

Supporting Information For:

Unusual transmetallation-induced formation of a C_2 -symmetric tetrapallada-macrocycle

Vincent T. Annibale, Liisa M. Lund, and Datong Song*

*Davenport Chemical Research Laboratories, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6. Email: dsong@chem.utoronto.ca ; Fax: +1 416 978 7013; Tel: +1 416 978 7014.

Experimental Section

General information: **1** was prepared from a literature procedure.¹ THF and benzene-d₆ were dried over Na/benzophenone and vacuum transferred before use, hexanes was dried after passing through a Pure Solv Innovative Technology Grubbs'-type solvent purification system, and degassed through three consecutive freeze-pump-thaw cycles. Pyridine was dried over CaH₂ and vacuum transferred before use. Methylolithium was titrated before use using *N*-benzylbenzamide according to a literature procedure.² ¹H, ¹¹B, and ¹³C NMR spectra were recorded on a Varian 400 MHz NMR instrument. All chemical shifts are reported in ppm relative the residual protio-solvent peaks: ¹H NMR, δ , ppm: dichloromethane-d₂, 5.32; chloroform-d, 7.26; benzene-d₆, 7.16. ¹³C NMR, δ : dichloromethane-d₂, 53.8; chloroform-d, 77.16; benzene-d₆, 175.82. Elemental analysis was performed by ANALEST at the University of Toronto.

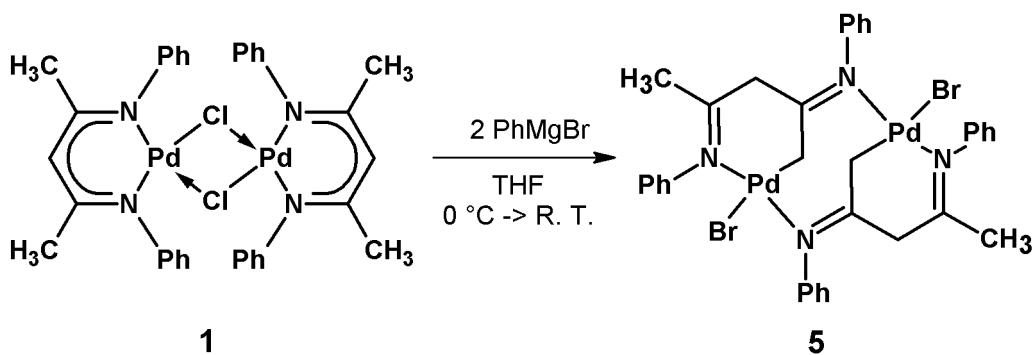
Synthesis of **2**: In air, 330 μ L (4.08 mmol) of pyridine was added to a dark green solution of 500 mg (0.639 mmol) of **1** in 150 mL of CH₂Cl₂, which turned orange-red within a minute. The reaction mixture was stirred for 15 min and the solvent was then removed under vacuum. The residue was washed with hexanes, and the material was recrystallized from a CH₂Cl₂/pentane solvent mixture. The orange-red crystals of **2** were dried under vacuum (580.0 mg, 97%). Crystals suitable for X-ray crystallographic analysis were grown by slow evaporation of a CH₂Cl₂ solution of **2**. ¹H NMR (400 MHz, CDCl₃): δ 8.26 (m, 2H), 7.36 (m, 1H), 7.28 (m, 2H), 7.13 (m, 2H), 6.90-6.79 (m, 5H), 6.75 (m, 2H), 4.83 (s, 1H, nacnac β -CH), 1.77 (s, 3H, nacnac-CH₃), 1.73 (s, 3H, nacnac-CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 158.51, 156.77, 152.43, 152.35, 150.68, 136.68, 128.21, 127.74, 127.66, 126.79, 124.68, 124.49, 124.27, 96.95, 24.33, 23.51. Anal. Calcd. for C₂₂H₂₂ClN₃Pd: C, 56.18; H, 4.71; N, 8.94. Found: C, 55.89; H, 4.72; N, 8.57.

Synthesis of **3**: In a Schlenk flask, 80.2 mg (0.171 mmol) of **2** was placed under argon and dissolved in 4 mL of diethyl ether and 6 mL of THF. The solution was chilled to -78 °C in a dry ice/acetone bath. To the orange-red solution 110 μ L methylolithium (titrated as 1.56 M in diethyl ether) was added dropwise. After the addition of methylolithium was complete a yellow solution resulted, and the mixture was stirred for 2 h. After the solvents were removed under vacuum, the

residue was brought into the glovebox for workup. The product was extracted into toluene and filtered through Celite. The solvent was removed from the toluene filtrate, and the yellow product was washed with cold hexanes and dried under vacuum. The final product was stored in a -35 °C freezer under nitrogen. The yield was 30.6 mg (40%). Crystals suitable for X-ray crystallographic analysis were grown by slow evaporation of a hexanes solution of **3**. ¹H NMR (400 MHz, C₆D₆): δ 7.93 (m, 2H), 7.22 (d, 4H, J=4.3 Hz), 6.95 (td, 1H, J = 4.3 Hz, J = 8.6 Hz), 6.63-6.46 (m, 5H), 6.38 (tt, 1H, J = 1.7 Hz, J = 7.7 Hz), 5.91 (ddd, 2H, J = 1.5 Hz, J = 4.9 Hz, J = 7.7 Hz), 4.98 (s, 1H, nacnac β-CH), 1.88 (s, 3H, nacnac-CH₃), 1.81 (s, 3H, nacnac-CH₃), 0.22 (s, 3H, Pd-CH₃). ¹³C NMR (400 MHz, C₆D₆): δ 158.83, 158.44, 155.05, 153.78, 153.07, 134.88, 127.48, 125.87, 123.76, 123.60, 122.29, 95.67, 26.41, 24.36, 3.57. Anal. Calcd. for C₂₃H₂₅N₃Pd: C, 61.40; H, 5.60; N, 9.34. Found: C, 61.69 ; H, 5.80; N, 9.11.

Synthesis of **4**: In air and with undried solvents and reagents from commercial sources, 27.3 mg (0.0349 mmol) of **1** was dissolved in 0.5 mL of a benzene-d₆:acetone-d₆ solvent mixture (9:1 v/v) and transferred to a 5 mm diameter J. Young NMR tube with re-sealable Teflon valve containing 5.4 mg (0.0443 mmol) of phenylboronic acid. After mixing the J. Young tube was sealed and gradually heated to 70 °C. After heated overnight, rhombus-shaped, orange, X-ray quality single crystals of **4** deposited on the insides of the J. Young tube. The mother-liquor was aspirated off and the crystals of **4** were washed with benzene, followed by hexanes and dried in vacuum (21.3 mg, 50%). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.02-8.00 (m, 1H, Ph), 7.50-7.46 (m, 2H, Ph), 7.38-7.30 (m, 5H, Ph), 7.27-7.20 (m, 2H, Ph), 7.13-7.10 (m, 3H, Ph), 6.95-6.91 (m, 1H, Ph), 6.88-6.85 (m, 1H, Ph), 3.89 (s, 1H, nacnac β-CH), 2.06 (s, 3H, nacnac-CH₃), 0.87 (s, 3H, nacnac-CH₃). ¹³C NMR (100 MHz, CD₂Cl₂): δ 185.81, 185.73, 147.96, 147.87, 141.95, 137.51, 136.38, 129.15, 128.78, 128.62, 127.72, 126.94, 126.91, 125.89, 124.84, 123.25, 56.90, 23.57, 23.22. Anal. Calcd. for C₄₆H₄₄Cl₄N₄Pd₄: C, 45.27; H, 3.63; N, 4.59. Found: C, 45.28; H, 3.83; N, 4.59.

Synthesis of (**5**) (poor reproducibility):



Magnesium turnings (358.1 mg, 14.73 mmol) were added to a flame-dried 2-neck flask fitted with a reflux condenser, which was then purged with argon three times. Dry THF (50 mL)

was added, followed by bromobenzene (1.4 mL, 13.3 mmol). The reaction was refluxed for ~2 h, after which the magnesium had fully disappeared. **1** (153.4 mg, 0.1961 mmol) was added to a Schlenk flask, which was then purged with argon three times. Dry THF (25 mL) was added, and the resulting dark green solution was cooled in an ice-water bath. The PhMgBr solution (~1.6 mL, 0.416 mmol) was then added. The reaction mixture was stirred under argon overnight, warming to room temperature, resulting in a dark red solution. H₂O (~15 mL) was added to quench the reaction, followed by the addition of CH₂Cl₂ (~25 mL). The CH₂Cl₂ layer was washed with H₂O (x5), followed by brine (x1), and then dried with Na₂SO₄. The solution was filtered and the solvent removed in vacuo. Crystals suitable for X-ray crystallographic analysis were grown by standing a CH₂Cl₂ solution of **5**. Anal. Calcd for C₃₄H₃₄Br₂N₄Pd₂: C, 46.87; H, 3.93; N, 6.43. Found: C, 47.45; H, 4.06; N, 6.28. Crystal data for **5**·(4CH₂Cl₂) at 150(2) K with Mo K α ($\lambda=0.71073\text{ \AA}$): C₃₈H₄₂Br₂Cl₈N₄Pd₂, $FW=1210.98$, monoclinic, space group $P2_1/n$, $Z=2$, $\mu=3.099\text{ mm}^{-1}$, $a=8.8468(2)\text{ \AA}$, $b=23.2955(7)\text{ \AA}$, $c=11.6038(3)$, $\beta=110.5891(13)^\circ$, $V=2238.68(10)\text{ \AA}^3$, $D_c=1.796\text{ Mg}\cdot\text{m}^{-3}$, θ range is 3.02 to 27.48°, 21574 reflections were collected of which 5089 were independent, 254 parameters, GOF on F^2 is 1.055, $R_1=0.0418$ for [$I>2\sigma(I)$] reflections, and $wR_2=0.1064$ (all data).

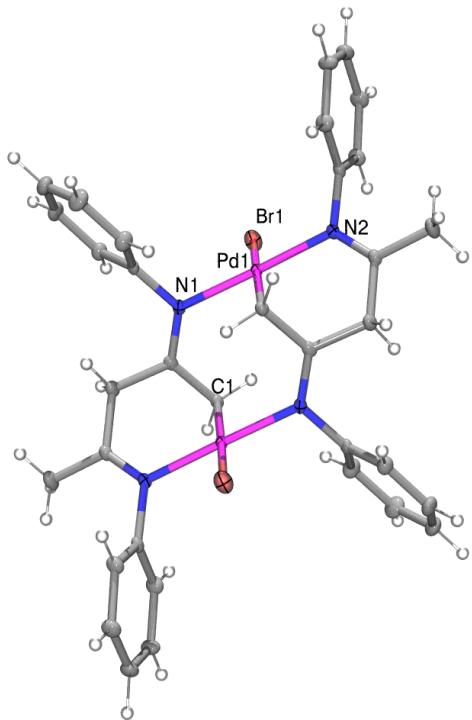


Figure S14: X-ray crystal structure of **5**, shown with 30% ellipsoids (except for H-atoms which are shown as spheres of arbitrary radius). CH₂Cl₂ solvent molecules are omitted for clarity.

X-ray crystallography:

The X-ray diffraction data for structures **2**, **4**, and **5**·(4CH₂Cl₂) were collected³ on a Nonius Kappa-CCD diffractometer and processed with the DENZO-SMN package.⁴ The X-ray diffraction data for structure **3** were collected on a Bruker Kappa Apex II diffractometer, and processed with the Bruker Apex 2 software package.⁵ All data were collected with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$), at 150 K controlled by an Oxford Cryostream 700 series low temperature system. All structures were solved by the direct methods and refined using SHELXTL V6.10.⁶ Whole-molecule disordering was found in the structure of compound **3**, this was modeled successfully over three sets of coordinates.

References:

- 1 A. Hadzovic, D. Song, *Organometallics* 2008, **27**, 1290.
- 2 A. Burchat, J. Chong, N. Nielsen, *J. Organomet. Chem.* 1997, **542**, 281.
- 3 *Collect. Data collection software*, B. V. Nonius., 1997-2002.
- 4 Z. Otwinowski, W. Minor, *Methods Enzymol.* 1997, **276**, 307.
- 5 *Apex 2 Software Package*, Bruker AXS Inc. , 2008.
- 6 G. M. Sheldrick, *Acta Crystallogr. , Sect. A: Found. Crystallogr.* 2008, **64**, 112.