

Rh-Catalyzed P-P Bond Activation

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Supplementary Data

Experimental Section

All preparations were done under an atmosphere of dry, O₂-free N₂ employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glove box. Solvents were purified employing a Grubbs' type column systems manufactured by Innovative Technology. ¹H, ¹³C and ³¹P NMR spectroscopy spectra were recorded on a Bruker Avance-300 spectrometer. ¹H and ¹³C NMR spectra are referenced to SiMe₄ using the residual solvent peak impurity of the given solvent. ³¹P NMR spectra were referenced to 85% H₃PO₄. Chemical shifts are reported in ppm and coupling constants in Hz. C₆D₆ and tol-d₈ were dried according to established procedures and used as the NMR solvents. Combustion analyses were performed in house employing a Perkin Elmer CHN Analyzer. RhNacNac(COE)N₂ was prepared according to the literature methods (Stephan, Can. J. Chem., 2005, 83, 324). Tetraphenyl biphosphine was purchased from the Aldrich Chemical Co., while other P₂ species were synthesized by reaction of the phosphine chloride with the corresponding lithium phosphide.

Typical procedure for Hydrogenation of P₂Ph₄ A J. Young's tube was charged with 20 mg P₂Ph₄ (0.056 mmol) and 3.5 mg **1** (0.0056 mmol, 10 mol%) in 0.75 mL tol-d₈. The tube was subjected to three freeze-pump-thaw cycles and subsequently exposed to 1 atm of H₂ at 78 K (~4 atm). The tube was subsequently heated to 50°C. After 12 hours the ³¹P NMR spectrum showed that hydrogenation of P₂Ph₄ to two equivalents of Ph₂PH had proceeded to 95% completion. Deuteration of Ph₂PH was accomplished in a similar manner, using 20 mg Ph₂PH (0.110 mmol) instead of P₂Ph₄ and 4 atm D₂ instead of H₂.

General procedure For Silylation: An NMR tube was charged with 20 mg Ph₂PH (0.110 mmol), 100 mg silane (~5 equivalents) and 3.5 mg **1** (0.0056 mmol, 5 mol% relative to Ph₂PH) and 0.75 mL tol-d₈. The reaction was heated and monitored by ³¹P NMR until no further reaction occurred. Reactions of biphosphines with silanes were performed in a similar fashion.

NMR data for silyl phosphines.

Et₃SiPPh₂: Spectroscopy identical that reported in: M. Hayashi, Y. Matsuura, Y. Watanabe, Tetrahedron Letters, 2004, 45, 1409-1411.

Ph₃SiPPh₂: Spectroscopy identical that reported in: A. Antoniadis, U. Kunze. Naturforsch, 1979, 34B, 116-117.

Ph₂(H)SiPPh₂: Spectroscopy identical that reported in: R. Shu, L. Hao, J.F. Harrod, H.-G. Woo and E. Samuel. J. Am. Chem.Soc., 1998, 120, 12988-12989.

Ph₂MeSiPPh₂: ¹H NMR (300 MHz, C₆D₆)δ: 0.62 (3H, d, J_{H-P}=3.3 Hz), 6.93-7.16, 7.32-7.53 (m, 20 H), ³¹P NMR (121 MHz, C₆D₆) δ: -59.2 (s), ²⁹S NMR (59 MHz, C₆D₆) δ: -8.2 (d, J_{Si-P}=25 Hz).

PhMe₂SiPPh₂: ¹H NMR (300 MHz, C₆D₆)δ: 0.35 (6H, J=3.6 Hz), 6.95-7.17, 7.33-7.56 (m, 15 H), ³¹P NMR (121 MHz, C₆D₆) δ: -58.2 (s), ²⁹S NMR (59 MHz, C₆D₆) δ: -3.8 (d, J_{Si-P}=23 Hz).