Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Catalysis of Kumada-Tamao-Corriu Coupling by a (P^OC^OP)Rh Pincer Complex

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Experimental

General Considerations. Unless otherwise specified, all manipulations were performed under an argon atmosphere using standard Schlenk line or glove box techniques. Toluene, THF, pentane, and isooctane were dried and deoxygenated (by purging) using a solvent purification system and stored over molecular sieves in an Ar-filled glove box. C_6D_6 and hexanes were dried over and distilled from NaK/Ph_2CO/18-crown-6 and stored over molecular sieves in an Ar-filled glove box. Fluorobenzene was dried with and then distilled or vacuum transferred from CaH_2. (P^OC^OP)H (**4**) and P^iPr_2(OPh) were synthesized according to published procedures.[1,2] Synthesis of (P^OC^OP)Rh(H)(Cl) (5) from 4 and $[(COE)_2RhCl]_2$ was accomplished according to the literature procedure.[3] All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 300 (^{1}H NMR, 299.951 MHz; ^{13}C NMR, 75.426 MHz, ^{31}P NMR, 121.422 MHz, ^{19}F NMR, 282.211 MHz) spectrometer. ^{2}H NMR spectra were recorded on a Varian iNova 400 (^{2}H NMR, 61.333 MHz). Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. ^{19}F NMR spectra were referenced externally using 1.0 M CF_3CO_2H in $CDCl_3$ at -78.5 ppm. ^{2}H NMR spectra were referenced externally using C_6D_6 at δ 7.15 ppm. Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ)**.**

Direct synthesis of (P^OC^OP)Rh(H)(Cl) (5) by reaction of $[(COD)RhCl]_2$ with (P^OC^OP)H (4) in toluene. In a J. Young tube, $[(COD)RhCl]_2$ (38.5 mg, 0.077 mmol) was combined with **4** (52.4 mg, 0.154) and dissolved in toluene. The reaction was heated in a 150 °C oil bath overnight producing a dark red-brown solution. The solution was passed through a pad of Celite and the volatiles were removed. Analysis by ^{31}P{^{1}H} NMR indicates 47% of **5**, 45% of one impurity

(assigned as **15)**, and another impurity (8%). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 197.4 (dd, J_{Rh-P} = 161 Hz, J_{P-P} = 16 Hz, **15**), 185.7 (d, J_{Rh-P} = 122 Hz, **5**), 182.2 (dt, J_{Rh-P} = 149 Hz, J_{P-P} = 16 Hz, **15**), 157.9 (d, J_{Rh-P} = 105 Hz)**.**

Synthesis of (P^OC^OP)Rh(H)(Cl)(Py) (6). In a Schlenk flask $[(cod)RhCl]_2$ (353 mg, 1.04 mmol) was combined with (P^OC^OP)H (**4**) (256 mg, 0.512 mmol) and dissolved in pyridine. The reaction was heated for 3 h at RT producing a light yellow solution. The solution was passed through Celite and the volatiles were removed. A yellow-white solid was collected (453 mg, 78% yield) by recrystallization in a minimum of fluorobenzene layered with pentane and dried under vacuum. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 181.3 (d, J_{Rh-P} = 120 Hz); ^{1}H NMR (C_6D_6): δ 10.32 (bs, 1H, Py-*H*), 7.72 (bs, 1H, Py-*H*), 6.90 (t, 1H, Ar-*H*, 7.2 Hz), 6.82(s, 1H, Py-*H*), 6.75 (d, 2H, Ar-*H*, 7.5 Hz), 6.63 (bs, 1H, Py-*H*), 6.12 (bs, 1H, Py-*H*), 2.33 (m, 2H, C*H*Me_2), 1.91 (m, 2H, C*H*Me_2), 1.42 (q, 6H, CH*Me*$_2$, 7.5 Hz), 1.22 (q, 6H, CH*Me*$_2$, 7.5 Hz), 1.06 (q, 6H, CH*Me*$_2$, 7.4 Hz), 1.00 (q, 6H, CH*Me*$_2$, 7.5 Hz), -16.58 (dt, 1H, Rh-*H,* J_{Rh-H} = 24.6, J_{P-H} = 5.7 Hz); ^{13}C (C_6D_6): δ 164.3 (t, 7.3 Hz, Ar), 152.6 (Py), 150.8 (Py), 136.5 (Py), 133.8 (dt, J_{P-C} = 31 Hz, J_{Rh-C} = 5.5 Hz, Ar), 125.4 (Ar), 124.1 (Ar), 123.9 (Py), 105.7 (t, 6.1 Hz, Py), 30.4 (dt, J_{Rh-C} = 85 Hz, J_{P-C} = 11 Hz), 17.9, 17.4 (t, 4.9 Hz), 16.7 (t, 2.4 Hz), 16.0**.**

Synthesis of (P^OC^OP)Rh(H)(Cl) (5) from 6. In a Schlenk flask **6** (200 mg, 360 mmol) was partially dissolved in a 5:1 mixture of pentane:toluene. BF_3-OEt_2 (60 μL, 478 mmol) was added to the flask resulting in a color change from light yellow to red. After stirring 3 h at RT, the solution was left without stirring for 3 h. The resultant mixture was passed through a pad of Celite and then through a thin pad of silica gel. The volatiles were removed. An orange-red solid was collected (101 mg, 59% yield) and dried under vacuum. An X-ray quality single crystal was obtained from the 5:1 pentane:toluene solution at RT. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 185.7 (d, J_{Rh-P} =

122 Hz); ^{1}H NMR (C_6D_6) 6.84 (t, 1H, Ar-*H*, 5.4 Hz), 6.68 (d, 2H, Ar-*H*, 6.3 Hz), 2.45 (m, 2H, C*H*Me$_2$), 2.11 (m, 2H, C*H*Me$_2$), 1.23 (q, 6H, CH*Me$_2$*, 5.4 Hz), 1.16 (q, 6H, CH*Me$_2$*, 5.1 Hz), 1.05 (m, 12H, CH*Me$_2$*), -25.32 (dt, 1H, Rh-*H*, J_{Rh-H} = 43.5, J_{P-H} = 12.6 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 166.7 (t, J_{P-C} = 7.4 Hz, Ar), 128.5 (s, Ar), 126.5 (s, Ar), 106.1 (t, J_{P-C} = 5.4 Hz, Ar), 29.7 (t, J_{P-C} = 11.0 Hz, P*C*H(CH$_3$)$_2$), 28.2 (t, J_{P-C} = 12.8 Hz, P*C*H(CH$_3$)$_2$), 17.2 (s, PCH(*C*H$_3$)$_2$), 17.1 (s, PCH(*C*H$_3$)$_2$), 16.7 (s, PCH(*C*H$_3$)$_2$), 16.2 (s, PCH(*C*H$_3$)$_2$). Elem. Anal. Calc. for $C_{18}H_{32}ClO_2P_2Rh$: C, 44.97; H, 6.71. Found: C, 44.90; H, 6.67%**.**

Reaction of (P^{O}C^{O}P)Rh(H)(Cl) (5) with pyridine to give 6. In a J. Young tube, **5** (15.2 mg, 0.031 mmol) was dissolved in pyridine. The reaction instantly became a light yellow. The solution was passed through a pad of Celite and the volatiles removed leaving a yellow-white solid. ^{31}P{^{1}H} and ^{1}H NMR are identical to that of **6.**

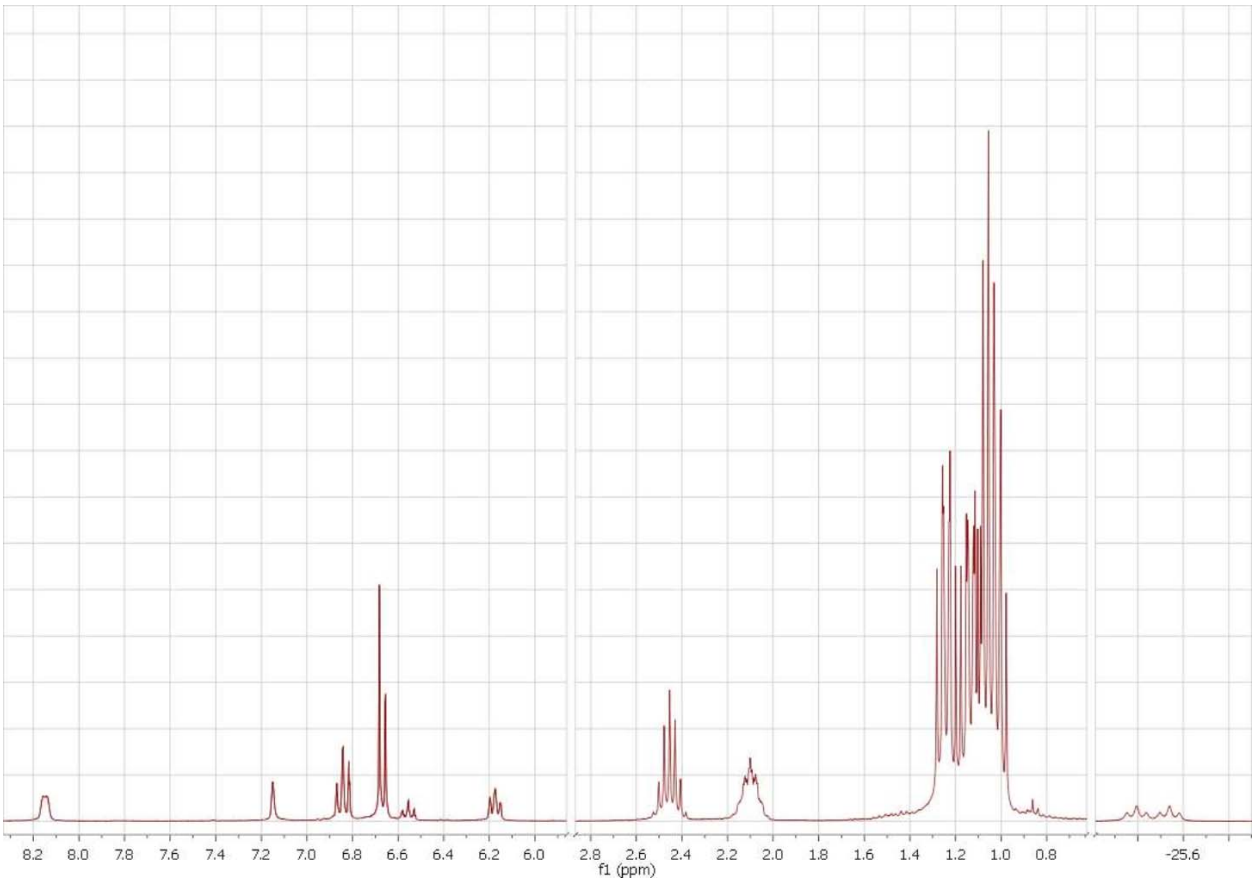

Figure S1. ^{1}H NMR spectrum of ($P^{O}C^{O}P$)Rh(H)(Cl)(Py) (**6**) in C_6D_6.

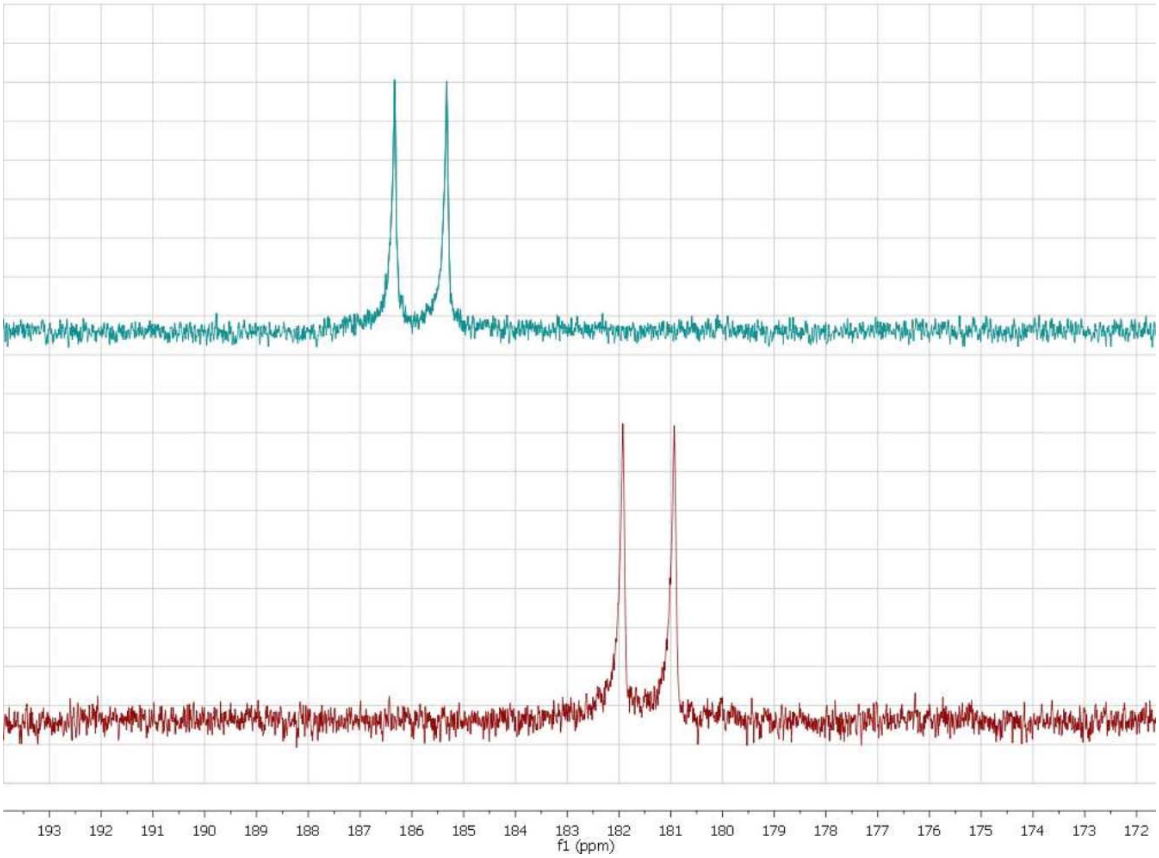

Figure S2. $^{31}P\{^{1}H\}$ NMR spectra of ($P^{O}C^{O}P$)Rh(H)(Cl)(Py) (**6**, bottom) and of ($P^{O}C^{O}P$)Rh(H)(Cl) (**5**, top) in C_6D_6.

Reaction of (P^OC^OP)Rh(H)(Cl) (5) with (P^OC^OP)H (4): observation of compounds 12, 13, 15. In a J. Young tube, **5** (21.2 mg, 0.044 mmol) was combined with **4** (9.1 μL, 0.027 mmol) and dissolved in C_6D_6. An instant color change to a light yellow-orange occurred. Analysis by $^{31}P\{^1H\}$ NMR indicated conversion to two new products in a 9:1 ratio. The major product is assigned as **12**, minor – as **13**. $^{31}P\{^1H\}$ NMR (C_6D_6) Major (**12**): δ 187.1 (dd, J_{Rh-P} = 112 Hz, J_{P-P} = 20 Hz), 173.2 (dt, J_{Rh-P} = 108 Hz, J_{P-P} = 20 Hz). ^1H NMR (C_6D_6): δ -16.34 (m, 1 H, Rh-*H*). $^{31}P\{^1H\}$ NMR (C_6D_6) Minor (**13**): δ 175.8 (dt, J_{Rh-P} = 105 Hz, J_{P-P} = 16 Hz), 170.8 (dt, J_{Rh-P} = 105 Hz, J_{P-P} = 16 Hz). $^{31}P\{^1H\}$ NMR data also showed the presence of uncoordinated phosphine at 151.8 ppm, probably belonging to **13**. The solution was heated in a 125 °C oil bath overnight resulting in the color darkening slightly and 75% conversion to a new product. The new major product is assigned as **15**. **16** could not be reliably identified in the mixture. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 197.4 (dd, J_{Rh-P} = 161 Hz, J_{P-P} = 16 Hz), 182.2 (dt, J_{Rh-P} = 149 Hz, J_{P-P} = 16 Hz). Additional heating (140 °C, 2 d) did not result in additional conversion to **15.**

Reaction of 5 with P^iPr_2(OPh): observation of compounds 14 and 17. In a J. Young tube, **5** (24.1 mg, 0.050 mmol) was combined with P^iPr_2(OPh) (11.0 μL, 0.050 mmol) and dissolved in C_6D_6. An instant color change to a light yellow solution occurred. $^{31}P\{^1H\}$ NMR analysis indicated conversion to a single product, assigned as **14**. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 187.1 (dd, J_{Rh-P} = 108 Hz, J_{P-P} = 16 Hz), 172.5 (dt, J_{Rh-P} = 105 Hz, J_{P-P} = 16 Hz); ^1H NMR (C_6D_6): δ 6.91 (m, 8 H, Ar-*H*), 3.90 (m, 2H, C*H*Me_2) 2.28 (m, 2H, C*H*Me_2), 2.02 (m, 2H, C*H*Me_2), 1.30 (m, 36 H, CH*Me*$_2$), -16.32 (m, 1H, Rh-*H*). The sample was heated in a 125 °C oil bath overnight resulting in approximately 50% conversion to a new product with some unreacted **14** remaining, as indicated by $^{31}P\{^1H\}$ NMR. The new product is assigned as **17**. $^{31}P\{^1H\}$ NMR (C_6D_6) for **17**: δ 197.5 (dd, J_{Rh-P} = 161 Hz, J_{P-P} = 16 Hz), 182.3 (dt, J_{Rh-P} = 149 Hz, J_{P-P} = 16 Hz). Another

unidentified product gave rise to an additional dd at 197.0 ppm; however, the presumed other resonance for this compound could not be identified (likely contained underneath the dt of **14** at 172.5 ppm). Additional heating (140 °C, 3 d) did not result in additional conversion to **17.**

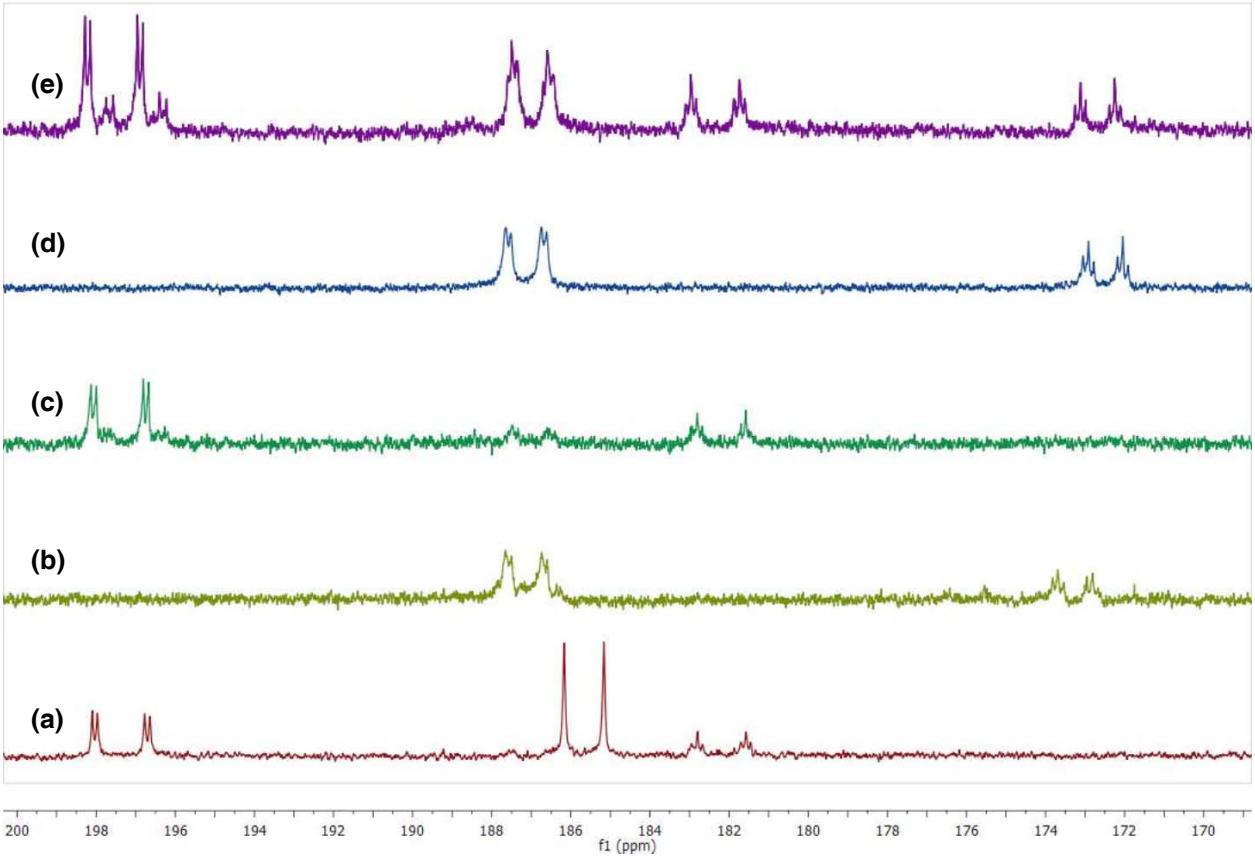

Figure S3. $^{31}P\{^{1}H\}$ NMR spectra of selected complexes collected in C_6D_6. (a) Synthesis of ($P^{O}C^{O}P$)Rh(H)(Cl) (**5)** by a direct route. Small resonance at 157.9 ppm not shown. (b) Reaction of **5** with 0.60 eq. of **4** at RT. The singlet resonance representing the uncoordinated phosphine at 151.8 ppm is not shown. (c) Reaction of **5** with 0.53 eq. of **4** after thermolysis at 125 °C. (d) Reaction of **5** with 1.0 eq. of $P^{i}Pr_2(OPh)$ at RT. (e) Reaction of **5** with 1.0 eq. of $P^{i}Pr_2(OPh)$ after thermolysis at 125 °C.

Deuterium exchange reactions. In a J. Young tube **5** (22.6 mg, 0.0472 mmol) was dissolved in C_6D_6 and heated in a 120 °C oil bath overnight. ^{2}H NMR indicated no exchange. A small amount (ca. 1 mL) of fluorobenzene saturated with D_2O was added to the sample and heated overnight in a 120 °C oil bath. The volatiles were removed in vacuo and the sample was redissolved in toluene. ^{2}H NMR showed a sharp singlet at -25.4 ppm indicating formation of (P^OC^OP)Rh(D)(Cl) (**5-*d***). The volatiles were removed from this solution in vacuo and the residue redissolved in 1,4-dioxane, shifting the ^{2}H NMR signal to -22.6 ppm. (P^OC^OP)H (**4**) (8.5 μL, 0.025 mmol) was added to the sample. ^{2}H NMR spectrum after the addition displayed a singlet at -16.1 ppm indicating the formation of **12-*d***. The sample was heated in a 115 °C oil bath overnight. The ^{2}H NMR spectrum displayed a new signal at 7.9 ppm (assigned to **17-*d***) in the aromatic region as the major resonance**.**

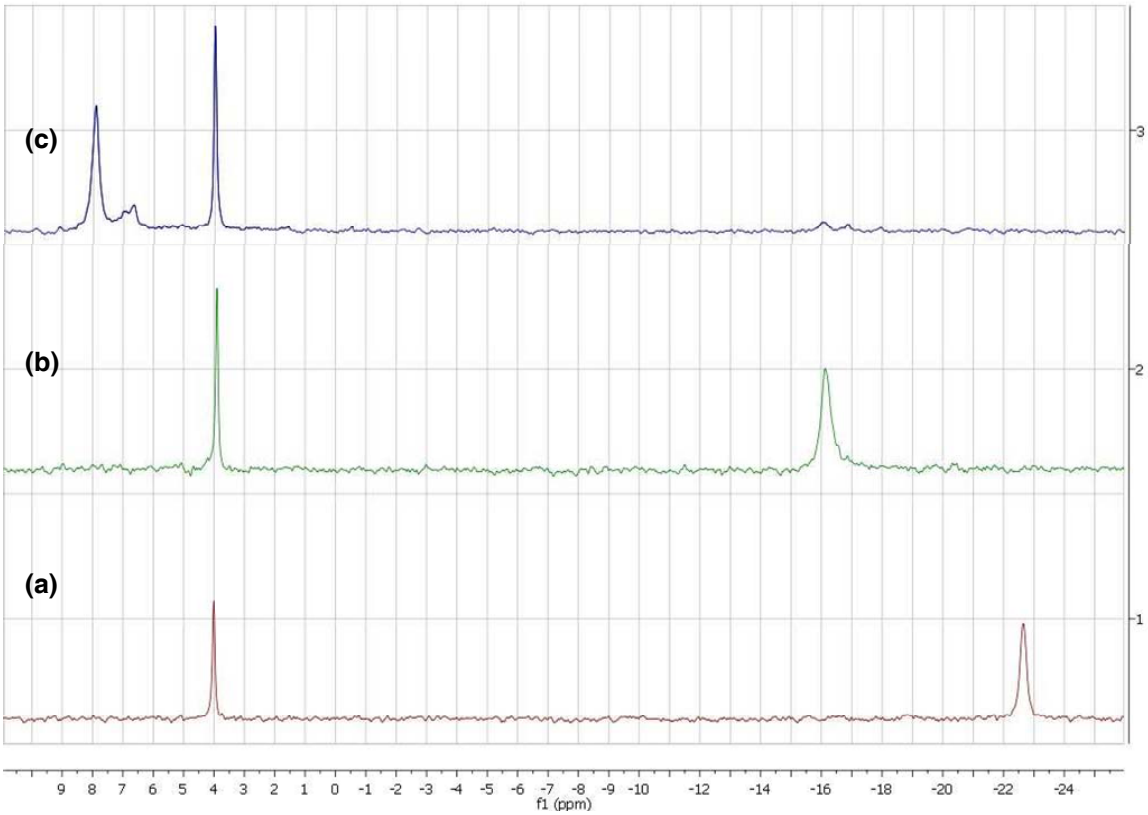

Figure S4. ^{2}H NMR spectra of deuterium exchange reactions collected in 1,4-dioxane. (a) Exchange of **5** with D_2O to give (POCOP)Rh(D)(Cl) (**5-*d***). (b) 0.53 eq of (POCOP)H added to **5-*d*** to give **12-*d***. (c) After overnight thermolysis of **12-*d*** at 115 °C to give **17-*d***.

Synthesis of (P^OC^OP)Rh(C_6H_5)(I) (10). In a J. Young tube **5** (28.8 mg, 0.603 mmol), *p*-FC_6H_5I (10.1. μL, 0.903 mmol), and $(CH_3)_3SiCH_2MgCl$ (80 μL, 0.080 μL) were combined and dissolved in C_6D_6. This resulted in an instant color change from orange to dark purple. The volatiles were removed in vacuo and the residue was recrystallized by dissolving in toluene and layering with pentane at -35 °C, giving a purple solid (33.1 mg, 84.7% yield). X-ray quality crystals were also obtained from toluene/pentane solution. $^{31}P\{^1H\}$ (C_6D_6): δ 176.8 (d, J_{Rh-P} = 120 Hz); ^1H NMR (C_6D_6): 8.03 (bs, 1H, Ph-*H*), 6.94 (t, 1H, Ar-*H*, 7.6 Hz), 6.77 (d, 2H, Ar-*H*, 7.8 Hz), 6.59 (bs, 1H, Ph-*H*), 6.53 (t, 1H, Ph-*H,* 6.9 Hz), 6.30 (bs, 1H, Ph-*H*), 5.99 (bs, 1H, Ph-*H*), 2.81 (m, 2H, C*H*Me_2), 2.10 (m, 2H, C*H*Me_2), 1.13 (m, 12H, CHMe_2), 1.01 (q, 6H, CHMe_2, 6.7 Hz), 0.75 (q, 6H, CHMe_2, 7.2 Hz); ^{13}C (C_6D_6): δ 164.6 (t, 6.1 Hz, Ar), 146.1 (dt, J_{Rh-C} = 36 Hz, J_{P-C} = 9.1 Hz, Ph), 141.6 (dt, J_{Rh-C} = 35 Hz, J_{P-C} = 4.8 Hz, Ar), 136.2 (Ph), 128.6 (Ar), 127.1 (Ar), 124.3 (Ph), 107.2 (t, 6.1 Hz, Ph), 31.8 (t, 11 Hz), 28.5 (t, 13 Hz), 18.1, 17.0, 16.6, 16.2. Elem. Anal. Calc. for $C_{24}H_{36}IO_2P_2Rh$: C, 44.46; H, 5.60. Found: C, 44.28; H, 5.45%**.**

Synthesis of (P^OC^OP)Rh(C_6H_4F-*p*)(I) (11). In a J. Young tube **5** (28.9 mg, 0.060 mmol) was combined with *p*-FC_6H_4I (11.2 μL, 0.0971 mmol) and dissolved in C_6D_6. $(CH_3)_3SiCH_2MgCl$ (81 μL, 0.081 mmol) was added to the sample resulting in an instant color change from orange to dark purple. Analysis by ^{19}F NMR shows the presence of unreacted FC_6H_4I (-115.5 ppm), $FC_6H_4CH_2Si(CH_3)_3$ (-120.9 ppm), and a signal at -121.8 ppm. The volatiles were removed in vacuo and the residue was redissolved in C_6D_6, resulting in only the signal at -121.8 ppm remaining in the ^{19}F NMR. The volatiles were again removed in vacuo and the residue was recrystallized by dissolving in toluene and layering with pentane at -35 °C, giving a purple solid (35 mg, 87% yield). $^{31}P\{^1H\}$ (C_6D_6): δ 176.4 (d, J_{Rh-P} = 119 Hz); ^1H NMR (C_6D_6): 7.91 (bs, 1H, Ph-*H*), 6.94 (t, 1H, Ar-*H*, 8.4 Hz), 6.75 (d, 2H, Ar-*H*, 8.4 Hz), 6.37 (bs, 1H, Ph-*H*), 6.05 (bs, 1H,

Ph-*H*), 5.82 (bs, 1H, Ph-*H*), 2.28 (m, 2H, C*H*Me$_2$), 2.05 (m, 2H, C*H*Me$_2$), 1.11 (m, 12H, CH*Me*$_2$), 0.98 (q, 6H, CH*Me*$_2$, 6.9 Hz), 0.71 (q, 6H, CH*Me*$_2$, 7.8 Hz); ^{19}F NMR (C_6D_6): -121.8 (s, Ph-*F*). ^{13}C (C_6D_6): δ 164.6 (t, 6.1 Hz, Ar), 162.6 (Ph), 159.3 (Ar), 141.5 (dt, J_{Rh-C} = 35 Hz, J_{P-C} = 6.0 Hz, Ph), 136.6 (dt, J_{Rh-C} = 37 Hz, J_{P-C} = 7.5 Hz, Ar), 127.3 (Ph), 113.9 (Ph), 107.0 (t, 6.1 Hz, Ph), 31.8 (t, 11 Hz), 28.5 (t, 15 Hz), 18.0, 17.0, 16.5, 16.2.

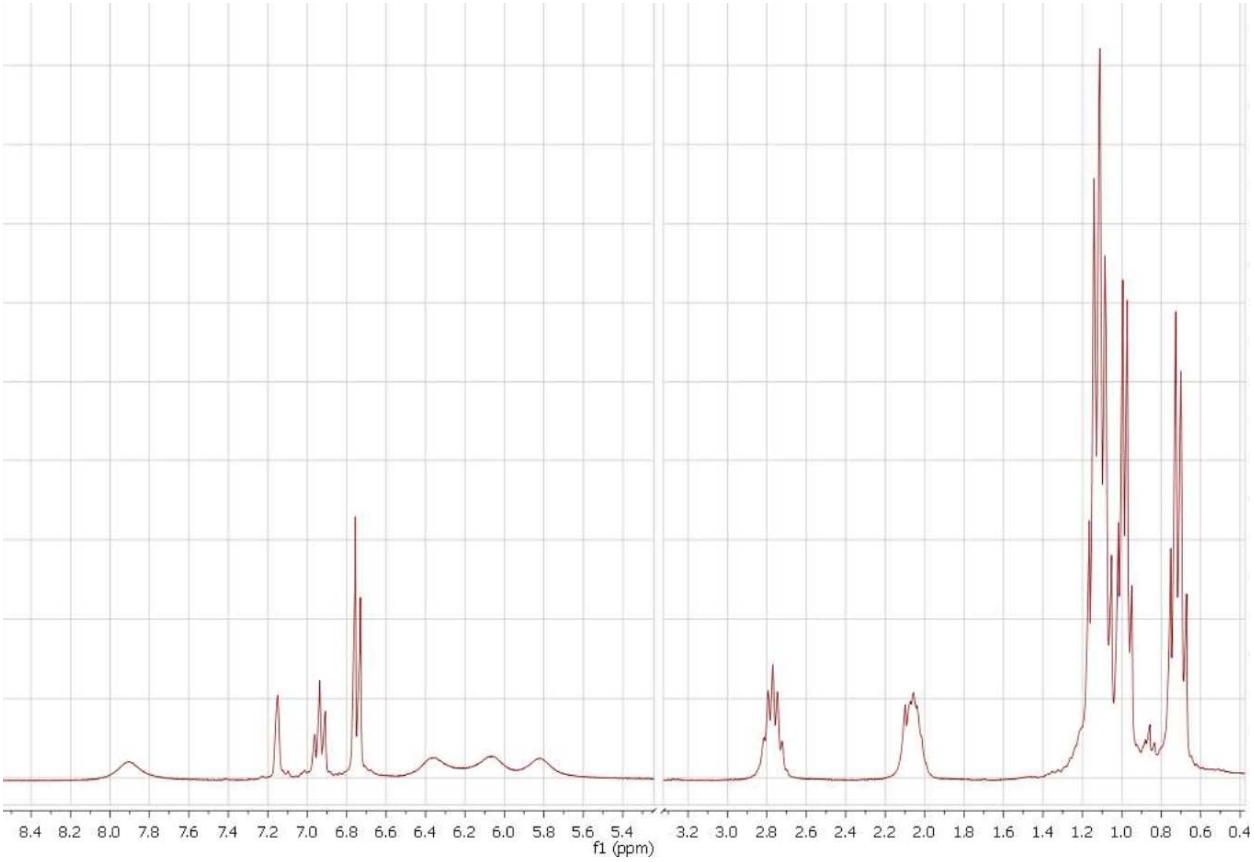

Figure S5. ^{1}H NMR spectrum of (P^OC^OP)Rh(C_6H_4F-*p*)(I) (**11**) in C_6D_6.

Catalytic reactions

Catalytic coupling reaction of *p*-FC_6H_4Br and PhMgBr with impure 5 as catalyst. **5** (5.7 mg, 0.012 mmol) was dissolved in 4-bromofluorobenzene (400 μL, 1.20 mmol) followed by addition of PhMgBr (135 μL, 1.23 mmol). The solution was heated at 100 °C for 18 h. Analysis of the solution by ^{19}F NMR revealed 4-bromofluorobenzene (80%) and 4-fluorobiphenyl (20%).

Catalytic coupling reaction of *p*-FC_6H_4I and PhMgBr with impure 5 as catalyst. **5** (5.8 mg, 0.012 mmol) was dissolved in 4-fluoro-iodobenzene (138.4 μL, 1.2 mmol) followed by addition of PhMgBr (400 μL, 1.2 mmol). The solution began to boil, a precipitate was formed and the solution became brown in color. Once the solution had stopped bubbling, analysis by ^{19}F NMR of the solution displayed only one resonance at -118.9 ppm. The solution was passed through a pad of silica gel and volatiles removed under vacuum. 4-Fluorobiphenyl (159 mg, 77 %) was isolated as a very light pink solid. ^1H NMR $(CD_3)_2CO$: δ 7.68 (m, 2H, Ar-*H*), 7.62 (d, 2H, *J* = 8 Hz, Ar-*H*), 7.45 (t, 2H, *J* = 7 Hz, Ar-*H*), 7.36 (t, 1H, *J* = 7 Hz, Ar-*H*), 7.22 (t, 2H, *J* = 8 Hz, Ar-*H*). ^{19}F NMR $(CD_3)_2CO$: δ -116.6.

Catalytic coupling reaction of *p*-MeC_6H_4Cl and PhMgBr with impure 5 as catalyst. **5** (5.8 mg, 0.012 mmol) was dissolved in 4-chlorotoluene (142.0 μL, 1.2 mmol) followed by addition of PhMgBr (400 μL, 1.2 mmol). No immediate change observed. A ^1H NMR spectrum was taken (unlocked) and only starting material was observed. The solution was heated at 100 °C for 20 h. No new products observed by NMR.

Catalytic coupling reaction of C_6H_5I and PhMgBr with impure 5 as catalyst. In a screw capped vial with a stir bar, 4-iodotoluene (262 mg, 1.2 mmol), PhMgBr (3.0 M in Et_2O, 400 μL, 1.2 mmol) and **5** (5.8 mg, 0.012 mmol) were combined and dissolved in toluene (2 mL). Immediately the solution became dark in red then changed to brown and began to boil. A

precipitate was observed. Once the solution appeared to stop boiling, in ca. 2-3 min the vial was brought out of the box, the solution passed through a plug of silica gel and extracted with pentane. A white fluffy solid was collected, 4-methylbiphenyl (159 mg, 79% yield). ^{1}H NMR $(CD_3)_2CO$: δ 7.62 (d, 2H, *J* = 8 Hz Ar-*H*), 7.53 (d, 2H, *J* = 7 Hz, Ar-*H*), 7.43 (t, 2H, *J* = 8 Hz, Ar-*H*), 7.32 (t, 1H, *J* = 7 Hz, Ar-*H*), 7.26 (d, 2H, *J* = 7 Hz, Ar-*H*), 2.36 (s, 3H, Ar-*Me*). GC-MS (EI) m/z: 168.

Catalytic coupling reaction of *p*-$MeOC_6H_4I$ and PhMgBr with impure 5 as catalyst. In a screw capped vial with stir bar 4-iodoanisole (281 mg, 1.2 mmol), PhMgBr (3.0 M in Et_2O, 400 μL, 1.2 mmol) and **5** (5.8 mg, 0.012 mmol) were combined. Immediately the solution became dark in color. The vial began to warm and bubbles were observed for ca. 10 min. The vial was brought out of the box, the solution passed through a plug of silica gel and extracted with pentane. A very light pink fluffy solid was collected, 4-methoxybiphenyl (182 mg, 83%). ^{1}H NMR $(CD_3)_2CO$: δ 7.60 (m, 4H, Ar-*H*), 7.42 (t, 2H, *J* = 7 Hz, Ar-*H*), 7.30 (t, 1H, *J* = 7 Hz, Ar-*H*), 7.01 (d, 2H, *J* = 8 Hz, Ar-*H*), 3.83 (s, 3H, O*Me*).

Catalytic coupling reaction of *p*-ClC_6H_4I and PhMgBr with impure 5 as catalyst. In a screw capped vial with a stir bar, 1-chloro-4-iodobenzene (286 mg, 1.2 mmol), PhMgBr (3.0 M in Et_2O, 400 μL, 1.2 mmol) and **5** (5.8 mg, 0.012 mmol) were combined. Immediately the solution began to heat up and became dark red in color. Reaction appeared complete after ca. 5 min. The vial was brought out of the box, the solution passed through a plug of silica gel and extracted with pentane. A very light pink fluffy solid was collected, 4-Chlorobiphenyl (178 mg, 79%). ^{1}H NMR $(CD_3)_2CO$: δ 7.66 (m, 4H, Ar-*H*), 7.47 (m, 4H, Ar-*H*), 7.38 (t, 1H, *J* = 8 Hz, Ar-*H*).

Catalytic coupling reaction of *o*-MeC_6H_4I and PhMgBr with impure 5 as catalyst. In a screw capped vial with a stir bar, 2-iodotoluene (153 μL, 1.2 mmol), PhMgBr (3.0 M in Et_2O, 400 μL, 1.2 mmol) and **5** (5.8 mg, 0.012 mmol) were combined. The solution was orange in color. The solution did not warm up. It was heated at 100 ^oC for 20 h. The solution had turned dark brown in color. The vial was brought out of the box, the solution passed through a plug of silica gel and extracted with pentane. A clear liquid was collected (186 μL). ^1H NMR and GC-MS analysis showed that it was a mixture of 88% of the desired 2-phenyltoluene product and 12% biphenyl. GC-MS: m/z 168 (2-phenyltoluene), 154 (biphenyl). In the ^1H NMR spectrum most of the aryl signals for both compounds are overlapped. To determine the percentages by ^1H NMR the integration ratios of the doublet at 7.65 ppm for biphenyl and the singlet at 2.24 ppm for 2-phenyl toluene were used. Assuming density of 1.0 g/mL (density of 3-phenyltoluene, which is a liquid at RT is 1.02 g/mol, according to Aldrich), these results correspond to 82% yield of 2-phenyltoluene and 11% yield of biphenyl.

Catalytic coupling reaction of *p*-FC_6H_4I and PhMgBr with impure 5 at 0.1% catalyst loading. In a J. Young tube 4-fluoro-iodobenzene (138.4 μL, 1.2 mmol), PhMgBr (3.0 M in Et_2O, 400 μL, 1.2 mmol) and **5** (0.040 M in C_6D_6, 30 μL, 0.0012 mmol) were combined. A ^{19}F NMR spectrum was collected upon mixing. Observed iodo-4-fluorobenzene (97%) and 4-fluorobiphenyl (3%). After heating the mixture at 90 ^oC for 1 h, ^{19}F NMR analysis revealed the presence of iodo-4-fluorobenzene (78%), 4-fluorobiphenyl (21%) and a trace of another compound resonating at -118.5 ppm. This resonance is consistent with *p*-FC_6H_4MgX. A similar resonance observed when iodo-4-fluorobenzene was treated with ^iPrMgCl. The solution was heated for a total of 20 h at 90 ^oC, resulting in >99% of 4-fluorobiphenyl 99.6% and <1% *p*-FC_6H_4MgX. The solution solidified upon cooling. GC-MS m/z = 172.

Catalytic coupling reaction of *p*-FC_6H_4I and EtMgBr with impure 5 as catalyst. **5** (14.3 μL of a 0.042 M solution in C_6D_6, $6.0x10^{-4}$ mmol), 4-fluoro-iodobenzene (138.4 μL, 1.2 mmol) and EtMgBr (3.0 M in Et_2O, 400 μL, 1.2 mmol) were combined. The solution became yellow gray in color. The solution was heated at 95 °C for 1 h. The solution was passed through silica gel and analyzed by GC-MS. The analysis revealed the presence of fluorobenzene, 4-fluoro-ethylbenzene, 4-fluoro-iodobenzene and 4,4'-fluorobiphenyl.

Catalytic coupling reaction of *p*-FC_6H_4I and Me_3SiCH_2MgCl with impure 5 as catalyst. **5** (5.8 mg, 0.012 mmol), 4-fluoro-iodobenzene (138 μL, 1.2 mmol) and Me_3SiCH_2MgCl (1 M in Et_2O; 1.2 mL, 1.2 mmol) were combined. The solution warmed to the touch. Analysis of the solution by ^{19}F NMR revealed only one resonance at -121.0 ppm. The solution was passed through a pad of silica gel and the volatiles removed under vacuum. 4-Fluorobenzyltrimethylsilane was isolated as a tan colored oily solid. ^1H NMR (C_6D_6): δ 7.05 (t, 2H, Ar-H), 6.92 (m, 2H, Ar-H), 2.05 (2H, CH_2), 0.15 (9H, $SiMe_3$); ^{19}F NMR (C_6D_6): δ -120.3 ppm.

Catalytic coupling reaction of *p*-FC_6H_4I and $PhMe_2CCH_2MgCl$ with impure 5 as catalyst. **5** (2.9 mg, 0.006 mmol), 4-fluoro-iodobenzene (69.2 μL, 0.6 mmol) and (2-methyl-2-phenylpropyl)MgCl (0.5 M in Et_2O; 1.2 mL, 0.6 mmol) were combined. The solution became red in color. Analysis of the solution by ^{19}F showed > 80% 4-fluoro-iodobenzene and ca. 20% of a new product. The solution was left at room temp. for 18 h. The solution had changed to yellow in color and a precipitate had formed. The solution was passed through a pad of silica gel and the volatiles removed under vacuum. 1-fluoro-4-(2-methyl-2-phenylpropyl)benzene was isolated as a tan colored oil (130 mg, 95%). ^1H NMR (C_6D_6): δ 7.21-7.00 (5H, Ar-H), 6.65 (t,

2H, Ar-H), 6.48 (m, 2H, Ar-H), 2.58 (2H, CH_2), 1.20 (6H, CMe_2); ^{19}F NMR (C_6D_6): δ -117.4 ppm.

Control catalytic reaction using $[(COD)RhCl]_2/PCy_3$. $[(COD)RhCl]_2$ (3.0 mg, 0.012 mmol) was combined with PCy_3 (6.8 mg, 0.024 mmol) and C_6D_6 (~0.2 mL) in a J. Young tube. This was followed by addition of 4-fluoroiodobenzene (138 μL, 1.2 mmol) and PhMgBr (3.0 M in Et_2O, 400 μL, 1.2 mmol). The solution became orange in color. ^{19}F NMR analysis showed only 4-fluoroiodobenzene present. The solution was placed in a 100 °C oil bath for 1 h. ^{19}F NMR analysis showed the presence of ~25% 4-fluoroiodobenzene, 25% 4-FC_6H_4MgX and 50% 4-fluorobiphenyl and 4,4'-fluorobiphenyl (signals overlap). The solution was heated an additional 17 h. ^{19}F NMR indicated that no more 4-fluoroiodobenzene was left. The solution was passed through a pad of silica gel. GC-MS analysis of the solution revealed the presence of 4-fluorobiphenyl, 4,4'-fluorobiphenyl and biphenyl.

Control catalytic reaction using $[(COD)RhCl]_2$. $[(COD)RhCl]_2$ (3.0 mg, 0.012 mmol) in a J. Young tube with 4-fluoroiodobenzene (138 μL, 1.2 mmol) and PhMgBr (3.0 M in Et_2O, 400 μL, 1.2 mmol). The solution became orange in color. ^{19}F NMR analysis showed only 4-fluoroiodobenzene present. The solution was placed in a 100 °C oil bath for 1 h. ^{19}F NMR analysis showed the presence of ~36% 4-fluoroiodobenzene, 40% 4-FC_6H_4MgX and 20% 4-fluorobiphenyl and 4,4'-fluorobiphenyl (signals overlap).

Preparation of stock solutions for the catalytic testing of impurities. Catalytic reactions were performed using 0.040 M stock solutions of **5** (Solution A), thermolyzed mixture of **5** and **4** (containing primarily **12** and **15**, Solution B), and thermolyzed mixture of **5** and $PhOPPr^i_2$ (containing primarily **14** and **17**, Solution C). The 0.040 M stock solution of **5** (Solution A) was prepared by dissolving **5** (57 mg, 0.120 mmol) in C_6D_6 (3.0 mL). The other two stock solutions

were prepared directly from the 0.040 M solution of **5**. Solution B was prepared by combining **4** (8.2 μL, 0.024 mmol) with the 0.040 M solution of **5** (1.0 mL, 0.040 mmol Rh) and heating overnight at 120 °C. Solution C was prepared by combining $P^iPr_2(OPh)$ (4.0 μL, 0.043 mmol) with the 0.040 M solution of **5** (1.0 mL, 0.040 mmol Rh) and heating overnight at 120 °C**.**

Catalytic coupling reaction of *p*-FC_6H_4I and PhMgBr with Solution A, 0.5% catalyst loading. In a J. Young *p*-FC_6H_4I (138 μL, 1.20 mmol) and Solution A (0.040 M Rh in C_6D_6, 150 μL, 0.0060 mmol) were combined. $PhCF_3$ (50 μL) was added to the sample as an internal standard. ^{19}F NMR indicated a 57:43 ratio of $PhCF_3$ (-63.1 ppm) to *p*-FC_6H_4I (-115.5 ppm). Additional C_6D_6 (1.5 mL) was added to help contain the heat evolved during the reaction and prevent evaporation of $PhCF_3$ and then PhMgBr (2.5 M in Et_2O, 480 μL, 1.2 mmol) was added to the reaction. The solution became hot to touch with some bubbling and became dark orange-brown in color. Analysis of the solution by ^{19}F NMR after 5 min indicated a 56:44 ratio of $PhCF_3$ to FC_6H_4-C_6H_5 (-116.9 ppm). Minor impurities do appear in the ^{19}F NMR spectrum, one at -116.5 ppm (0.5 %) and one at -117.4 ppm (0.5 %).

Catalytic coupling reaction of *p*-FC_6H_4I and PhMgBr with Solution B, 0.5% catalyst loading. In a J. Young tube, *p*-FC_6H_4I (138 μL, 1.20 mmol) and Solution B (0.040 M in C_6D_6, 150 μL, 0.0060 mmol Rh) were combined. $PhCF_3$ (50 μL) was added to the sample as an internal standard. ^{19}F NMR indicate a 57:43 ratio of $PhCF_3$ to *p*-FC_6H_4I. Additional C_6D_6 (1.5 mL) was added to help contain the heat evolved during the reaction and prevent evaporation of $PhCF_3$ and then PhMgBr (2.5 M in Et_2O, 480 μL, 1.2 mmol) was added to the reaction. The solution became warm to the touch and the color became slightly darker. Analysis by ^{19}F NMR after 5 min indicated approximately 3% conversion to FC_6H_4-C_6H_5 and approximately 68% conversion after 24 h.

Catalytic coupling reaction of *p*-FC_6H_4I and PhMgBr with Solution C, 0.5% catalyst loading. In a J. Young *p*-FC_6H_4I (138 μL, 1.20 mmol) and Solution C (0.040 M in C_6D_6, 150 μL, 0.0060 mmol) were combined. $PhCF_3$ (50 μL) was added to the sample as an internal standard. ^{19}F NMR indicated a 53:47 ratio of $PhCF_3$ to *p*-FC_6H_4I, respectively. Additional C_6D_6 (1.5 mL) added to help contain the heat evolved during the reaction and prevent evaporation of $PhCF_3$ and then PhMgBr (2.5 M in Et_2O, 480 μL, 1.2 mmol) was added to the reaction. No heat evolution or color change accompanied the addition of the Grignard. Analysis of ^{19}F NMR after 5 min indicated approximately 9% conversion to FC_6H_4-C_6H_5 and approximately 98% conversion after 2.5 h.

X-ray crystallography.

X-Ray data collection, solution, and refinement for 5. A fragment of suitable size and quality (0.2 × 0.1 × 0.6 mm) was broken off of an orange, multi-faceted crystal selected from a representative sample of crystals of the same habit using an optical microscope, mounted onto a nylon loop and placed in a cold stream of nitrogen (110 K). Low-temperature X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[4] An absorption correction was applied using SADABS.[5] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the triclinic P-1 space group using XS[6] (incorporated in SHELXTL). No obvious missed symmetry was reported by PLATON.[7] The absence of higher symmetry appears to derive from the bending of one of the chloride atoms out of the plane of the metal, phosphorus and ipso carbon. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using riding model with the exception of the hydrogen bound to rhodium which was located from the difference map. The structure was refined (weighted least squares refinement on F^2) to convergence. Slight disorder of the peripheral isopropyl groups is responsible for the large $U_{eq(max)}/U_{eq(min)}$ ratios noted in the CheckCIF report.

X-Ray data collection, solution, and refinement for 10. A fragment of suitable size and quality (0.1 x 0.06 x 0.05 mm) was broken off of a red, multi-faceted crystal selected from a representative sample of crystals of the same habit using an optical microscope, mounted onto a nylon loop and placed in a cold stream of nitrogen (110 K). Low-temperature X-ray data were

obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[4] An absorption correction was applied using SADABS.[5] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the monoclinic p21/c space group using XS[6] (incorporated in X-Seed). This symmetry was reported by PLATON.[7] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on F^2) to convergence. Slight disorder exists among the isopropyl carbons, but this is to be expected for the terminal atoms. Modeling of this disorder did not improve the R or wR2 value.

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