New approach to Phosphinoalkynes based on Pd- and Ni-Catalyzed Cross-coupling of terminal alkynes with Chlorophosphanes

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Supporting Information

Manipulations of air and moisture sensitive materials were conducted under argon atmosphere using standard vacuum line and Schlenk techniques.

Solvents were dried and purified under argon before use: PhH, PhMe and heptane were distilled from sodium benzophenone, MeCN and CH₂Cl₂ were distilled from P₂O₅.

NMR ¹H, ¹³C and ³¹P spectra were recorded on Varian VXR-400 instrument. Chemical shift values for ¹H and ¹³C are referenced to Me₄Si, and these for ³¹P are referenced to H₃PO₄ (85% solution in D₂O, 0 ppm).

Catalysts, alkynes and chlorophosphanes were either commercially available or prepared by a reported procedure: Chlorodibutylphosphane¹, Bis(triphenylphosphano)nickel dibromide², Bis(cyclooctadienyl)nickel³, Tetrakis(triethylphosphite)nickel⁴, Tetrakis(triphenylphosphano)palladium⁵.

General procedure. A Schlenk flask was charged with chlorophosphane, Ni(acac)₂ (3 mol%), triethylamine, alkyne, and solvent. The solution was stirred for specified period at maintained temperature. The reaction was followed using ³¹P NMR. Ammonia salt was removed by filtration, solvent was evaporated under a reduced pressure. The crude product was then purified by column chromatography (SiO₂, CH₂Cl₂/hexane) or distilled under reduced pressure.

[1] Diphenyl(2-phenylethynyl)phosphane⁶. Yield 95%, light yellow solid, mp= 43°C. ³¹P{H} NMR (162.6 MHz, CDCl₃) δ: -33.50.

[2] Diphenyl[(4-methylphenyl)ethynyl]phosphane⁷. Yield 96%, light yellow solid, mp= 51°C. ³¹P{H} NMR (162.6 MHz, CDCl₃) δ: -33.41.

[3] Diphenyl(1-pentynyl)phosphane⁸. Yield 91%, colorless oil, bp= 132-134°C/0.05 Torr. ³¹P{H} NMR (162.6 MHz, CDCl₃) δ: -33.65.

[4] Diphenyl(1-heptynyl)phosphane⁶. Yield 93%, colorless oil, bp= 154-159°C/0.05 Torr. ³¹P{H} NMR (162.6 MHz, CDCl₃) δ: -33.62.

[5] Diphenyl(3,3-dimethylbutynyl-1)phosphane^{9,10}. Yield 87%, colorless solid, mp= 33-34°C. ³¹P{H} NMR (162.6 MHz, CDCl₃) δ: -34.21.

[6] Diisopropyl(2-phenylethynyl)phosphane⁸. Yield 79%, colorless oil, bp= 125-130°C/0.75 Torr. ³¹P{H} NMR (162.6 MHz, CDCl₃) δ: -11.56.

[7] Diisopropyl(1-heptynyl)phosphane. Yield 82%, colorless oil, bp= 110-115°C/0.02 Torr. ¹H NMR (400 MHz, CDCl₃) δ: 0.79 (t, 3H), 1.08 (d. d., 6H, J=4.47, 7.10 Hz), 1.29 (m, 4H), 1.78 (m, 2H), 2.90 (d.

t., 2H, J=3Hz). ^{13}C NMR (100.6 MHz, CDCl_3) δ : 14.18, 19.42 (d, J=14.0 Hz), 20.31, 22.46, 28.49, 30.28 (d, J=8.9 Hz), 74.57 (d, J=9.16 Hz), 107.40 (d, J=3 Hz). $^{31}\text{P}\{\text{H}\}$ NMR (162.6 MHz, CDCl_3) δ : -11.50.

[8] Diisopropyl(3,3-dimethylbutynyl-1)phosphane. Yield 86%, colorless oil, bp= 105-110°C/0.02 Torr. ^1H NMR (400 MHz, CDCl_3) δ : 1.11 (c, 9H), 1.24 (d. d., 6H, J=4.53, 8.10 Hz), 1.75 (m, 2H). ^{13}C NMR (100.6 MHz, CDCl_3) δ : 19.29 (d, J=14.21 Hz), 28.27, 29.0 (d, J=32.09 Hz), 30.84, 72.90 (d, J=9.15 Hz), 114.0. $^{31}\text{P}\{\text{H}\}$ NMR (162.6 MHz, CDCl_3) δ : -12.20.

[9] Isopropyl(phenyl)(2-phenylethynyl)phosphane. Yield 89%, colorless oil, bp= 155-160°C/0.2 Torr. ^1H NMR (400 MHz, CDCl_3) δ : 1.10 (d. q, 6H, J=7.0, 22.0 Hz), 2.02 (d. h., 1H, J=2.27, 7.30 Hz), 7.30 (m, 6H), 7.48 (m, 2H), 7.68 (d. t., 2H, J=1.6 Hz). ^{13}C NMR (100.6 MHz, CDCl_3) δ : 19.92 (d, J=15.3 Hz), 30.90, 29.0 (d, J=7.70 Hz), 86.90 (d, J=15.30 Hz), 107.79, 123.85, 129.13, 129.20, 129.64 (d, J=29 Hz), 132.46, 133.65 (d, J=15.60 Hz), 135.73 (d, J=10.50 Hz). $^{31}\text{P}\{\text{H}\}$ NMR (162.6 MHz, CDCl_3) δ : -23.35.

[10] Dibutyl(2-phenylethynyl)phosphane¹¹. Yield 82%, colorless oil, bp= 165-170°C/0.75 Torr. $^{31}\text{P}\{\text{H}\}$ NMR (162.6 MHz, CDCl_3) δ : -49.80.

[11] Dibutyl(1-heptynyl)phosphane. Yield 86%, colorless oil, bp= 148-150°C/0.02 Torr. ^1H NMR (400 MHz, CDCl_3) δ : 0.82 (m, 9H), 1.28 (m, 6H), 1.45 (m, 6H), 1.60 (m, 8H), 2.41 (q, 2H). ^{13}C NMR (100.6 MHz, CDCl_3) δ : 14.18, 20.37, 22.51, 24.56 (d, J=10.68 Hz), 27.89 (d, J=9.50 Hz), 28.55, 28.76 (d, J=7.63 Hz), 30.40, 31.23 (d, J=9.15 Hz), 68.60, 105.89. $^{31}\text{P}\{\text{H}\}$ NMR (162.6 MHz, CDCl_3) δ : -46.20.

[12] Phenyl[bis(2-phenylethynyl)]phosphane¹². Yield 96%, light yellow solid, mp= 48-53°C. $^{31}\text{P}\{\text{H}\}$ NMR (162.6 MHz, CDCl_3) δ : -60.94.

[13] Phenyl[bis(1-heptynyl)]phosphane. Yield 95%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 0.87 (t, 6H), 1.33 (m, 6H), 1.52 (m, 4H), 3.31 (d. t., 4H, J=1.48 Hz), 7.33 (m, 3H), 7.70 (m, 2H). ^{13}C NMR (100.6 MHz, CDCl_3) δ : 12.49, 18.86, 20.88, 26.77, 29.79, 72.47 (d, J=3.82 Hz), 107.28 (d, J=6.01 Hz), 127.17 (d, J=7.63 Hz), 127.62, 130.20 (d, J=21.30 Hz), 133.47 (d, J=2.30 Hz). $^{31}\text{P}\{\text{H}\}$ NMR (162.6 MHz, CDCl_3) δ : -66.2.

[14] Bis(3,3-dimethyl-1-butynyl)(phenyl)phosphane. Yield 94%, light yellow solid, mp=31°C. ^1H NMR (400 MHz, CDCl_3) δ : 1.01 (s, 18H), 7.32 (m, 3H), 7.71 (m, 2H). ^{13}C NMR (100.6 MHz, CDCl_3) δ : 30.02, 30.51, 73.21 (d, J=3.85 Hz), 110.34 (d, J=6.01 Hz), 127.17 (d, J=7.63 Hz), 127.62, 130.20 (d, J=21.30 Hz), 133.47 (d, J=2.30 Hz). $^{31}\text{P}\{\text{H}\}$ NMR (162.6 MHz, CDCl_3) δ : -61.23.

[15] Tris(2-phenylethynyl)phosphane¹³. Yield 95%, colorless solid, mp= 90°C. NMR (162.6 MHz, CDCl_3) δ : -88.40.

[16] Tris[2-(4-methylphenyl)ethynyl]phosphane¹⁴. Yield 96%, colorless solid, mp= 125°C. $^{31}\text{P}\{\text{H}\}$ NMR (162.6 MHz, CDCl_3) δ : -87.95.

[17] Tris(3,3-dimethyl-1-butynyl)phosphane¹⁵. Yield 96%, colorless solid, mp= 84°C. $^{31}\text{P}\{\text{H}\}$ NMR (162.6 MHz, CDCl_3) δ : -86.56.

Journals:

1. Komkov, I. P.; Karavanov, N. V. *Zh. Obsh. Chim.* **1958**, 28, 2963.
2. Venanzi, L.M. *J. Chem. Soc.* **1958**, 2, 719.
3. Leto, J.R.; Leto, M.F. *J. Am. Chem. Soc.* **1961**, 83, 2944.
4. Berdnik, I.V.; Krasil'nikova, E.A.; Sentemov V.V. *Zh. Obsh. Chim.* **1989**, 59, 2508.
5. Graeves E.O.; Lock C.E.; Maitlis P.M. *Can. J. Chem.* **1968**, 46, 3879.
6. Bharathy, P.; Periasamy, M. *Organometallics*. **2000**, 19, 5511-13.
7. Carty, J.; Hota, N. K.; Ng, T.W.; Patel, H. A.; O'Connor, T. J. *Can. J. Chem.* **1971**, 49, 2706.

8. Aguar A. M.; Preyeau, G. W.; Irelan, J. R. S.; Morrow, C. J. *J. Org. Chem.* **1969**, 34, 4024.
9. Montllo, D.; Suades, J.; Dalah, F.; Mathien, R. *Organometallics*. **1990**, 9, 2933.
10. Loutani, E.; Suades, J.; Mathien, R. *J. Organomet. Chem.* **1991**, 335.
11. Rosenberg, D.; Drenth, W. *Tetrahedron* **1971**, 27, 3893.
12. Hengefeld, A.; Nast, R. *Chem. Ber.* **1983**, 116, 2035.
13. Hartmann, H. *Lieb. Ann. Chem.* **1968**, 714, 1.
14. Hartmann, H.; Meixner, A. *Naturwiss.* **1963**, 50, 403.
15. Rieff, H. F.; Pant, B. C. *J. Organomet. Chem.* **1969**, 17, 165.