

**Direct observation of a carbonylation reaction relevant to CO/alkene copolymerization in a methylpalladium carbonyl complex containing a bis(N-heterocyclic carbene) ligand**

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**SUPPLEMENTARY INFORMATION**

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## EXPERIMENTAL

**General Considerations.** All manipulations were performed under inert atmosphere. Hexanes (Pharmco), *n*-hexane (Acros), THF (Pharmco) and diethyl ether (Acros) were dried over and vacuum distilled from Na/benzophenone ketyl prior to use. Dichloromethane (Pharmco) was washed with concentrated H<sub>2</sub>SO<sub>4</sub>, water, aqueous NaHCO<sub>3</sub>, and again water, and then dried over and vacuum distilled from P<sub>2</sub>O<sub>5</sub> prior to use. CH<sub>3</sub>CN (Pharmco) was pre-dried over CaCl<sub>2</sub>, then boiled over and distilled from CaH<sub>2</sub>, and finally stored over and vacuum distilled from 4 Å molecular sieves prior to use. NMR solvents were purchased from Cambridge Isotopes Laboratories. CD<sub>3</sub>CN and DMSO-*d*<sub>6</sub> were dried by stirring over activated 4Å molecular sieves followed by vacuum distillation at room temperature. CD<sub>2</sub>Cl<sub>2</sub> was dried similarly and then stored over and vacuum distilled from P<sub>2</sub>O<sub>5</sub> before use. Carbon monoxide (Aldrich, 99.0+%) was used as received. All other reagents were purchased from Aldrich or Acros and used as received. [Pd(TMEDA)(CH<sub>3</sub>)<sub>2</sub>]<sup>1</sup> and 1,1'-dimesityl-3,3'-methylene-diimidazolium dibromide<sup>2</sup> were prepared by literature procedures. NMR spectra were recorded on Varian GEMINI 2000 (300 MHz) and Varian Unity INOVA (400 and 600 MHz) spectrometers. Reported chemical shifts are referenced to residual solvent peaks (<sup>13</sup>C, <sup>1</sup>H). For low temperature studies, the NMR probe temperature was calibrated within 2 d of the experiment using a methanol standard. IR spectra were acquired from Nujol mulls on a Nicolet Protégé 460 FT-IR spectrometer. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana.

### Synthetic Procedures

[Pd(DIMes<sup>Me</sup>)(CH<sub>3</sub>)<sub>2</sub>] (**3**). To a solid mixture of 1,1'-dimesityl-3,3'-methylene-diimidazolium dibromide (100 mg, 0.546 mmol) and potassium *tert*-butoxide (125 mg, 1.093 mmol) was added THF (40 mL) at -78 °C. The mixture was stirred for 45 minutes at -78 °C to give a cloudy, light pink suspension. This reaction mixture was transferred onto a solution of [Pd(TMEDA)(CH<sub>3</sub>)<sub>2</sub>] (138 mg, 0.546 mmol) in THF (15 mL) at -78 °C via cannula, and the resulting mixture was stirred for another 45 minutes at -78 °C. The volatiles were removed under vacuum, the residue was extracted with methylene chloride, and diethyl ether was added to obtain colorless crystals, which were collected by filtration. Yield 166 mg, 59%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN-*d*<sub>3</sub>): δ 7.57 (2H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 7.04 (2H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 6.90 (4H, s, mesityl *m*-CH), 6.19 (2H, s, CH<sub>2</sub>), 2.51 (6H, s, *p*-CH<sub>3</sub>), 1.96 (12H, s, *o*-CH<sub>3</sub>), -1.11 (6H, s, Pd-CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN): δ 189.1 (carbene), 136.9 (mesityl *o*-C), 136.8 (mesityl *p*-C), 134.6 (mesityl *ipso*), 128.1 (mesityl *m*-C), 121.7 (*imid.*-C), 119.9 (*imid.*-C), 62.5 (CH<sub>2</sub>), 20.6 (mesityl *p*-CH<sub>3</sub>), 18.05 (mesityl *o*-CH<sub>3</sub>), -5.38 (Pd-CH<sub>3</sub>). Anal. Calc. for C<sub>27</sub>H<sub>34</sub>N<sub>4</sub>Pd: C, 62.24; H, 6.58; N, 10.76 %. Found: C, 62.16; H, 6.65; N, 10.57 %.

[Pd(DIMes<sup>Me</sup>)(CH<sub>3</sub>)I] (**4**). Methyl iodide (39 μL, 0.61 mmol) was added to a solution of **3** (100 mg, 0.19 mmol) in THF (30 mL) at -78 °C. The reaction mixture was warmed to 0 °C and stirred for 1 h to give a bright white powder. The solid was isolated by filtration, followed by washing with diethyl ether. Yield 87 mg, 72%. Complex **4** darkened rapidly with concomitant decomposition upon standing at room temperature for >1 h, even in inert atmosphere. This prevented characterization by elemental analysis. Complex **4** was only significantly soluble in DMSO, and it decomposed too rapidly in solution to collect adequate <sup>13</sup>C NMR data. Samples of **4** could be stored at -35 °C for several weeks without significant decomposition. <sup>1</sup>H NMR (400

MHz, DMSO-*d*<sub>6</sub>): δ 7.80 (1H, s, *imid.*), 7.71 (1H, s, *imid.*), 7.35 (1H, s, *imid.*), 7.20 (1H, s, *imid.*), 6.98 (2H, s, mesityl *m-CH*), 6.96 (2H, s, mesityl *m-CH*), 6.40 (2H, s, *CH*<sub>2</sub>), 2.27 (6H, s, *p-CH*<sub>3</sub>), 2.03 (6H, s, *o-CH*<sub>3</sub>), 1.95 (6H, br s, *o-CH*<sub>3</sub>), -0.54 (3H, s, Pd-*CH*<sub>3</sub>).

**[Pd(DIMes<sup>Me</sup>)(CH<sub>3</sub>)(NCCH<sub>3</sub>)] [BF<sub>4</sub>] (5).** AgBF<sub>4</sub> (31 mg, 0.16 mmol) was added to a solution of **4** (100 mg, 0.16 mmol) in CH<sub>3</sub>CN (10 mL) at 25 °C. The reaction mixture was stirred for one hour to give an ash brown precipitate. The precipitate was removed by filtration through celite, volatiles were stripped under vacuum, and the residue was dried for an additional 2 h. The solid was redissolved in CH<sub>3</sub>CN and filtered through celite to removed residual AgI. The solution was then concentrated, and diethyl ether was added to obtain white crystals, which were isolated by filtration. Yield 74 mg, 74%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 7.53 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 7.51 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 7.05 (2H, s, mesityl *m-CH*), 7.03 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 7.02 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 6.97 (2H, d, <sup>3</sup>J<sub>HH</sub> = 0.8 Hz, mesityl *m-CH*), 6.19 (2H, s, *CH*<sub>2</sub>), 2.32 (3H, s, *p-CH*<sub>3</sub>), 2.29 (3H, s, *p-CH*<sub>3</sub>), 2.04 (6H, s, *o-CH*<sub>3</sub>), 1.97 (6H, s, *o-CH*<sub>3</sub>), 1.95 (3H, s, CH<sub>3</sub>CN), -0.65 (3H, s, Pd-*CH*<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.75 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 7.72 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 7.01 (2H, s, mesityl *m-CH*), 6.94 (2H, s, mesityl *m-CH*), 6.86 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 6.85 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 6.40 (2H, bs, *CH*<sub>2</sub>), 2.34 (3H, s, *p-CH*<sub>3</sub>), 2.31 (3H, s, *p-CH*<sub>3</sub>), 2.08 (6H, s, *o-CH*<sub>3</sub>), 2.01 (6H, s, *o-CH*<sub>3</sub>), 1.84 (3H, s, CH<sub>3</sub>CN), -0.59 (3H, s, Pd-*CH*<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN): δ 182.5 (carbene), 167.9 (carbene), 140.4 (mesityl *p-C*), 140.2 (mesityl *p-C*), 136.7 (mesityl *ipso-C*), 136.4 (mesityl *ipso-C*), 136.4 (mesityl *o-C*), 135.9 (mesityl *o-C*), 129.7 (mesityl *m-C*), 129.6 (mesityl *m-C*), 124.6 (*imid.*), 123.3 (*imid.*), 122.7 (*imid.*), 122.0 (*imid.*), 64.1 (*CH*<sub>2</sub>), 27.0 (*p-CH*<sub>3</sub>), 21.1 (*p-CH*<sub>3</sub>), 18.8 (*o-CH*<sub>3</sub>), 17.9 (*o-CH*<sub>3</sub>), 1.4 (CNCH<sub>3</sub>), -8.3 (Pd-*CH*<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 182.0 (carbene), 167.3 (carbene), 139.5 (mesityl *p-C*), 139.5 (mesityl *p-C*), 135.9 (mesityl *ipso-C*), 135.9 (mesityl *ipso*), 135.8 (mesityl *o-C*), 135.2 (mesityl *o-C*), 129.1 (2 overlapped mesityl *m-C*), 123.6 (*imid.*), 122.4 (*imid.*), 122.3 (*imid.*), 121.7 (*imid.*), 120.6 (CN), 63.2 (*CH*<sub>2</sub>), 21.1 (*p-CH*<sub>3</sub>), 21.1 (*p-CH*<sub>3</sub>), 18.8 (*o-CH*<sub>3</sub>), 17.9 (*o-CH*<sub>3</sub>), 3.3 (CNCH<sub>3</sub>), -8.5 (Pd-*CH*<sub>3</sub>). Anal. Calc. for C<sub>28</sub>H<sub>34</sub>BF<sub>4</sub>N<sub>5</sub>Pd: C, 53.06; H, 5.41; N, 11.05 %. Found: C, 52.78; H, 5.33; N, 10.91 %.

**[Pd(DIMes<sup>Me</sup>)(CH<sub>3</sub>)(CO)] [BF<sub>4</sub>] (6).** Complex **5** (100 mg, 0.16 mmol) was dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> in a sealable reaction vessel, and 1 atm of CO was admitted. The solution was stirred for 15 minutes, volatiles were removed, and the resulting solid was dried under vacuum overnight. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and the solution was filtered through celite. Diethyl ether and hexanes were added, forming white crystals that were collected by filtration. Yield 75 mg, 77%. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.92 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 7.90 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 7.03 (2H, s, mesityl *m-CH*), 7.03 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 6.98 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 6.96 (2H, s, mesityl *m-CH*), 6.50 (2H, s, *CH*<sub>2</sub>), 2.34 (3H, s, *p-CH*<sub>3</sub>), 2.32 (3H, s, *p-CH*<sub>3</sub>), 2.01 (6H, s, *o-CH*<sub>3</sub>), 1.96 (6H, s, *o-CH*<sub>3</sub>), -0.29 (3H, s, Pd-*CH*<sub>3</sub>). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 183.0 (CO), 178.3 (carbene), 169.9 (carbene) 140.8 (mesityl *p-C*), 140.0 (mesityl *p-C*), 135.5 (mesityl *o-C*), 135.4 (mesityl *ipso-C*), 135.3 (mesityl *ipso*), 135.0 (mesityl *o-C*), 129.7 (mesityl *m-C*), 129.4 (mesityl *m-C*), 124.3 (*imid.*), 123.2 (*imid.*), 123.0 (*imid.*), 122.7 (*imid.*), 63.2 (*CH*<sub>2</sub>), 21.2 (*p-CH*<sub>3</sub>), 21.1 (*p-CH*<sub>3</sub>), 18.5 (*o-CH*<sub>3</sub>), 17.8 (*o-CH*<sub>3</sub>), -13.2 (Pd-*CH*<sub>3</sub>). IR (Nujol, cm<sup>-1</sup>): 2105 (s). Anal. Calc. for C<sub>27</sub>H<sub>31</sub>OBF<sub>4</sub>N<sub>4</sub>Pd: C, 52.24; H, 5.03; N, 9.03 %. Found: C, 52.29; H, 5.27; N, 8.88 %.

**[Pd(DIMes<sup>Me</sup>)(COCH<sub>3</sub>)(CO)][BF<sub>4</sub>] (7)**. Complex **6** (40 mg, 0.064 mmol) was dissolved in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> in a sealable vessel, and 1 atm CO was admitted. The solution was stirred for 1 h at 25 °C, and volatiles were removed under vacuum. The solid was slurried in hexanes and collected by filtration. Yield 35 mg, 84.0%. <sup>1</sup>H NMR analysis in CD<sub>2</sub>Cl<sub>2</sub> showed the product to be a mixture of **7** (95%) and **6** (5%), so elemental analysis data were not obtained. NMR data were recorded for a sample of this mixture placed under 1 atm CO, which resulted in quantitative conversion to **7** in solution. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.94 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 7.92 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 7.05 (2H, s, mesityl *m*-CH), 7.04 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 6.98 (2H, s, mesityl *m*-CH), 6.91 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2 Hz, *imid.*), 6.55 (2H, s, CH<sub>2</sub>), 2.35 (3H, s, *p*-CH<sub>3</sub>), 2.32 (3H, s, *p*-CH<sub>3</sub>), 1.99 (6H, s, *o*-CH<sub>3</sub>), 1.94 (6H, s, *o*-CH<sub>3</sub>), 1.29 (3H, s, COCH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 234.5 (COCH<sub>3</sub>) 178.1 (carbene), 168.2 (carbene), 140.9 (mesityl *p*-C), 140.8 (mesityl *p*-C), 135.7 (mesityl *o*-C), 135.5 (mesityl *o*-C), 135.1 (mesityl *ipso*-C), 134.6 (mesityl *ipso*), 129.8 (mesityl *m*-C), 129.8 (mesityl *m*-C), 123.7 (2 overlapped *imid.*-C), 123.4 (*imid.*), 123.2 (*imid.*), 63.1 (CH<sub>2</sub>), 44.3 (COCH<sub>3</sub>), 21.2 (*p*-CH<sub>3</sub>), 21.1 (*p*-CH<sub>3</sub>), 18.2 (*o*-CH<sub>3</sub>), 17.8 (*o*-CH<sub>3</sub>). IR (Nujol, cm<sup>-1</sup>): 2112 (s), 1667 (s).

### Equilibria and Kinetics

**Equilibrium between [Pd(DIMes<sup>Me</sup>)(CH<sub>3</sub>)(CO)][BF<sub>4</sub>] (6) and [Pd(DIMes<sup>Me</sup>)(COCH<sub>3</sub>)(CO)][BF<sub>4</sub>] (7)**. Complex **5** (2 mg, 0.003 mmol) was dissolved in 0.7 mL of CD<sub>2</sub>Cl<sub>2</sub> in a J Young NMR tube, and 1 atm of CO was added at 25 °C. After 15 min, CO was added again to adjust the pressure to exactly 1 atm. The sample tube was placed in the NMR probe set at the desired temperature (probe temperature pre-calibrated). The sample was equilibrated for 20 min at each temperature before taking data. Only **6** and **7** were detected under these conditions. The solubility of CO in CD<sub>2</sub>Cl<sub>2</sub> 1 atm was calculated using Bryndza's equation, which also accounts for the temperature dependence of [CO].<sup>3</sup> Uncertainties are reported at the 95% confidence level. These were derived from a least-squares linear regression analysis of the temperature dependence of  $K_{\text{eq}}$ .

**Kinetics of conversion of 6 to 7**. A sample of **6** (2.5 mg, 0.004 mol) was dissolved in 0.7 mL of CD<sub>2</sub>Cl<sub>2</sub> under vacuum in a J Young NMR tube. An initial NMR spectrum of the sample was taken at -50 °C to establish a starting concentration of **6** prior to CO addition. The sample was then cooled to -84 °C in an ethyl acetate slush bath. CO (1 atm or 0.5 atm) was added with the liquid held at -84 °C. In the sample tubes used, this corresponded to 22 equiv of CO per Pd at 1 atm and 11 equiv CO at 0.5 atm. The sample tube was briefly shaken and then placed in the pre-cooled, calibrated NMR probe at -50 °C. Collection of data was begun after a 5 min equilibration period. The residual CH<sub>2</sub>Cl<sub>2</sub> solvent peak was used as an internal reference to convert the integrated intensity of the methyl peak of **6** into concentration units. The disappearance of **6** was monitored over 4.7 hours at both 1.0 atm CO (3.8 half-lives) and 0.5 atm CO (~3 half-lives). Rates ( $k_{\text{obs}}$ ) and uncertainties were determined from linear least-squares regression analyses of the plots of ln[**6**] versus time (see pp. S8-S9). Uncertainties are reported at the 95% confidence level.

## X-RAY CRYSTALLOGRAPHIC ANALYSES

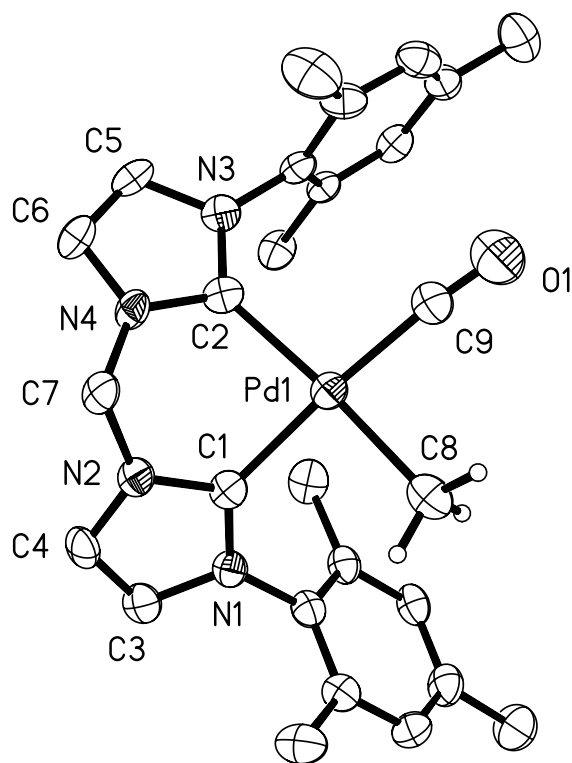
**General Considerations.** X-ray diffraction data were collected on a Bruker SMART APEX II diffractometer with a CCD detector using a combination of  $\phi$  and  $\omega$  scans. The crystal-to-detector distance was 6.0 cm. A Bruker Kryoflex liquid nitrogen cooling device was used for low-temperature data collections. Unit cell determination and data collection utilized the Bruker APEX2 software package.<sup>4</sup> Data integration employed SAINT.<sup>5</sup> Multiscan absorption corrections were implemented using SADABS.<sup>6</sup> X-ray diffraction experiments employed graphite-monochromated Mo K $\alpha$  radiation ( $\lambda=0.71073$  Å). Structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL software suite.<sup>7</sup> Non-hydrogen atoms were assigned anisotropic temperature factors, with hydrogen atoms included in calculated positions (riding model). Further details of the structural determinations are given below. Supplementary crystallographic data for **5** and **6** have been deposited in CIF format with the Cambridge Crystallographic Data Centre (CCDC 729935 for **5**, CCDC 736964 and 730056 for **6**) and can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**X-ray Crystallographic Analysis of 5.** Slow diffusion of diethyl ether into an acetonitrile solution of **5** afforded large, colorless blocks that were suitable for X-ray analysis. A sample measuring 0.43 x 0.23 x 0.20 mm was cut from a larger block and placed in the cold stream at 115 K for data collection using 20 s scans. During refinement, one uncoordinated CH<sub>3</sub>CN molecule per asymmetric unit was located in the difference Fourier map and refined as part of the model. Refined formula C<sub>28</sub>H<sub>34</sub>BF<sub>4</sub>N<sub>5</sub>Pd·C<sub>2</sub>H<sub>3</sub>N,  $M = 674.87$ , monoclinic, space group  $P2_1/n$ ,  $a = 11.5389(1)$  Å,  $b = 19.0724(2)$  Å,  $c = 15.1677(2)$  Å,  $\beta = 108.068(1)^\circ$ ,  $U = 3173.42(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.413$  g cm<sup>-3</sup>,  $\mu = 0.638$  mm<sup>-1</sup>,  $T = 115(2)$  K,  $2\theta_{\max} = 61.7^\circ$ , 54834 total reflections, 9914 independent ( $R_{\text{int}} = 0.033$ ), 8388 observed [ $I > 2\sigma(I)$ ]. Final  $R1$  [ $I > 2\sigma(I)$ ] = 0.0278,  $wR2$  (all data) = 0.0726. Deposition number CCDC 729935..

**X-ray Crystallographic Analysis of 6.** Slow diffusion of *n*-hexane into a concentrated solution of **6** in diethyl ether/dichloromethane led to formation of flat, colorless rods. A sample measuring 0.27 x 0.21 x 0.10 mm was placed in the cold stream at 115 K for data collection using 50 s scans. One CH<sub>2</sub>Cl<sub>2</sub> molecule per asymmetric unit was located in the difference Fourier map and refined as part of the model. Refined formula C<sub>27</sub>H<sub>31</sub>BF<sub>4</sub>N<sub>4</sub>OPd·CH<sub>2</sub>Cl<sub>2</sub>,  $M = 705.69$ , triclinic, space group  $P-1$ ,  $a = 7.3442(5)$ ,  $b = 14.0019(9)$ ,  $c = 15.747(1)$  Å,  $\alpha = 101.273(4)$ ,  $\beta = 101.577(4)$ ,  $\gamma = 96.190(4)^\circ$ ,  $U = 1537.5(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.524$  g cm<sup>-3</sup>,  $\mu(\text{Mo-}\alpha) = 0.830$  mm<sup>-1</sup>,  $T = 115(2)$  K,  $2\theta_{\max} = 51.4^\circ$ , 21988 total reflections, 5799 independent ( $R_{\text{int}} = 0.025$ ), 5179 observed [ $I > 2\sigma(I)$ ]. Final  $R1$  [ $I > 2\sigma(I)$ ] = 0.0375,  $wR2$  (all data) = 0.1066. Deposition number CCDC 736964.

A second, unsolvated crystalline form of **6** was obtained from some of the crystallization vials, presumably as a result of slight differences in solvent ratios and/or diffusion rates. The crystals were well formed but small (maximum dimensions 0.10 – 0.13 mm), and all examples tested showed very weak or no diffraction past  $2\theta=45^\circ$ . A sample measuring 0.13 x 0.10 x 0.03 mm was placed in the cold stream at 115 K for data collection. Because of the small crystal size, 60 s scans were utilized, but usable data could only be obtained to  $2\theta=47.1^\circ$ . Refined formula C<sub>27</sub>H<sub>31</sub>BF<sub>4</sub>N<sub>4</sub>OPd,  $M = 620.77$ , triclinic, space group  $P-1$ ,  $a = 10.7458(3)$ ,  $b = 12.1565(4)$ ,  $c = 12.6369(4)$  Å,  $\alpha = 68.230(2)$ ,  $\beta = 73.986(2)$ ,  $\gamma = 67.495(2)^\circ$ ,  $U = 1398.94(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c =$

1.474 g cm<sup>-1</sup>,  $\mu(\text{Mo-K}\alpha) = 0.717 \text{ mm}^{-1}$ ,  $T = 115(2) \text{ K}$ ,  $2\theta_{\text{max}} = 47.1^\circ$ , 15017 total reflections, 4140 independent ( $R_{\text{int}} = 0.047$ ), 3346 observed [ $I > 2\sigma(I)$ ]. Final  $R1$  [ $I > 2\sigma(I)$ ] = 0.0467,  $wR2$  (all data) = 0.1209. Deposition number CCDC 730056. Metric parameters of **6** determined for this crystalline form generally differed by less than 2% from those of the dichloromethane solvate form reported in the main text. An exception is the C9-O1 distance of 1.118(6) Å, which is 5.6% longer than that observed in the solvated form. A thermal ellipsoid plot and selected metric parameters are shown below in Figure S1.

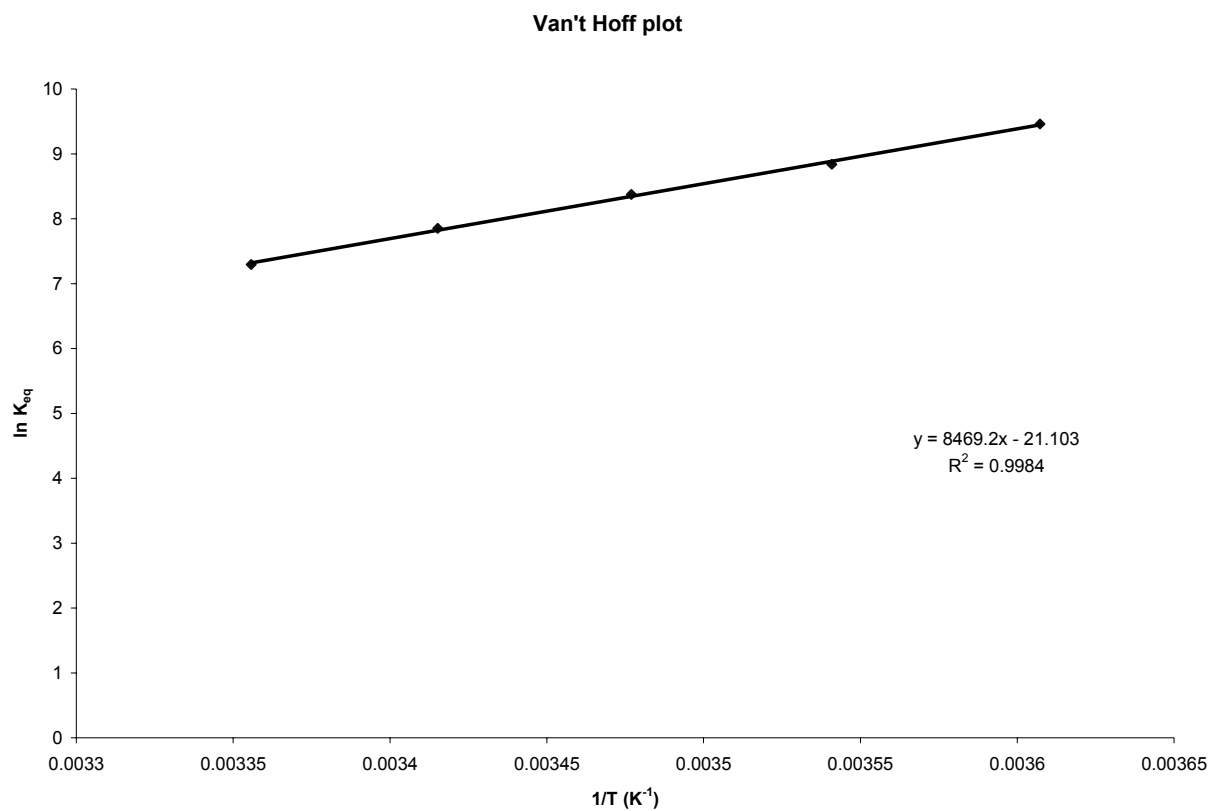


**Figure S1.** Structure of a second, unsolvated form of **6**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and the  $\text{BF}_4^-$  anion are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Pd1-C1 2.034(5), Pd1-C2 2.081(5), Pd1-C8 2.101(5), Pd1-C9 1.918(6), C9-O1 1.118(6), C1-Pd1-C2 85.4(2), C1-Pd1-C8 90.9(2).

## EQUILIBRIUM DATA

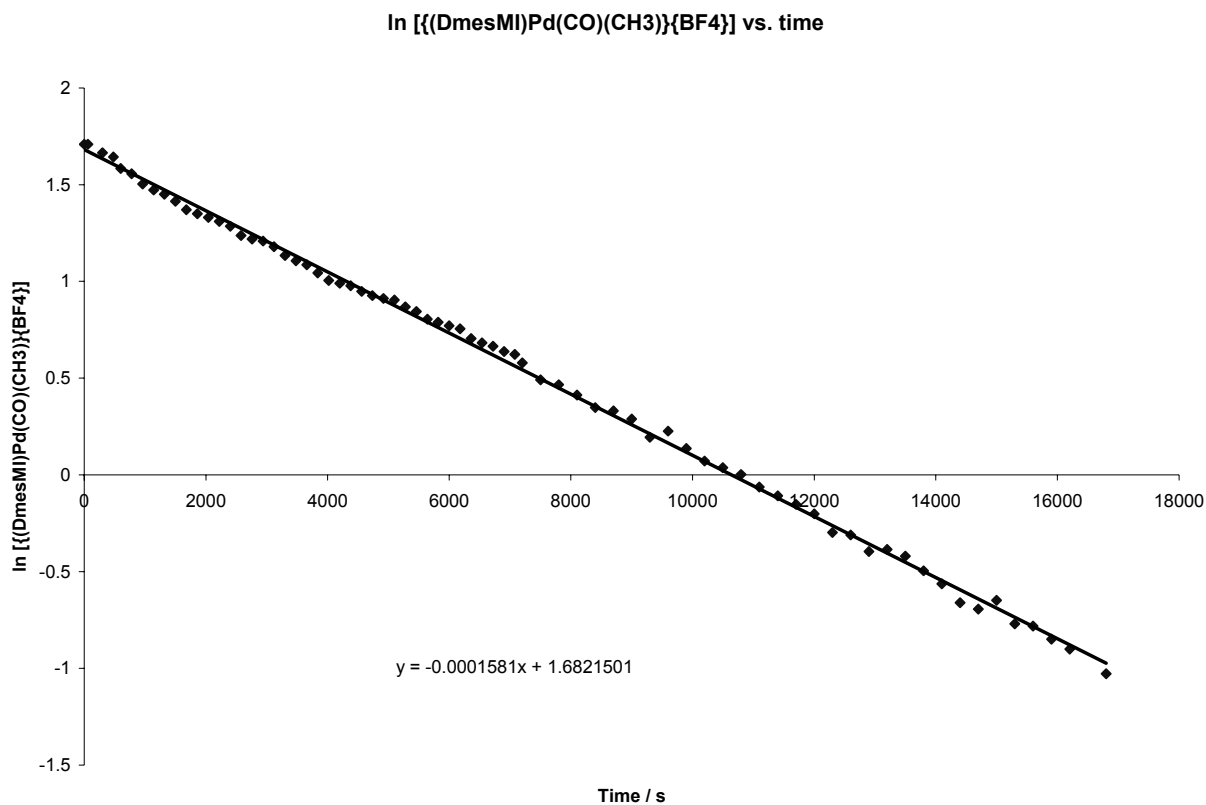
### Equilibrium between 6 and 7

Temperature		$K_{eq}$ (dm <sup>3</sup> /mol)
°C	K	
4.1	277.3	12845
9.3	282.5	6895.0
14.5	287.7	4324.3
19.7	292.9	2567.1
24.85	298.0	1469.9



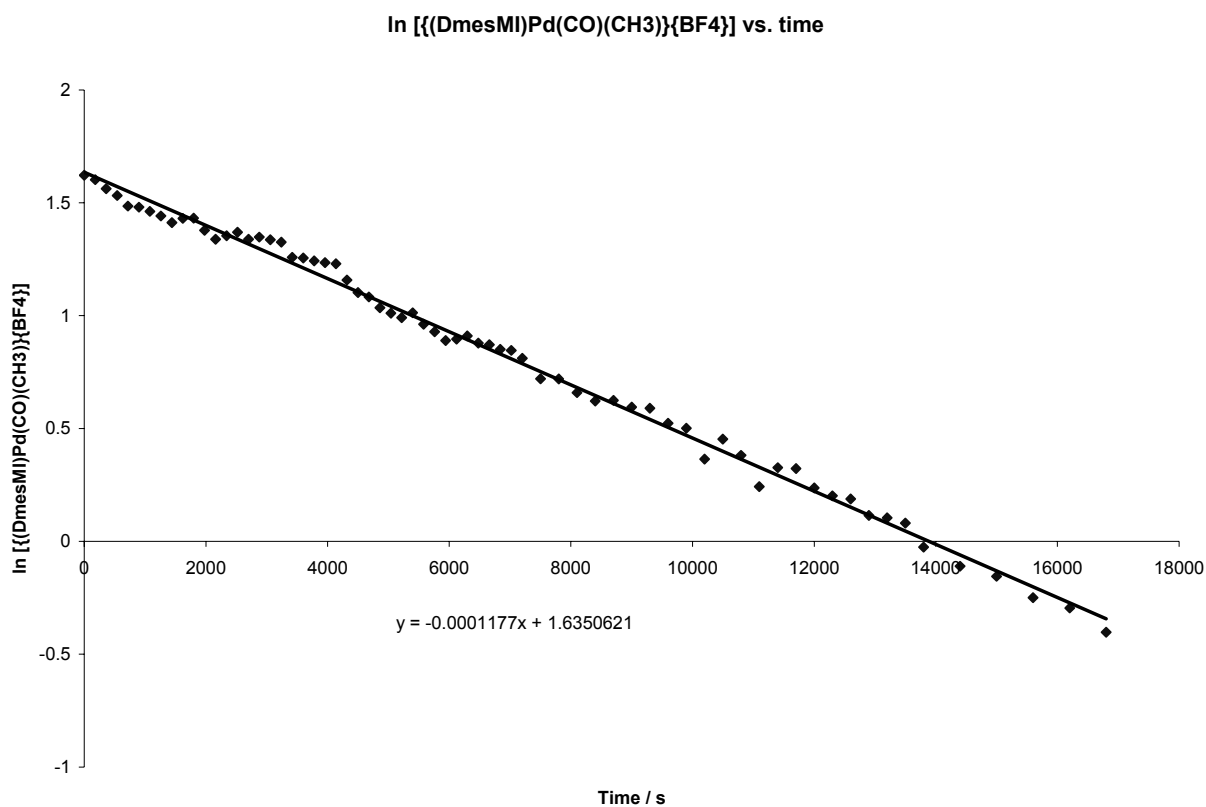
# KINETIC DATA

Conversion of 6 to 7 at -50 °C and 1 atm CO

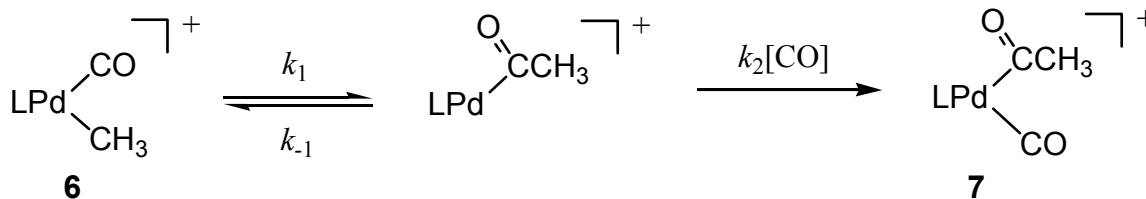




# Conversion of 6 to 7 at -50 °C and 0.5 atm CO



### KINETIC DERIVATION FOR ESTIMATION OF $k_1$



$$\frac{d[\mathbf{6}]/dt}{k_{-1} + k_2[\text{CO}]} = \frac{k_1 k_2 [\text{CO}][\mathbf{6}]}{k_{-1} + k_2[\text{CO}]} \quad k_{\text{obs}} = \frac{k_1 k_2 [\text{CO}]}{k_{-1} + k_2[\text{CO}]}$$

[CO] at 1 atm and -50 °C was estimated by Bryndza's equation.<sup>3</sup> Henry's Law behavior was assumed; i.e. [CO] at 0.5 atm was assumed to be one-half its value at 1.0 atm CO.

$$\frac{k_{\text{obs}}(1\text{atm})}{k_{\text{obs}}(0.5\text{atm})} = \frac{k_1 k_2 (0.00631)}{k_{-1} + k_2 (0.00631)} \times \frac{k_{-1} + k_2 (0.00316)}{k_1 k_2 (0.00316)} = \frac{1.58(1) \times 10^{-4} \text{ s}^{-1}}{1.18(2) \times 10^{-4} \text{ s}^{-1}} = 1.34(2)$$

$$k_{-1} = [0.00326(22)]k_2$$

Plug into  $k_{\text{obs}}$  expression with [CO] = 0.00631 M (i.e. 1 atm and -50 °C):

$$k_{\text{obs}} = 1.58(1) \times 10^{-4} \text{ s}^{-1} = \frac{k_1 k_2 [0.00631]}{[0.00326(22)]k_2 + k_2 (0.00631)}$$

$$k_1 = 1.58(1) \times 10^{-4} \text{ s}^{-1} / 0.659(15) = 2.40(6) \times 10^{-4} \text{ s}^{-1}$$

Note that for pseudo-first order conditions, the kinetic plot should have the following form:

$$\ln[\mathbf{6}] = -k_{\text{obs}}t + \ln[\mathbf{6}]_0$$

As shown below, the y-intercepts of the kinetic plots were very close to the expected values of  $\ln[\mathbf{6}]_0$  based on starting concentrations. This indicates that the steady state model shown above, with the  $k_2$  step effectively irreversible, is very likely valid under the conditions used.

$P_{\text{CO}}$	y intercept	expected $\ln[\mathbf{6}]_0$
1.0 atm	1.68(1)	1.71
0.5 atm	1.64(2)	1.62

## REFERENCES

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