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 CH_2Cl_2 were distilled from P_2O_5.

NMR ^1H, ^{13}C and ^{31}P spectra were recorded on Varian VXR-400 instrument. Chemical shift values for ^1H and ^{13}C are referenced to Me_4Si, and these for ^{31}P are referenced to H_3PO_4 (85% solution in D_2O, 0 ppm).

Catalysts, alkynes and chlorophosphanes were either commercially available or prepared by a reported procedure: Chlorodibuthylphosphane[1], Bis(triphenylphosphano)nickel dibromide[2], Bis(cyclooctadienyl)nickel[3], Tetrakis(triethylphosphite)nickel[4], Tetrakis(triphenylphosphano)palladium[5].

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 ^{31}P NMR. Ammonia salt was removed by filtration, solvent was evaporated under a reduced pressure. The crude product was then purified by column chromatography (SiO_2, CH_2Cl_2/hexane) or distilled under reduced pressure.

[1] Diphenyl(2-phenylethynyl)phosphane[6]. Yield 95%, light yellow solid, mp= 43°C. $^{31}P\{H\}$ NMR (162.6 MHz, $CDCl_3$) δ: -33.50.

[2] Diphenyl[(4-methylphenyl)ethynyl]phosphane[7]. Yield 96%, light yellow solid, mp= 51°C. $^{31}P\{H\}$ NMR (162.6 MHz, $CDCl_3$) δ: -33.41.

[3] Diphenyl(1-penthynyl)phosphane[8]. Yield 91%, colorless oil, bp= 132-134°C/0.05 Torr. $^{31}P\{H\}$ NMR (162.6 MHz, $CDCl_3$) δ: -33.65.

[4] Diphenyl(1-hepthynyl)phosphane[6]. Yield 93%, colorless oil, bp= 154-159°C/0.05 Torr. $^{31}P\{H\}$ NMR (162.6 MHz, $CDCl_3$) δ: -33.62.

[5] Diphenyl(3,3-dimethylbuthynyl-1)phosphane[9,10]. Yield 87%, colorless solid, mp= 33-34°C. $^{31}P\{H\}$ NMR (162.6 MHz, $CDCl_3$) δ: -34.21.

[6] Diisopropyl(2-phenylethynyl)phosphane[8]. Yield 79%, colorless oil, bp= 125-130°C/0.75 Torr. $^{31}P\{H\}$ NMR (162.6 MHz, $CDCl_3$) δ: -11.56.

[7] Diisopropyl(1-hepthynyl)phosphane. Yield 82%, colorless oil, bp= 110-115°C/0.02 Torr. ^1H NMR (400 MHz, $CDCl_3$) 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}P{H} NMR (162.6 MHz, $CDCl_3$) δ: -11.50.

[8] Diisopropyl(3,3-dimethylbuthynyl-1)phosphane. Yield 86%, colorless oil, bp= 105-110^{o}C/0.02 Torr. ^{1}H 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}P{H} NMR (162.6 MHz, $CDCl_3$) δ: -12.20.

[9] Isopropyl(phenyl)(2-phenylethynyl)phosphane. Yield 89%, colorless oil, bp= 155-160^{o}C/0.2 Torr. ^{1}H 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}P{H} NMR (162.6 MHz, $CDCl_3$) δ: -23.35.

[10] Dibutyl(2-phenylethynyl)phosphane[11] . Yield 82%, colorless oil, bp= 165-170^{o}C/0.75 Torr. ^{31}P{H} NMR (162.6 MHz, $CDCl_3$) δ: -49.80.

[11] Dibutyl(1-hepthynyl)phosphane. Yield 86%, colorless oil, b_p= 148-150^{o}C/0.02 Torr. ^{1}H 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}P{H} NMR (162.6 MHz, $CDCl_3$) δ: -46.20.

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

[13] Phenyl[bis(1-hepthynyl)]phosphane. Yield 95%, colorless oil. ^{1}H 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}P{H} NMR (162.6 MHz, $CDCl_3$) δ: -66.2.

[14] Bis(3,3-dimethyl-1-butynyl)(phenyl)phosphane. Yield 94%, light yellow solid, m_p=31^{o}C. ^{1}H 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}P{H} NMR (162.6 MHz, $CDCl_3$) δ: -61.23.

[15] Tris(2-phenylethynyl)phosphane[13]. Yield 95%, colorless solid, mp= 90^{o}C. NMR (162.6 MHz, $CDCl_3$) δ: -88.40.

[16] Tris[2-(4-methylphenyl)ethynyl]phosphane[14]. Yield 96%, colorless solid, mp= 125^{o}C. ^{31}P{H} NMR (162.6 MHz, $CDCl_3$) δ: -87.95.

[17] Tris(3,3-dimethyl-1-butynyl)phosphane[15]. Yield 96%, colorless solid, mp= 84^{o}C. ^{31}P{H} NMR (162.6 MHz, $CDCl_3$) δ: -86.56.

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