Supplementary Material (ESI) for Chemical Communications

Cross-Coupling Reaction of Alkyl Halides with Grignard Reagents Using Nickel and Palladium Complexes Bearing η^3-Allyl Ligand as Catalysts

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Typical Experimental Procedures and Analytical Data of Products.

General

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-Alice 400 spectrometer (400 MHz and 100 MHz, respectively). Chemical shifts are given in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer FT-IR (Model 1600). Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC Mass analyses (EI) were run using a JEOL JMS-mate operating in the electron impact mode (70 eV) equipped with a RTX-5 30MX.25MMX.25U column. Elemental analyses were performed on a Perkin Elmer 240C apparatus.

1-Cycropropylnonane

See ref. 8 for the synthetic procedure. IR (neat): 3076, 3000, 2957, 2923, 2864, 2360, 1464, 1378, 1014, 911, 820, 721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=-0.02-0.01 (m, 2H), 0.34-0.43 (m, 2H), 0.60-0.78 (m, 1H), 0.89 (t, *J*=6.8 Hz, 3H), 1.15-1.38 (m, 16H), ^{13}C NMR (100MHz, $CDCl_3$): δ_u=11.1, 14.3, δ_d =4.6, 22.9, 29.5, 29.7, 29.8, 29.9, 32.1, 34.9; MS (EI) *m/z* (relative intensity, %) 168 (M^+, 1.48), 125 (4), 111 (19), 97 (49), 83 (74), 69 (91), 55 (100), 41 (59); HR-MS: calcd for $C_{12}H_{24}$ (M^+): 168.1878, found 168.1879; elemental analysis: calcd for $C_{12}H_{24}$: C, 85.63; H, 14.37. found: C, 85.32; H, 14.02.

Bis(η^3-allyl)palladium CAS Registry Number: 12240-87-8

Allylmagnesium bromide (0.5 M in Et_2O, 4.0 mL, 2.0 mmol) was added drop wise to a stirred solution of $PdCl_2$ (179.0 mg, 1.0 mmol) in Et_2O (4.0 mL) at -40 °C over 1 h, and then the solution was cooled to -78 °C. After stirring for 15 h, the Et_2O was removed at -78 °C in vacuo. The resulting solid was

extracted with pentane at -40 °C, filtered at -40 °C to remove insoluble salts, and concentrated under high vacuum at -78 °C to give yellow solids (47.2 mg, 26%).

***cis*- Bis(η^3-allyl)palladium**

^{1}H NMR (400MHz, toluene-d_8, -30 °C): δ=2.74(d, *J*=13.2 Hz, 2H), 4.35(d, *J*=7.1 Hz, 2H), 4.96(tt, *J*=7.1, 13.2 Hz, 1H), ^{13}C NMR (100 MHz, toluene-d_8, -30 °C): δ=54.8, 116.1.

***trans*- Bis(η^3-allyl)palladium**

^{1}H NMR (400MHz, toluene-d_8, -30 °C): δ=2.65(d, *J*=13.2 Hz, 2H), 4.35(d, *J*=7.1 Hz, 2H), 5.04(tt, *J*=7.1, 13.4 Hz, 1H), ^{13}C NMR (100 MHz, toluene-d_8, -30 °C): δ=55.6, 115.8.

Bis(η^3-allyl)nickel CAS Registry Number: 12077-85-9

Allylmagnesium bromide (0.5 M in Et_2O, 4.0 mL, 2.0 mmol) was added drop wise to a stirred solution of $NiCl_2$ (129.6 mg, 1.0 mmol) in Et_2O (4.0 mL) at -40 °C over 1 h, and then the solution was cooled to -78 °C. After stirring for 15 h, the Et_2O was removed at -78 °C in vacuo. The resulting solid was extracted with pentane at -40 °C, filtered at -40 °C to remove insoluble salts, and concentrated under high vacuum at -78 °C to give yellow solids (195.7 mg, 69%).

***cis*-Bis(η^3-allyl)nickel**

^{1}H NMR (400MHz, toluene-d_8, -50 °C): δ=2.26(d, *J*=14.4 Hz, 2H), 3.70(d, *J*=7.6 Hz, 2H), 4.96(tt, *J*=7.6, 14.4 Hz, 1H), ^{13}C NMR (100 MHz, toluene-d_8, -30 °C): δ=53.5, 112.8.

***trans*- Bis(η^3-allyl)nickel**

^{1}H NMR (400MHz, toluene-d_8, -50 °C): δ=1.81(d, *J*=13.9 Hz, 2H), 3.92(d, *J*=7.3 Hz, 2H), 4.96(tt, *J*=7.3 13.9 Hz, 1H), ^{13}C NMR (100 MHz, toluene-d_8, -30 °C): δ=53.5, 112.7.

$[(C_2H_5)Pd(\eta^1,\eta^3\text{-}C_3H_5)_2]^-[MgBr^+]$

To a THF-d_8 solution (1.0 mL) of bis(η^3-allyl)palladium (110 mg, 0.58 mmol) was added a THF-d_8 solution of EtMgBr (0.90 M, 1.0 mL, 0.90 mmol) at -60 °C under argon. After stirring the mixture for 1 h, the ^{1}H NMR spectrum indicated that $[(C_2H_5)Pd(\eta^1,\eta^3\text{-}C_3H_5)_2]^-[MgBr^+]$ was formed in 94% NMR yield. ^{1}H NMR (400 MHz, THF-d_8, -60 °C): δ=0.6-0.9 (m, 2H) 1.26 (t, *J*=7.7 Hz, 3H), 1.51 (d, *J*=14.9 Hz, 1H), 1.55 (d, *J*=14.4 Hz, 1H), 1.71 (d, *J*=8.8 Hz, 2H), 2.01 (d, *J*=6.9 Hz, 1H), 2.15 (d, *J*=6.6 Hz, 1H), 3.41 (d, *J*=9.3 Hz, 1H), 3.91 (d, *J*=16.4 Hz, 1H), 4.3-4.6 (m, 1H), 6.1-6.4 (m, 1H), ^{13}C NMR (100 MHz, THF-d_8, -60 °C): δ=8.3, 22.8, 23.4, 45.9, 50.0, 91.1, 113.3, 152.7.

Registry No of other products and their references

The following compounds are known and their spectral data (^{1}H NMR, ^{13}C NMR, and Mass spectra) were consistent with those previously reported.

Octhylbenzene. CAS Registry Number: 2189-60-8

1-Decene. CAS Registry Number: 872-05-9

1-Bromo-4-butyl-benzene. CAS Registry Number: 41492-05-1