Simple rhodium-chlorophosphine precatalysts for the ortho-arylation of Phenols

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Electronic Supplementary Information

General

All reaction were performed under nitrogen using standard Schlenk techniques and all solvents used were anhydrous unless otherwise stated.

Catalysis (as given in table 2).

To a solution of chlorodiisopropylphosphine (0.008 ml, 0.05 mmol) and [{RhCl(COD)}$_2$] (0.006 g, 0.0125 mmol) in toluene (5 ml) was added the appropriate phenol (0.5 mmol), Cs_2CO_3 (0.277 g, 0.85 mmol) and the appropriate aryl halide (0.6 mmol). The mixture was heated at reflux temperature for 18h, allowed to cool then quenched with $HCl_{(aq)}$ (2 M, 2.5 ml). The organic phase was extracted with CH_2Cl_2 (3 × 8 ml), dried ($MgSO_4$), then filtered and the solvent was removed under reduced pressure. The crude product mixture was dissolved in $CDCl_3$ solution and 1,3,5-$MeO_3C_6H_3$ (internal standard, 0.5 M, 1.00 ml) and the conversion to the ortho-arylated phenol was determined by ^{1}H NMR spectroscopy. The spectroscopic data for the known phenols where verified against those prepared previously.[1]

2-*tert*-butyl-6-(2',6'-dimethylphenyl)phenol (table 2, entry 7). To a solution of chlorodiisopropylphosphine (0.008 ml, 0.05 mmol) and [{RhCl(COD)}$_2$] (0.006 g, 0.0125 mmol) in toluene (5 ml) was added 2-*tert*-butylphenol (0.075 g, 0.5 mmol), Cs_2CO_3 (0.277 g, 0.85 mmol) and 2-bromo-*meta*-xylene (0.111 g, 0.6 mmol). The mixture was heated to reflux temperature for 18h, allowed to cool then quenched with $HCl_{(aq)}$ (2 M, 2.5 ml). The organic phase was extracted with CH_2Cl_2 (3 × 8 ml), dried ($MgSO_4$), then filtered and the solvent was removed under reduced pressure. The crude mixture was dissolved in $CDCl_3$ solution and 1,3,5-$MeO_3C_6H_3$ (internal standard, 0.5 M, 1.00 ml) and the conversion to the *ortho*-arylated phenol was determined by ^{1}H NMR spectroscopy. The crude product was purified by column chromatography (SiO_2) to give the product as a colourless oil: 0.106 g (83.3 %); R_f 0.58 ($CHCl_3$/hexane, 1:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (s, 9H, ^{t}Bu), 2.07 (s, 6H, Me), 4.77 (s, 1H, OH), 6.89 (dd, J = 1.96 & 7.36 Hz, 1H, ArH), 6.95 (t, J = 7.32 Hz, 1H, ArH), 7.15 – 7.23 (m, 3H, *meta*-xylene ArH), 7.32 (dd, J = 1.96 & 7.56 Hz, 1H, ArH); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 20.4 (s, CH_3), 29.6 (s, CH_3), 34.9 (s, C), 120.1 (s, C), 126.2 (s, C), 127.1 (s, CH), 127.3 (s, CH), 128.2 (s, CH), 128.6 (s, CH), 135.1 (s, CH), 136.1 (s, CH), 138.4 (s, CH), 150.9 (s, C); HRMS (CI) calcd for $C_{18}H_{23}O$ [M^+ + H] 255.1749, found 255.1760.

Synthesis of complex 2. Chlorodiisopropylphosphine (0.132 ml, 0.832 mmol) was added to a solution of [{RhCl(COD}$_2$] (0.205 g, 0.416 mmol) in CH_2Cl_2 (10 ml) the resultant solution stirred at room temperature for 2h. The solvent was removed under reduced pressure to give analytically pure [RhCl(COD)(P^{i}Cl^{i}Pr$_2$)], **2** as a yellow powder. 0.325 g (98 %); Crystals of complex **2** suitable for X-ray analysis were grown from a concentrated CH_2Cl_2 solution; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, J = 6.8 Hz, 3H, CH(CH_3)$_2$), 1.31 (d, J = 6.8 Hz, 3H, CH(CH_3)$_2$), 1.40 (d, J = 7.2 Hz, 3H, CH(CH_3)$_2$), 1.27 (d, J = 7.2 Hz, 3H, CH(CH_3)$_2$), 2.05 – 2.15 (m, 4H, 2 × CH_2), 2.28 – 2.45 (m, 4H, 2 × CH_2), 2.64 (hept, J = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 3.58 – 3.62 (m, 2H, =CH *trans* to Cl), 5.38 – 5.42 (m, 2H, =CH *trans* to P); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5 (s, CH_3), 19.1 (s, CH_3), 19.2 (s, CH_3), 28.7 (s, CH_2), 28.8 (s, CH_2), 32.5 (d, $J_{P\text{-}C}$ = 1.5 Hz, CH), 32.6 (d, $J_{P\text{-}C}$ = 1.5Hz, CH), 32.8 (s, CH_2), 32.9 (s, CH_2), 73.4 (d, $J_{Rh\text{-}C}$ = 13.8 Hz, =CH), 101.6 (dd, $J_{Rh\text{-}C}$ = 12.7 Hz, $J_{P\text{-}C}$ = 6.5 Hz, =CH); ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 173.2 (d, $J_{Rh\text{-}P}$ = 175 Hz); HRMS (ESI) calcd for $C_{14}H_{26}Cl_2PRh$ [M^+ + Na] 421.009 643, found 421.011 276. Anal. calcd for $C_{14}H_{26}Cl_2PRh$: C, 42.13; H, 6.57. Found: C, 42.37; H, 6.42.

Synthesis of complex 4. A solution of [{RhCl(COD)}$_2$] (0.493 g, 1.0 mmol) and P^{i}Pr$_2$(OC$_6$H$_3$-2,4-^{t}Bu$_2$) (0.645 g, 2.0 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature for 1h. The solvent was then removed under reduced pressure and the yellow solid washed with hexane (3 x 12 ml) and then dried under reduced pressure to give complex **4**. 1.09 g (96 %); ^{1}H NMR (400 MHz, d$_8$-toluene) δ 1.25 (s, 9H, ^{t}Bu), 1.28 (d, J = 7.3, 3H, CH(CH_3)$_2$), 1.32 (d, J = 7.3, 3H, CH(CH_3)$_2$), 1.41 (s, 9H, ^{t}Bu), 1.48 (d, J = 7.2, 3H, CH(CH_3)$_2$), 1.52 (d, J = 7.2, 3H, CH(CH_3)$_2$), 1.62 – 1.68 (m, 4H, 2 × CH_2), 2.02 – 2.10 (m, 4H, 2 × CH_2), 2.68 – 2.81 (m, 2H, CH(CH$_3$)$_2$), 4.27 – 4.36 (m, 2H, =CH *trans* to Cl), 5.73 – 5.78 (m, 2H, =CH *trans* to P), 7.21 (dd, J = 2.4 Hz & 8.5 Hz, 1H, aromatic *meta* CH), 7.42 (d, J = 2.4 Hz, 1H, aromatic *meta* CH), 8.15 (dd, J = 8.5 & $J_{P\text{-}H}$ = 2.2 Hz, aromatic *ortho* CH); ^{13}C NMR (100 MHz, d$_8$-toluene) δ 18.1 (s, CH_3), 18.2 (s, CH_3), 19.7 (s, CH_3), 28.0 (s, CH_2), 28.1 (s, CH_2), 29.7 (s, CH_3), 30.7 (d, $J_{P\text{-}C}$ = 1.5 Hz, CH), 30.9 (d, $J_{P\text{-}C}$ = 1.5 Hz, CH), 31.4 (s, CH_3), 32.8 (s, CH_2), 32.9 (s, CH_2), 34.8 (s, C(CH$_3$)$_3$), 34.9 (s, C(CH$_3$)$_3$), 78.0 (d, $J_{Rh\text{-}C}$ = 13.8 Hz, =CH), 107.4 (dd, $J_{Rh\text{-}C}$ = 13.1 Hz, $J_{P\text{-}C}$ = 6.2 Hz, =CH) 118.7 (d, $J_{P\text{-}C}$ = 10.8 Hz, aromatic *ortho* CH), 123.5 (s, aromatic *meta* CH), 123.8 (s, aromatic *meta* CH), 141.8 (s, aromatic C), 144.7 (s, aromatic C), 153.0 (s, aromatic C); ^{31}P {^{1}H} NMR (121.4 MHz, $CDCl_3$) δ 152.2 (d, $J_{Rh\text{-}P}$ = 170 Hz) HRMS (ESI) calcd for $C_{28}H_{47}OPRh$ [M^+ - Cl] 533.241 4081, found 533.241 0940. Anal. Calcd for $C_{28}H_{47}ClOPRh$: C, 59.10; H, 8.32. Found: C, 58.88; H, 8.25.

Synthesis of complex 3, method a. A solution of complex **4** (0.150 g, 0.264 mmol) and NaO^{t}Bu (0.030 g, 0.311 mmol) in toluene (4 ml) was heated at 80^{o}C for 1h. During this time the yellow solution slowly turned orange/red in colour. The solvent was removed under reduced pressure to give an orange solid. The crude product was dissolved in Et_2O (5 ml) and the solution filtered through Celite. The solvent was removed under reduced pressure to give an orange powder. 0.128 g (91 %); ^{1}H NMR (400 MHz, d$_8$-toluene) δ 0.96 (d, J = 7.3, 3H, CH(CH_3)$_2$), 1.01 (d, J = 7.3, 3H, CH(CH_3)$_2$), 1.08 (d, J = 6.8, 3H, CH(CH_3)$_2$), 1.11 (d, J = 6.8, 3H, CH(CH_3)$_2$), 1.39 (s, 9H, ^{t}Bu), 1.59 (s, 9H, ^{t}Bu), 2.08 – 2.16 (m, 4H, 2 × CH_2), 2.38 – 2.43 (m, 2H, CHP^{i}r$_2$), 2.44 – 2.52 (m, 4H, 2 × CH_2), 4.57 – 4.62 (m, 2H, =CH *trans* Cl), 6.07 – 6.13 (m, 2H, =CH *trans* P), 7.27 (dd, J = 2.2 Hz &

J_{Rh-H} = 1.5 Hz, 1H, aromatic *meta* CH), 7.36 (dd, J_{Rh-H} = 4.1 Hz & J = 2.1 Hz, 1H, aromatic *meta* CH); ^{13}C NMR (100 MHz, d_8-toluene) δ 17.4 (s, CH_3), 17.5 (s, CH_3), 17.6 (s, CH_3), 29.3 (s, CH_2), 29.4 (s, CH_2), 30.3 (s, CH_3), 30.8 (d, J_{P-C} = 3.0 Hz, CH), 31.0 (d, J_{P-C} = 3.0 Hz, CH), 32.0 (s, CH_3), 32.1 (s, CH_2), 32.2 (s, CH_2), 34.7 (s, $C(CH_3)_3$), 34.9 (s, $C(CH_3)_3$), 80.2 (d, J_{Rh-C} = 7.7 Hz, =CH *cis* P), 99.1 (d, J_{Rh-C} = 7.7 Hz, =CH *trans* P), 99.2 (d, J_{Rh-C} = 7.7 Hz, =CH *trans* P), 123.4 (s, aromatic *meta* CH), 123.6 (s, aromatic *meta* CH), 141.2 (s, aromatic C), 142.0 (s, aromatic C), 150.2 (dd, J_{Rh-C} = 35.4 Hz & J_{P-C} = 9.2 Hz, aromatic *ortho* C), 152.6 (s, aromatic C); ^{31}P {^{1}H} NMR (121.4 MHz, d_8-toluene) δ 188.3 (d, J_{Rh-P} = 198 Hz); HRMS (ESI) calcd for $C_{28}H_{46}OPRh$ [M^+ + H] 533.241 4081, found 533.241 9830. Anal. calcd for $C_{28}H_{46}OPRh$: C, 63.15; H, 8.70. Found: C, 61.75; H, 8.70.

Method b. A solution of complex **2** (0.040 g, 0.1 mmol), 2,4-di-*tert*-butylphenol (0.021 g, 0.1 mmol) and NaO^{t}Bu (0.021 g, 0.21 mmol) in toluene (2 ml) was heated at 80^{o}C for 1h. During this time the yellow solution slowly turned orange/red in colour. The solvent was removed under reduced pressure to give an orange solid. The crude product was dissolved in Et_2O (10 ml) and filtered through Celite. The solvent was removed under reduced pressure to give an orange powder. 0.051 g (96%); Data as above.

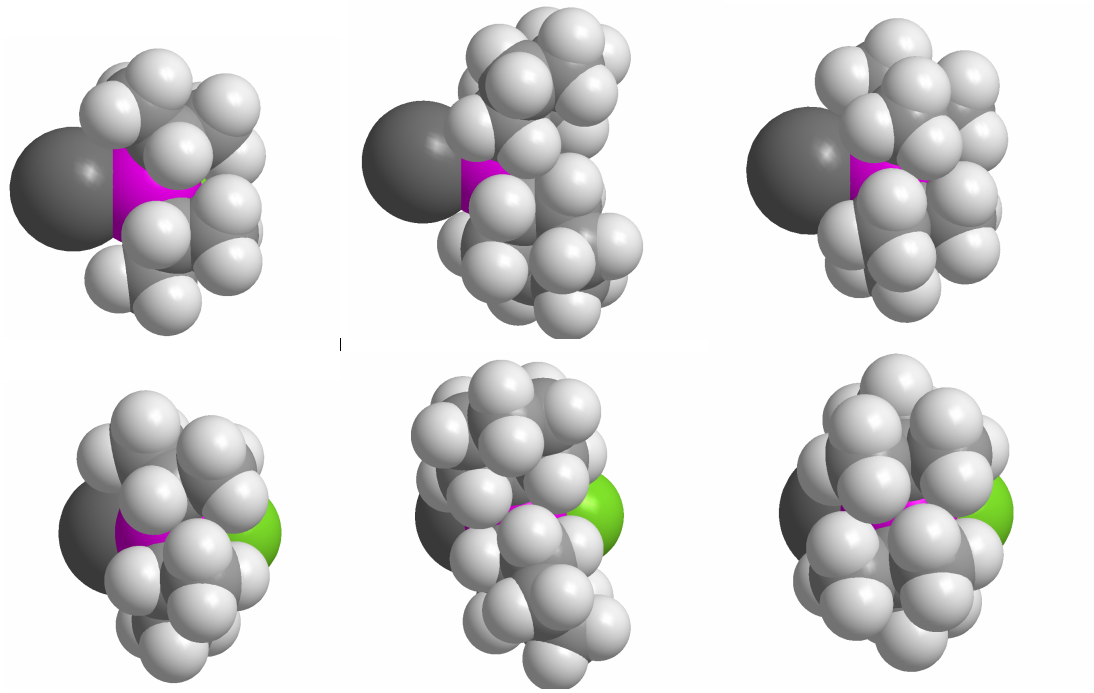

Figure S1. Comparison of the steric hindrance to nucleophilic attack for the fragments 'Rh-PCl^{i}Pr$_2$' (left), 'Rh-PClCy$_2$' (centre) and 'Rh-PClP^{t}Bu$_2$' (right) with Rh-P aligned along x-axis (top row) and Rh-P-Cl aligned with XZ plane (bottom row). MM2 models with bond lengths and angles about P optimised to those obtained from the X-ray analysis of complex **2**.

[1] R. B. Bedford and M. E. Limmert, *J. Org. Chem.*, 2003, **68**, 8669.