Supporting information for

# γ-Agostic Interactions Stabilize the Propagating Species in the Vinyl Addition Polymerization of Norbornene

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#### 1. Experimental Details

**General Considerations.** All manipulations were carried out using standard vacuum, Schlenk, cannula, or glovebox techniques. Argon was purified by passage through BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. All palladium catalysts were stored under argon in an MBraun glovebox at -35°C. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>1</sup>H-<sup>1</sup>H COSY, <sup>1</sup>H-<sup>13</sup>C HSQC, <sup>1</sup>H-<sup>1</sup>H NOESY, <sup>1</sup>H-<sup>1</sup>H TOCSY and <sup>13</sup>C DEPT135 and DEPT90 NMR spectra were recorded on a Bruker DRX 500 MHz spectrometer. Chemical shifts are referenced relative to residual CH(D)Cl<sub>2</sub> (δ 5.32 for <sup>1</sup>H), CHCl<sub>2</sub>F (δ 7.47 for <sup>1</sup>H), <sup>13</sup>CD<sub>2</sub>Cl<sub>2</sub> (δ 53.8 for <sup>13</sup>C) and <sup>13</sup>CDCl<sub>2</sub>F (δ 104.2 for <sup>13</sup>C). Elemental analyses were carried out by Robertson Microlit Laboratories of Madison, NJ.

**Materials.** All solvents were deoxygenated and dried by passage over columns of activated alumina.<sup>1,2</sup> CD<sub>2</sub>Cl<sub>2</sub>, purchased from Cambridge Laboratories, Inc., was dried over CaH<sub>2</sub>, vacuum transferred to a Teflon sealable Schlenk flask containing 4 Å molecular sieves, and degassed via three freeze-pump-thaw cycles. Freon (CDCl<sub>2</sub>F) was prepared according to a literature procedure and stored over activated 4Å molecular sieves at -25 °C.<sup>3</sup> Norbornene was purchased from Aldrich and dried by refluxing over activated 4Å molecular sieves, followed by distillation.<sup>4</sup> PdCl<sub>2</sub> was purchased from J&J Materials and used as received. (tmeda)PdMe<sub>2</sub> and [H(OEt<sub>2</sub>)<sub>2</sub>][B(Ar<sub>F</sub>)<sub>4</sub>]were synthesized according to literature methods.<sup>5, 6</sup>

**Spectral data for [B(Ar<sub>F</sub>)<sub>4</sub><sup>-</sup>].** The <sup>1</sup>H and <sup>13</sup>C spectral data for the [B(Ar<sub>F</sub>)<sub>4</sub>]<sup>-</sup> annion (B(Ar<sub>F</sub>)<sub>4</sub> = [3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H3)]<sub>4</sub>) were unchanged for all cationic complexes and therefore are not included in the characterization unless otherwise stated. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  7.72 (s, 4H, Ar<sub>F</sub> H<sub>p</sub>), 7.57 (s, 8H, Ar<sub>F</sub> H<sub>o</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  162.1 (q, <sup>1</sup>*J*<sub>C-B</sub> = 49.8 Hz, Ar<sub>F</sub> C<sub>*ipso*</sub>), 135.2 (s, Ar<sub>F</sub> C<sub>o</sub>), 129.2 (qq, <sup>3</sup>*J*<sub>C-B</sub> = 3.0 Hz, <sup>3</sup>*J*<sub>C-F</sub> = 34.4 Hz, Ar<sub>F</sub> CF<sub>3</sub>), 122.3 (q, <sup>1</sup>*J*<sub>C-F</sub> = 273.2 Hz, Ar<sub>F</sub> CF<sub>3</sub>), 117.8 (bt, Ar<sub>F</sub> C<sub>p</sub>).

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Synthesis of  $[(\text{tmeda})Pd(\text{Me})(\text{OEt}_2)][B(\text{Ar}_F)_4]$  (4). A Schlenk flask was charged with  $(\text{tmeda})\text{Pd}(\text{Me})_2$  (0.114 g, 0.5 mmol) and  $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{Ar}_F)_4]$  (0.46 g, 0.5 mmol). The flask was cooled to -78 °C, CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and Et<sub>2</sub>O (0.1 mL) were added -78 °C and the reaction mixture was stirred at this temperature for 30 min, then allowed to warm to 0 °C to dissolve both reactants completely and then cooled to -30 °C. Stirring was continued at this temperature for 1 h, and the solvent was removed under dynamic vacuum (-30 °C) to give a pale yellow powder which was washed with pentane (2 x 10 mL) to remove excess ether and dried in vacuo (-30 °C) Yield: 0.45 g (0.38 mmol, 77 %). Complex 4 was very thermally sensitive and to prevent thermal decomposition it was stored at -38 °C in a glovebox; in solution complex 4 degraded at room temperature within minutes. <sup>1</sup>H NMR (500 MHz, CDCl<sub>2</sub>F, -120 °C): δ 3.57 (dq, 2H, OEt<sub>2</sub>, H<sub>3,a/a'</sub>/H<sub>3,b/b'</sub>), 3.48 (dq, 2H, OEt<sub>2</sub>, H<sub>3,b/b'</sub>/H<sub>3,a/a'</sub>), 2.87 (dd, 1H, tmeda CH<sub>2</sub>, H<sub>1,e</sub>/H<sub>1,a</sub>), 2.58 (dd, 1H, tmeda CH<sub>2</sub>, H<sub>2,e</sub>/H<sub>2,a</sub>), 2.50 (s, 3H, tmeda Me<sub>1,a</sub>/Me<sub>1,e</sub>) 2.35 (s, 3H, tmeda Me<sub>1,e</sub>/Me<sub>1,a</sub>), 2.30 (s, 3H, tmeda Me<sub>2,a</sub>/Me<sub>2,e</sub>) 2.29 (s, 3H, tmeda Me<sub>2,e</sub>/Me<sub>2,a</sub>), 2.15 (dd, 1H, tmeda CH<sub>2</sub>, H<sub>1,e</sub>/H<sub>1,a</sub>), 2.07 (dd, 1H, tmeda CH<sub>2</sub>, H<sub>2,e</sub>/H<sub>2,a</sub>), 1.39 (br.s, 6H, OEt<sub>2</sub>, Me<sub>4/4</sub>), 0.19 (s, 3H, Pd-Me). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>2</sub>F, -120 °C): δ 71.8 (OCH<sub>2</sub>CH<sub>3</sub>), 63.2 (C<sub>1</sub>), 56.7 (C<sub>2</sub>), 53.0 (Me<sub>1.a</sub>/Me<sub>1.e</sub>), 50.0 (Me<sub>2.a</sub>/Me<sub>2.e</sub>), 49.3 (Me<sub>1.e</sub>/Me<sub>1.a</sub>), 45.6 (Me<sub>2.e</sub>/Me<sub>2.a</sub>), 15.6 (OCH<sub>2</sub>CH<sub>3</sub>), 0.92 (Pd-Me). Anal. Calcd for C<sub>43</sub>H<sub>41</sub>BF<sub>24</sub>N<sub>2</sub>OPd: C, 44.0; H, 3.52; N, 2.39. Found: C, 44.1; H, 3.60; N, 2.36 (Sample shipped on dry ice).

Single crystals suitable for an X-ray diffraction experiment were grown from a concentrated  $CHCl_3$  solution at -60 °C on addition of a layer of pentane.



#### Generation of $[(tmeda)Pd(C_{15}H_{23})][B(Ar_F)_4)]$ (4).

*Method 1:* In a screw-cap NMR tube 4 (20 mg,  $1.7 \times 10^{-2}$  mmol) was dissolved in dry, degassed CDCl<sub>2</sub>F at -140 °C, and 2 equiv of a NB stock solution (60 µL,  $3.4 \times 10^{-2}$  mmol) in CD<sub>2</sub>Cl<sub>2</sub> was added. The reaction mixture was inserted into a precooled NMR probe (-120 °C). At this temperature two equivalents of NB had inserted into the Pd-Me bond, and no other intermediates were observed.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>2</sub>F, -75 °C):

*tmeda moiety:*  $\delta$  3.00 (m, 1H, C<sub>3</sub>-*H<sub>a</sub>*/C<sub>3</sub>-*H<sub>e</sub>*), 2.88 (s, 3H, C<sub>5</sub>/C<sub>6</sub>-*Me*), 2.67 (m, 1H, C<sub>4</sub>-*H<sub>a</sub>*/C<sub>4</sub>-*H<sub>e</sub>*), 2.58 (s, 3H, C<sub>6</sub>/C<sub>5</sub>-*Me*), 2.55 (s, 3H, C<sub>1</sub>/C<sub>2</sub>-*Me*), 2.41 (s, 3H, C<sub>2</sub>/C<sub>1</sub>-*Me*), 2.37 (m, 1H, C<sub>3</sub>-*H<sub>e</sub>*/C<sub>3</sub>-*H<sub>a</sub>*), 2.17 (m, 1H, C<sub>4</sub>-*H<sub>e</sub>*/C<sub>4</sub>-*H<sub>a</sub>*).

*NB moiety:*  $\delta$  2.58 (s, 1H, C<sub>13</sub>-*H*), 2.56 (dq, not resolved due to signal overlap, 1H, C<sub>8</sub>-H), 2.49 (dd, 1H, C<sub>16</sub>-*H*), 2.40 (s, 1H, C<sub>17</sub>-*H*), 2.17 (s,1H, C<sub>20</sub>-*H*), 1.96 (br.s, 2H, C<sub>10</sub>-*H* and C<sub>21</sub>-*H*), 1.72 (d, <sup>2</sup>*J*<sub>HH</sub>= 14 Hz, 1H, C<sub>14</sub>-*H*), 1.48 (m, 2H, C<sub>11/12</sub>-*H* and C<sub>18/19</sub>-*H*), 1.31 (m, 5H, C<sub>7</sub>-*H*, C<sub>11/12</sub>-*H*, and C<sub>18/19</sub>-*H*), 1.20 (d,

 ${}^{2}J_{\text{HH}}$ = 13 Hz, 1H, C<sub>21</sub>-*H*), 1.14 (m, 1H, C<sub>11/12</sub>-*H*), 1.00 (m, 1H, C<sub>11/12</sub>-*H*), 0.96 (m, 1H, C<sub>18/19</sub>-*H*), 0.91 (m, 1H, C<sub>18/19</sub>-*H*), 0.77 (d,  ${}^{3}J_{\text{HH}}$ = 10 Hz, 1H, C<sub>15</sub>-*H*), 0.74 (d,  ${}^{3}J_{\text{HH}}$ = 14 Hz, 1H, C<sub>15</sub>-*H*), -4.15 ("dd", 1H, C<sub>9</sub>-*H*,  ${}^{3}J_{\text{HH}}$ = 13.2 Hz,  ${}^{3}J_{\text{HH}}$ = 8.2 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>2</sub>F, -75 °C):

*tmeda moiety:* δ 62.1 (C<sub>4</sub>), 55.8 (C<sub>3</sub>), 52.8 (C<sub>5/6</sub>), 51.1 (C<sub>1/2</sub>), 49.4 (C<sub>6/5</sub>), 45.6 (C<sub>2</sub>/C<sub>1</sub>)

*NB moiety*: δ 53.7 (C<sub>16</sub>), 43.8 (C<sub>10</sub>), 41.7 (C<sub>8</sub>), 41.0 (C<sub>17</sub>), 40.8 (C<sub>13</sub>), 39.0 (C<sub>20</sub>), 36.3 (C<sub>21</sub>), 31.6 (C<sub>15</sub>), 30.3 (C<sub>14</sub>), 29.2 (C<sub>11/12</sub>), 28.7 (C<sub>18/19</sub>), 27.8 (C<sub>19/18</sub>), 27.6 (C<sub>12/11</sub>), 16.6 (C<sub>7</sub>), 11.9 (C<sub>9</sub>, <sup>1</sup>*J*<sub>CH</sub>= 87 Hz)

It is noteworthy that at -120 °C the agostic resonances split in two resonances at  $\delta$  -4.04 and -4.20 in an intensity ratio of 1 : 5.4, both signals show identical coupling pattern ("dd",  ${}^{3}J_{HH}$ = 13.2 Hz,  ${}^{3}J_{HH}$ = 8.2 Hz) and  ${}^{1}J_{CH}$  coupling constants (87 Hz). The are of unequal population and their presence is attributed to the ring inversion of the (tmeda)Pd moiety which gives rise to two isomers of unequal populations where one species is slightly more energetically favorable than the other. The resonances in the chemical shift range  $\delta$  0-10 ppm show an analogue splitting pattern. However, when warmed to -75 °C the resonances merge at  $\delta$  -4.15 as the weighted average of both species, and the coupling pattern is lost, the full fast exchange spectrum has not been reached.



Figure S1. Temperature dependence of γ-agostic C-H resonance.

Single crystals suitable for an X-ray diffraction experiment were grown from a concentrated CHCl<sub>3</sub> solution at -60 °C on addition of a layer of pentane. Crystal growth was extremely slow and very dependent on crystallization conditions. Crystals dissolved readily when allowed to warm in the presence of residual solvent vapor and as isolated material the crystals had to be handled quickly during crystal selection and mounting on the diffractometer to prevent sample degradation and loss of crystallinity.

*Method 1:* Alternatively, complex 5' was generated from (tmeda)PdMe<sub>2</sub> on addition of 1 equiv of  $B(C_6F_5)_3$  in  $CD_2Cl_2$ . Me abstraction was instantaneous and complex  $[(tmeda)Pd(Me)(CD_2Cl_2)][MeB(C_6F_5)_3]$  was formed, addition of 2 equiv of NB resulted in double NB insertion no mono-insertion intermediate was observed similar to *Method 1* described above.

# 2. Crystal Structure Determination of 4 and 5

## Table S1. X-Ray Crystal Structure Data for 4 (internal number: c09219; CCDC 743857)

Crystal data	
Chemical formula	$C_{11}H_{29}N_2OPd\cdot C_{32}H_{12}BF_{24}$
$M_r$	1174.99
Cell setting, space group	Orthorhombic, Pbca
Temperature (K)	100 (2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.9055 (8), 19.9639 (9), 27.1312 (13)
$V(\text{\AA}^3)$	9698.4 (8)
Ζ	8
$D_x$ (Mg m <sup>-3</sup> )	1.609
Radiation type	Μο Κα
$\mu (mm^{-1})$	0.51
Crystal form, colour	Block, colourless
Crystal size (mm)	$0.30\times0.25\times0.25$
Data collection	
Diffractometer	Bruker APEX-II CCD

Data collection method	$\phi$ and $\omega$ scans	
Absorption correction	Multi-scan (based on symmetry-related measurements)	
$T_{\min}$	0.862	
$T_{\max}$	0.883	
No. of measured, independent and observed reflections	62819, 9916, 7556	
Criterion for observed reflections	$I > 2\sigma(I)$	
R <sub>int</sub>	0.049	

### Refinement

 $\theta_{max}$  (°)

Refinement on	$F^2$
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.058, 0.166, 1.02
No. of relections	9916 reflections
No. of parameters	725
No. of restraints	111
H-atom treatment	Constrained to parent site
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0834P)^2 + 24.6288P]$ where $P = (F_o^2 + 2F_c^2)/3$

26.4

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 $(\Delta/\sigma)_{\rm max}$  0.002

 $\Delta \rho_{max}, \Delta \rho_{min} (e \text{ Å}^{-3})$  2.16, -1.10

Computer programs: Bruker APEX2; Bruker SAINT; SHELXS-97 (Sheldrick, 2008); SHELXL-97 (Sheldrick, 2008); Bruker SHELXTL.

*Note:* Significant thermal motion in the tmeda moiety. The disorder in the structure of complex **4** was modeled using a model of split *N*- and *C*-atoms, restraints were introduced and the data refined.

### Table S2. X-Ray Crystal Structure Data for 5 (internal number: c09205; CCDC 743856)

Crystal data	
Chemical formula	$C_{32}H_{12}BF_{24}.C_{21}H_{39}N_2Pd$
$M_r$	1289.17
Cell setting, space group	Monoclinic, $P2_1/c$
Temperature (K)	100 (2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.9847 (3), 31.1704 (6), 17.3760 (5)
β (°)	109.9810 (10)
$V(\text{\AA}^3)$	6609.4 (3)
Ζ	4
$D_x$ (Mg m <sup>-3</sup> )	1.296
Radiation type	Cu Ka
$\mu (mm^{-1})$	3.17
Crystal form, colour	Block, yellow
Crystal size (mm)	$0.30 \times 0.30 \times 0.25$
Data collection	
Diffractometer	Bruker APEX-II CCD
Data collection method	$\phi$ and $\omega$ scans
Absorption correction	Multi-scan (based on symmetry-related
	measurements)
$T_{\min}$	0.450
$T_{\max}$	0.505
No. of measured, independent and observed reflections	81207, 12241, 11021
Criterion for observed reflections	$I > 2\sigma(I)$
$R_{\rm int}$	0.039
$\theta_{max}$ (°)	71.7
Pafinoment	
Refinement on	$F^2$
$P[F^2 > 2\sigma(F^2)] \rightarrow P(F^2) $	0.063.0.167.1.06
R[r > 20(r)], wR(r), 5	122/1 reflections
No. of parameters	751
H-atom treatment	Mixture of independent and constrained
	refinement
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0898P)^2 +$
	16.8136 <i>P</i> ] where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$	0.008
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	1.54, -1.15

Computer programs: Bruker APEX2; Bruker SAINT; SHELXS-97 (Sheldrick, 2008); SHELXL-97 (Sheldrick, 2008); Bruker SHELXTL.

**Note:** During the refinement, severely disordered solvent molecules (pentane and CHCl<sub>3</sub>) were located in two solvent accessible cavities (total volume 1683  $Å^3$ ). The disordered molecules could not be successfully modeled, therefore their contribution was eliminated from the reflection data, using the BYPASS method as implemented in the SQUEEZE routine<sup>7</sup> of the PLATON-98 package.<sup>8</sup>

Hydrogen atoms were included in calculated positions using a riding model, but not refined, except the hydrogen atoms on C8, C9, C15 and C16, which have been refined isotropically. It should be noted that the "X-ray determined" bond length is a measure of the distance between the centroids of the electron density of the two atoms concerned, and the centroid of the electron density around a covalently bonded hydrogen atom is not coincident with its nuclear position but is displaced significantly in the direction of the hydrogen-(other atom)  $\sigma$ bond.<sup>9</sup>

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