Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Synthesis of Cp*CH_2PPh_2 and Its Use as a Ligand for Nickel-Catalysed Cross-Coupling Reaction of Alkyl Halides with Aryl Grignard Reagents

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Instrumentation and Materials

^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on Varian UNITY INOVA 500 spectrometers unless otherwise noted. Chemical shifts (δ) are in parts per million relative to benzene at 7.16 ppm for ^{1}H and at 128.0 ppm for ^{13}C or chloroform at 7.26 ppm for ^{1}H and at 77.2 ppm for ^{13}C. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 1,2,3,4,5-Pentamethyl-1,3-cyclopentadiene was purchased from Kanto Chemical Co. THF (dehydrated, stabilizer free) was purchased from Kanto Chemical Co., stored under nitrogen, and used without distillation. Butyllithium and diphenylphosphine were purchased from Nacalai Tesque and TCI, respectively. Borane-dimethyl sulfide complex and commercially available phosphine ligands were obtained from Aldrich. Hexamethylcyclopentadiene (**4**) was prepared according to the literature.[1]

All reactions were carried out under argon atmosphere.

Preparation of Phosphine–borane Complex, $P(CH_2{}^tC_4H_9)Ph_2{\bullet}BH_3$ (Table 1, entry 5)

A solution of ^{n}BuLi in hexane (1.58 M, 2.78 mL, 4.4 mmol) was added to a solution of diphenylphosphine (0.69 mL, 4.0 mmol) in THF (20 mL) at 0 ºC. The mixture was stirred for 10 min at the same temperature. Neopentyl iodide (0.64 mL, 4.8 mmol) was added to the reaction mixture, and the mixture was stirred for 3 h at 70 ºC. Borane–dimethyl sulfide complex (0.46 mL, 4.8 mmol) was added to the mixture at 0 ºC, and the resulting mixture was

stirred for 30 min at 0 ºC. The reaction was quenched with water, and the mixture was extracted with ethyl acetate. The combined organic parts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give a crude oil. The oil was purified by chromatography on silica gel (Wakogel C–200, hexane – ethyl acetate=20:1) to afford **$P(CH_2{}^tC_4H_9)Ph_2$•BH_3** (940 mg, 3.48 mmol, 87%). IR (nujol) 823, 1000, 1025, 1062, 1108, 1136, 1239, 1365, 1436, 2368 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80–1.55 (br, 3H), 1.02 (s, 9H), 2.37 (d, J = 12.0 Hz, 2H), 7.38–7.78 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 31.57 (d, J = 5.8 Hz, 3C), 32.40, 40.04 (d, J = 30.6 Hz), 128.63 (d, J = 10.0 Hz, 4C), 130.82 (d, J = 2.4 Hz, 2C), 131.31 (d, J = 54.9 Hz, 2C), 132.10 (d, J = 9.1 Hz, 4C). ^{31}P NMR ($CDCl_3$) δ 9.04 (m), Found: C, 75.19; H, 8.81%. Calcd for $C_{17}H_{24}BP$: C, 75.58; H, 8.95%. mp.: 141.5–143.0 ˚C.

Preparation of Phosphine–borane Complex, Cp*$CH_2CH_2PPh_2$•BH_3 (Table 1, entry 6)

A solution of ^{n}BuLi in hexane (1.58 M, 6.96 mL, 11 mmol) was added to a solution of pentamethylcyclopentadiene (1.72 mL, 11 mmol) in THF (50 mL) at –20 ºC. The mixture was stirred for 30 min at the same temperature. 1, 2–Dibromoethane (0.86 mL, 10 mmol) was added to the reaction mixture, and the mixture was stirred for 12 h at 70 ºC to afford 5-(2-bromoethyl)-1,2,3,4,5-pentamethyl-1,3-cyclopentadiene. The solution was used for the next step without quenching. A solution of ^{n}BuLi in hexane (1.58 M, 7.59 mL, 12 mmol) was added to a solution of diphenylphosphine (2.07 mL, 12 mmol) in THF (50 mL) at 0 ºC. The mixture was stirred for 10 min at the same temperature. The solution of 5-(2-bromoethyl)-1,2,3,4,5-pentamethyl-1,3-cyclopentadiene was added to the reaction mixture, and the mixture was stirred for 8 h at 70 ºC. Borane–dimethyl sulfide complex (1.23 mL, 13 mmol) was added to the mixture at 0 ºC, and the resulting mixture was stirred for 30 min at 0 ºC. The reaction was quenched with water, and the mixture was extracted with ethyl acetate. The combined organic parts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give a crude oil. The oil was purified by chromatography on silica gel (Wakogel C–200, hexane – ethyl acetate=30:1) to afford **Cp*$CH_2CH_2PPh_2$•BH_3** (2.33 g, 6.43 mmol, 64%). IR (nujol) 696, 737, 955, 999, 1066, 1106, 1436, 2364 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.50–1.35 (br, 3H), 0.83 (s, 3H), 1.40–1.60 (m, 10H), 1.78 (s, 6H), 7.37–7.63 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 9.53 (2C), 11.06 (2C), 19.88 (d, J = 37.8 Hz), 21.60, 27.56, 55.90 (d, J = 13.4 Hz), 128.69 (d, J = 9.5 Hz, 4C), 129.75 (d, J = 54.9 Hz, 2C), 131.01 (d, J = 2.4 Hz, 2C), 132.14 (d, J = 9.1 Hz, 4C), 134.83 (2C), 138,94 (2C). ^{31}P NMR ($CDCl_3$) δ 14.51 (m), Found: C, 79.44; H, 9.01%. Calcd for $C_{24}H_{32}BP$: C, 79.56; H, 8.90%. mp.: 103.0–103.5 ˚C.

Characterization Data

The products (entry 1–5, 8, and 10) in Table 2 and in eq 3 are commercially available, and showed reasonable ^{1}H NMR spectra. Compounds in eq 4 are found in the literature.[2]

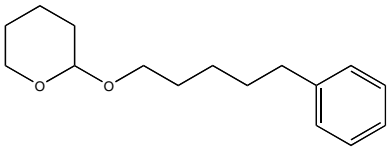
Phosphine 1

^{1}H NMR ($CDCl_3$) δ 0.96 (d, *J* = 1.8 Hz, 3H), 1.38 (d, *J* = 0.9 Hz, 6H), 1.71 (d, *J* = 0.9 Hz, 6H), 2.26 (d, *J* = 3.0 Hz, 2H), 7.20–7.35 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 9.6 (d, *J* = 2.9 Hz, 2C), 10.91 (2C), 23.52 (d, *J* = 7.6 Hz), 35.32 (d, *J* = 13.9 Hz), 54.60 (d, *J* = 15.3 Hz), 127.80 (d, *J* = 6.3 Hz, 4C), 127.94 (2C), 128.62 (d, *J* = 101.6 Hz, 2C), 133.26 (d, *J* = 19.5 Hz, 4C), 134.57 (2C), 140.02 (d, *J* = 2.9 Hz, 2C). ^{31}P NMR (C_6D_6) δ –23.58.

The oxide of 1

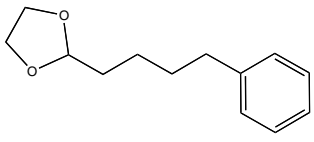
^{1}H NMR ($CDCl_3$) δ 0.97 (d, *J* = 2.7 Hz, 3H), 1.49 (d, *J* = 0.3 Hz, 6H), 1.59 (d, *J* = 0.6 Hz, 6H), 2.54 (d, *J* = 11.1 Hz, 2H), 7.34–7.64 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 10.02 (2C), 10.85 (2C), 24.96 (d, *J* = 16.8 Hz), 34.46 (d, *J* = 72.0 Hz), 53.00 (d, *J* = 3.3 Hz), 127.95 (d, *J* = 11.4 Hz, 4C), 130.79 (d, *J* = 9.0 Hz, 4C), 131.28 (d, *J* = 2.4 Hz, 2C), 133.33 (d, *J* = 98.3 Hz, 2C), 135.01 (2C), 138.79 (2C). ^{31}P NMR (C_6D_6) δ 20.16.

5–Phenylpentyl 2–tetrahydropyranyl ether (Table 2, entry 6)



IR (neat) 699, 747, 870, 1023, 1078, 1121, 1201, 1353, 1453, 1496, 2858, 2937 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.38–1.92 (m, 12H), 2.62 (t, *J* = 7.8 Hz, 2H), 3.34–3.58 (m, 2H), 3.68–3.94 (m, 2H), 4.57 (t, *J* = 4.5 Hz, 1H), 7.18–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.67, 25.47, 25.89, 29.58, 30.74, 31.35, 35.88, 62.34, 67.51, 98.84, 125.59, 128.22 (2C), 128.39 (2C), 142.68. Found: C, 77.17; H, 9.80%. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74%.

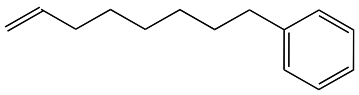
4–Phenyl–1–(2, 5–dioxacyclopentyl)butane (Table 2, entry 7)



IR (neat) 699, 749, 858, 945, 1030, 1134, 1360, 1410, 1454, 1496, 1604, 2860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44–1.74 (m, 6H), 2.63 (t, *J* = 7.7 Hz, 2H), 3.80–4.00 (m, 4H), 4.85 (t, *J* = 4.8 Hz, 1H), 7.14–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 23.81, 31.43, 33.76, 35.88, 64.83 (2C), 104.54, 125.63, 128.25 (2C), 128.38 (2C), 142.50. Found: C, 75.90; H, 8.90%. Calcd for

$C_{13}H_{18}O_2$: C, 75.69; H, 8.80%.

7–Octenylbenzene (Table 2, entry 9)



IR (neat) 698, 725, 746, 909, 994, 1030, 1453, 1496, 1605, 1641, 2855, 2929 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28–1.69 (m, 8H), 2.00–2.10 (m, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 4.90–5.04 (m, 2H), 5.81 (ddt, *J* = 6.6, 10.2, 17.1 Hz, 1H), 7.14–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 28.82, 28.96, 29.13, 31.44, 33.76, 35.94, 114.16, 125.54, 128.20 (2C), 128.38 (2C), 139.15. 142.86. Found: C, 89.14; H, 10.77%. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71%.

References:

(1) C. Zou, M. S. Wrighton and J. P. Blaha, *Organometallics,* 1987*,* **6***,* 1452.

(2) (a) H. Ohmiya, K. Wakabayashi, H. Yorimitsu and K. Oshima, *Tetrahedron,* 2006*,* **62***,* 2207. (b) A. Padwa, W. Dent, H. Nimmesgern, M. K. Venkatramanan and G. S. K. Wong, *Chem. Ber.,* 1986, **119**, 813.