Structure and Reactivity of "Unusual" *N*-Heterocyclic Carbene (NHC) Palladium Complexes Synthesized from Imidazolium Salts.

Hélène Lebel,*[‡] Marc K. Janes,[‡] André B. Charette,[‡] Steven P. Nolan[§]
Département de chimie, Université de Montréal, C.P. 6128, Succursale Centre-ville, Montréal, Québec, Canada, H3C 3J7; Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148.

Supporting Information

[‡] Université de Montréal.
[§] University of New Orleans.

General: Unless otherwise noted, all reactions were carried out using standard Schlenk techniques under a dry argon atmosphere or in an MBraun glovebox containing dry argon (less than 1 ppm of oxygen and water). Dioxane was distilled over sodium/benzophenone under argon and degassed prior to use. Anhydrous *N*,*N*-Dimethylacetamide 99.8% was purchased from Aldrich and degassed prior to use. 4-Chlorotoluene was freshly distilled over CaH_2 under argon and degassed prior to use. Bromobenzene was refluxed and freshly distilled from sodium under argon. Cesium carbonate was purchased from Aldrich, dried at 175 °C for 15 hours under vacuum and kept in a glove-box. $Pd(OAc)_2$ and $PdCl_2$ were purchased from Strem, stored in a glove-box under an argon atmosphere and used as received. IMesHCl,[1] 4-MeOPhB$(OH)_2$,[2] butyl acrylate,[3] were synthesized according to literature procedures and are also commercially available from Strem or Aldrich. All reported yields are of isolated pure material obtained from an average of at least two runs. Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, iodine, or aqueous potassium permanganate. Flash chromatography was performed using Silicycle, Ultra Pur Silica Gel 60 Å (230-400 mesh) with the indicated solvent system. ^{1}H NMR spectra were recorded in deuterated chloroform, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (400, 400, 300 and 300 MHz respectively). For complex **1** and **2**, deuterated chloroform for NMR analysis was passed through a pad of basic alumina prior to use. Chemical shifts are reported in ppm on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, integration. ^{13}C NMR spectra were recorded in deuterated chloroform, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (100, 100, 75 and 75 MHz respectively) with complete proton decoupling. Chemical shifts are reported in ppm from the central peak of deuterated chloroform (77.36 ppm) on the δ scale. The elemental analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal or by the Canadian Microanalytical Service ltd. Melting points are uncorrected.

Synthesis of normal $IMes_2PdCl_2$ (1)

Under an argon atmosphere a flask was charged with IMesHCl (150 mg, 0.44 mmol), $PdCl_2$ (37 mg, 0.21 mmol) and Cs_2CO_3 (681 mg, 2.09 mmol). The flask was then fitted with a condenser and a septum. Dioxane (4.4 mL) was added *via* syringe and the reaction mixture was heated to 80 °C for 5 hours. Heating was discontinued and the reaction mixture was allowed to cool to room temperature. Volatiles were removed under reduced pressure. Purification by flash column chromatography (CH_2Cl_2) afforded **1** as a white solid (112 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) 6.94 (s, 8H, ArH), 6.79 (s, 4H, NCH=CHN), 2.49 (s, 12H, *p*-ArCH_3), 1.96 (s, 24H, *o*-ArCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) 171.2 (s), 137.9 (s), 136.5 (s), 136.1 (s), 129.1 (s), 122.8 (s), 21.6 (s), 19.3 (s).

Calcd. for $C_{42}H_{48}Cl_2N_4Pd$: C, 64.16; H, 6.15; N, 7.13. Found: C, 64.26; H, 6.20; N, 7.00.

Dec. point: ca. 250 °C

Synthesis of abormal $IMes_2PdCl_2$ (2)

Under an argon atmosphere, a flask was charged with IMesHCl (109 mg, 0.32 mmol) and $Pd(OAc)_2$ (35 mg, 0.16 mmol). The flask was then fitted with a condenser and a septum. Dioxane (1.6 mL) was added *via* syringe and the reaction mixture was heated to 80 °C for 6 hours. Heating was discontinued and the reaction mixture was allowed to cool to room temperature. Volatiles were removed under reduced pressure. Purification by flash column chromatography (100% DCM) afforded **2** as a white solid (91 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) 7.47 (d, J = 1.7 Hz, 1 H, NCHN), 6.99 (s, 4 H, mes-CH), 6.91 (s, 4 H, mes-CH), 6.85 (s, 2 H, NCH=CHN), 6.57 (d, J = 1.7 Hz, 1 H, CH(=C)N), 2.46 (s, 3 H, mes-CH_3), 2.43 (s, 6 H, mes-CH_3), 2.30 (s, 3 H, mes-CH_3), 2.20 (s, 12 H, mes-CH_3), 1.98 (s, 6 H, mes-CH_3), 1.95 (s,6 H, mes-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) 175.9 (Pd-$\underline{C}N_2$), 150.7 (Pd-$\underline{C}$(=C)N), 139.9 (1 mes-CR_4), 137.9 (1+2 mes-CR_4), 136.6 (4 mes-CR_4), 136.4 (2 mes-CR_4), 135.7 (2 mes-CR_4), 135.4 (1 mes-CR_4), 134.7 (2 mes-CR_4), 132.2 (1 mes-CR_4), 131.6 (N$\underline{C}$HN), 129.3 (2 mes-$\underline{C}$H), 129.1 (4 mes-$\underline{C}$H), 128.9 (2 mes-$\underline{C}$H), 125.5 ($\underline{C}$H(=C)N), 122.8 (N$\underline{C}$H=$\underline{C}$HN), 21.5 (mes-CH_3), 21.4 (mes-CH_3), 21.2 (mes-CH_3), 19.1 (mes-CH_3), 18.9 (mes-CH_3), 17.6 (mes-CH_3).

Calcd. for $C_{42}H_{48}Cl_2N_4Pd$: C, 64.16; H, 6.15; N, 7.13. Found: C, 63.95; H, 6.17; N, 7.10.

Dec. point: ca. 240 °C

Typical Suzuki procedure using preformed catalysts 1 or 2

Under an atmosphere of argon, a flask was charged with abnormal $IMes_2PdCl_2$ **2** (20 mg, 0.025 mmol) and Cs_2CO_3 (652 mg, 2.00 mmol). Dioxane (1 mL) was added *via* syringe, followed by 4-chlorotoluene (119 μL, 1.00 mmol). A solution of 4-MeO-PhB$(OH)_2$ (228 mg, 1.50 mmol) in dioxane (2 mL) was added *via* cannula. The argon inlet was removed, the septum was covered with parafilm and the reaction vessel was placed in a oil bath at 80 °C. Stirring was continued for 23 hours. The reaction mixture was then cooled to room temperature, diluted with dichloromethane (20 mL), filtered through a pad of celite using dichloromethane (100 mL). The volatiles were evaporated under reduced pressure. Purification by flash column chromatography (1% EtOAc / Hex) yielded 4-methoxy-4'-methylbiphenyl as a white solid (87 mg, 0.44 mmol, 44%). All coupling products were found to be identical by NMR to literature data.[4]

Typical Suzuki procedure using *in situ* formation of the catalyst[5]

Under an atmosphere of argon, a flask was charged with $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), IMesHCl (17 mg, 0.05 mmol) and Cs_2CO_3 (652 mg, 2.00 mmol). Dioxane (2 mL) was added *via* syringe. After 30 min at 80 °C, the reaction mixture was cooled to room temperature and 4-chlorotoluene (119 μL, 1.0 mmol) was added to the reaction mixture. A solution of 4-MeO-PhB$(OH)_2$ (228 mg, 1.5 mmol) in dioxane (1 mL) was then added *via* cannula. The argon inlet was removed, the septum was covered with parafilm and the reaction vessel was placed in a oil bath at 80 °C. Stirring was continued for 23 hours. The reaction mixture was then cooled to room temperature, diluted with dichloromethane (20 mL), filtered through a pad of celite using dichloromethane (100 mL) and volatiles were evaporated under reduced pressure. Purification by column chromatography (1% EtOAc / Hex) yielded 4-methoxy-4'-methylbiphenyl as a white solid (151 mg, 0.76 mmol, 76%). All coupling products were found to be identical by NMR to literature data.[4]

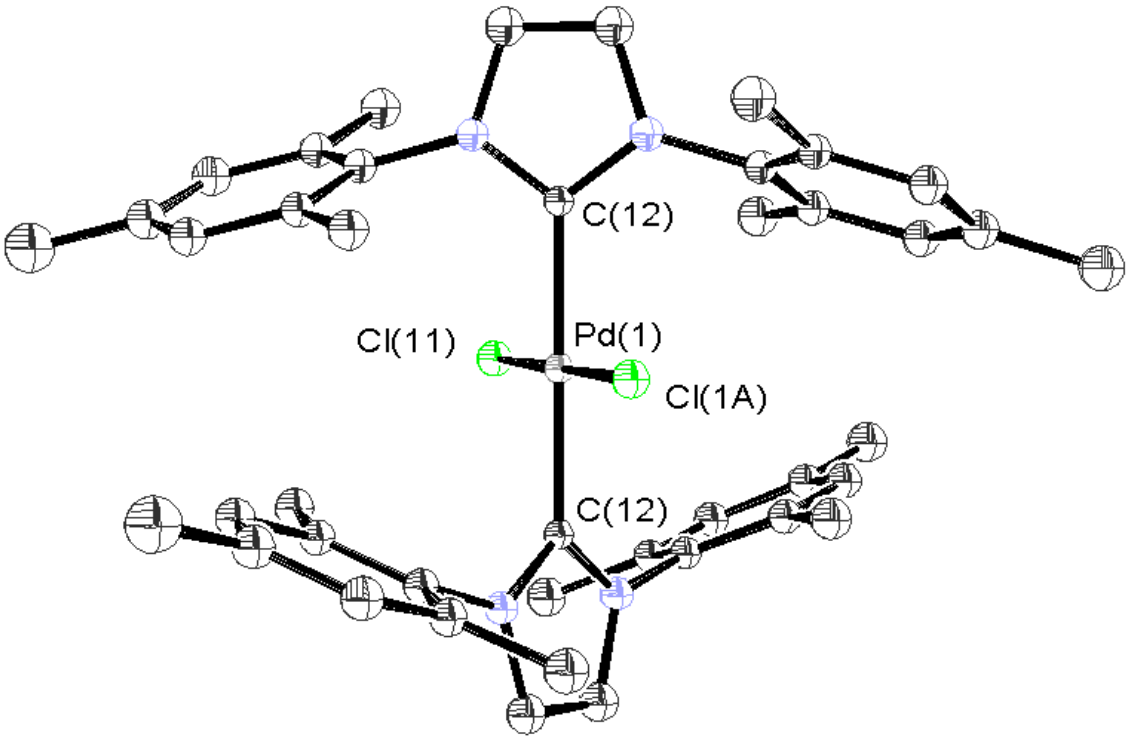
Typical Heck procedure using preformed catalysts 1 or 2

Under an atmosphere of argon a flask was charged with abnormal $IMes_2PdCl_2$ **2** (20 mg, 0.02 mmol) and Cs_2CO_3 (652 mg, 2.00 mmol). *N*,*N*-dimethylacetamide (2 mL) was added *via* syringe followed by butyl acrylate (229 μL, 1.60 mmol) and then bromobenzene (105 μL, 1.00 mmol). The argon inlet was removed, the septum was covered with parafilm and the reaction vessel was placed in a oil bath at 120 °C. Stirring was continued for 7 hours. The reaction mixture was then cooled to room temperature, diluted with diethyl ether (20 mL) and washed with water (15 mL). The aqueous phase was then extracted twice with diethyl ether (20 mL), the organic phases were combined and dried over Na_2SO_4. The volatiles were removed under reduced pressure. Flash column chromatography (4% EtOAc / Hex) yielded *n*-butylcinnamate as a white solid (157mg, 0.77 mmol, 77%). All coupling products were found to be identical by NMR to literature data.[6]

Typical Heck procedure using *in situ* formation of catalyst [7]

Under an atmosphere of argon, a flask was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), IMesHCl (13.6 mg, 0.04 mmol) and Cs_2CO_3 (652 mg, 2.00 mmol). *N*,*N*-dimethylacetamide (2 mL) was added *via* syringe and the reaction mixture was stirred for 15 minutes at room temperature. Butyl acrylate (229 μL, 1.60 mmol) was then added, followed by bromobenzene (105 μL, 1.00 mmol). The argon inlet was removed, the septum was covered with parafilm and the reaction vessel was placed in a oil bath at 120 °C. Stirring was continued for 4 hours. The reaction mixture was then cooled to room temperature, diluted with diethyl ether (20 mL) and washed with water (15 mL). The aqueous phase was then extracted twice with diethyl ether (20 mL), the organic phases were combined and dried over Na_2SO_4. The volatiles were removed under reduced pressure. Flash column chromatography (4% EtOAc / Hex) yielded *n*-butylcinnamate as a white solid (135 mg, 0.66 mmol, 66%). All coupling products were found to be identical by NMR to literature data.[6]

ORTEP representation of complex **1** (elipsoid drawn at 30% propability level)



(1) (a) Arduengo, A.J. III. US patent 5 077 414, 1991; (b) Arduengo, A.J. III; Krafczyk, R.; Schmutzler, R. *Tetrahedron*, **1999**, *55*, 14523-14534.
(2) (a) Schmid, M.; Eberhardt, R.; Klinga, M. Leskelä, Rieger, B. *Organometallics*, **2001**, *20*, 2321-2330; (b) Steele, M.; Watkinson, M.; Whiting, A. *J. Chem. Soc., Perkin Trans. 1*, **2001**, *6*, 588-598.
(3) Serra, A.C.; da Silva Corrêa, C.M.M.; do Vale, M.L.C. *Tetrahedron*, **1991**, *47*, 9463-9488.
(4) Farina, V.; Krishnan, B.; Marshall, D.R.; Roth, G.P. *J. Org. Chem.* **1993**, *58*, 5434-5444.
(5) Grasa, G.A.; Viciu, M.S.; Huang, J.; Zhang, C.; Trudell, M.L.; Nolan, S.P. *Organometallics*, **2002**, *21*, 2866-2873.
(6) Feuerstein, M.; Doucer, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 5923-5925.
(7) Yang, C.; Nolan, S.P. *Synlett*, **2001**, *10*, 1539-1542.