Supporting Information

Borylation of Aryl Diazonium Ions with N-Heterocyclic Carbenes Formed without Added Base

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General Procedure:
Aryldiazonium tetrafluoroborate (1.0 mmol), bis(pinacolato) diboron (1.0 mmol), $Pd(OAc)_2$ (0.01 mmol, 1 mol%, 2.24 mg) and N,N-diisopropyl-4,5-dihydroimidazolium chloride salt **5** (0.02 mmol, 2 mol%, 8.50 mg) were added to a reaction flask which was purged thoroughly with N_2. Deoxygenated, anhydrous THF (2 mL) was added via syringe and the reaction was allowed to proceed at rt. TLC was used to monitor the progress of the reaction. The solution was concentrated, water was added (5 mL) and the mixture was extracted with EtOAc/hexanes (20%). The combined organic layer was dried ($MgSO_4$) and the product was purified by silica gel chromatography (5-10%, EtOAc/hexanes). Data for the product compounds, all of which are known, was obtained:

$C_6H_5B(O_2C_2Me_4)$: Yield: 87%, R_f: 0.75 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.78 (d, 2H), 7.45-7.27 (m, 3H), 1.36 (s, 12H); ^{11}B NMR ($CDCl_3$) 26,71; MS (EI) *m/z* 204.

4-$MeC_6H_4B(O_2C_2Me_4)$: Yield: 92%, R_f: 0.75 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71 (d, 2H, *J*=8.2), 6.88 (d, 2H, *J*=8.2), 1.33 (s, 12H); MS (EI) *m/z* 218.

2-$MeC_6H_4B(O_2C_2Me_4)$: Yield: 90%, R_f: 0.75 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84-7.32 (m, 4H), 1.33 (s, 12H); MS (EI) *m/z* 218.

4-$MeOC_6H_4B(O_2C_2Me_4)$: Yield: 85%, R_f: 0.60 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66 (d, 2H, *J*=8.3), 6.88 (d, 2H, *J*=8.3), 3.88 (s, 3H), 1.31 (s, 12H); ^{11}B NMR ($CDCl_3$) 30.63; MS (EI) *m/z* 234.

2-$MeOC_6H_4B(O_2C_2Me_4)$: Yield: 81%, R_f: 0.60 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62-7.23 (m, 4H), 3.86 (s, 3H), 1.31 (s, 12H); MS (EI) *m/z* 234.

4-$MeC(O)C_6H_4B(O_2C_2Me_4)$: Yield: 87%, R_f: 0.60 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.82 (d, 2H, *J*=8.3), 6.94 (d, 2H, *J*=8.3), 2.58 (s, 3H),1.32 (s, 12H); ^{11}B NMR ($CDCl_3$) 30.57; MS (EI) *m/z* 246.

4-$MeO_2CC_6H_4B(O_2C_2Me_4)$: Yield: 80%, R_f: 0.55 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.98 (d, 2H, *J*=8.1), 7.74 (d, 2H, *J*=8.1), 3.91 (s, 3H),1.36 (s, 12H); ^{11}B NMR ($CDCl_3$) 30.57; MS (EI) *m/z* 262.

4-$O_2NC_6H_4B(O_2C_2Me_4)$: Yield: 88%, R_f: 0.45 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.12 (d, 2H, *J*=8.6), 7.92 (d, 2H, *J*=8.6), 1.35 (s, 12H); MS (EI) *m/z* 249.

4-$BrC_6H_4B(O_2C_2Me_4)$: Yield: 95%, R_f: 0.70 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62 (d, 2H, *J*=7.8), 7.32 (d, 2H, *J*=7.8), 1.32 (s, 12H); MS (EI) *m/z* 284.

4-$NCC_6H_4B(O_2C_2Me_4)$: Yield: 79%, R_f: 0.60 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.78 (d, 2H, *J*=8.1), 7.56 (d, 2H, *J*=8.0), 1.32 (s, 12H); ^{11}B NMR ($CDCl_3$) 30.57; MS (EI) *m/z* 229.

2,6-$Me_2C_6H_3B(O_2C_2Me_4)$: Yield: 63%, R_f: 0.70 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34-6.81 (m, 3H), 2.35 (d, 6H),1.33 (s, 12H); ^{11}B NMR ($CDCl_3$) 32.78; MS (EI) *m/z* 232.

1,4-$C_6H_4[B(O_2C_2Me_4)]$: Yield: 71%, R_f: 0.55 (10 %, EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80 (s, 3H), 7.78 (s,1H), 1.33(s, 24H); MS (EI) *m/z* 330.

Crystal Preparation:

PdI_2-**5** Formed with base: Palladium (II) acetate (42.5 mg, 0.19 mmol), sodium iodide (140 mg, 0.94 mmol), sodium *tert*-butoxide (47.5 mg, 0.50 mmol) and imidazolium chloride **2** (200 mg. 0.47 mmol) were dissolved in dry THF (20 mL) and the solution was heated at reflux for 12 h. The solution was evaporated in vacuo and the dark red NHC complex PdI_2-**2** was purified by silica gel chromatography (Et_2O/hexanes, 1:1). Crystals suitable for single crystal X-ray crystallography (42% yield, 305-307 °C mp) were obtained by slow evaporation of a solution of PdI_2-**2** in 1:1 Et_2O/hexanes. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42 (t, *J*=8.0 Hz, 4 H), 7.28 (dd, *J*=8.0, 8.0 Hz, 4 H), 7.19 (dd, *J*=8.0, 8.0 Hz, 4H), 4.01 (m, 4H), 3.90 (m, 4H), 3.64 (m, 4H), 3.61 (m, 4H), 1.55 (d, *J*=6.0 Hz, 12H), 1.32 (d, *J*=7.0 Hz, 12H), 1.19 (d, *J*=6.0 Hz, 12H), 1.10 (d, *J*=7.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.76, 146.84, 136.09, 129.66, 125.26, 124.96, 54.29, 29.17, 17.41, 27.27, 25.26; MS (FAB) *m/z* 1247 (M-2I).

Table 1-S. Crystal data and structure refinement for PdI_2-**5** formed with added base.

Identification code	PdI_2-**5**	
Empirical formula	C54 H76 I4 N4 Pd2	
Formula weight	1501.59	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.3173(16) Å	α= 110.479(10)°.
	b = 12.3785(17) Å	β= 93.757(11)°.
	c = 12.5477(17) Å	γ = 104.671(12)°.
Volume	1431.1(4) $Å^3$	
Z	1	
Density (calculated)	1.742 Mg/m^3	
Absorption coefficient	2.822 mm^{-1}	
F(000)	732	
Crystal size	0.74 x 0.18 x 0.16 mm^3	
Theta range for data collection	2.33 to 27.50°.	
Index ranges	-13<=h<=1, -14<=k<=14, -16<=l<=16	
Reflections collected	7494	
Independent reflections	6421 [R(int) = 0.0300]	
Completeness to theta = 27.50°	97.4 %	
Absorption correction	Empirical	
Max. and min. transmission	0.5511 and 0.4815	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6421 / 0 / 297	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0298, wR2 = 0.0739	
R indices (all data)	R1 = 0.0405, wR2 = 0.0789	
Largest diff. peak and hole	0.857 and -0.535 $e.Å^{-3}$	

$PdCl_2$-**5** Formed without added base: Palladium (II) acetate (21.3 mg, 0.095 mmol), and imidazolium chloride **2** (100 mg. 0.24 mmol) were dissolved in dry THF (20 mL) and the solution was heated at reflux for 18 h. The solution was evaporated in vacuo and the orange NHC complex $PdCl_2$-**5** was purified by silica gel chromatography (Et_2O/hexanes, 1:1). Crystals suitable for single crystal X-ray crystallography (37% yield, >350 °C, decomp.) were obtained by slow evaporation of a solution of $PdCl_2$-**5** in 1:1 Et_2O/hexanes. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.44 (t, *J*=8.0 Hz, 4H), 7.28 (d, *J*=9.0 Hz, 4H), 7.21 (d, *J*=7.0 Hz, 4H), 3.88 (m, 8H), 3.30 (m, 4H), 3.01 (m, 4H), 1.43 (d, *J*=6.0 Hz, 12H), 1.33 (d, *J*=6.5 Hz, 12H), 1.18 (d, *J*=7.0 Hz, 12H), 1.11 (d, *J*=7.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.32, 147.60, 147.21, 147.23, 134.66, 129.78, 124.93, 124.91, 124.74, 124.55, 54.13, 53.90, 53.68, 29.10, 29.00, 28.76, 28.66, 27.04, 26.97, 26.90, 26.83, 24.72, 24.61, 24.51, 24.45, 24.37; MS (FAB) *m/z* 1156 (M+Na).

Table 2-S. Crystal data and structure refinement for $PdCl_2$-**5** formed without base.

Identification code	$PdCl_2$-**5**	
Empirical formula	C27 H38 Cl2 N2 Pd	
Formula weight	567.89	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4(1)2(1)2	
Unit cell dimensions	a = 15.9400(18) Å	α= 90°.
	b = 15.9400(18) Å	β= 90°.
	c = 26.756(3) Å	γ = 90°.
Volume	6798.1(14) $Å^3$	
Z	8	
Density (calculated)	1.110 Mg/m^3	
Absorption coefficient	0.717 mm^{-1}	
F(000)	2352	
Crystal size	0.54 x 0.51 x 0.42 mm^3	
Theta range for data collection	2.62 to 25.01°.	
Index ranges	-1<=h<=18, -1<=k<=18, -1<=l<=31	
Reflections collected	7877	
Independent reflections	5975 [R(int) = 0.0436]	
Completeness to theta = 25.01°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5975 / 0 / 297	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.0968	
R indices (all data)	R1 = 0.0654, wR2 = 0.1104	
Absolute structure parameter	0.02(4)	
Largest diff. peak and hole	0.325 and -0.446 $e.Å^{-3}$	