

## Supplementary Information for:

### The First Palladium(IV) Aryldiazenido Complex: Relevance for C-C Coupling

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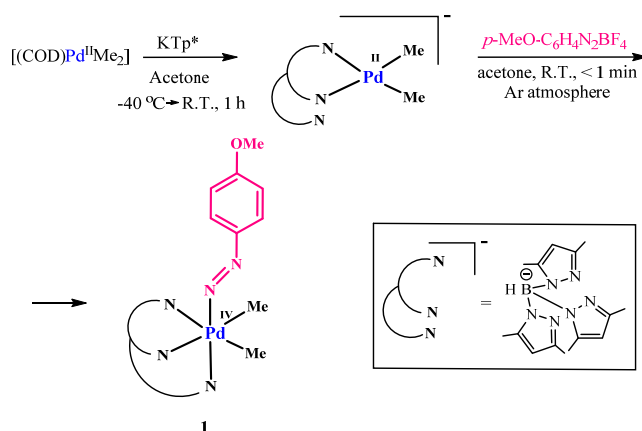
#### General specifications

All manipulations were carried out under an inert (N<sub>2</sub> or Ar) atmosphere using standard glove box (M Braun UniLab) and Schlenk-type techniques except where noted, and using oven-dried glassware. All reagents for which synthesis is not given were commercially available from Sigma Aldrich, Alfa Aesar, or STREM and were used as received without further purification. Solvents were purified prior to use by passing through a column of activated alumina using an MBRAUN SPS. NMR solvents were obtained from Cambridge Isotope Laboratories. Diethyl ether (Et<sub>2</sub>O), dimethoxyethane (DME), tetrahydrofuran (THF), and benzene-*d*<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>) were further purified using by vacuum distillation from purple sodium benzophenone ketyl. Acetone and acetone-*d*<sub>6</sub> were dried/degassed over molecular sieves (3Å) before use. [(COD)PdMe<sub>2</sub>] was prepared by a modified literature procedure by addition of two equivalents of commercial methylmagnesium bromide solution (Aldrich, 3 M in Et<sub>2</sub>O) to a slurry of [(COD)PdCl<sub>2</sub>] in dimethoxyethane at - 30 °C.<sup>1</sup> All NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. Standard VNMR pulse sequences for heteronuclear multiple bond correlation (gHMBC) were used. The 2-D experiment (<sup>15</sup>N-<sup>1</sup>H gHMBC) was also optimized for an average <sup>3</sup>J<sub>NH</sub> coupling of 3.5 Hz. Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks. Abbreviations for the multiplicity of NMR signals are s (singlet), d (doublet), t (triplet), q (quartet),

m (multiplet), br (broad). Elemental analyses were conducted at Guelph (Chemisar) Laboratories, Guelph, ON, Canada.

### Procedure for synthesis of Pd(IV) aryldiazenido complex

A solid sample of [(COD)PdMe<sub>2</sub>] (61.1 mg, 0.25 mmol) was placed into an cooled 25 mL air-free round-bottom flask equipped with a magnetic stirring bar. The flask was cooled to -40 °C, after which 5 mL of acetone was added. A solution of KTp\* (84.1 mg, 0.25 mmol) in 2 mL acetone was then added at -40 °C and the reaction mixture was allowed to stir while coming to room temperature under Ar over a period of 1 h. A solution of pmbd-BF<sub>4</sub> (55.5 mg, 0.25 mmol) in 3 mL acetone was added at room temperature immediately resulted in a rapid color change within mixing from colorless to dark orange without any intermediate colour observed. The solvent was removed by evaporation under high vacuum at room temperature and the resulting solid residue was transferred to the glove box, extracted with 20 mL of diethyl ether, filtered using a 0.2 μm Whatman disk filter and 30 mL glass syringe, and evaporated to dryness to give an orange solid of [(Tp\*)PdMe<sub>2</sub>(pmbd)] (**1**) in 94% (133.6 mg, 0.23 mmol) (Scheme S1).

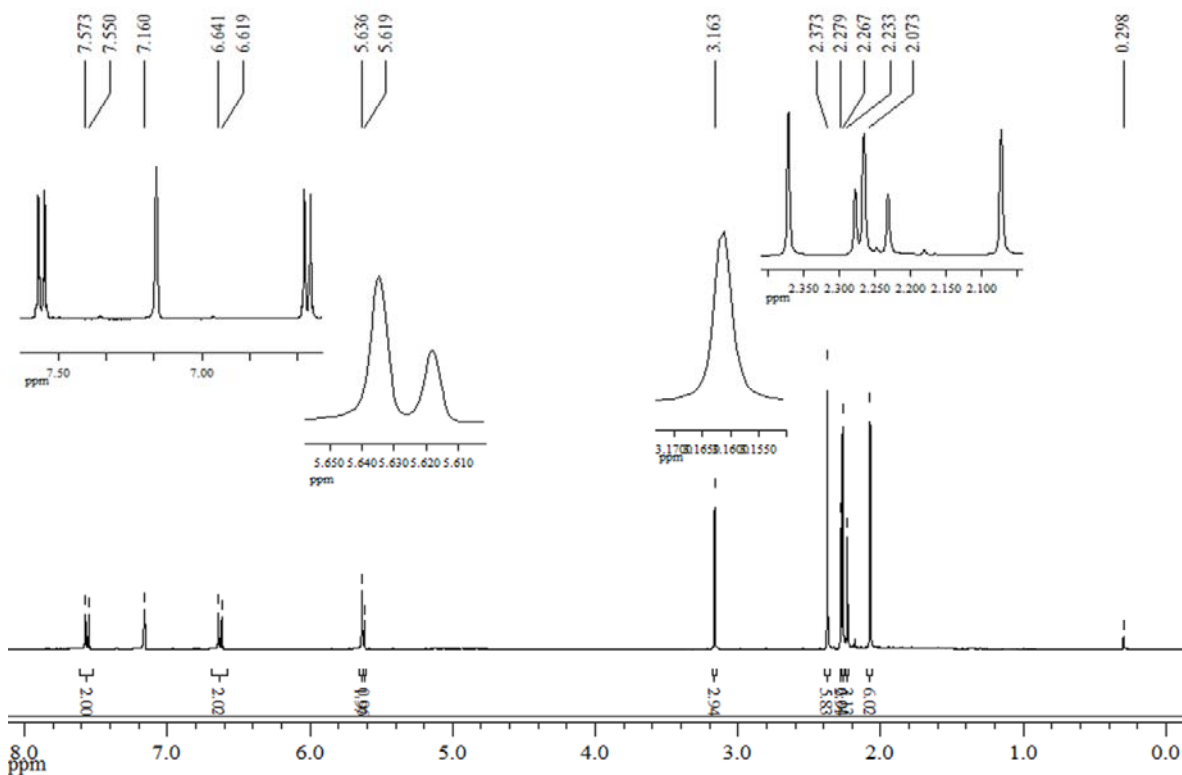


**Scheme S1** Synthesis of [(Tp\*)PdMe<sub>2</sub>(pmbd)] (**1**).

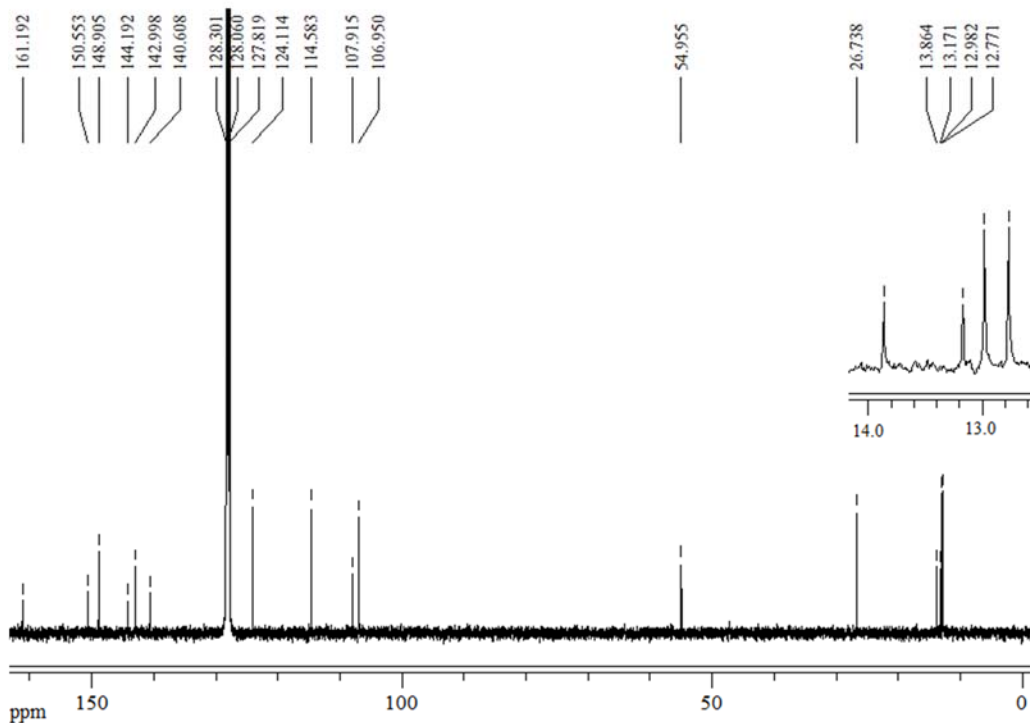
### Characterization of [(Tp\*)PdMe<sub>2</sub>(pmbd)] (1)

**1** was prepared using the procedure above. It was characterized by X-ray crystallography, elemental analysis, and <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>15</sup>N-<sup>1</sup>H gHMBC NMR spectroscopies (Figures S1-S4):

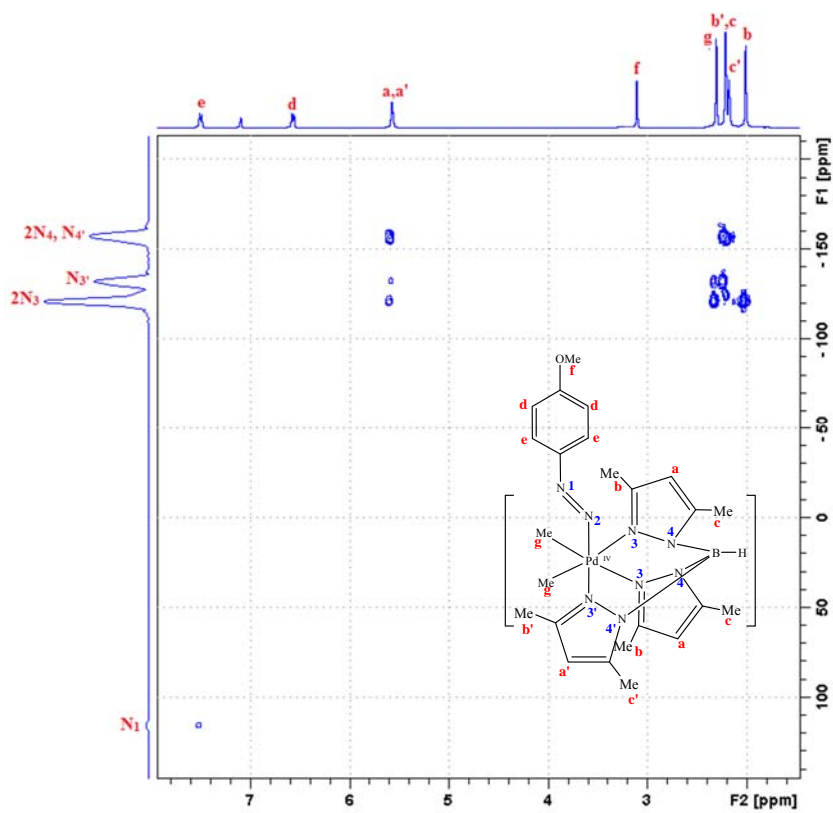
<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ (ppm)): 2.073 (s, 6H, pz-Me), 2.233 (s, 3H, pz-Me), 2.267 (s, 6H, pz-Me), 2.279 (s, 3H, pz-Me), 2.373 (s, 6H, Pd-Me), 3.163 (s, 3H, Ph-OMe), 5.619 (s, 1H, pz-CH), 5.636 (s, 2H, pz-CH), 6.630 (d, 2H, *o*-Ph), 7.561 (d, 2H, *m*-Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ (ppm)): 12.771 (2C, pz-Me), 12.982 (2C, pz-Me), 13.171 (1C, pz-Me), 13.864 (1C, pz-Me), 26.738 (2C, Pd-Me), 54.955 (1C, Ph-OMe), 106.950 (2C, pz-CH), 107.915 (1C, pz-CH), 114.583 (2C, *o*-Ph), 124.114 (2C, *m*-Ph), 140.608 (1C, *p*-Ph), 142.998 (2C, pz-C(Me)), 144.192 (1C, pz-C(Me)), 148.905 (2C, pz-C(Me)), 150.553 (1C, pz-C(Me)), 161.192 (1C, *ipso*-Ph). Anal. Calcd for C<sub>24</sub>H<sub>35</sub>BN<sub>8</sub>OPd (568.81 g mol<sup>-1</sup>): C, 50.67; H, 6.20; N, 19.69. Found: C, 50.52; H, 6.01; N, 19.47.



**Fig. S1** <sup>1</sup>H NMR spectrum of [(Tp\*)PdMe<sub>2</sub>(pmbd)] (1) in C<sub>6</sub>D<sub>6</sub> at 25 °C.



**Fig. S2**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{Tp}^*)\text{PdMe}_2(\text{pmbd})]$  (**1**) in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$ .

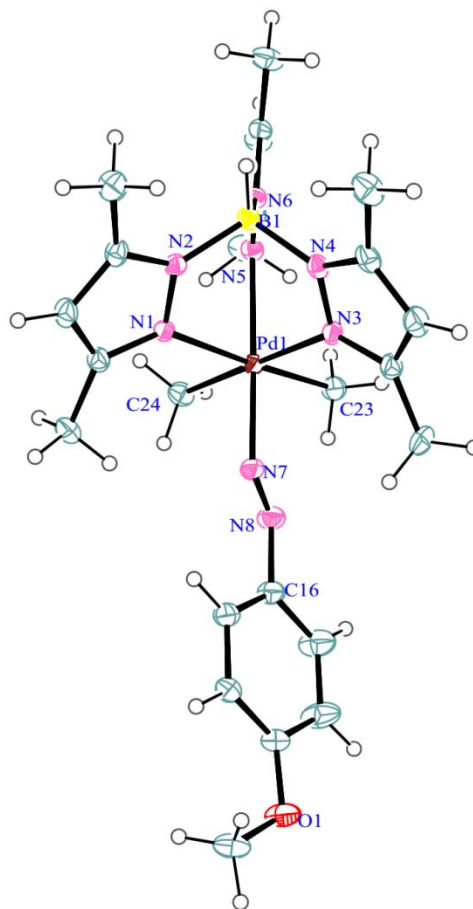


**Fig. S3**  $^{15}\text{N}-^1\text{H}$  gHMBC NMR spectrum of  $[(\text{Tp}^*)\text{PdMe}_2(\text{pmbd})]$  (**1**) in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$ .

### X-ray structure determination of [(Tp\*)PdMe<sub>2</sub>(pmbd)]

X-ray quality crystals for **1** were obtained from a concentrated diethyl ether solution after three days at -35 °C. An orange single crystal with dimensions of 0.10 × 0.10 × 0.03 mm was chosen for the single-crystal X-ray diffraction study. Data were collected<sup>2</sup> on a Nonius-Kappa CCD diffractometer using graphite monochromatized Mo *K*α radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 150(2) K using the  $\omega$ -scan technique. Unit cell parameters were refined and data were reduced with Denzo-SMN.<sup>3</sup> The absorption correction performed was semi-empirical from equivalents. The structure was solved using direct methods<sup>4</sup> and refined, full-matrix least-squares on  $F^2$ , using SHELXTL V6.1.<sup>5</sup>

**Fig. S4** ORTEP representation (35% probability ellipsoids) of **1**. Selected bond distances (Å) and angles (deg): Pd1–C23, 2.036(2); Pd1–C24, 2.042(3); Pd1–N1, 2.212(2); Pd1–N3, 2.212(2); Pd1–N5, 2.174(2); Pd1–N7, 2.009(2); N7–N8, 1.212(3); N8–C16, 1.456(4); C23–Pd1–C24, 87.98(14); N7–Pd1–C23, 91.26(11); N7–Pd1–C24, 88.87(12); N5–Pd1–N7, 175.20(10); N7–N8–C16, 115.5(3); Pd1–N7–N8, 119.8(2).



**Table S1** Crystal data and structure refinement for [(Tp\*)PdMe<sub>2</sub>(pmbd)].

Chemical formula	C <sub>24</sub> H <sub>35</sub> BN <sub>8</sub> OPd
Formula weight	568.81
Temperature (K)	150(2) K
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	7.9636(7)
<i>b</i> (Å)	12.4983(12)
<i>c</i> (Å)	13.5112(12)
$\beta$ (°)	87.268(2)
<i>V</i> (Å <sup>3</sup> )	1329.8(2)
<i>Z</i>	2
Calculated density (Mg/m <sup>3</sup> )	1.421
Crystal size (mm)	0.10 × 0.10 × 0.03
<i>F</i> (000)	588
$\theta$ range (°)	1.51 to 27.49
Reflections collected	22570
Independent reflections ( <i>R</i> <sub>int</sub> )	6073 [ <i>R</i> <sub>(int)</sub> = 0.0540]
Data / restraints / parameters	6073 / 0 / 329
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.020
Final <i>R</i> indices	<i>R</i> <sub><i>I</i></sub> = 0.0372, <i>wR</i> <sub>2</sub> = 0.0790
<i>R</i> indices (all data)	<i>R</i> <sub><i>I</i></sub> = 0.0548, <i>wR</i> <sub>2</sub> = 0.0862
Range of <i>h, k, l</i>	-10/8, -16/16, -17/17

**Table S2** Selected bond lengths (Å) and angles (deg) for [(Tp\*)PdMe<sub>2</sub>(pmbd)].

<i>Bond lengths (Å)</i>	
Pd(1)–N(7)	2.009(2)
Pd(1)–C(23)	2.036(3)
Pd(1)–C(24)	2.042(3)
Pd(1)–N(5)	2.174(2)
Pd(1)–N(1)	2.212(2)
Pd(1)–N(3)	2.212(2)
N(7)–N(8)	1.212(3)

N(8)–C(16)	1.456(4);
<i>Bond angles (deg)</i>	
N(7)–Pd(1)–C(23)	91.26(11)
N(7)–Pd(1)–C(24)	88.87(12)
C(23)–Pd(1)–C(24)	87.98(14)
N(7)–Pd(1)–N(5)	175.20(10)
C(23)–Pd(1)–N(5)	92.72(11)
C(24)–Pd(1)–N(5)	93.95(11)
N(7)–Pd(1)–N(1)	91.40(9)
C(23)–Pd(1)–N(1)	177.10(10)
C(24)–Pd(1)–N(1)	93.25(11)
N(5)–Pd(1)–N(1)	84.58(8)
N(7)–Pd(1)–N(3)	89.44(10)
C(23)–Pd(1)–N(3)	93.69(12)
C(24)–Pd(1)–N(3)	177.65(11)
N(5)–Pd(1)–N(3)	87.62(9)
N(1)–Pd(1)–N(3)	85.16(9)
N(7)–N(8)–C(16)	115.5(3)
Pd(1)–N(7)–N(8)	119.8(2)

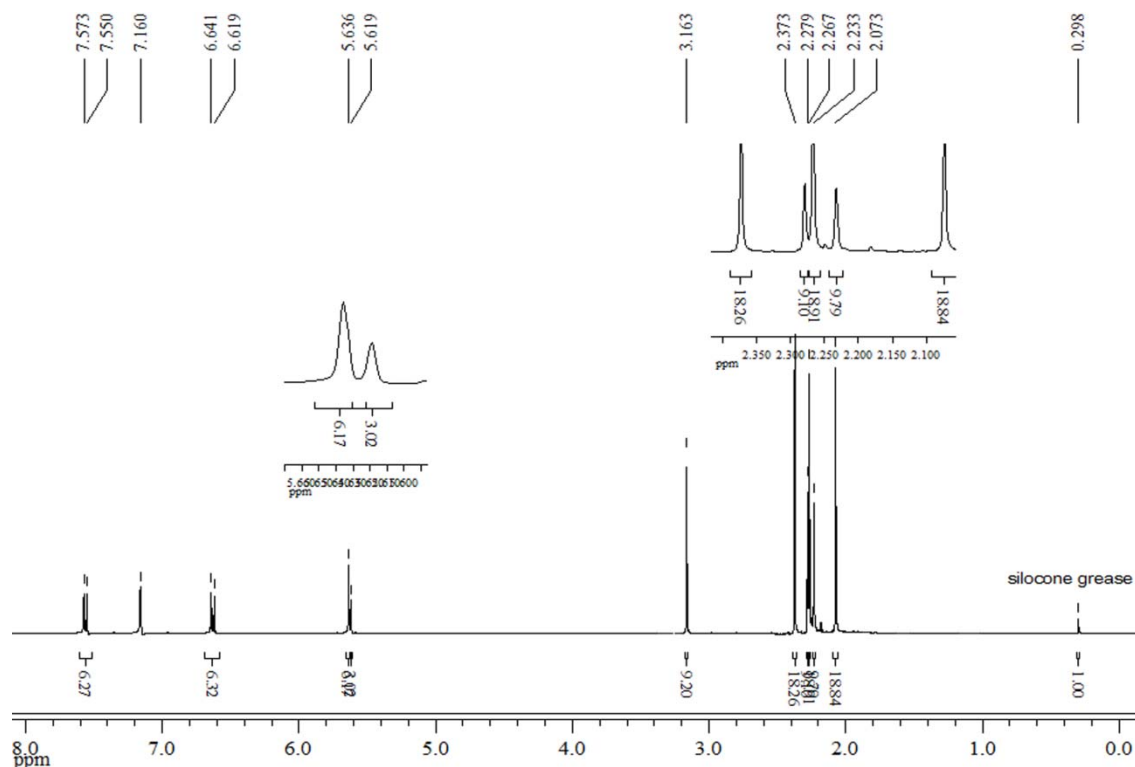
### Thermolysis of [(Tp\*)PdMe<sub>2</sub>(pmbd)] in C<sub>6</sub>D<sub>6</sub>

A solution of [(Tp\*)PdMe<sub>2</sub>(pmbd)] (**1**) in C<sub>6</sub>D<sub>6</sub> was prepared under N<sub>2</sub> atmosphere, placed into a Young tube. The reaction mixture was heated at 70 °C and periodically analyzed by <sup>1</sup>H NMR spectroscopy. **1** disappeared to give one major organometallic product, [(Tp\*)PdMe<sub>3</sub>] (**2**), and one major organic product, 4,4'-dimethoxybiphenyl, in ~34% and ~36% yield, respectively, after heating for 1 h at 70 °C. The yields of products were determined by <sup>1</sup>H NMR integration relative to an internal standard (The silicone 'grease' signal was used as the internal standard, which was set to an integration of 1.0 in each spectrum and integration intensities of the least obscured peaks were used to determine NMR yields, namely aromatic C-H peaks for 4,4'-dimethoxybiphenyl and pyrazole C-H peaks for **2**).

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$  (ppm)):

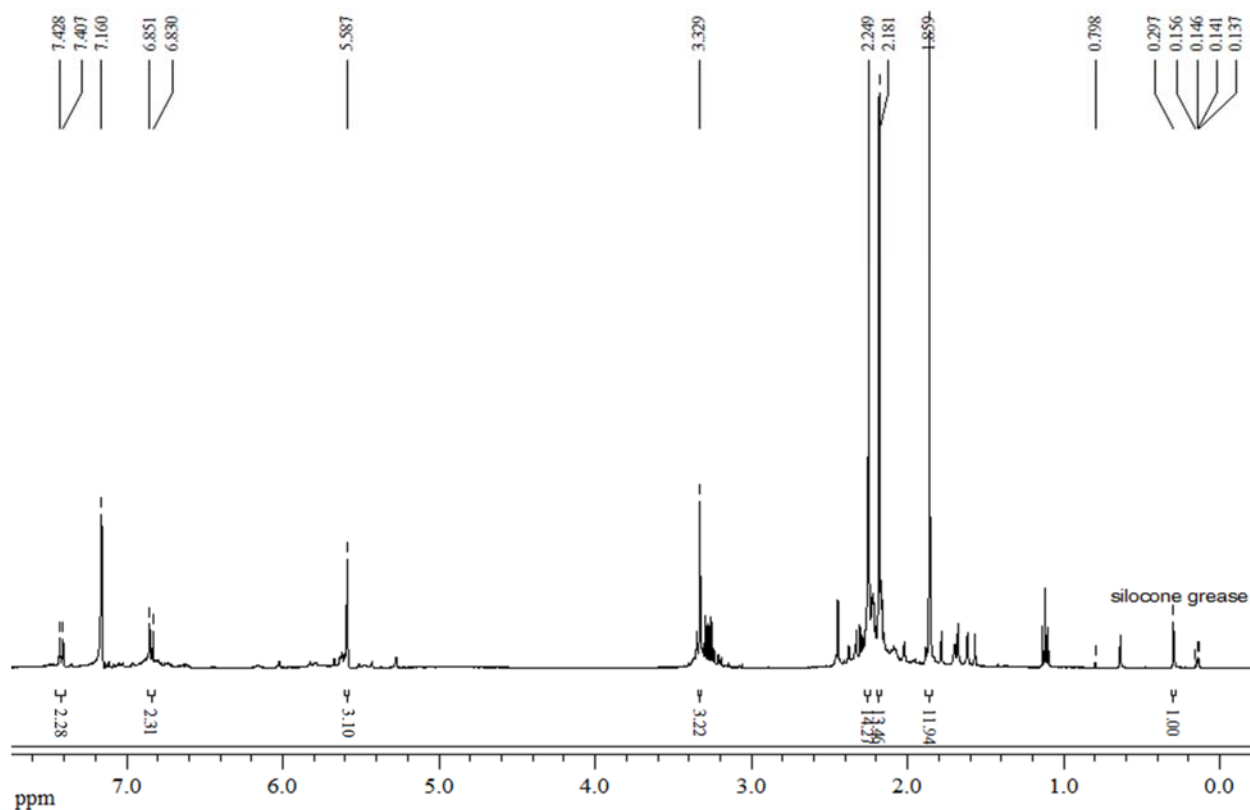
4,4'-Dimethoxybiphenyl: 3.329 (s, 6H, Ph-OMe), 6.841 (d, 4H, *o*-Ph), 7.417 (d, 4H, *m*-Ph);

**2**: 1.859 (s, 9H, Pd-Me), 2.181 (s, 9H, pz-Me), 2.249 (s, 9H, pz-Me), 5.587 (s, 3H, pz-CH).



**Fig. S5**  $^1\text{H}$  NMR spectrum of  $[(\text{Tp}^*)\text{PdMe}_2(\text{pmbd})]$  in  $\text{C}_6\text{D}_6$  before heating at  $70\text{ }^\circ\text{C}$  with integration toward the silicone grease signal as the internal standard.





**Fig. S6**  $^1\text{H}$  NMR spectrum of  $[(\text{Tp}^*)\text{PdMe}_2(\text{pmbd})]$  in  $\text{C}_6\text{D}_6$  after heating for 1 h at  $70\text{ }^\circ\text{C}$  with integration toward the silicone grease signal as the internal standard.

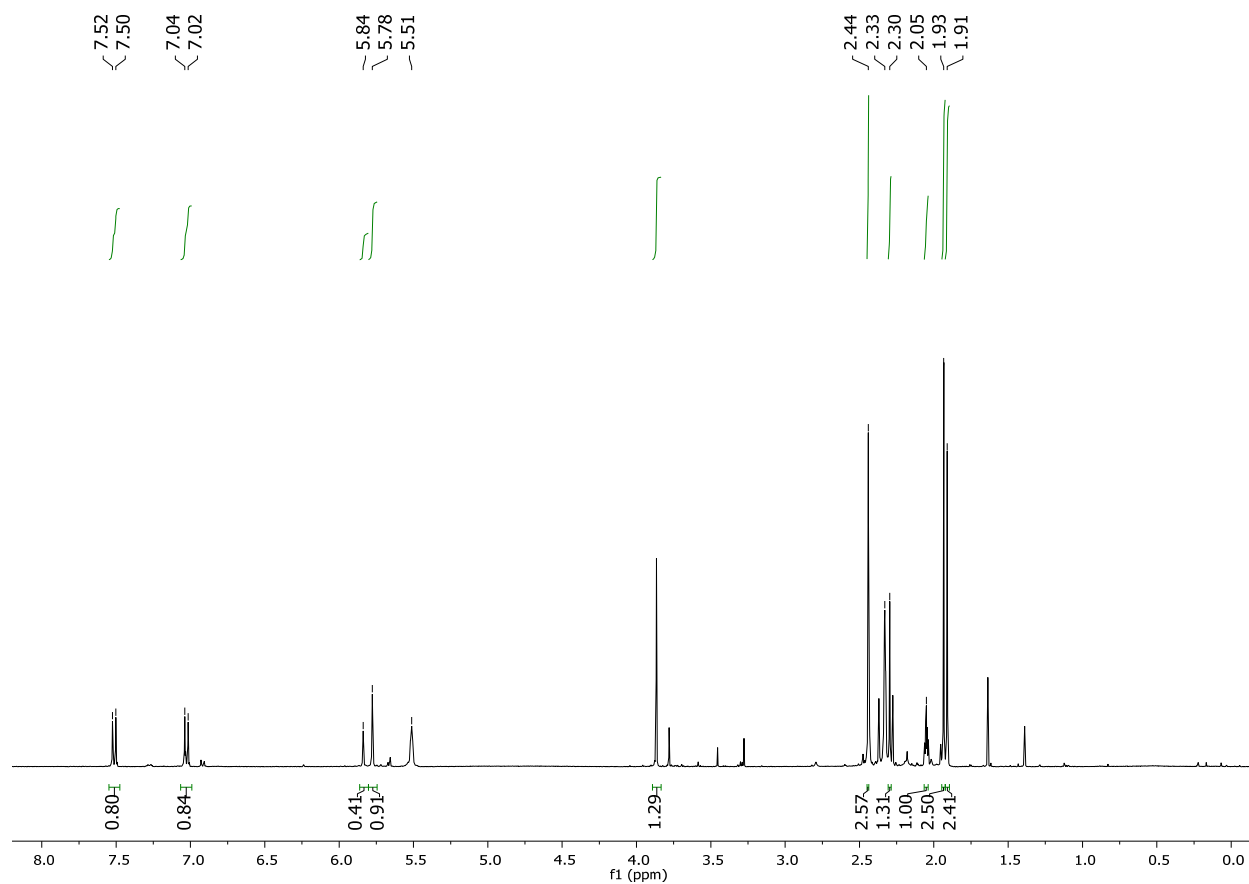
### Thermolysis of $[(\text{Tp}^*)\text{PdMe}_2(\text{pmbd})]$ in $\text{Acetone-}d_6$

A solution of  $(\text{COD})\text{PdMe}_2$  in  $\text{acetone-}d_6$  was prepared under  $\text{N}_2$  atmosphere, placed into a J. Young tube. The solution was cooled to  $-50\text{ }^\circ\text{C}$  and one equivalent of  $\text{KTp}^*$  in  $\text{acetone-}d_6$  was added and allowed to react for 30 minutes to afford  $\text{K}[(\text{Tp}^*)\text{PdMe}_2]$  *in situ*. One equivalent of  $[\text{pmbd}][\text{BF}_4]$  in  $\text{acetone-}d_6$  was then added to give  $[(\text{Tp}^*)\text{PdMe}_2(\text{pmbd})]$  (**1**), and a  $^1\text{H}$  NMR spectrum was immediately recorded. The reaction mixture was heated at  $70\text{ }^\circ\text{C}$  and periodically analyzed by  $^1\text{H}$  NMR spectroscopy. **1** disappeared to give one major organometallic product,  $[(\text{Tp}^*)\text{PdMe}_3]$  (**2**), and one major organic product,  $\text{anisole-}d_1$  in  $\sim 50\%$  and  $\sim 49\%$  yield,

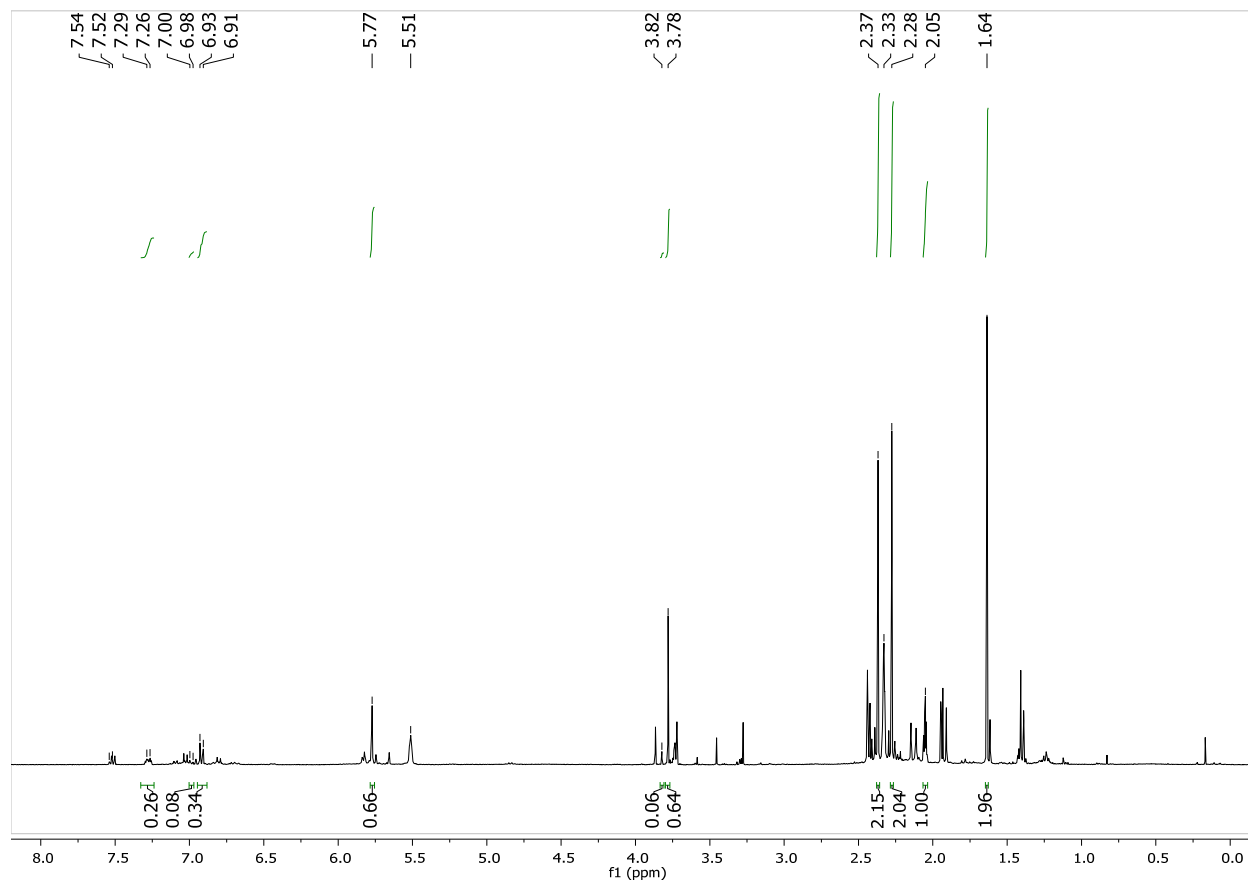
respectively, after heating for 1 h at 70 °C. 4,4'-dimethoxybiphenyl was formed in ~5% yield. The yields of products were determined by <sup>1</sup>H NMR integration relative to an internal standard (The acetone-*d*<sub>5</sub> residual solvent signal was used as the internal standard, which was set to an integration of 1.0 in each spectrum and integration intensities of the least obscured peaks were used to determine NMR yields, namely methoxy C-H peaks for anisole-*d*<sub>1</sub> and 4,4'-dimethoxybiphenyl, and pyrazole C-H peaks for **2**).

<sup>1</sup>H NMR (Acetone-*d*<sub>6</sub>, δ (ppm)):

1,5-COD: 5.51 (bs, 4H, CH). 2.33 (bs, 8H, CH<sub>2</sub>); Anisole-*d*<sub>1</sub>: 3.78 (s, 3H, Ph-OMe), 7.27 (m, 2H, Ph), 6.92 (d, 2H, Ph); 4,4'-Dimethoxybiphenyl: 3.82 (s, 6H, Ph-OMe), 7.53 (d, 4H, *o*-Ph), 6.99 (d, 4H, *m*-Ph); **2**: 1.64 (s, 9H, Pd-Me), 2.28 (s, 9H, pz-Me), 2.37 (s, 9H, pz-Me), 5.77 (s, 3H, pz-CH).



**Fig. S7**  $^1\text{H}$  NMR spectrum of  $[(\text{Tp}^*)\text{PdMe}_2(\text{pmbd})]$  in  $\text{acetone-}d_6$  before heating at  $70\text{ }^\circ\text{C}$  with integration toward the solvent residual signal as the internal standard.



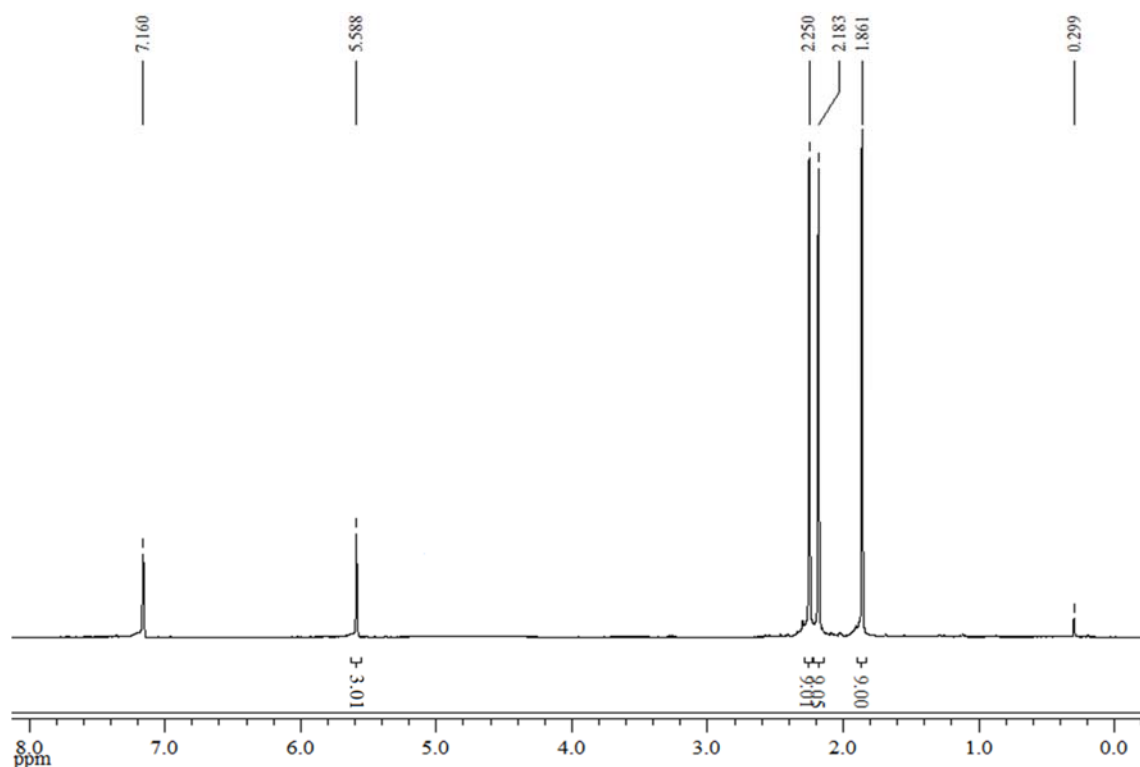
**Fig. S8**  $^1\text{H}$  NMR spectrum of  $[(\text{Tp}^*)\text{PdMe}_2(\text{pmbd})]$  in acetone- $d_6$  after heating for 1 h at 70 °C with integration toward the solvent residual signal as the internal standard.

### Isolation and characterization of $[(\text{Tp}^*)\text{PdMe}_3]$ (**2**)

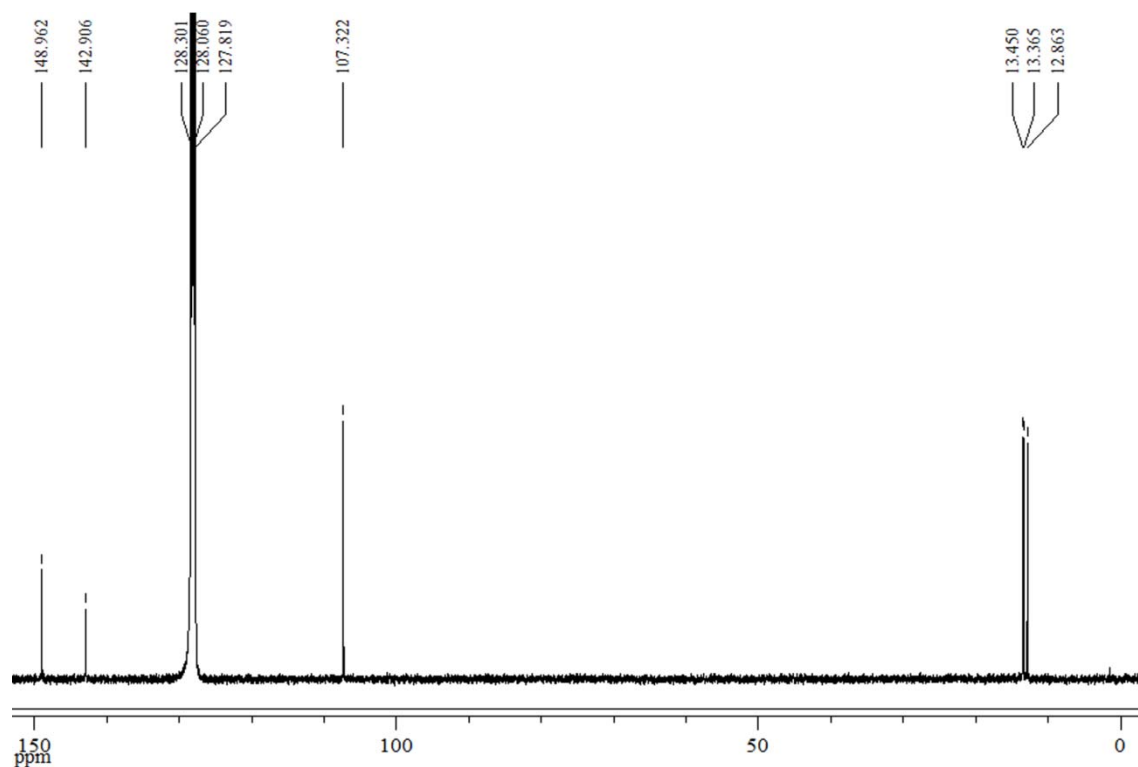
**2** was isolated from the crude reaction mixture of thermolysis of  $[(\text{Tp}^*)\text{PdMe}_2(\text{pmbd})]$  in  $\text{C}_6\text{D}_6$  at 70 °C after 1 h. The solvent of the reaction mixture was removed by evaporation under high vacuum at room temperature and the resulting solid residue was transferred to the glove box, extracted with 2 mL of diethyl ether, filtered using a 0.2  $\mu\text{m}$  Whatman disk filter, and recrystallized at -35 °C to give the colorless crystals of  $[(\text{Tp}^*)\text{PdMe}_3]$  in ~43% yield (16.5 mg, 0.036 mmol). It was also characterized by X-ray crystallography, elemental analysis, and  $^1\text{H}$  and  $^{13}\text{C}\{\text{H}\}$  NMR spectroscopies. It is worth noting that the isolated yield of **2** is greater than the reported NMR

yield. This is likely due to the use of Et<sub>2</sub>O in the isolation of the product, since the product appears to have better solubility in Et<sub>2</sub>O than in C<sub>6</sub>D<sub>6</sub>.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ (ppm)): 1.861 (s, 9H, Pd–Me), 2.183 (s, 9H, pz–Me), 2.250 (s, 9H, pz–Me), 5.588 (s, 3H, pz–CH). <sup>13</sup>C{H} NMR (C<sub>6</sub>D<sub>6</sub>, δ (ppm)): 12.863 (3C, Pd–Me), 13.365 (3C, pz–Me), 13.450 (3C, pz–Me), 107.322 (3C, pz–CH), 142.906 (3C, pz–C(Me)), 148.962 (3C, pz–C(Me)).  
Anal. Calcd for C<sub>18</sub>H<sub>31</sub>BN<sub>6</sub>Pd (448.70 g mol<sup>-1</sup>): C, 48.14; H, 6.90; N, 18.72. Found: C, 47.95; H, 6.72; N, 18.56.



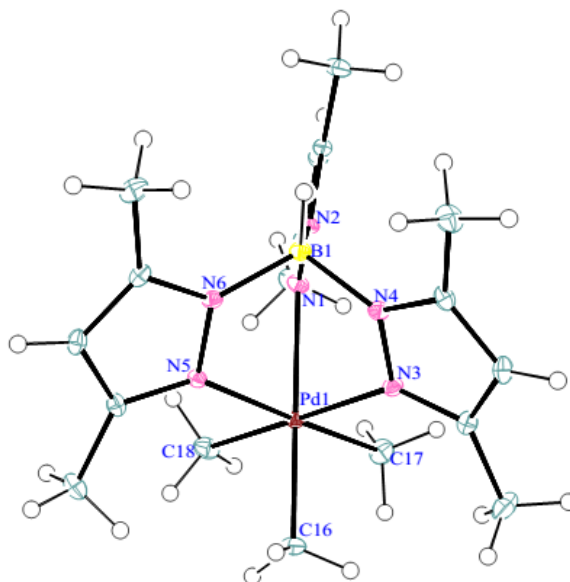
**Fig. S9** <sup>1</sup>H NMR spectrum of [(Tp\*)PdMe<sub>3</sub>] (2) in C<sub>6</sub>D<sub>6</sub> at 25 °C.



**Fig. S10**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of  $[(\text{Tp}^*)\text{PdMe}_3]$  (**2**) in  $\text{C}_6\text{D}_6$  at  $25\text{ }^\circ\text{C}$ .

### X-ray structure determination of $[(\text{Tp}^*)\text{PdMe}_3]$

X-ray quality crystals for **2** were obtained from a concentrated diethyl ether solution after a week at  $-35\text{ }^\circ\text{C}$ . A colorless single crystal with dimensions of  $0.38 \times 0.23 \times 0.15\text{ mm}$  was chosen for the single-crystal X-ray diffraction study. Data were collected<sup>2</sup> on a Nonius-Kappa CCD diffractometer using graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) at  $110(2)\text{ K}$  using the  $\omega$ -scan technique. The structure refinement was performed using similar methods and techniques as used for **1**.



**Fig. S11** ORTEP representation (35% probability ellipsoids) of **2**. Selected bond distances (Å) and angles (deg): Pd1–C16, 2.0439(16); Pd1–C17, 2.0397(15); Pd1–C18, 2.0399(15); Pd1–N1, 2.2304(13); Pd1–N3, 2.2122(12); Pd1–N5, 2.1925(12); C16–Pd1–C17, 87.65(7); C16–Pd1–C18, 87.96(7); C17–Pd1–C18, 87.49(7).

**Table S3** Crystal data and structure refinement for [(Tp\*)PdMe<sub>3</sub>].

Chemical formula	C <sub>18</sub> H <sub>31</sub> BN <sub>6</sub> Pd
Formula weight	448.70
Temperature (K)	110(2) K
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> (Å)	16.3066(9)
<i>b</i> (Å)	9.8567(6)
<i>c</i> (Å)	25.2093(14)
$\beta$ (°)	90
<i>V</i> (Å <sup>3</sup> )	1329.8(2)
<i>Z</i>	8
Calculated density (Mg/m <sup>3</sup> )	1.471

$F(000)$	1856
$\theta$ range (°)	1.62 to 33.17
Reflections collected	32099
Independent reflections ( $R_{\text{int}}$ )	7727 [ $R_{\text{int}} = 0.0282$ ]
Data / restraints / parameters	7727 / 0 / 248
Goodness-of-fit on $F^2$	1.067
Final $R$ indices	$R_1 = 0.0271$ , $wR_2 = 0.0585$
$R$ indices (all data)	$R_1 = 0.0354$ , $wR_2 = 0.0621$
Range of $h, k, l$	-25/20, -11/15, -38/38

**Table S4** Selected bond lengths (Å) and angles (deg) for [(Tp\*)PdMe<sub>3</sub>].

<i>Bond lengths (Å)</i>	
Pd(1)–C(17)	2.0397(15)
Pd(1)–C(18)	2.0399(15)
Pd(1)–C(16)	2.0439(16)
Pd(1)–N(5)	2.1925(12)
Pd(1)–N(3)	2.2122(12)
Pd(1)–N(1)	2.2304(13)
<i>Bond angles (deg)</i>	
C(17)–Pd(1)–C(18)	87.49(7)
C(17)–Pd(1)–C(16)	87.65(7)
C(18)–Pd(1)–C(16)	87.96(7)
C(17)–Pd(1)–N(5)	177.87(6)
C(18)–Pd(1)–N(5)	92.27(6)
C(16)–Pd(1)–N(5)	94.46(6)
C(17)–Pd(1)–N(3)	94.33(6)
C(18)–Pd(1)–N(3)	178.17(6)
C(16)–Pd(1)–N(3)	91.86(6)
N(5)–Pd(1)–N(3)	85.93(4)
C(17)–Pd(1)–N(1)	93.05(6)
C(18)–Pd(1)–N(1)	93.21(6)
C(16)–Pd(1)–N(1)	178.66(6)
N(5)–Pd(1)–N(1)	84.85(4)
N(3)–Pd(1)–N(1)	86.94(4)



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