Nickel-Catalyzed Cross-Coupling of Diphenylphosphine with Vinyl Bromides and Chlorides as a Route to Diphenylvinylphosphines

Mstilsav O. Shulyupin, Evgeniy A. Chirkov, Marina A. Kazankova,* Irina P. Beletskaya

Department of Chemistry, Moscow State University (MSU), Leninskie Gory 1, Building 3, 119992 Moscow, Russia
Fax +7(095)9328846; E-mail: kazank@org.chem.msu.ru

Received 15 December 2004

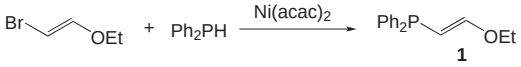
Abstract: An efficient nickel-catalyzed reaction for the phosphination of vinyl bromides and chlorides was developed. The procedure uses a combination of up to 1 mol% of nickel acetylacetonate, triethylamine and dimethylformamide as a solvent. The double bond geometry of the vinyl halides was retained under the reaction conditions.

Key words: cross-coupling, phosphorus, nickel, alkenylphosphines

Tertiary alkenylphosphines play an important role in organophosphorus synthesis[1] (preparation of polyphosphines), polymer chemistry[2] and coordination chemistry.[3] There are three main approaches to the synthesis of these compounds: hydrophosphination of alkynes,[4] coupling of chlorophosphines with vinylmagnesium or lithium reagents,[5] or the reaction of phosphide anion with vinyl halides.[6]

Recently, a new general method of P-C bond formation was developed via cross-coupling of secondary phosphines with aryl iodides, bromides and triflates using complexes of Pd, Ni or Cu as catalyst.[7] These conditions can be applied to the synthesis of alkenylphosphines from vinyl triflates,[8] iodides[9] and activated vinyl bromides.[10] However, some types of alkenyl bromides were unactive under reported conditions and there were no reports about coupling of vinyl chlorides with secondary phosphines. In this communication we wish to report a protocol for nickel-catalyzed synthesis of tertiary alkenylphosphines from alkenyl bromides and vinylidene chlorides.

1-Bromo-2-ethoxy-ethene and diphenylphosphine were chosen as reaction partners for the discovery of appropriate reaction conditions (Equation 1).



Equation 1 Nickel-catalyzed phosphination of 1-bromo-2-ethoxy-ethene

We were pleased to find (Table 1, entry 1) that using ligand-free nickel acetylacetonate as the catalyst precursor,[11] triethylamine as the base and dimethylformamide as the solvent, the cross-coupling took place and the product was isolated in high yield. The reaction was stereospecific. Pure *E*-isomer of 2-ethoxyethenyldiphenylphosphine was received from the pure *E*-isomer of 1-bromo-2-ethoxy-ethene according to ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra. The choice of the solvent was crucial for the success. HMPA was good for the reaction as well as DMF (entry 2), the yield of **1** dropped dramatically in the case of HMPA–toluene mixture and the reaction did not proceed totally in the toluene or THF media (entries 4 and 5).

Table 1 Cross-Coupling of 1-Bromo-2-ethoxy-ethene with Diphenylphosphine[a]

Entry	Solvent	Temp (°C)	Time (h)	Isolated yield
1	DMF	120	1	90
2	HMPA	120	1	80
3	HMPA/toluene (1:1)	120	1	58
4	Toluene	120	50	3[b]
5	THF	120	50	2[b]

[a] Reaction conditions: diphenylphosphine (1.5 mmol), 1-bromo-2-ethoxy-ethene (1.5 mmol), Et_3N (1.5 mmol), solvent (2 mL), catalyst (5 mol%).
[b] Conversion according to ^{31}P NMR.

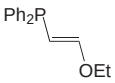
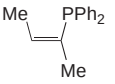
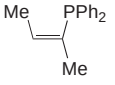
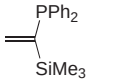
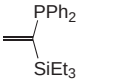
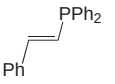
Under the indicated optimized conditions, cross-coupling of several substituted alkenyl halides was carried out. It should be pointed out that the reaction is more efficient in DMF rather than in HMPA (Table 2, compare entries 2 and 3). Moreover, for the scaled-up preparative experiments the quantity of the catalyst can be reduced to 1 mol% and reaction time to 30 minutes without prejudice to the yield.

Vinylidene tertiary phosphines are used as bidentate ligands in coordination chemistry because the 'bite-angle' of these chelated ligands is sufficiently changed by the sp^2-hybridized carbon.[12] 1,1-Bis(diphenylphosphino)ethene is a precursor for synthesis of other polydentate ligands.[13] The challenge was to synthesize 1,1-bis(diphenylphosphino)ethene using the cross-coupling reaction of 1,1-dichloroethene and diphenylphosphine (Scheme 1).

As can be seen from Table 3, complexes of Ni were able to catalyze the cross-coupling reaction (entries 1–4) but under these conditions the side reaction – oxidative

SYNLETT 2005, No. 4, pp 0658–0660
Advanced online publication: 22.02.2005
DOI: 10.1055/s-2005-863714; Art ID: G46004ST

Table 2 Nickel Acetylacetonate-Catalyzed Phosphination of Alkenyl Halides[a]

Entry	Vinyl-Br	Product	Time (h)	Yield (%)[b]
1		 **1**	0.5	90
2		 **2**	0.5	90
3[c]		 **2**	0.5	75
4		 **3**	0.5	93
5		 **4**	0.5	96
6		 **5**	0.5	90

[a] Reaction conditions: diphenylphosphine (5 mmol), alkenyl bromide (5 mmol), Et_3N (5 mmol), $Ni(acac)_2$ (1 mol%), 120 °C, DMF (5 mL).
[b] Isolated yield.
[c] HMPA was used as a solvent.

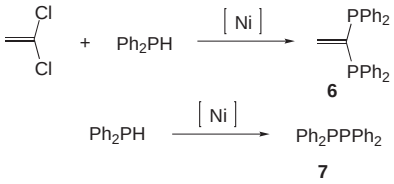
Table 3 Cross-Coupling of 1,1-Dichloroethene with Diphenylphosphine[a]

Entry	Catalyst	Solvent/additive	Temp (°C)	Time (h)	Ratio of **6**:**7**[b]
1	$Ni(acac)_2$	PhMe	120	7	34:66
2	$Ni(acac)_2$	DMF	120	1	40:60
3	$NiCl_2(PPh_3)_2$	PhMe	120	7	38:62
4	$NiCl_2(PPh_3)_2$	DMF	120	1	45:55
5[c]	$NiCl_2(PPh_3)_2$	DMF/Et_3N	120	3	100:0 (94)
6[c]	$Ni(acac)_2$	DMF/Et_3N	120	3	100:0 (81)

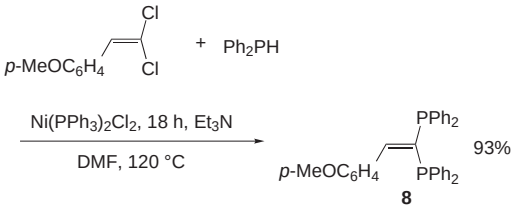
[a] Reaction conditions: diphenylphosphine (2 mmol), 1,1-dichloroethene (2.5 mmol), Et_3N (4 mmol), solvent (3 mL), catalyst (2 mol%).
[b] According to ^{31}P NMR, isolated yield of **6** in parentheses.
[c] 8 mmol of Et_3N were used.

dimerization of diphenylphosphine to form tetraphenyldiphosphine – took place. We found that, in the presence of a double molar excess of triethylamine, this side reaction was completely suppressed (entry 5, 6).

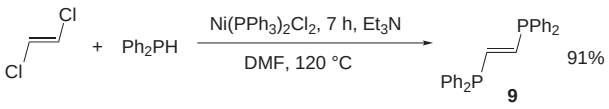
The reactivity of substituted 1,1-dichloroethenes was much less, for example in the case of 1-(*p*-methoxyphenyl)-2,2-dichloroethene 18 hours of heating was



Scheme 1



Equation 2 Nickel-catalyzed phosphination of 1-(*p*-methoxyphenyl)-2,2-dichloroethene



Equation 3 Nickel-catalyzed phosphination of *trans*-1,2-dichloroethene

necessary for the completion of the reaction (Equation 2) and 1-cyclohexyl-2,2-dichloroethene did not react at all for 40 hours at 120 °C.

The same method was applicable for the reaction of *trans*-1,2-dichloroethene with diphenylphosphine to form *trans*-1,2-diphenylphosphinoethene (according to ^{31}P NMR) in 91% yield (Equation 3). The latter compound is used as a ligand for synthesis of organometallic macrocycles,[14] metal complexes[15] and as a precursor to synthesis of chiral ligands.[16]

In conclusion, we have developed an efficient nickel-catalyzed carbon-phosphorus bond-forming protocol[17] for vinyl bromides and chlorides, which leads to corresponding phosphines with high yield and has some advantages over known organometallic methods of synthesis.

Acknowledgment

We thank RFBR (grant 04-03-32709), Uniros 05.03.044/04-1, the Grant of Russian Federation President supporting Leading Scientific Schools – 1611.2003.03 for financial support.

References

(1) *The Chemistry of Organophosphorus Compounds*, Vol. 1; Hartley, F. R., Ed.; Wiley: Chichester, UK, **1990**, 191.
(2) (a) Edge, M.; Faulds, P.; Kelly, D. G.; McMahon, A.; Ranger, G. C.; Turner, D. *Eur. Pol. J.* **2001**, *37*, 349.
(b) Maraval, V.; Laurent, R.; Donnadieu, B.; Mauzac, M.; Caminade, A.-M.; Majoral, J.-P. *J. Am. Chem. Soc.* **2000**, *122*, 2499.

(3) Some recent references: (a) Tunik, S. P.; Koshevoy, I. O.; Poe, A. J.; Norlander, E.; Haukka, M.; Pakkanen, T. A. *J. Chem. Soc., Dalton Trans.* **2003**, 2457. (b) Grachova, E. V.; Haukka, M.; Heaton, B. T.; Nordlander, E.; Pakkanen, T. A.; Podkorytov, I. S.; Tunik, S. P. *J. Chem. Soc., Dalton Trans.* **2003**, 2468. (c) Maitra, K.; Nelson, J. H. *Polyhedron* **1998**, *18*, 203. (d) Barthel-Rosa, L. P.; Maitra, K.; Fischer, J.; Nelson, J. H. *Organometallics* **1997**, *16*, 1714.

(4) For reviews, see: (a) Beletskaya, I. P.; Kazankova, M. A. *Russ. J. Org. Chem.* **2002**, *38*, 1391. (b) Tanaka, M. *Top. Curr. Chem.* **2004**, *232*, 25. (c) Some recent papers: Takaki, M.; Koshoji, G.; Komeyama, K.; Takeda, M.; Shishido, T.; Kitani, A.; Takehira, K. *J. Org. Chem.* **2003**, *68*, 6554. (d) See also: Mimeau, D.; Gaumont, A. *J. Org. Chem.* **2003**, *68*, 7016. (e) Jerome, F.; Monnier, F.; Lawicka, H.; Derien, S.; Dixneuf, P. H. *Chem. Commun.* **2003**, 696.

(5) (a) *The Chemistry of Organophosphorus Compounds*, Vol. 1; Hartley, F. R., Ed.; Wiley: Chichester, UK, **1990**, 309–401. (b) *The Chemistry of Organophosphorus Compounds*, Vol. 1; Hartley, F. R., Ed.; Wiley: Chichester, UK, **1990**, 496–499.

(6) (a) Colquhoun, I. J.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1982**, 1915. (b) Bookham, J. L.; McFarlane, W. *Polyhedron* **1988**, *7*, 239.

(7) For reviews see ref.[4a] and: (a) Schwan, A. L. *Chem. Soc. Rev.* **2004**, *33*, 218. (b) Some recent papers: Gelman, D.; Jiang, L.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2315. (c) Allen, D. V.; Venkataraman, D. *J. Org. Chem.* **2003**, *68*, 4590. (d) Moncarz, J. R.; Brunker, T. J.; Jewett, J. C.; Orchowski, M.; Glueck, D. S.; Sommer, R. D.; Lam, K.-C.; Incarvito, C. D.; Concolino, T. E.; Ceccarelli, C.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2003**, *22*, 3205. (e) Murata, M.; Buchwald, S. L. *Tetrahedron* **2004**, *60*, 7397.

(8) Gilbertson, S. R.; Fu, Z.; Starkey, G. W. *Tetrahedron Lett.* **1999**, *40*, 8509.

(9) See ref. 7b and: Trostyanskaya, I. G.; Titskiy, D. Y.; Anufrieva, E. A.; Borisenko, A. A.; Kazankova, M. A.; Beletskaya, I. P. *Russ. Chem. Bull.* **2001**, *50*, 2095.

(10) Kazankova, M. A.; Chirkov, E. A.; Kochetkov, A. N.; Efimova, I. V.; Beletskaya, I. P. *Tetrahedron Lett.* **1999**, *40*, 573.

(11) There was a report that secondary phosphines were successfully used as ligands for the Heck reaction. See: Schnyder A., Aemmer T., Indolese A. F., Pittelkow U., Studer M.; *Adv. Synth. Catal.;* **2002,** *244:* 495.

(12) Some recent articles: (a) Vila, J. M.; Lopez-Torres, M.; Fernandez, A.; Pereira, M. T.; Ortigueira, J. M.; Fernandez, J. J. *Inorg. Chim. Acta* **2003**, *342*, 185. (b) Mosteiro, R.; Fernandez, A.; Lopez-Torres, M.; Vazquez-Garcia, D.; Suarez, A.; Fernandez, J. J.; Vila, J. M. *New J. Chem.* **2002**, *26*, 1425. (c) Higgins, S. J.; La Pensee, A.; Stuart, C. A.; Charnock, J. M. *J. Chem. Soc., Dalton Trans.* **2001**, 902. (d) Goli, M. B.; Grim, S. O. *Tetrahedron Lett.* **1991**, *32*, 363; and references therein.

(13) (a) Izod, K.; McFarlane, W.; Tyson, B. V.; Clegg, W.; Harrington, R. W.; Liddle, S. T. *Organometallics* **2003**, *22*, 3684. (b) Clegg, W.; Izod, K.; McFarlane, W.; O'Shaughnessy, P. *Organometallics* **1998**, *17*, 5231.

(14) (a) Mohr, F.; Eisler, D. J.; McArdle, C. P.; Atieh, K.; Jennings, M. C.; Puddephatt, R. J. *J. Organomet. Chem.* **2003**, *670*, 27. (b) Hunks, W. J.; Lapierre, J.; Jenkins, H. A.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **2002**, 2885. (c) McArdle, C. P.; Van, S.; Jennings, M. C.; Puddephatt, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 3959. (d) McArdle, C. P.; Irwin, M. J.; Jennings, M. C.; Vittal, J. J.; Puddephatt, R. J. *Chem.–Eur. J.* **2002**, *8*, 723.

(15) Some recent articles: (a) Chen, J.-L.; Zhang, L.-Y.; Chen, Z.-N.; Gao, L.-B.; Abe, M.; Sasaki, Y. *Inorg. Chem.* **2004**, *43*, 1481. (b) Ares, R.; Lopez-Torres, M.; Fernandez, A.; Pereira, M. a. T.; Alberdi, G.; Vazquez-Garcia, D.; Fernandez, J. J.; Vila, J. M. *J. Organomet. Chem.* **2003**, *665*, 76. (c) Ares, R.; Lopez-Torres, M.; Fernandez, A.; Castro-Juiz, S.; Suarez, A.; Alberdi, G.; Fernandez, J. J.; Vila, J. M. *Polyhedron* **2002**, *21*, 2309.

(16) Brown, J. M.; Lucy, A. R. *J. Organomet. Chem.* **1986**, *314*, 241.

(17) **General Procedure (for Compounds 1–5).**
A Schlenk flask was charged with 5 mmol of alkenyl bromide, 5 mmol of Et_3N, 5 mmol of diphenylphosphine, 5 mL of DMF and 1 mol% of $Ni(acac)_2$. The reaction mixture was stirred for specified period at maintained temperature (Table 2). To this mixture 20 mL of H_2O and 20 mL of benzene were added after cooling. The benzene phase was separated, washed with 10 mL of H_2O, and dried under $MgSO_4$. Then, 20 mg of dimethylglyoxime were added to the benzene solution. After 1 h the solution was passed through short layer of silica gel and evaporated in vacuum. The crude product was then distilled under reduced pressure.
***E*-(2-Ethoxyvinyl)diphenylphosphine (1)**: yield 90%, colorless oil, bp 120–124 °C/4 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25–1.28 (t, 3), 3.82–3.88 (q, 2), 5.32–5.35 (d, 1 , J_{HH} = 14 Hz), 6.86–6.92 (dd, 1 , J_{HH} = 14 Hz, J_{PH} = 9 Hz), 7.21–7.40 (m, 10). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.51 (-H_3), 65.24 (-O-CH_2), 97.63, 128.01, 128.21, 132.20, 159. ^{31}P{H} NMR (162.6 MHz, $CDCl_3$): δ = –18.0. Anal. Calcd for $C_{16}H_{17}OP$ (%): C, 74.99; H, 6.69. Found: C, 75.02; H, 6.52.
***Z*-(1-Methylpropenyl)diphenylphosphine (2)**: yield 90%, colorless oil, bp 110 °C/3 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72 (dt, 3 H, =(P)CH_3, J_{PH} = 1.0 Hz, J_{HH} = 7.4 Hz), 1.77 (d, 3 H, =(P)CH_3, J_{PH} = 6.7 Hz), 5.95 (m, -H), 7.32 (m, 10 H, C_6H_5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 137.09 (d, =C-P, J_P = 32.1 Hz), 133.22 (d, C=C-P, J_P = 19.8 Hz), 136.51 (d, J_P = 10.7 Hz, ipso), 128.65 (m, $_6H_5$), 15.00 (d, CH_3-C=C-P, J_P = 15.2 Hz), 15.00 [d, C=C(PPh_2)CH_3, J_P = 39.6 Hz]. ^{31}P{H} NMR (162.6 MHz, $CDCl_3$): δ = 5.9. Anal. Calcd for $C_{16}H_{17}P$ (%): C, 79.98; H, 7.13; P, 12.89. Found: C, 79.35; H, 6.96; P, 12.83.
General Procedure (for Compounds 6, 8, 9).
A Schlenk flask was charged with 2.5 mmol of alkenyl chloride, 8 mmol of Et_3N, 2 mmol of diphenylphosphine, 3 mL of DMF, and 2 mol% of $Ni(PPh_3)_2Cl_2$. The solution was stirred for specified period at maintained temperature. To this solution 20 mL of H_2O and 20 mL of benzene were added after cooling. The benzene phase was separated, washed with 10 mL of H_2O and dried under $MgSO_4$. Then, 20 mg of dimethylglyoxime were added to benzene solution and after 1 h the solution was passed through short layer of silica gel and evaporated in vacuum. The crude product was then purified by column chromatography (Al_2O_3, THF).
1,1-Bis(diphenylphosphino)-2-(*p*-methoxyphenyl)ethane (8): yield 93%, mp 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.68 (s, 3), 6.74 (d, 1 H), 7.03–7.39 (m, 25). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 55.10 (d, O-CH_3, J = 9.0 Hz), 113.25 (d, J = 4.5 Hz), 127.68, 128.27 (dd), 130.0 (t), 131.29 (t), 132.39 [dd, Ph_2P-C(PPh_2)=C, J = 33.6 Hz, J = 48.8 Hz], 133.83 (d, J = 21.4 Hz), 134.27 (d, J = 19.8 Hz), 135.84 (dd, J = 6.1 Hz, J = 9.2 Hz), 136.47 (d, J = 15.0 Hz), 152.79 (dd, J = 9.0 Hz, J = 23.0 Hz), 159.48. ^{31}P{H} NMR (162.6 MHz, $CDCl_3$): δ = –3.8 (d, J = 1.5 Hz), –12.0 (d, J = 1.5 Hz). Anal. Calcd for $C_{33}H_{28}P_2O$ (%): C, 78.80; H, 5.62. Found: C, 77.49; H, 5.79.