Cross-Coupling Reaction of Alkyl Halides with Grignard Reagents Using Nickel and Palladium Complexes Bearing $\eta^3$-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$_d$ = 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($\eta^3$-allyl)palladium CAS Registry Number: 12240-87-8
Allylmagnesium bromide (0.5 M in Et$_2$O, 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$_2$O (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$_2$O 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(η₃-allyl)palladium

$^1$H NMR (400MHz, toluene-$d_8$, -30 °C): $\delta=2.74$(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): $\delta=54.8, 116.1$.

trans- Bis(η₃-allyl)palladium

$^1$H NMR (400MHz, toluene-$d_8$, -30 °C): $\delta=2.65$(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): $\delta=55.6, 115.8$.

Bis(η₃-allyl)nickel

CAS Registry Number: 12077-85-9

Allylmagnesium bromide (0.5 M in Et₂O, 4.0 mL, 2.0 mmol) was added drop wise to a stirred solution of NiCl₂ (129.6 mg, 1.0 mmol) in Et₂O (4.0 mL) at -40 °C over 1 h, and then the solution was cooled to -78 °C. After stirring for 15 h, the Et₂O 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(η₃-allyl)nickel

$^1$H NMR (400MHz, toluene-$d_8$, -50 °C): $\delta=2.26$(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): $\delta=53.5, 112.8$.

trans- Bis(η₃-allyl)nickel

$^1$H NMR (400MHz, toluene-$d_8$, -50 °C): $\delta=1.81$(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): $\delta=53.5, 112.7$.

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

To a THF-$d_8$ solution (1.0 mL) of bis(η₃-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 $[(C_2H_5)Pd(\eta^1,\eta^3-C_3H_5)_2][MgBr^+]$ was formed in 94% NMR yield. $^1$H NMR (400 MHz, THF-$d_8$, -60 °C): $\delta=0.6-0.9$ (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): $\delta=8.3, 22.8, 23.4, 45.9, 50.0, 91.1, 113.3, 152.7.$
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