was allowed to react with methanol (0.5 mL) in toluene (5 mL) for 3 h at rt. Chromatography on silica gel with hexane/dichloromethane 4:1 afforded **8** as a white powder (0.14 g, 75%): ^{31}P NMR ($CDCl_3$) δ 112.5 $^1J(^{31}P-^{183}W) = 287.0$ Hz; ^{1}H NMR ($CDCl_3$) δ 3.38 (d, 3H, ^3J(H−P) = 12.9 Hz, OMe), 6.54 (*A*BX, 1H, ^3J(A−B) = 8.6 Hz, J(A−X) = 12.3 Hz, =CH), 6.91 (A*B*X, 1H, J(B−X) = 24.9 Hz, =CH), 7.23−7.63 (m, 5H, Ph); MS (^{184}W,^{35}Cl) *m*/*z* 524 (M , 13), 369 (M − 5 CO − Me, 100). Anal. Calcd for $C_{14}H_{10}ClO_6PW$: C, 32.06; H, 1.92. Found: C, 32.11; H, 2.08.

[(*trans*-2-Chlorovinyl)phenylchlorophosphine]pentacarbonyltungsten 7. A solution of **1** (1.9 g, 3 mmol) and 2 mL of *trans*-1,2-dichloroethene in 15 mL of toluene was heated at 120 °C overnight. The purification on silica gel with hexane/dichloromethane 5:1 as the eluent gave **7** (0.53 g, 35%). ^{31}P NMR (CH_2Cl_2) δ 79.1, $^1J(^{31}P-^{183}W)$ = 289.3 Hz; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.78 (*A*BX, ^3J(A−B) ≈ J(A−X) = 14 Hz, =CH), 6.84 (A*B*X, J(B−X) = 22.3 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ 133.17 (d, J(C−P) = 25.3 Hz, =CH), 135.39 (d, J(C−P) = 18.3 Hz, =CH), 137.11 (d, ^1J(C−P) = 36.6 Hz, Ph *C* ipso), 195.46 (d, ^2J(C−P) = 7.3 Hz, cis CO), 198.35 (d, ^2J(C−P) = 31.9 Hz, trans CO); MS (^{184}W,^{35}Cl) *m*/*z* 528 (M , 34), 352 (M − 5 CO − HCl, 100). Anal. Calcd for $C_{13}H_7Cl_2O_5PW$: C, 29.52; H, 1.33. Found: C, 29.93; H, 1.19.

[Methyl (*trans*-2-chlorovinyl)phenylphosphinite]pentacarbonyltungsten 9. The same conditions as for the conversion of **6** into **8** were used with **7**: yield of **9** ca. 70%; ^{31}P NMR ($CDCl_3$) δ 113.3, $^1J(^{31}P-^{183}W) = 286.1$ Hz; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.54 (d, 3H, ^3J(H−P) = 13.1 Hz, OMe), 6.65 (*A*BX, 1H, ^3J(A−B) = 14.3 Hz, J(A−X) = 15.3 Hz, =CH), 6.83 (A*B*X, 1H, J(B−X) = 10.6 Hz, =CH), 7.49−7.60 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 132.07 (d, J(C−P) = 31.9 Hz, =CH), 135.05 (d, J(C−P) = 18.0 Hz, =CH), 196.11 (d, ^2J(C−P) = 7.8 Hz, *cis* CO); MS (^{184}W,^{35}Cl) *m*/*z* 524 (M , 22), 369 (M − 5 CO − Me, 100).

(1-Phenyl-2,2-dichlorophosphirane)pentacarbonyltungsten 10. From **1** (2.7 g, 4 mmol) and 1,1-dichloroethene (3 mL) heated in toluene at 110 °C for 14 h was obtained phosphirane **10** as a white powder (1.7 g, 80%): ^{31}P NMR ($CDCl_3$) δ −99.5, $^1J(^{31}P-^{183}W) = 274.0$ Hz; ^{1}H NMR ($CDCl_3$) δ 2.32 (*A*BX, 1H, ^2J(A−B) = 10.8 Hz, ^2J(A−X) = 2.3 Hz, ring H), 2.74 (A*B*X, 1H, ^2J(B−X) = 7.9 Hz, ring H), 7.47 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 31.89 (d, ^1J(C−P) = 6.4 Hz, CH_2), 63.78 (d, ^1J(C−P) = 13.2 Hz, CCl_2), 132.94 (d, ^1J (C−P) = 28.9 Hz, Ph *C* ipso), 194.67 (d, ^2J (C−P) = 7.7 Hz, cis CO), 196.80 (d, ^2J(C−P) = 31.9 Hz, trans CO); MS (^{184}W,^{35}Cl) *m*/*z* 528 (M , 3), 350 (M − 5 CO − HCl, 100). Anal. Calcd for $C_{13}H_7Cl_2O_5PW$: C, 29.52; H, 1.33. Found: C, 29.71; H, 1.31.

[(1-Chlorovinyl)phenylchlorophosphine]pentacarbonyltungsten 11. From **10** (1.7 g, 3 mmol), chlorophosphine complex **11** was obtained using the same conditions as for the transformation of **5** into **6**: yield 1.2 g (70%); ^{31}P NMR ($CDCl_3$) δ 91.6, $^1J(^{31}P-^{183}W) = 292.2$ Hz; ^{1}H NMR ($CDCl_3$) δ 6.18 (*A*BX, 1H, ^2J(A−B) = 2.7 Hz, ^3J(A−X) = 27.5 Hz, =CH_2), 6.35 (A*B*X,-1H, ^3J(B−X) = 10.0 Hz, =CH_2); ^{13}C NMR ($CDCl_3$) δ 126.39 (d, ^2J(C−P) = 14.2 Hz, =CH_2), 134.67 (d, ^1J(C−P) = 35.1 Hz, Ph *C* ipso), 140.91 (d, ^1J(C−P) = 26.0 Hz, =CCl), 195.37 (d, ^2J(C−P) = 7.7 Hz, cis CO), 197.89 (d, ^2J(C−P) = 33.7 Hz, trans CO); MS (^{184}W, ^{35}Cl) *m*/*z* 528 (M).

[Methyl (1-chlorovinyl)phenylphosphinite]pentacarbonyltungsten 12. From **11** (0.26 g, 0.49 mmol), the phosphinite complex **12** was obtained using the same conditions as for the transformation of **6** into **8**: yield 0.2 g (60%); ^{31}P NMR ($CDCl_3$) δ 125.6, $^1J(^{31}P-^{183}W)$ = 289.0 Hz; ^{1}H NMR ($CDCl_3$) δ 3.54 (d, 3H, ^3J(H−P) = 13.3 Hz, OMe), 6.20−6.25 (m, 2H, =CH_2), 7.47−7.66 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 54.60 (d, ^2J(C−P) = 2.8 Hz, OMe), 126.92 (d, ^2J(C−P) = 15.0 Hz, =CH_2), 135.09 (d, ^1J(C−P) = 45.1 Hz, Ph*C* ipso), 141.52 (d,^1J(C−P) = 29.9 Hz, =CCl), 196.00 (d, ^2J(C−P) = 7.7 Hz, cis CO), 198.33 (d, ^2J(C−P) = 27.4 Hz, trans CO); MS (^{184}W,^{35}Cl) *m*/*z* 524 (M , 41), 384 (M − 5CO, 91), 369 (M − 5CO − Me, 100). Anal. Calcd for $C_{14}H_{10}ClO_6PW$: C, 32.06; H,1.92. Found: C, 31.96; H, 1.79.

Methyl (1-Chlorovinyl)phenylphosphinate 13. A solution of the phosphinite complex **12** (0.2 g, 0.38 mmol) and Me_3NO, $2H_2O$ (0.4 g, 3.6 mmol) in toluene (2 mL) was heated at 110 °C for 4 h. The product was chromatographed with CH_2Cl_2/MeOH as the eluent: yield 0.05 g (60%); ^{31}P NMR ($CDCl_3$) δ 25.6; ^{1}H NMR ($CDCl_3$) δ 3.83 (d, 3H, ^3J(H−P) = 11.6 Hz, OMe), 6.23 (dd, 1H, ^2J(H−H) = 1.5 Hz, ^3J(H−P) = 30.7 Hz, =CH_2), 6.57 (dd, 1H, ^2J(H−H) = 1.5 Hz, ^3J(H−P) = 11.7 Hz, =CH_2), 7.5 (m, 3H, Ph *m*, *p*), 7.9 (m, 2H, Ph *o*); ^{13}C NMR ($CDCl_3$) δ 52.10 (d, ^2J(C−P) = 6.2 Hz, OMe), 131.02 (d, ^2J(C−P) = 14.6 Hz, =CH_2); MS (^{35}Cl) *m*/*z* 216 (M , 25), 181 (M − Cl, 52), 155 (100). Anal. Calcd for $C_9H_{10}ClO_2P$: C, 49.91; H, 4.65. Found: C, 50.04; H, 5.24.

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