



Connecting Binuclear Pd(III) and Mononuclear Pd(IV) Chemistry by Pd–Pd Bond Cleavage

Citation

Powers, David C., Eunsung Lee, Alireza Ariafard, Melanie S. Sanford, Brian F. Yates, Allan J. Canty, and Tobias Ritter. 2012. Connecting binuclear Pd(III) and mononuclear Pd(IV) chemistry by Pd–Pd bond cleavage. *Journal of the American Chemical Society* 134 (29): 12002-12009

Published Version

doi:10.1021/ja304401u

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Supporting Information

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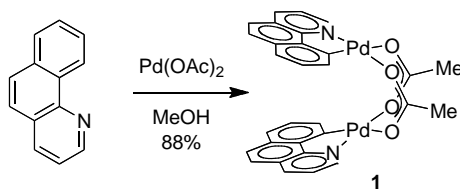
Materials and Methods

Reactions were carried out under ambient atmosphere unless otherwise specified. Anhydrous solvents were obtained either by filtration through drying columns¹ (ether, CH₂Cl₂, THF) on an mBraun system or by distillation over sodium (ether, pentane). Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds unless otherwise noted. NMR spectra were recorded on either a Varian Unity/Inova 600 spectrometer operating at 600 MHz for ¹H acquisitions, a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ¹H and ¹³C acquisitions, respectively, or a Varian Mercury 400 spectrometer operating at 400 MHz and 375 MHz for ¹H and ¹⁹F acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. The following solvent chemical shifts were used as reference values (ppm): CDCl₃ = 7.26 (¹H), 77.0 (¹³C); CD₂Cl₂ = 5.32 (¹H), 53.8 (¹³C); C₂D₄Cl₂ = 3.72 (¹H); benzene-*d*₆ = 7.15 (¹H), 128.0 (¹³C). Data is reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. UV-vis spectra were obtained on a Varian Cary 50 Probe UV-visible spectrophotometer. High-resolution mass spectra were obtained on Jeol AX-505 or SX-102 spectrometers at the Harvard University Mass Spectrometry Facilities. Pd(OAc)₂ was purchased from Strem. XeF₂ was purchased from Matrix Scientific. Benzo[*h*]quinoline was obtained from TCI America. 2-Iodobenzoic acid was obtained from Sigma Aldrich. All other chemicals were used without purification.

Experimental Data

Experimental Procedures and Compound Characterization

Benzo[*h*]quinoliny] palladium acetate dimer (**1**)

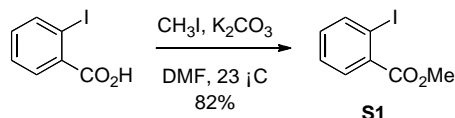


Complex **1** was prepared according to a published procedure.² To benzo[*h*]quinoline (1.00 g, 5.58 mmol, 1.00 equiv) in MeOH (75 mL) at 23 °C was added Pd(OAc)₂ (1.25 g, 5.58 mmol, 1.00 equiv). After 8 h, the precipitate was isolated by filtration and washed sequentially with MeOH (50 mL) and Et₂O (50 mL). The solid was dissolved in CH₂Cl₂ (250 mL) and filtered through a plug of Celite. Solvent was removed in vacuo to afford 1.68 g of the title compound as a yellow solid (88% yield).

NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 7.82 (dd, *J* = 5.0 Hz, 1.1 Hz, 2H), 7.44 (dd, *J* = 8.0 Hz, 1.1 Hz, 2H), 7.25–7.20 (m, 6H), 7.09 (dd, *J* = 6.9 Hz, 1.1 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.48 (dd, *J* = 8.0 Hz, 5.0 Hz, 2H), 2.38 (s, 6H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 182.3, 152.9,

148.6, 148.5, 139.7, 135.0, 132.2, 128.7, 127.6, 127.4, 124.7, 122.6, 121.8, 119.5, 24.9. These spectroscopic data correspond to those reported in the literature.ⁱⁱ UV-vis Spectroscopy (CH₂Cl₂, 23 °C): 425 nm ($\epsilon = 2.00 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); 376 nm ($\epsilon = 4.30 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); 346 nm ($\epsilon = 4.18 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). Mass Spectrometry: LRMS-APCI (m/z): 686.0 [C₃₀H₂₂N₂O₄Pd₂⁺]. Cyclic voltammogram included in Electrochemical Data Section. X-ray data has been submitted to the Cambridge Crystal Structure Database as CCDC 705005 and CCDC 832191.

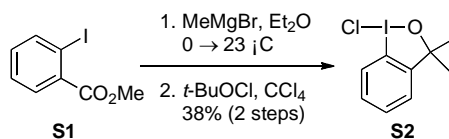
Methyl 2-iodobenzoate (S1)



Compound **S1** was prepared according to a published procedure.⁴ To 2-iodobenzoic acid (100.0 g, 0.4032 mol, 1.000 equiv) in DMF (300 mL) at 23 °C was added K₂CO₃ (66.84 g, 0.4836 mol, 1.199 equiv). After gas evolution ceased, CH₃I (27.60 mL, 62.93 g, 0.4433 mol, 1.099 equiv) was added and the reaction mixture was stirred at 23 °C for 14 h. The reaction mixture was added to H₂O (300 mL) and the aqueous phase was extracted with Et₂O (3 × 100 mL). The organic layers were combined, washed with H₂O (2 × 100 mL), brine (1 × 50 mL), and dried with MgSO₄. Solvent was removed in vacuo to afford 86.59 g of the title compound as a yellow oil (82% yield).

R_f = 0.39 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 7.99 (d, $J = 7.9$ Hz, 1H), 7.79 (d, $J = 7.8$ Hz, 1H), 7.39 (dd, $J = 7.5$ Hz, 0.7 Hz, 1H), 7.14 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H), 3.93 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, 23 °C, δ): 166.9, 141.3, 135.0, 132.6, 130.9, 127.8, 94.0, 52.4. These spectroscopic data correspond to those reported in the literature.ⁱⁱⁱ

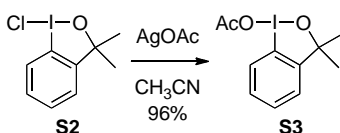
1-Chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (S2)



Compound **S2** was prepared according to a published procedure.⁵ To methyl 2-iodobenzoate (**S1**) (10.0 g, 38.2 mmol, 1.00 equiv) in Et₂O (200 mL) at 0 °C under an N₂ atmosphere was added MeMgBr (3.0 M in Et₂O, 28 mL, 84 mmol, 2.2 equiv) over 30 min. The reaction mixture was stirred for 30 min, warmed to 23 °C and stirred for an additional 2 h. The reaction mixture was extracted with Et₂O (3 × 50 mL). The organic layers were combined, washed with H₂O (2 × 100 mL), brine (1 × 50 mL), and dried with MgSO₄. Solvent was removed in vacuo. The residue was taken up in CCl₄ (20 mL) and *tert*-butyl hypochlorite (7.10 mL, 6.82 g, 63.0 mmol, 1.20 equiv) was added in one portion. The reaction mixture was stirred at 23 °C. After one hour the precipitate was collected by filtration and washed with hexane (30 mL) to afford 4.26 g of the title compound as a yellow solid (38% yield).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 8.02 (dd, $J = 8.3$ Hz, 1.0 Hz, 1H), 7.57 (ddd, $J = 8.3$ Hz, 8.3 Hz, 1.6 Hz, 1H), 7.52 (ddd, $J = 7.3$ Hz, 7.3 Hz, 1.2 Hz, 1H), 7.17 (dd, $J = 7.3$ Hz, 1.6 Hz, 1H), 1.55 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3 , 23 °C, δ): 149.4, 130.9, 130.4, 128.4, 126.1, 114.6, 85.1, 29.2. These spectroscopic data correspond to those reported in the literature.^{iv}

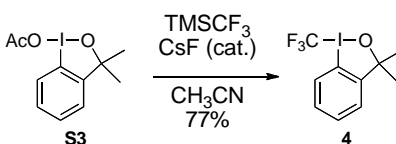
1-Acetoxy-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**S3**)



Compound **S3** was prepared according to a published procedure.⁶ This reaction was carried out in a nitrogen-filled dry box. To 1-chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**S2**) (3.00 g, 10.1 mmol, 1.00 equiv) in CH_3CN (40 mL) at 23 °C was added AgOAc (1.68 g, 10.1 mmol, 1.00 equiv) as a solid in one portion. The reaction mixture was stirred for 16 h at 23 °C in the dark. The reaction mixture was filtered through a pad of celite. The filtrate was concentrated in vacuo to afford 3.11 g of the title compound as a colorless solid (96% yield).

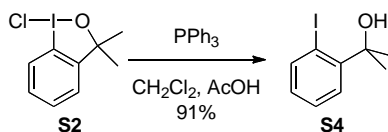
NMR Spectroscopy: ^1H NMR (400 MHz, benzene- d_6 , 23 °C, δ): 7.81 (d, $J = 8.1$ Hz, 1H), 6.95 (ddd, $J = 7.3$ Hz, 7.3 Hz, 1.5 Hz, 1H), 6.88 (ddd, $J = 7.3$ Hz, 7.3 Hz, 1.1 Hz, 1H), 6.56 (dd, $J = 7.3$ Hz, 1.1 Hz, 1H), 1.94 (s, 3H), 1.28 (s, 6H). ^{13}C NMR (100 MHz, benzene- d_6 , 23 °C, δ): 176.2, 150.1, 130.4, 130.1, 129.6, 126.1, 116.3, 84.2, 29.2, 21.2. These spectroscopic data correspond to those reported in the literature.^v

1-Trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**4**)



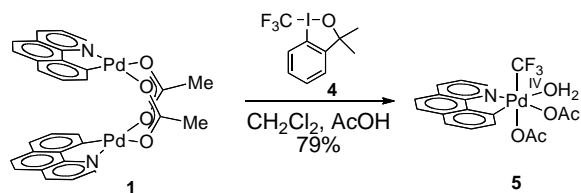
Compound **4** was prepared according to a published procedure.⁶ To 1-acetoxy-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**S3**) (1.10 g, 3.44 mmol, 1.00 equiv) in CH_3CN (20 mL) at 23 °C was added TMSCF₃ (0.770 mL, 0.732 g, 5.15 mmol, 1.50 equiv) in one portion. CsF (50 mg, 0.33 mmol, 0.096 equiv) was added and the reaction mixture was stirred for 16 h at 23 °C in the dark. Solvent was removed in vacuo and pentane (50 mL) was added. The reaction mixture was filtered through a pad of celite. The filtrate was concentrated in vacuo to afford 877 mg of the title compound as a yellow solid (77% yield).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 7.54–7.51 (m, 2H), 7.44–7.38 (m, 2H), 1.48 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 149.2, 130.6, 129.8, 127.9 (q, $J = 3.0$ Hz), 127.80, 110.5 (q, $J = 3.1$ Hz), 109.0 (q, $J = 210.5$ Hz), 76.5, 30.8. ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): –39.5. These spectroscopic data correspond to those reported in the literature.⁶

2-(2-iodophenyl)propan-2-ol (S4)

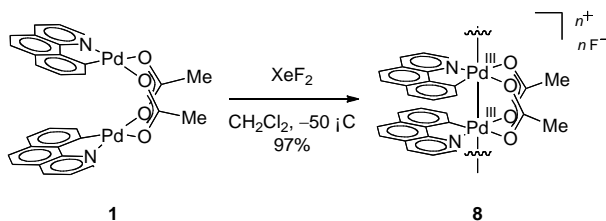
To 1-chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**S2**) (256 mg, 0.863 mmol, 1.00 equiv) in CH_2Cl_2 (8 mL) and AcOH (0.1 mL) at 23 °C was added PPh_3 (226 mg, 0.863 mmol, 1.00 equiv) as a solid in one portion. The reaction mixture was stirred for 5 min at 23 °C before solvent was removed in vacuo. The residue was purified by chromatography on SiO_2 gel eluting with EtOAc / hexanes (1 : 9 (v/v)) to afford 206 mg of the title compound as a pale yellow oil (91% yield).

$R_f = 0.47$ (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 7.96 (dd, $J = 7.9$ Hz, 1.5 Hz, 1H), 7.62 (dd, $J = 7.9$ Hz, 1.6 Hz, 1H), 7.33 (ddd, $J = 8.6$ Hz, 7.2 Hz, 1.3 Hz, 1H), 6.90 (ddd, $J = 8.9$ Hz, 7.3 Hz, 1.8 Hz, 1H), 1.76 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 148.4, 142.7, 128.6, 128.1, 126.7, 93.1, 73.56, 29.8. These spectroscopic data correspond to those reported in the literature.^{vi}

Benzo[*h*]quinolinyll trifluoromethyl palladium(IV) diacetate aquo complex (5)

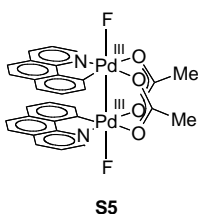
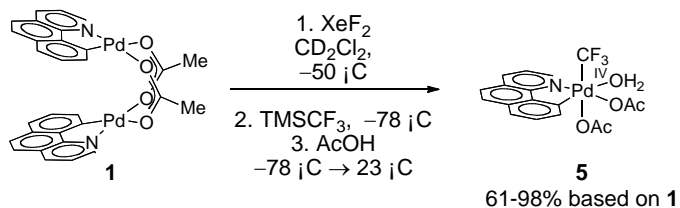
Compound **5** was prepared according to a published procedure.⁸ To benzo[*h*]quinolinyll palladium acetate dimer (**1**) (552 mg, 0.803 mmol, 1.00 equiv) in CH_2Cl_2 (15 mL) at 23 °C was added AcOH (0.92 mL, 970 mg, 16 mmol, 20 equiv) and 1-trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**4**) (1.06 g, 3.21 mmol, 4.00 equiv), sequentially. The reaction mixture was stirred at 23 °C for 15 min before solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 (5 mL) and hexanes (40 mL) was added. The precipitate was isolated by filtration on a plug of celite and was washed with hexanes (100 mL). The residue was recovered from the celite plug with Et_2O (200 mL). Solvent was removed in vacuo to afford 620 mg of the title compound as a green solid (79% yield).

NMR Spectroscopy: ^1H NMR (600 MHz, CDCl_3 , 23 °C, δ): 9.67 (br s, 2H), 9.06 (d, $J = 5.3$ Hz, 1H), 8.52 (dd, $J = 8.1$ Hz, 1.0 Hz, 1H), 7.99 (d, $J = 7.6$ Hz, 1H), 7.97 (d, $J = 8.8$ Hz, 1H), 7.92 (d, $J = 7.9$ Hz, 1H), 7.81 (d, $J = 8.6$ Hz, 1H), 7.77–7.74 (m, 2H), 2.34 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 23 °C, δ): 151.3, 147.4, 139.4, 136.2, 135.5, 130.9, 129.5, 128.6, 126.4, 126.1, 124.3, 122.9, 24.6, 24.2. ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): –23.7. These spectroscopic data correspond to those reported in the literature.^{vii} X-ray data has been submitted to the Cambridge Crystal Structure Database as CCDC 831838.

Palladium(III) fluoride **8**

Compound **8** was prepared according to a published procedure.⁹ All manipulations were carried out in a dry box under a N₂ atmosphere. Benzo[*h*]quinolinyl palladium acetate dimer (**1**) (21 mg, 3.1×10^{-5} mol, 1.0 equiv) was dissolved in 1.0 mL CH₂Cl₂ at -50 °C. XeF₂ (5.3 mg, 3.1×10^{-5} mol, 1.0 equiv) was added as a solid in one portion. The yellow solution immediately became a dark red-brown suspension. After stirring for five min at -50 °C, solvent was removed in vacuo at -50 °C. The residue was washed with Et₂O (1.0 mL) at -50 °C. The Et₂O was decanted, and the residue was dried under vacuum at -50 °C to afford 22 mg of the title compound (97% yield) as a dark red solid.

NMR Spectroscopy: ¹H-NMR (500 MHz, CD₂Cl₂, -10 °C, δ): 7.87 (d, $J = 5.1$ Hz, 2H), 7.71 (d, $J = 7.7$ Hz, 2H), 7.47–7.40 (m, 4H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 7.0$ Hz, 2H), 7.15 (d, $J = 8.8$ Hz, 2H), 6.86 (dd, $J = 4.8$ Hz, $J = 4.8$ Hz, 2H), 2.72 (s, 6H). ¹⁹F-NMR (375 MHz, CD₂Cl₂, -10 °C, δ): -170.4 (br s, $h_{1/2} = 317.8$ Hz). UV-VIS Spectroscopy (CH₂Cl₂, 0 °C): 1021 nm (absorbance at this wavelength is non-linear with concentration); 464 nm (absorbance at this wavelength is non-linear with concentration); 376 nm ($\epsilon = 2.47 \times 10^3$ M⁻¹ cm⁻¹). ¹³C NMR signals were not observed due to signal broadness. The reported spectral data correspond to those reported in the literature.^{viii} In addition to compound **8**, the structure of which has been submitted to the Cambridge Crystal Structure Database (CCDC 841654), complex **S5**, in which the fluoride ligands are Pd-bound, have also been characterized (CCDC 841653). In solution, extended chain **8** is exclusively observed.

Observation of **5** from Treatment of **8** with AcOH

This reaction was carried out in a nitrogen-filled dry box. To benzo[*h*]quinolinyl palladium acetate dimer

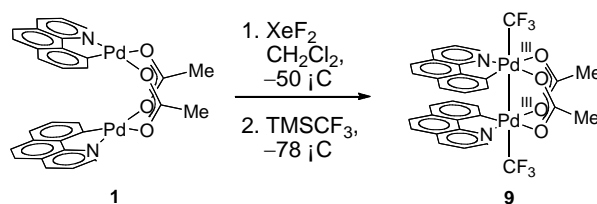
(**1**) (45.1 mg, 6.56×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (2.0 mL) at -50°C was added XeF_2 (11.1 mg, 6.56×10^{-5} mol, 1.00 equiv) as a solid in one portion. After 45 min, the reaction was cooled to -78°C and TMSCF_3 (29.5 μL , 28.0 mg, 0.196 mmol, 3.00 equiv) was added. The reaction vessel was removed from the cold bath and allowed to briefly warm until the color of the reaction mixture was observed to change from red to dark brown green. The reaction mixture was re-cooled to -78°C . After one minute, AcOH (38.0 μL , 39.9 mg, 0.656 mmol, 10.0 equiv) was added to the reaction mixture and the reaction mixture was warmed to 23°C . ^1H and ^{19}F NMR spectra were obtained which confirmed the formation of **5**. Mesitylene (3.0 μL , 2.6 mg, 2.2×10^{-5} mol, 0.33 equiv) was added and the amount of **5** formed was quantified by comparison of the integral of mesitylene at 6.78 ppm with the integral of **5** at 8.52 ppm. Yields of 61–98% based on **1** were observed. The yields of TMSF and CF_3H (40–52% and 21–30%) were determined by integration of ^{19}F NMR signals versus added 1-bromo-4-(trifluoromethyl)benzene.

The spectral data (^1H and ^{19}F NMR) of the **5** obtained by the above procedure is identical to authentic material and ^1H and ^{19}F peaks were coincident with the peaks of an authentic sample of **5** added to the NMR sample prepared above.^x Spectral data of compound **1** obtained by this procedure is identical to that of an authentic sample prepared above.

CHF_3 : NMR Spectroscopy: ^{19}F NMR (375 MHz, CD_2Cl_2 , -80°C , δ): -76.5 (d, $J = 77.8$ Hz).

TMSF : NMR Spectroscopy: ^1H -NMR (400 MHz, CD_2Cl_2 , 23°C , δ): 0.21 (d, $J = 8.8$ Hz, 9H). ^{19}F -NMR (375 MHz, CD_2Cl_2 , 23°C , δ): -160.3 . ^{29}Si -NMR (80 MHz, CD_2Cl_2 , 23°C , δ) 31.3 (d, $J = 273$ Hz).

Observation of Benzo[*h*]quinolinyll trifluoromethyl palladium(III) acetate dimer (**9**)



The following reaction was carried out in an N_2 -filled dry box. To benzo[*h*]quinolinyll palladium acetate dimer (**1**) (12.9 mg, 1.88×10^{-5} mol, 1.00 equiv) in CD_2Cl_2 (0.8 mL) at -50°C was added XeF_2 (3.5 mg, 2.1×10^{-5} mol, 1.1 equiv). The reaction mixture was stirred at -50°C for 45 min, at which time a dark red solution was observed. The reaction mixture was transferred to an NMR tube and frozen. TMSCF_3 (8.4 μL , 8.0 mg, 5.6×10^{-5} mol, 3.0 equiv) was added to the NMR tube. The reaction mixture was removed from the dry box and placed in a dry ice / acetone bath, at which temperature the reaction mixture melted resulting in a dark green brown solution. NMR spectra of the reaction mixture were obtained at -80°C . The ^1H NMR spectrum indicated the presence of TMSF as well as a complex with signals consistent with the structure **9** as drawn above.^x ^{19}F NMR analysis showed TMSF , which was quantified (40-52%) by integration versus internal standard 1-bromo-4-(trifluoromethyl)benzene.

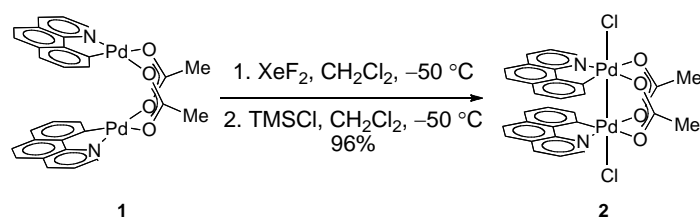
NMR Spectroscopy: ^1H NMR (500 MHz, CD_2Cl_2 , -80°C , δ): 7.85 (br s, 2H), 7.72 (br s, 2H), 7.45–7.44 (m, 4H), 7.32 (br s, 2H), 7.26 (br s, 2H), 7.19–7.14 (m, 2H), 6.85 (br s, 2H), 2.74 (s, 6H).

Discussion of Structure of **9**

Thermal instability of **9** has prevented independent characterization of the structure of **9**. The proposed structure of **9** is based on analogy to reactions of **8** with TMSX reagents (X = OAc, Cl), *vide infra*, and based on the similarity of the ^1H NMR spectrum of **9** with binuclear Pd(III) complexes **2** and **3**. Below, previously published procedures for the synthesis of **2** and **3**, by treatment of **8** with TMSCl and TMSOAc, respectively, are reproduced.

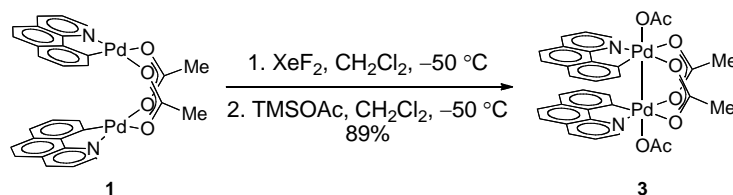
The acetate chemical shift for **9** is at 2.74 ppm. This is similar to the corresponding chemical shifts of **2** (2.69 ppm) and of **3** (2.71 ppm). By contrast, the corresponding shift in binuclear Pd(II) complex **1** is at 2.38 ppm. The acetate resonances of Pd(IV) complex **5** are at 2.34 and 1.72 ppm, respectively. Thermal instability of **9** prevented the acquisition of ^{13}C NMR and UV-vis spectra as well as mass spectrometric analysis. ^{19}F NMR analysis of the reaction mixture containing proposed structure **9** showed TMSF ($\delta = -160.3$). A single resonance attributable to **9** was not observed.

Benzo[*h*]quinolinyl chloro palladium(III) acetate dimer (**2**) by Oxidation with XeF_2



Complex **2** was prepared according to a published procedure.³ To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**1**) (71.4 mg, 1.04×10^{-4} mol, 1.00 equiv) in CH_2Cl_2 (2.0 mL) at -50 °C was added XeF_2 (17.6 mg, 1.04×10^{-4} mol, 1.00 equiv) as a solid in one portion. The color of the solution immediately changed from pale yellow to dark red-brown. After 10 min, TMSCl (27.0 μL , 2.13×10^{-4} mol, 2.05 equiv) was added in one portion. The reaction was stirred for an additional 10 min before solvent was removed in vacuo at -50 °C. The residue was triturated with 3 mL Et_2O at -50 °C. The residue was dried under vacuum to afford 75.4 mg of the title compound (96% yield).

^1H -NMR (500 MHz, CD_2Cl_2 , -50 °C, δ): 7.71 (br s, 2H), 7.58 (d, $J = 7.8$ Hz, 2H), 7.45 (dd, $J = 7.3$ Hz, $J = 7.3$ Hz, 2H), 7.35 (d, $J = 7.8$ Hz, 2H), 7.22 (d, $J = 8.8$ Hz, 2H), 7.18 (d, $J = 7.8$ Hz, 2H), 7.03 (d, $J = 8.3$ Hz, 2H), 6.71 (bs, 2H), 2.69 (s, 6H). UV-VIS Spectroscopy (CH_2Cl_2 , 0 °C): 582 nm ($\epsilon = 2.99 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); 491 nm ($\epsilon = 7.39 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); 417 nm ($\epsilon = 2.61 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$); 270 nm ($\epsilon = 3.69 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). These data are in accord with those reported in the literature.^{xi}

Benzo[*h*]quinolinyl acetoxy palladium(III) acetate dimer (3) by Oxidation with XeF₂

Complex **3** was prepared according to a published procedure.³ To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**1**) (61.3 mg, 8.92×10^{-5} mol, 1.00 equiv) in CH₂Cl₂ (2.0 mL) was added XeF₂ (15.1 mg, 8.92×10^{-5} mol, 1.00 equiv) at -50 °C in an N₂-filled dry box. The reaction mixture immediately became dark red. After stirring for 5 min at -50 °C, TMSOAc (40.1 μL, 2.68×10^{-4} mol, 3.00 equiv) was added in one portion. After 15 min, solvent was removed in vacuo at -50 °C. The dark red residue was washed with pre-cooled (-50 °C) Et₂O (2 × 3 mL) and dried at -50 °C to afford 63.9 mg of the title compound (89% yield) as a 15:1 mixture of isomers (benzoquinolinyl ligand head to tail vs. head to head). The title compound is a moisture sensitive dark red solid.

NMR Spectroscopy: ¹H-NMR (500 MHz, CD₂Cl₂, -30 °C, δ): Head to Tail Isomer: 7.89 (d, *J* = 5.4 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.47–7.41 (m, 4H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.71 (dd, *J* = 7.8 Hz, 5.4 Hz, 2H), 2.71 (s, 6H), 1.47 (s, 6H). Head to Head Isomer: 8.26 (d, *J* = 5.2 Hz, 2H), 7.84 (d, 7.8 Hz, 2H), 6.88 (d, *J* = 7.3 Hz, 2H). ¹³C-NMR (125 MHz, CD₂Cl₂, -30 °C, δ): Head to Tail Isomer: 187.4, 175.9, 157.4, 150.6, 149.9, 136.8, 136.7, 133.4, 130.4, 127.4, 126.3, 125.6, 124.8, 124.5, 121.2, 25.0, 23.0. UV-VIS Spectroscopy (CH₂Cl₂, 0 °C): 419 nm ($\epsilon = 1.03 \times 10^4$ M⁻¹ cm⁻¹); 281 nm ($\epsilon = 2.48 \times 10^4$ M⁻¹ cm⁻¹). These data are in accord with those reported in the literature.³

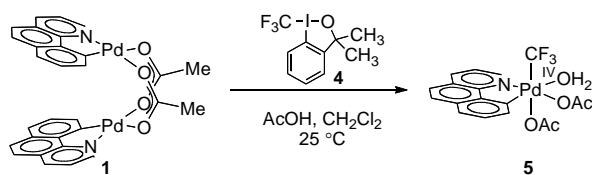
Reaction Kinetics

Initial Rate Kinetics of Oxidation of **1** with **4**

The rate-law of oxidation of binuclear Pd(II) complex **1** with **4** to afford mononuclear Pd(IV) complex **5** was determined by examination of the initial rate kinetics of formation of **5** as a function of concentration of each reaction component. This analysis revealed that the rate law is $\text{rate} = k [\mathbf{1}] [\mathbf{4}] [\text{AcOH}]$, consistent with rate-determining oxidation of binuclear Pd complexes to afford a binuclear Pd(III) complex. Experimental details are reported below.

In general, initial rate measurements were carried out as follows. Individual samples were prepared as described below and were inserted into a temperature-controlled NMR spectrometer. The concentration of **5** was assayed by integration of the ^{19}F NMR signal versus the integration of the internal standard signal. For each set of experiments in which the concentration of a reaction component was varied, the initial rate of the fastest reaction (generally, the sample with the highest concentration of the reagent being varied), was determined using a single data point. Examination of the full time course of product formation confirmed that the first data point was representative. The conversion at the first data point in this experiment established the conversion to which subsequent experiments were monitored. Each experimental point is based on a different number of data points, between 1 and 8. We chose to collect data in this way because we were endeavoring to obtain initial rate data at 5-10% yield. To insure that this approach was reproducible, the entire data set used for each of the kinetic order determinations was performed in duplicate.

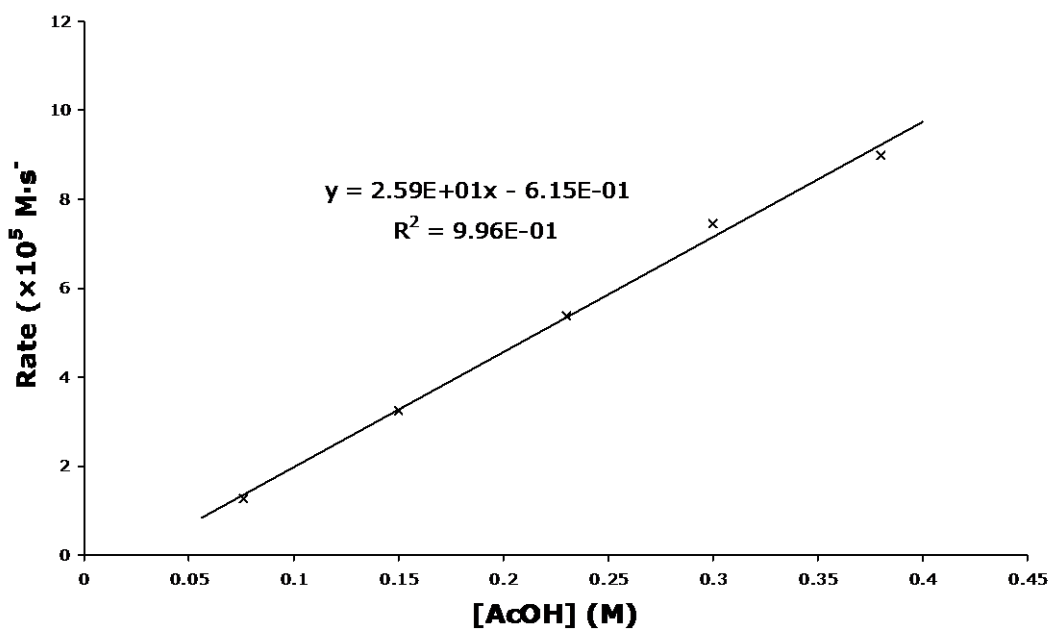
Reaction order of AcOH in the oxidation of **1** to **5**ⁱⁱⁱ



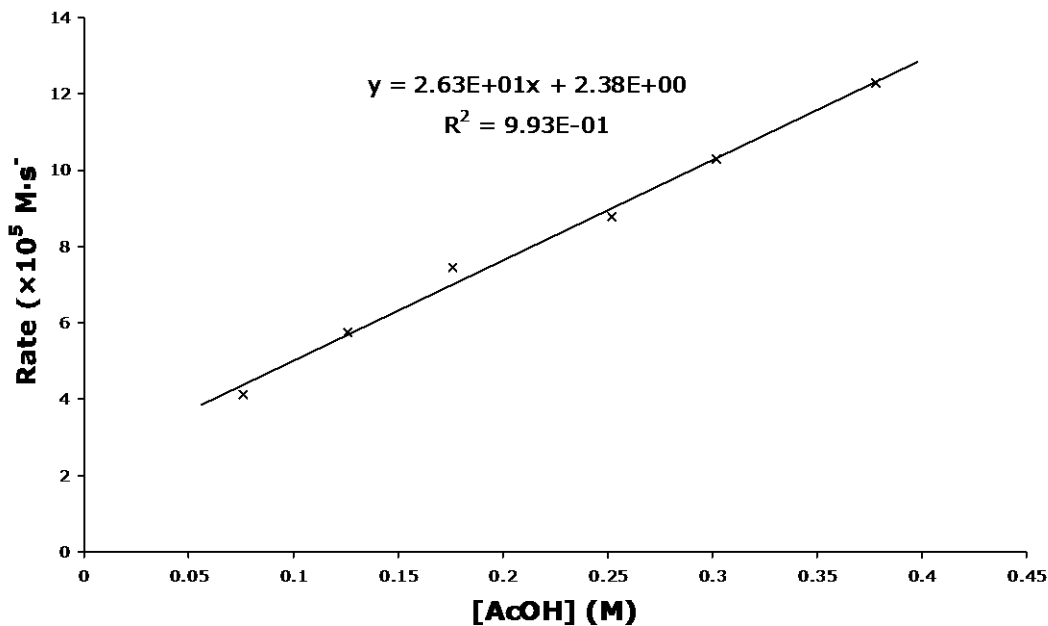
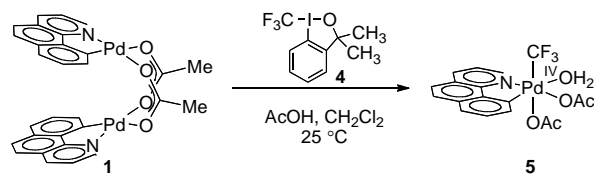
A solution of benzo[*h*]quinolinyll palladium acetate dimer (**1**) (65 mM; 130 mM in Pd) was prepared by dissolving 180 mg of **1** in CH₂Cl₂ (4.0 mL). This solution also contained 200 mM CCl₃F (72 μL). A solution of AcOH in CH₂Cl₂ (4.0 M) was prepared by dissolving AcOH (314 mg, 0.300 mL) in 1.0 mL CH₂Cl₂. A solution of **4** (0.26 M) in CH₂Cl₂ was prepared by dissolving 258 mg of **4** in CH₂Cl₂ (3.0 mL). Samples were prepared with total volumes by combining the following volumes of the above-described solutions (see table below); the solution of **4** was added last. Following addition of **4**, ^{19}F NMR spectra were obtained and the concentration of **5** was quantified by integration of the ^{19}F NMR signal at -25.5 ppm versus the ^{19}F signal of CCl₃F at 1.05 ppm. Initial rates of oxidation were determined from the data obtained.

| Run | Pd V (μL); C (M) | 4 V (μL); C (M) | AcOH V (μL); C (M) | CH ₂ Cl ₂ V (μL) | rate (M/s) (yield (%)) |
|-----|----------------------------------|---------------------------------|------------------------------------|--|------------------------------|
| 1 | 400; 0.065 | 300; 0.098 | 15; 0.076 | 85 | 1.27×10^{-5} (8.6) |
| 2 | 400; 0.065 | 300; 0.098 | 30; 0.15 | 70 | 3.25×10^{-5} (14.4) |
| 3 | 400; 0.065 | 300; 0.098 | 45; 0.23 | 55 | 5.38×10^{-5} (14.6) |
| 4 | 400; 0.065 | 300; 0.098 | 60; 0.30 | 40 | 7.45×10^{-5} (14.2) |
| 5 | 400; 0.065 | 300; 0.098 | 75; 0.38 | 25 | 8.99×10^{-5} (14.2) |

Oxidation Rate vs. [AcOH]



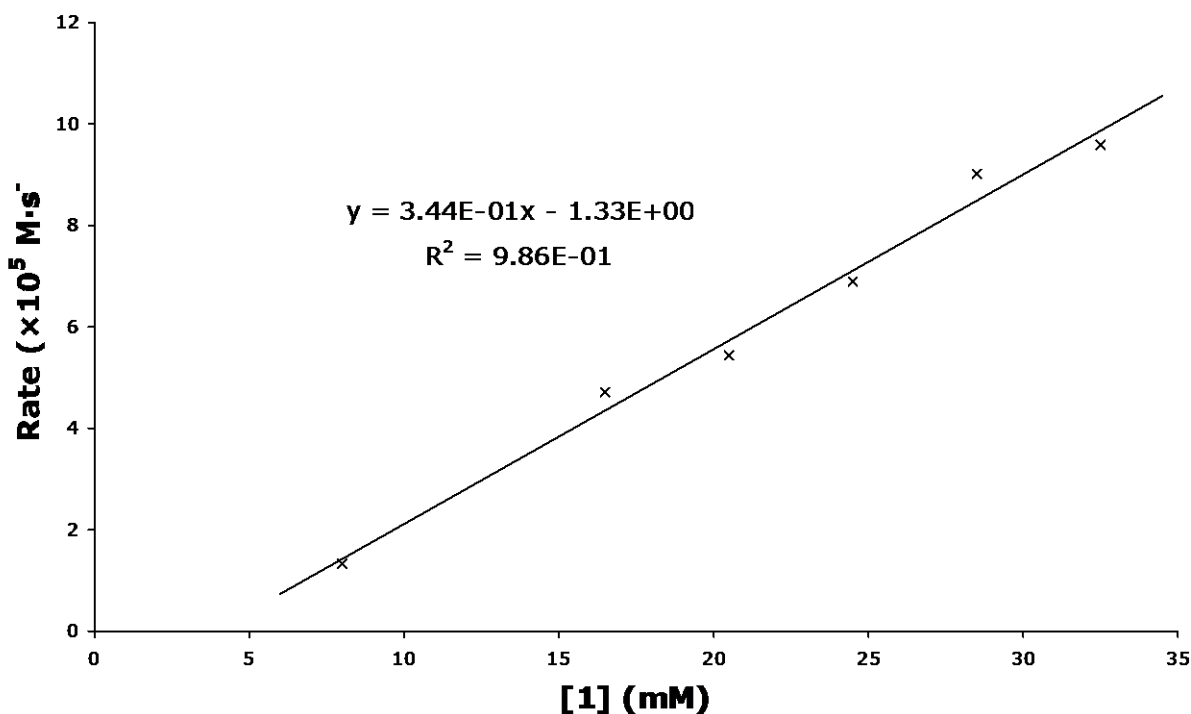
To evaluate the reliability of the y-intercept on the above plot, a completely independent data set was collected and is plotted below. Based on the close agreement of the slope of the line and the divergent y-intercept, two-term rate laws based on the non-zero intercept are likely not relevant.

Oxidation Rate vs. [AcOH]**Reaction order of 1 in the oxidation of 1 to 5**

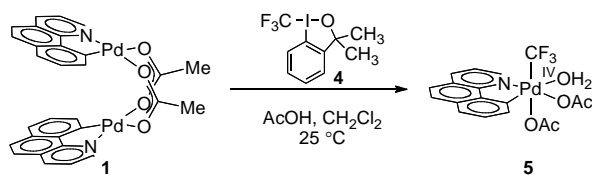
A solution of benzo[*h*]quinolinylnickel(II) dimer (**1**) (65 mM; 130 mM in Pd) was prepared by dissolving 180 mg of **1** in CH₂Cl₂ (4.0 mL). A solution of AcOH in CH₂Cl₂ (4.0 M) was prepared by dissolving AcOH (314 mg, 0.300 mL) in 1.0 mL CH₂Cl₂. A solution of oxidant (**4**) (0.26 M) in CH₂Cl₂ was prepared by dissolving 258 mg of **4** in CH₂Cl₂ (3.0 mL) and 72 μL CCl₃F. Samples were prepared with total volumes by combining the following volumes of the above-described solutions (see table below); the solution of **4** was added last. Following addition of **4**, ¹⁹F NMR spectra were obtained and the concentration of **5** was quantified by integration of the ¹⁹F NMR signal at -25.5 ppm versus the ¹⁹F signal of CCl₃F at 1.05 ppm. Initial rates of oxidation were determined from the data obtained.

| Run | Pd V (μL); C (M) | 4 V (μL); C (M) | AcOH V (μL); C (M) | CH ₂ Cl ₂ V (μL) | rate (M/s) (yield (%)) |
|-----|----------------------------------|---------------------------------|------------------------------------|--|------------------------------|
| 1 | 100; 0.016 | 300; 0.098 | 50; 0.25 | 350 | 1.32×10^{-5} (12.4) |
| 2 | 200; 0.033 | 300; 0.098 | 50; 0.25 | 250 | 4.71×10^{-5} (7.4) |
| 3 | 250; 0.041 | 300; 0.098 | 50; 0.25 | 200 | 5.44×10^{-5} (10.5) |
| 4 | 300; 0.049 | 300; 0.098 | 50; 0.25 | 150 | 6.89×10^{-5} (11.8) |
| 5 | 350; 0.057 | 300; 0.098 | 50; 0.25 | 100 | 9.02×10^{-5} (15.8) |
| 6 | 400; 0.065 | 300; 0.098 | 50; 0.25 | 50 | 9.59×10^{-5} (13.8) |

Oxidation Rate vs. [1]



Reaction order of 4 in the oxidation of 1 to 5

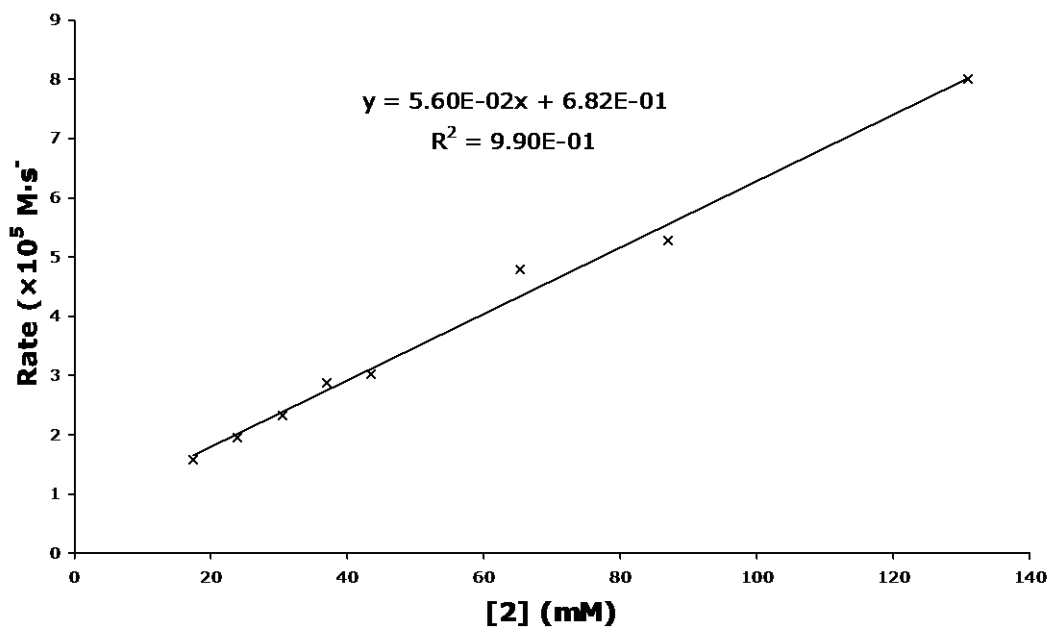


A solution of benzo[*h*]quinolinylligand palladium acetate dimer (**1**) (87 mM; 174 mM in Pd) was prepared by dissolving 360 mg of **1** in CH₂Cl₂ (6.0 mL). This solution also contained 200 mM CCl₃F (108 μL). A solution of AcOH in CH₂Cl₂ (4.0 M) was prepared by dissolving AcOH (314 mg, 0.300 mL) in 1.0 mL CH₂Cl₂. A solution of oxidant (**4**) (0.35 M) in CH₂Cl₂ was prepared by dissolving 138 mg of **4** in CH₂Cl₂

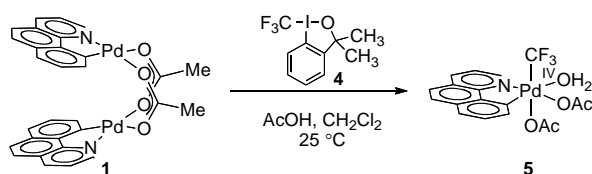
(1.2 mL). Samples were prepared with total volumes by combining the following volumes of the above-described solutions (see table below); the solution of **4** was added last. Following addition of **4**, ^{19}F NMR spectra were obtained and the concentration of **5** was quantified by integration of the ^{19}F NMR signal at -25.5 ppm versus the ^{19}F signal of CCl_3F at 1.05 ppm. Initial rates of oxidation were determined from the data obtained.

| Run | Pd V (μL); C (M) | 4 V (μL); C (M) | AcOH V (μL); C (M) | CH_2Cl_2 (V (μL)) | rate (M/s) (yield (%)) |
|-----|----------------------------------|--|------------------------------------|---|-----------------------------|
| 1 | 400; 0.087 | 40; 0.017 | 30; 0.15 | 330 | 1.58×10^{-5} (7.9) |
| 2 | 400; 0.087 | 55; 0.024 | 30; 0.15 | 315 | 1.96×10^{-5} (7.9) |
| 3 | 400; 0.087 | 70; 0.031 | 30; 0.15 | 300 | 2.33×10^{-5} (7.4) |
| 4 | 400; 0.087 | 85; 0.037 | 30; 0.15 | 285 | 2.88×10^{-5} (7.0) |
| 5 | 400; 0.087 | 100; 0.044 | 30; 0.15 | 270 | 3.03×10^{-5} (7.3) |
| 6 | 400; 0.087 | 150; 0.065 | 30; 0.15 | 220 | 4.79×10^{-5} (8.5) |
| 7 | 400; 0.087 | 200; 0.087 | 30; 0.15 | 170 | 5.28×10^{-5} (6.7) |
| 8 | 400; 0.087 | 300; 0.13 | 30; 0.15 | 70 | 8.01×10^{-5} (6.9) |

Reaction Rate vs. [4]



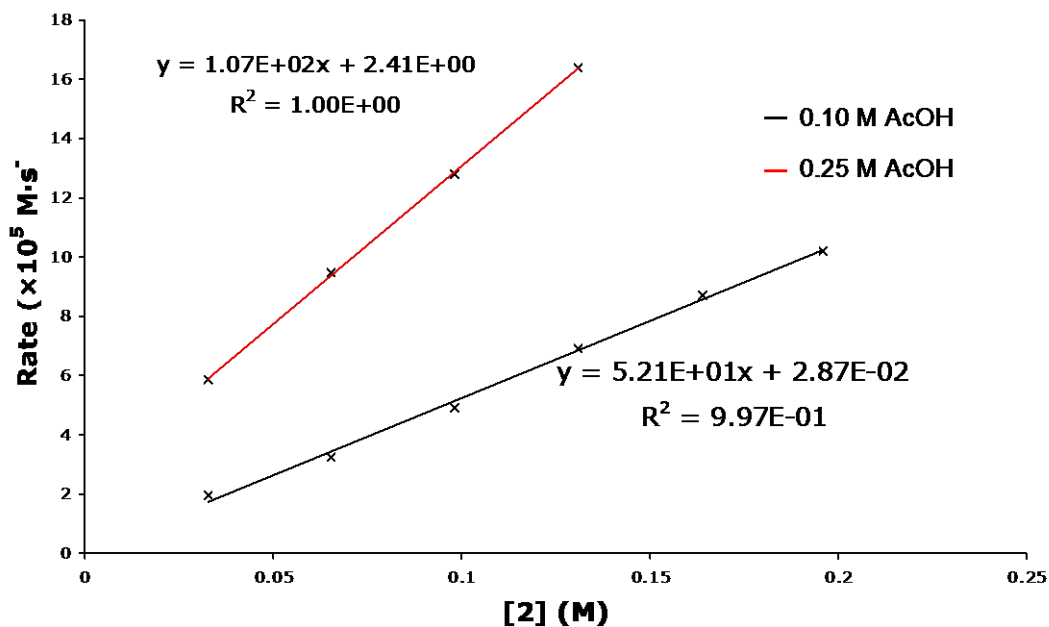
Rate of Oxidation of **1** as a function of [4] at two concentrations of AcOH



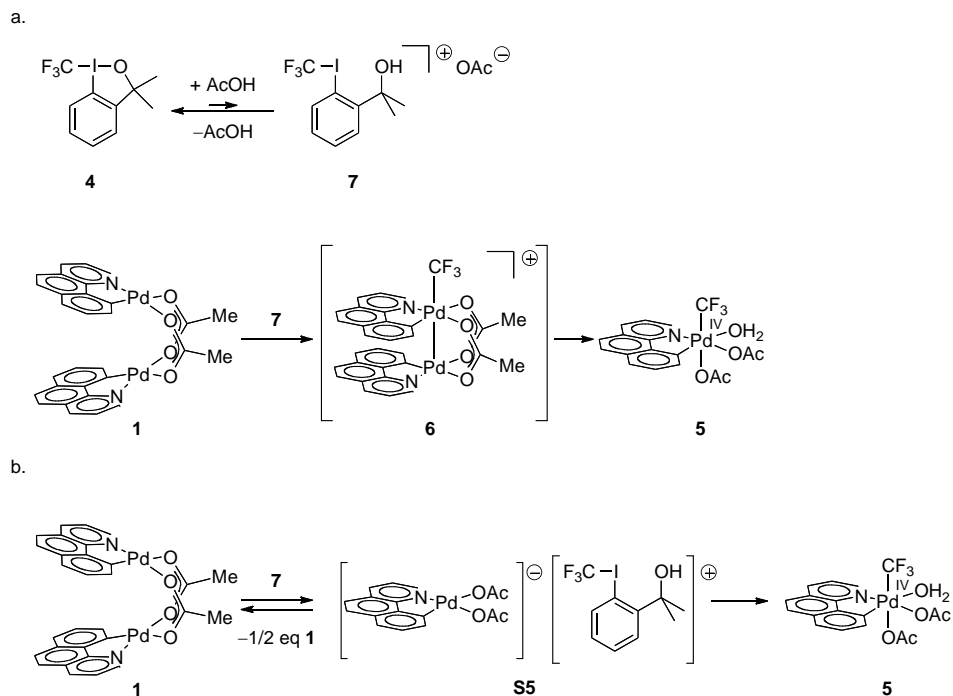
To confirm the results reported regarding the reaction order of both AcOH and oxidant, the following experiment was carried out in which the rate dependence on oxidant (**4**) was determined at two concentrations of AcOH.

A solution of benzo[*h*]quinolinyl palladium acetate dimer (**1**) (65 mM; 130 mM in Pd) was prepared by dissolving 252 mg of **1** in CH₂Cl₂ (5.6 mL). This solution also contained 200 mM CCl₃F (100 μL). A solution of AcOH in CH₂Cl₂ (4.0 M) was prepared by dissolving AcOH (314 mg, 0.300 mL) in 1.0 mL CH₂Cl₂. A solution of oxidant (**4**) (0.52 M) in CH₂Cl₂ was prepared by dissolving 414 mg of **4** in CH₂Cl₂ (2.4 mL). Samples were prepared with total volumes by combining the following volumes of the above-described solutions (see table below); the solution of **4** was added last. Following addition of **4**, ¹⁹F NMR spectra were obtained and the concentration of **5** was quantified by integration of the ¹⁹F NMR signal at –25.5 ppm versus the ¹⁹F signal of CCl₃F at 1.05 ppm. Initial rates of oxidation were determined from the data obtained.

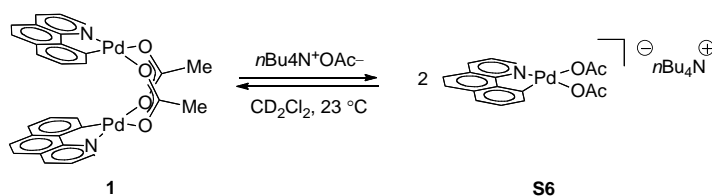
| Run | Pd V (μL); C (M) | 4 V (μL); C (M) | AcOH V (μL); C (M) | CH ₂ Cl ₂ V (μL) | rate (M/s) (yield (%)) |
|-----|---------------------|---------------------------|-----------------------|---|--------------------------------|
| 1 | 400; 0.087 | 50; 0.033 | 20; 0.10 | 330 | 1.96 × 10 ⁻⁵ (10.6) |
| 2 | 400; 0.087 | 100; 0.065 | 20; 0.10 | 280 | 3.25 × 10 ⁻⁵ (11.1) |
| 3 | 400; 0.087 | 150; 0.098 | 20; 0.10 | 230 | 4.91 × 10 ⁻⁵ (8.3) |
| 4 | 400; 0.087 | 200; 0.13 | 20; 0.10 | 180 | 6.92 × 10 ⁻⁵ (8.6) |
| 5 | 400; 0.087 | 250; 0.16 | 20; 0.10 | 130 | 8.73 × 10 ⁻⁵ (7.6) |
| 6 | 400; 0.087 | 300; 0.20 | 20; 0.10 | 80 | 1.02 × 10 ⁻⁴ (8.9) |
| 7 | 400; 0.087 | 50; 0.033 | 50; 0.25 | 300 | 5.86 × 10 ⁻⁵ (11.3) |
| 8 | 400; 0.087 | 100; 0.065 | 50; 0.25 | 250 | 9.48 × 10 ⁻⁵ (11.0) |
| 9 | 400; 0.087 | 150; 0.098 | 50; 0.25 | 200 | 1.28 × 10 ⁻⁴ (9.3) |
| 10 | 400; 0.087 | 200; 0.13 | 50; 0.25 | 150 | 1.64 × 10 ⁻⁴ (8.1) |

Rate vs. [4] at 0.10 M and 0.25 M AcOH**Discussion of Potential Oxidation Pathways via Mononuclear Pd Complexes**

The experimentally derived rate law is: $\text{rate} = k [\mathbf{1}] [\mathbf{4}] [\text{AcOH}]$. This rate law is consistent with pre-equilibrium protonation of **4** by acetic acid followed by oxidation of binuclear Pd(II) complex **1** (a, scheme below). This rate law is also consistent with pre-equilibrium association of the acetate counterion of **7** participating in bridge-splitting equilibrium with binuclear Pd(II) complex **1** to afford mononuclear Pd(II) palladate complex **S5**, which undergoes subsequent oxidation to afford the observed mononuclear Pd(IV) complex **5**. While we can not differentiate between these two possibilities by reaction kinetics analysis, below are outlined a series of experiments that we carried out which suggest that a mononuclear complex is not required for oxidation. First, we showed that acetate ions can bind to the Pd(II) centers of **1** by treating **1** with *n*-Bu₄NOAc to afford **S6**. We next prepared a protonated derivative of Togni reagent (**S7**) bearing a weakly coordinating counterion by treating **4** with CSA. Finally, we have shown that oxidation of **1** to **5** proceeds in the absence of exogenous anions to promote monomerization of **1**; oxidation of **1** with **S7** affords mononuclear Pd(IV) complex **5** in 36% yield (based on Pd). The reaction of **1** with **S7** suggests that an anionic donor to monomerize **1** is not required for oxidation to afford **5**.



Benzo[*h*]quinolinyl bis-acetato palladate (S6)

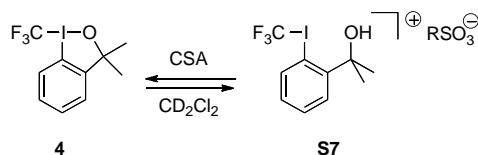


To benzo[*h*]quinolinyl palladium acetate dimer (**1**) (2.7 mg, 3.9 μmol , 1.0 equiv) in CD_2Cl_2 (0.50 mL) at 23 $^\circ\text{C}$ was added *n*-Bu₄NOAc (2.8 mg, 9.4 μmol , 2.4 equiv). After 10 min, a ¹H NMR spectrum was obtained. The spectrum contained both signals attributable to **1** as well as signals attributable to a new species, assigned as **S6**. The assignment of **S6** as a monomer is based primarily on the large downfield shift of the benzo[*h*]quinolinyl protons that is observed.

The concentration of **S6** was found to be dependent on the concentration of *n*-Bu₄NOAc added. Above, at 19 mM *n*-Bu₄NOAc (2.4 equiv), a ratio of 84 : 16 (**1** : **S6**) was observed. In a second experiment, at 190 mM *n*-Bu₄NOAc (24 equiv), a ratio of 14 : 86 (**1** : **S6**) was observed. The ¹H NMR spectra of these two conditions are reproduced in the 'NMR Data' section.

NMR Spectroscopy: ¹H NMR (500 MHz, CD_2Cl_2 , 23 $^\circ\text{C}$, δ): 8.67 (d, *J* = 5.4, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.41 (dd, *J* = 8.5 Hz, 5.4 Hz, 1H), 7.36–7.33 (m, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 2.07 (s, 3H).

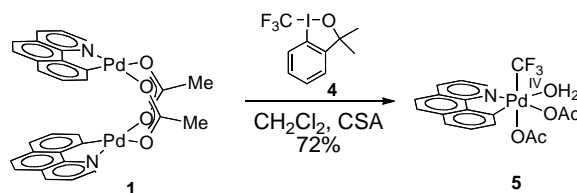
Protonation of **4** with CSA



To 1-trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**4**) (38 mg, 0.12 mmol, 1.0 equiv) in CD_2Cl_2 (0.60 mL) at 23 °C was added CSA (27 mg, 0.12 mmol, 1.0 equiv) in one portion. ^1H and ^{19}F NMR spectra were obtained which showed the disappearance of the signals attributable to **4** and the appearance of a new set of signals, assigned to **S7**. Stacked ^1H and ^{19}F NMR spectra of **4** and **S7** are reproduced in the ‘NMR Data’ section.

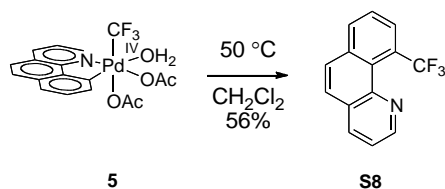
NMR Spectroscopy: ^1H NMR (400 MHz, CD_2Cl_2 , 23 °C, δ): 7.69–7.63 (m, 2H), 7.57–7.50 (m, 2H), 1.70 (s, 6H). ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): –26.0.

Benzo[*h*]quinolinyll trifluoromethyl palladium(IV) diacetate aquo complex (**5**)



To benzo[*h*]quinolinyll palladium acetate dimer (**1**) (10 mg, 0.015 mmol, 1.0 equiv) in CD_2Cl_2 (0.60 mL) in a J. Young NMR tube at 23 °C was added CSA (27 mg, 0.12 mmol, 8.0 equiv) and 1-trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**4**) (38 mg, 0.12 mmol, 8.0 equiv), sequentially. The homogeneous reaction mixture was kept at 23 °C for 11 h and fluorobenzene (2.0 μL , 2.1 mg) was added to the reaction before a ^1H and ^{19}F NMR spectra were obtained. The yield for **5** (36% based on Pd) was determined by comparing the integration of the ^{19}F NMR resonance of **5** and that of fluorobenzene (–113.2 ppm). In addition to compound **5**, 10-(trifluoromethyl)benzo[*h*]quinoline (**S8**) was observed (36% yield, based on Pd).

Spectral data for compound **5** prepared by this procedure are identical to those reported above. Spectral data for **S8** prepared by this procedure are identical to those reported in the literature and correspond to those obtained from an authentic sample (see below).

10-(trifluoromethyl)benzo[*h*]quinoline (S8)

A solution of benzo[*h*]quinolinyl trifluoromethyl palladium(IV) diacetate aquo complex (**5**) (220 mg, 0.449 mmol, 1.00 equiv) in CH₂Cl₂ was heated to 50 °C. After 12 h, solvent was removed in vacuo and the residue was purified by chromatography on SiO₂ gel eluting with EtOAc / hexanes (1 : 4 (v/v)) to afford 62.2 mg of the title compound as a colorless solid (56% yield).

R_f = 0.51 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 9.07 (dd, *J* = 4.2 Hz, 1.9 Hz, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.20 (dd, *J* = 8.1 Hz, 1.9 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.74 (dd, *J* = 8.2 Hz, 8.2 Hz, 1H), 7.57 (dd, *J* = 8.1 Hz, 4.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, 23 °C, δ): 147.8, 145.13, 135.5, 135.4, 132.9, 128.1 (q, *J* = 8.0 Hz), 128.0, 127.7, 126.9, 126.7, 122.1. ¹⁹F NMR (375 MHz, CDCl₃, 23 °C, δ): -57.2. These spectroscopic data correspond to those reported in the literature.^{xiii}

X-ray Crystallographic Analysis

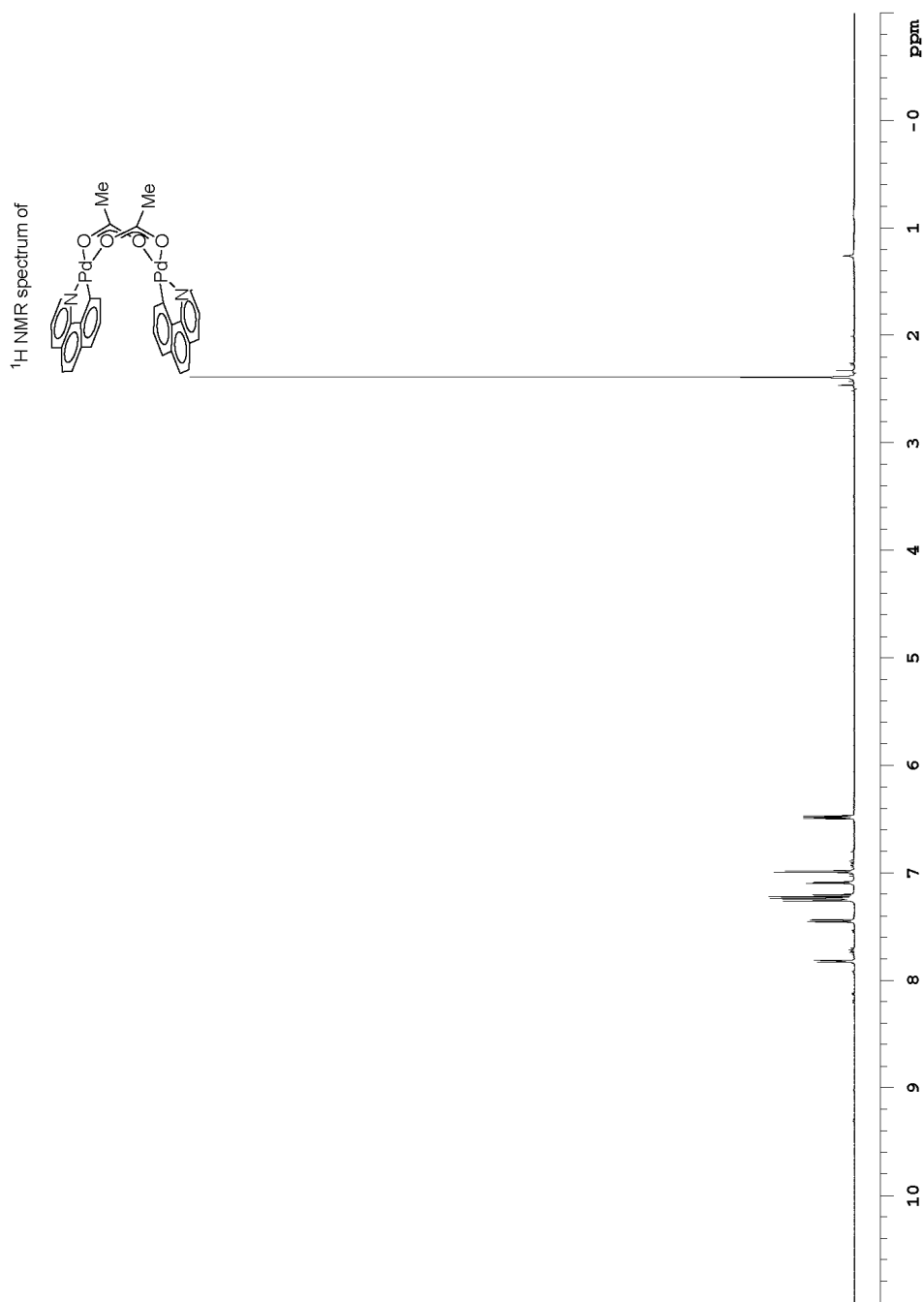
Complex **1** has been crystallized by vapor diffusion of pentane into a concentrated CH₂Cl₂ solution of **1**. Two crystal morphologies have been obtained: needle-like and prismatic crystals have been observed. The structure of the needle-shaped crystals has previously been reported⁹ and has been deposited in the Cambridge Crystal Structure Database as CCDC 705005. The structure of the prismatic morphology of **1** is reported here for the first time and has been deposited in the Cambridge Crystal Structure Database as CCDC 832191. Experimental data is included below.

Benzo[*h*]quinolinyl Palladium Acetate Dimer (1) (Prismatic Morphology) (CCDC 832191)

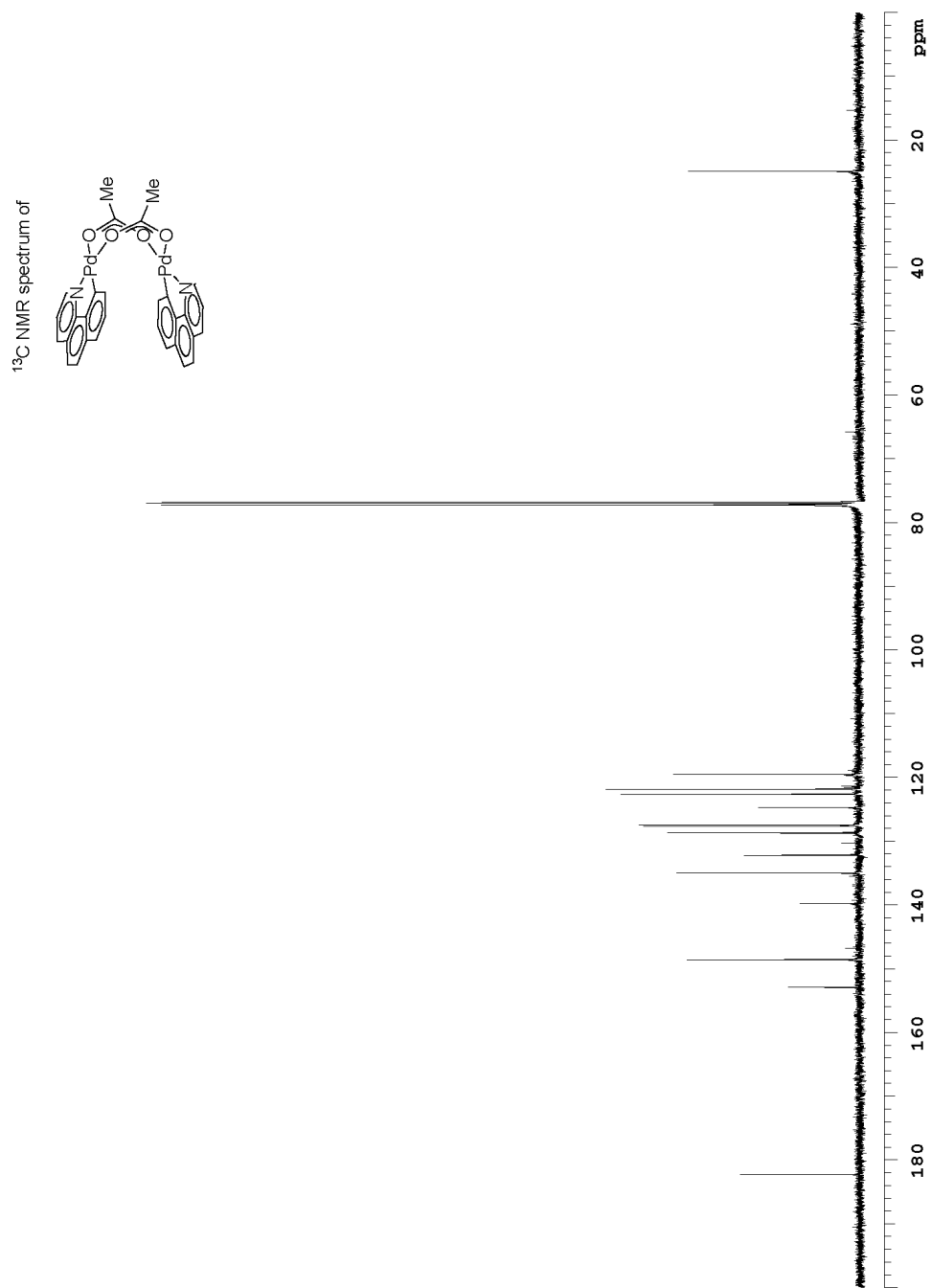
An orange prismatic crystal suitable for x-ray diffraction was obtained by vapor diffusion of pentane into a saturated CH₂Cl₂ solution of **1**. Data was collected on a crystal mounted on a diffractometer at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer (MoK radiation, λ = 0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5 scans in at 28 in 2. Data integration down to 0.82 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program TWINABS. The structure was solved by the direct methods procedure and refined by least-squares methods again F2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table 1 and geometric parameters are shown in Table 2.

Table 1. Experimental details

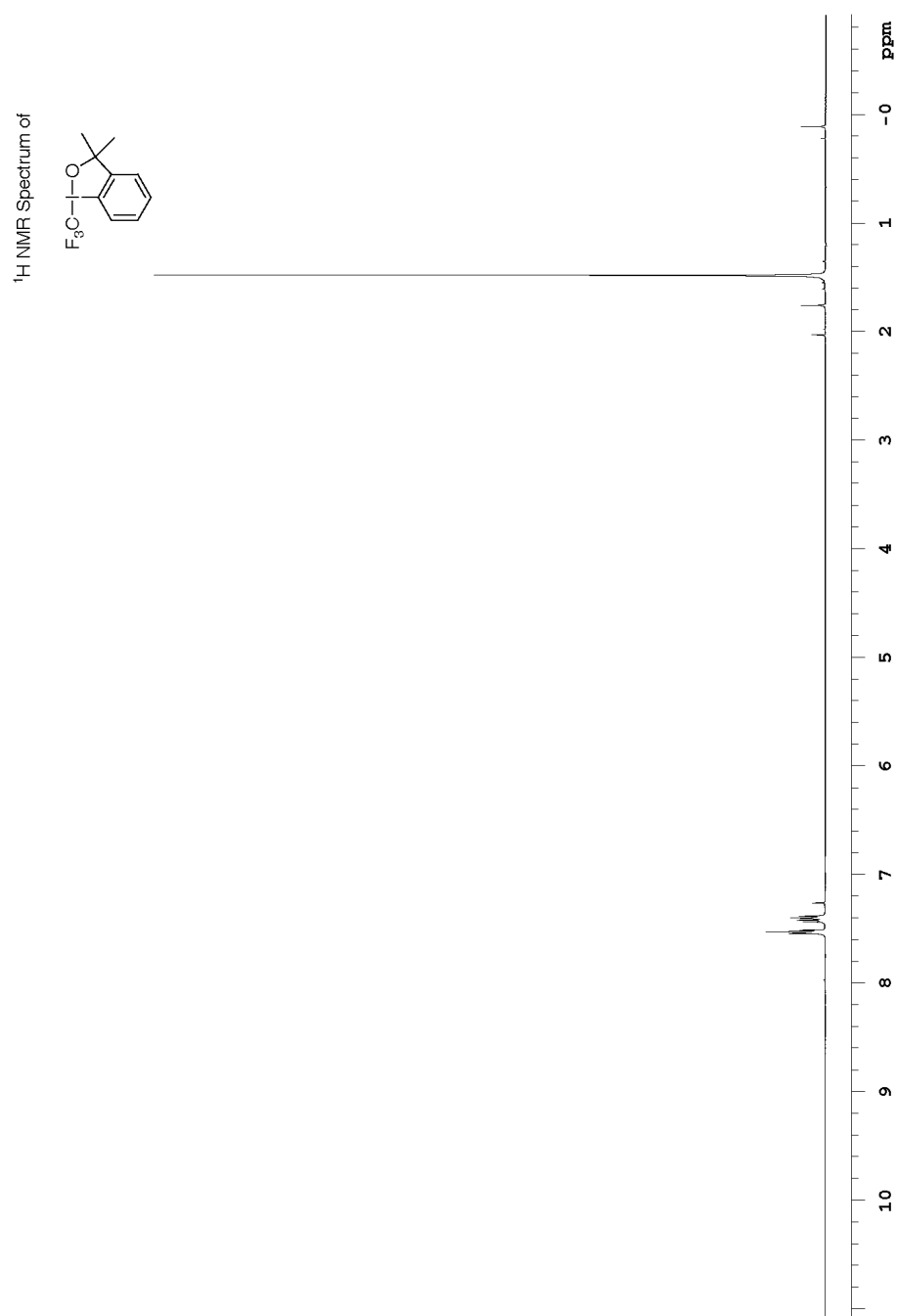
| | |
|--|---|
| Identification Code | 1 (CCDC 832191) |
| Chemical formula | $C_{184}H_{140}Cl_8N_{12}O_{24}Pd_{12}$ |
| M_r | 4463.48 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 100 |
| a, b, c (Å) | 17.1241 (6), 20.2806 (7), 23.2979 (9) |
| α, β, γ (°) | 89.559 (2), 89.230 (2), 88.773 (2) |
| V (Å ³) | 8088.3 (5) |
| Z | 2 |
| Radiation type | Mo $K\alpha$ |
| μ (mm ⁻¹) | 1.51 |
| Crystal size (mm) | 0.20 × 0.14 × 0.12 |
| Data collection | |
| Absorption correction | Multi-scan TWINABS |
| T_{\min}, T_{\max} | 0.753, 0.840 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 60924, 60924, 45721 |
| R_{int} | 0.0000 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ | 0.048, 0.107, 1.04 |
| No. of reflections | 60924 |
| No. of parameters | 2178 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $D_{\text{max}}, D_{\text{min}}$ (e Å ⁻³) | 1.39, -1.03 |

NMR Data

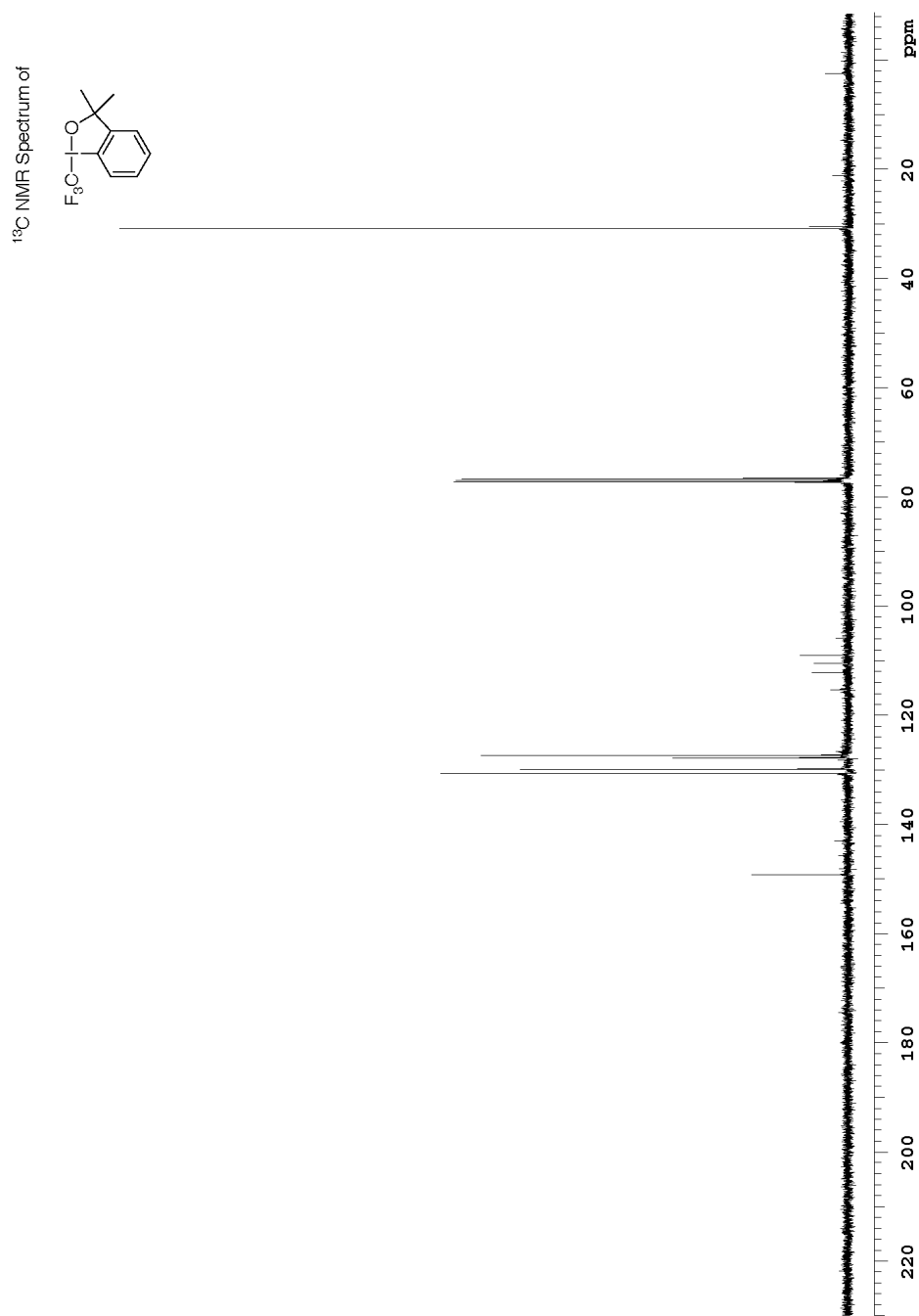
¹H NMR spectrum of **1** in CDCl₃ at 23 °C.



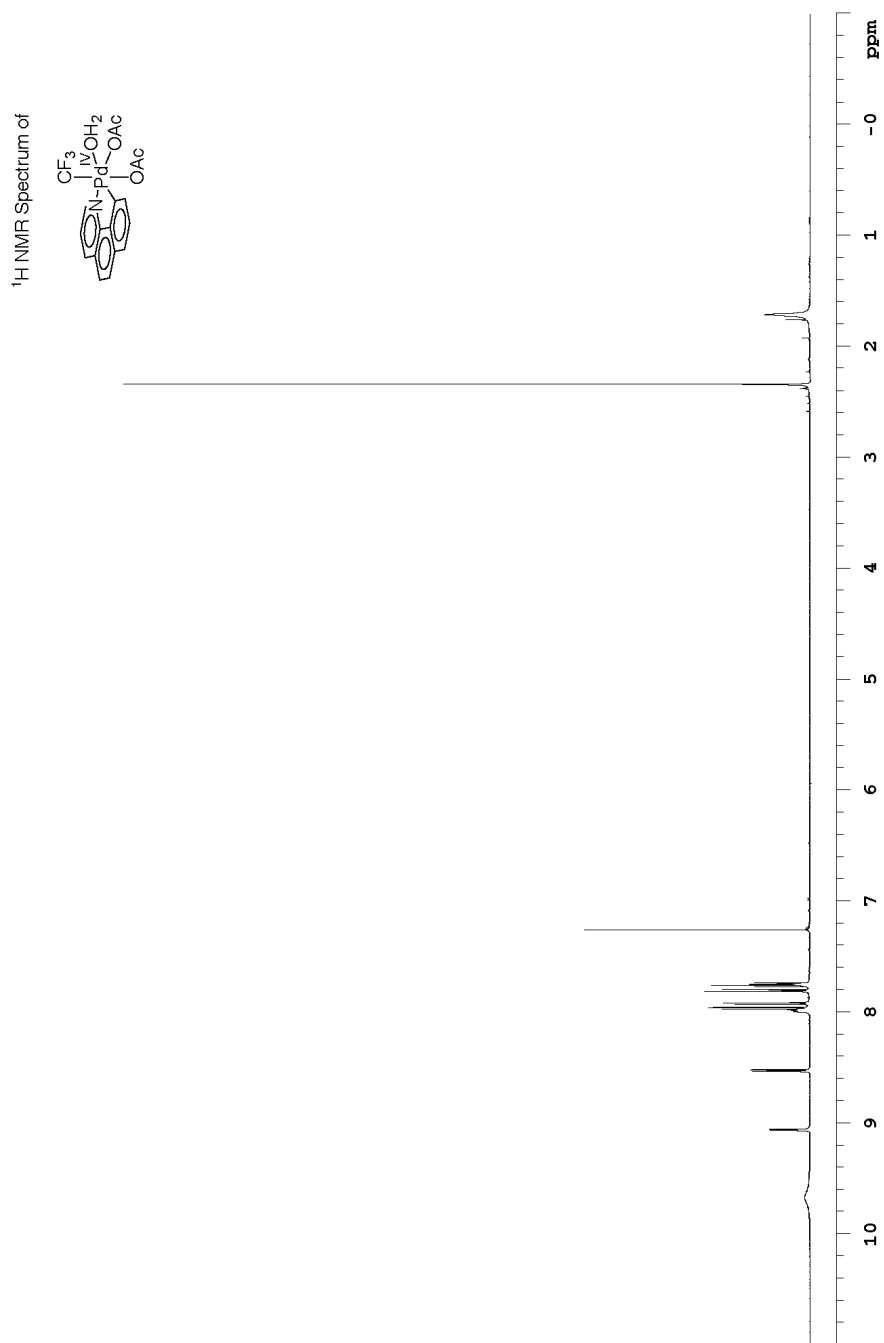
¹³C NMR spectrum of **1** in CDCl₃ at 23 °C.



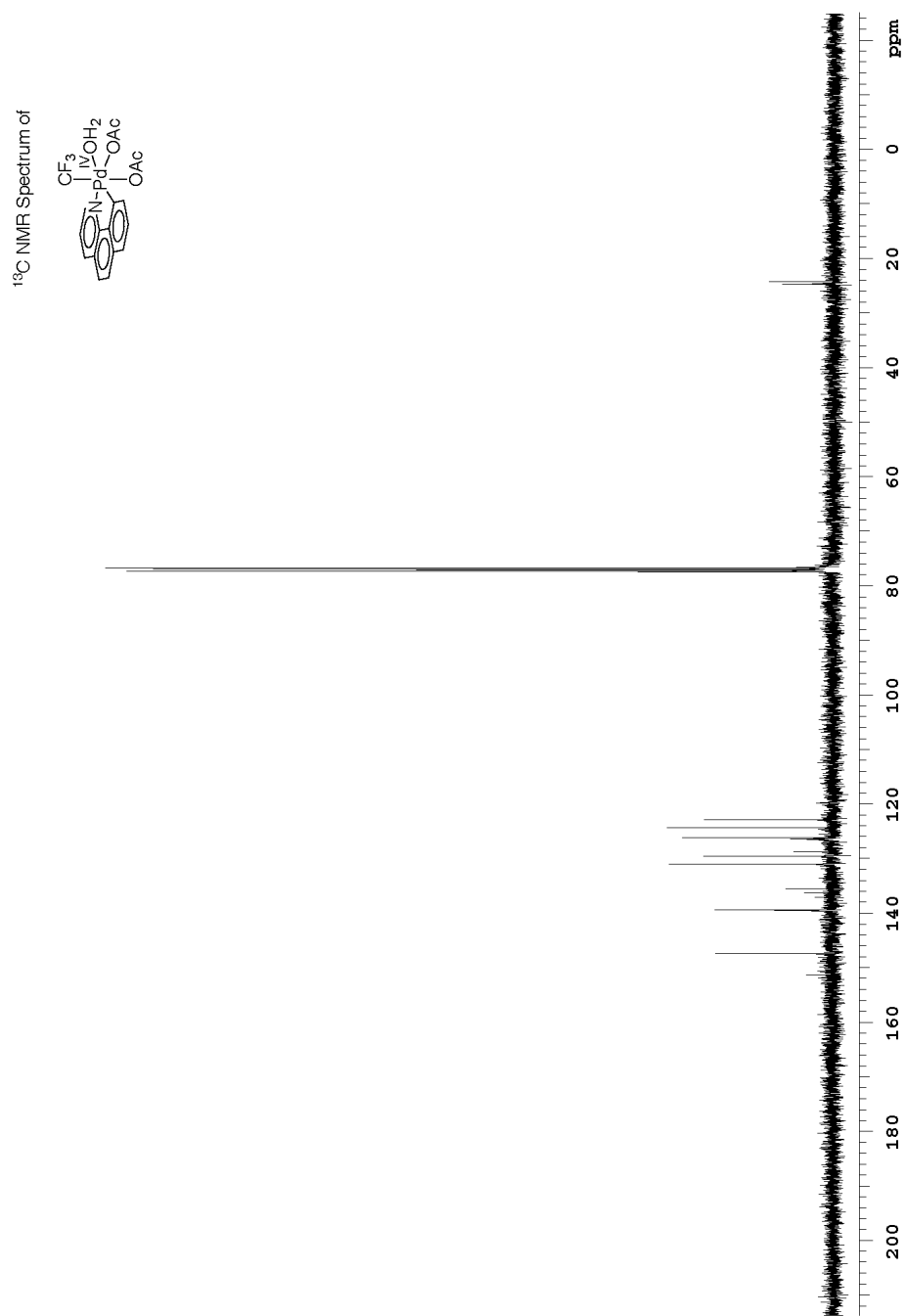
¹H NMR spectrum of **4** in CDCl₃ at 23 °C.



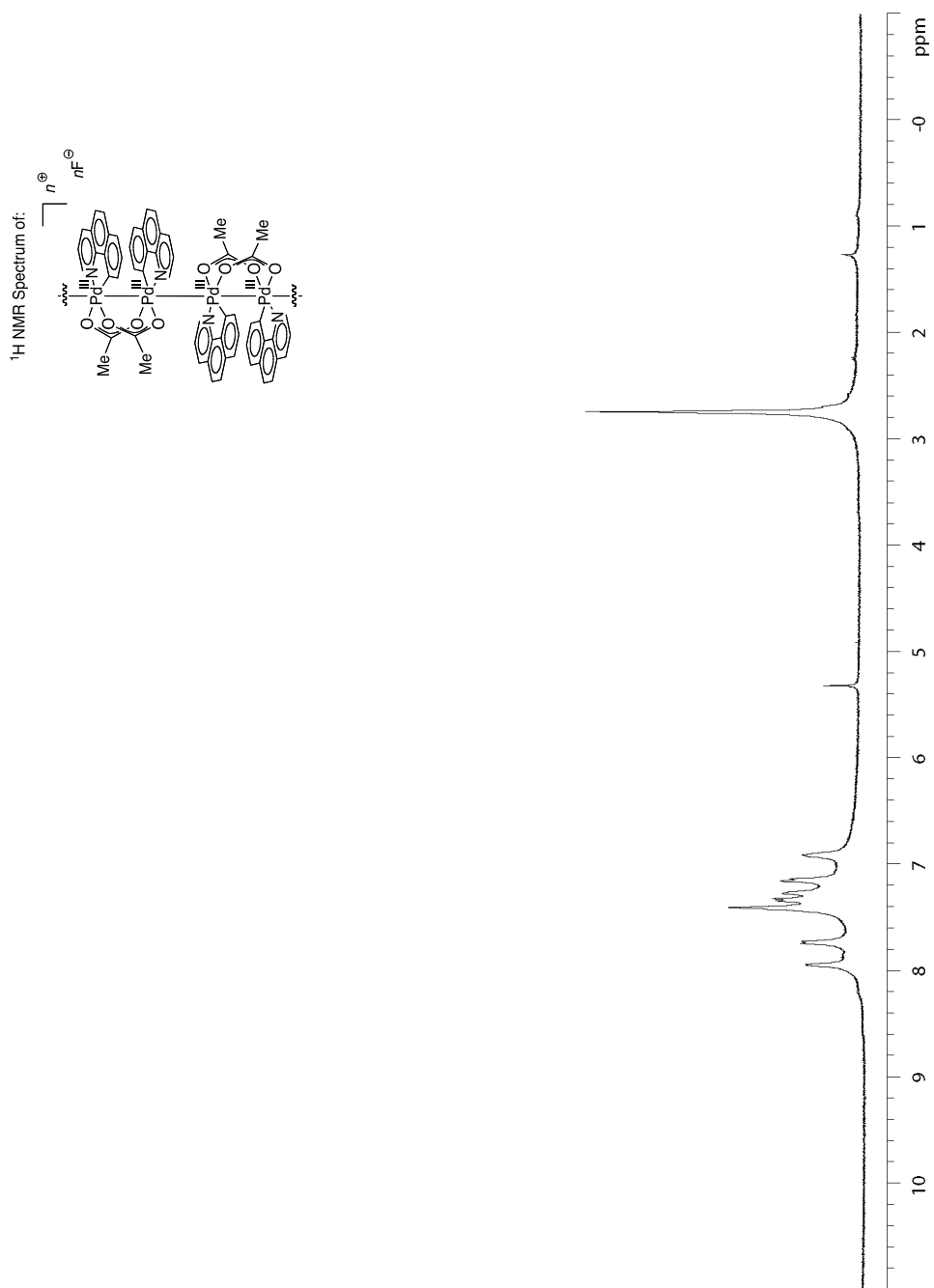
¹³C NMR spectrum of **4** in CDCl₃ at 23 °C.



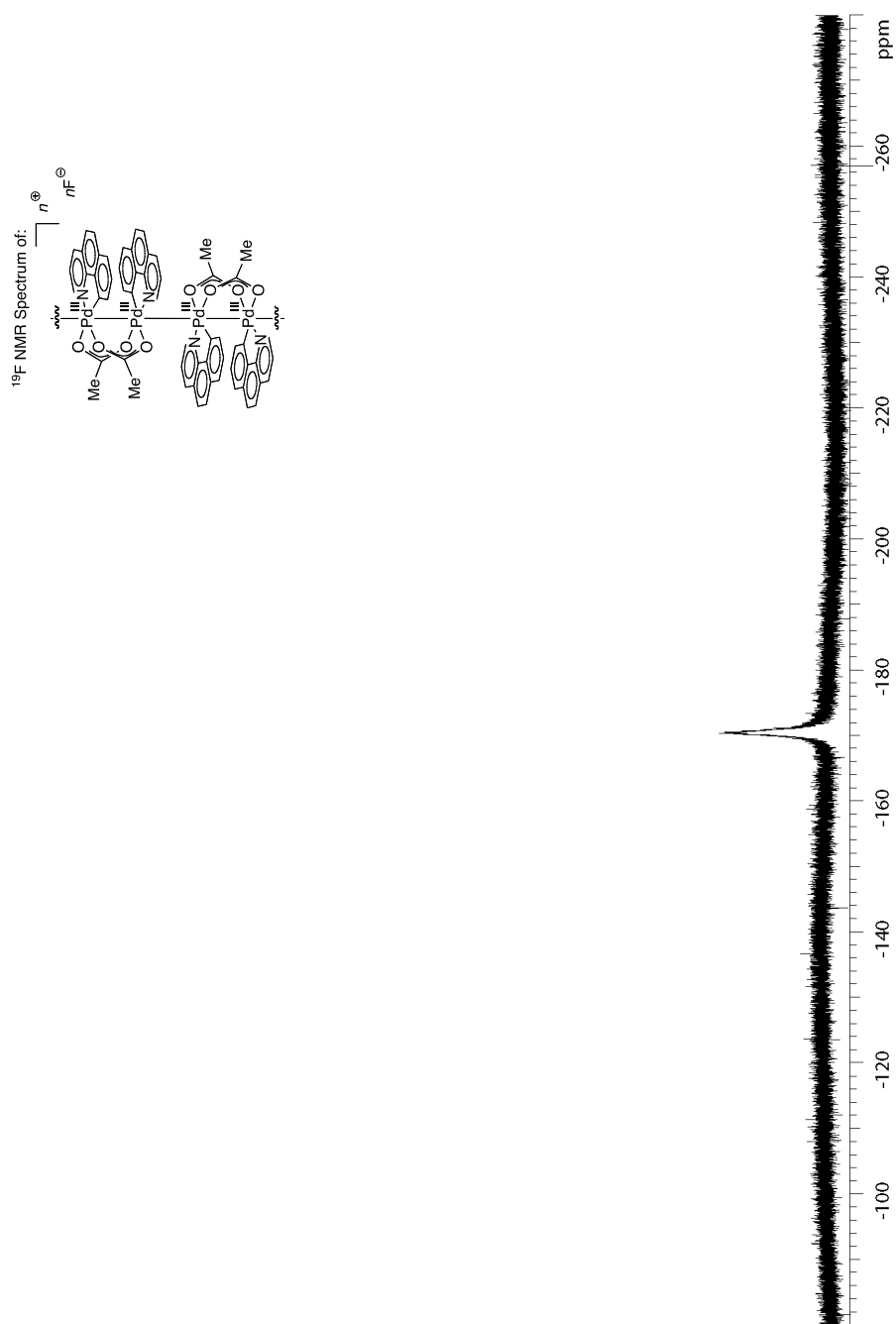
¹H NMR spectrum of **5** in CDCl₃ at 23 °C.



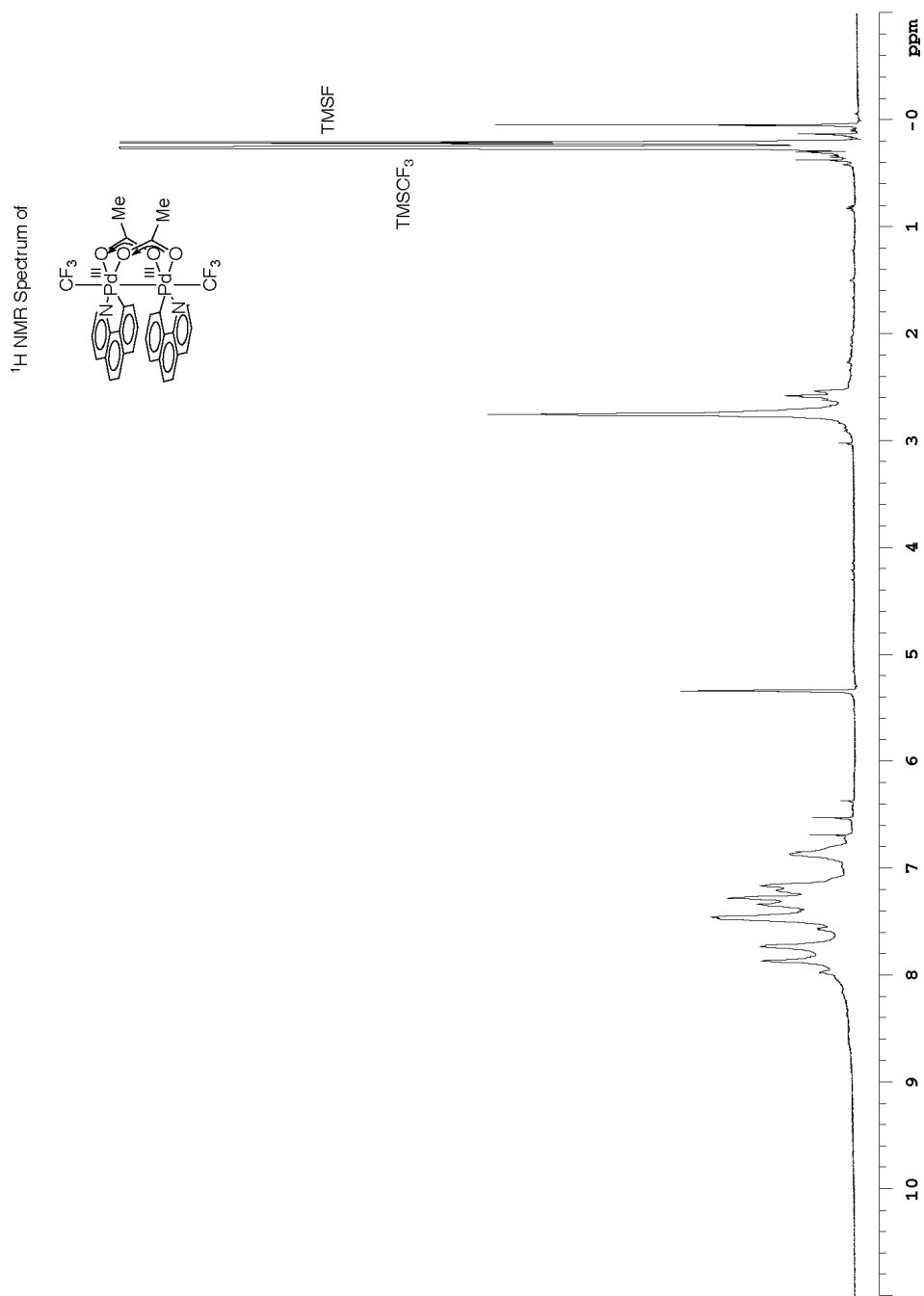
¹³C NMR spectrum of **5** in CDCl₃ at 23 °C.



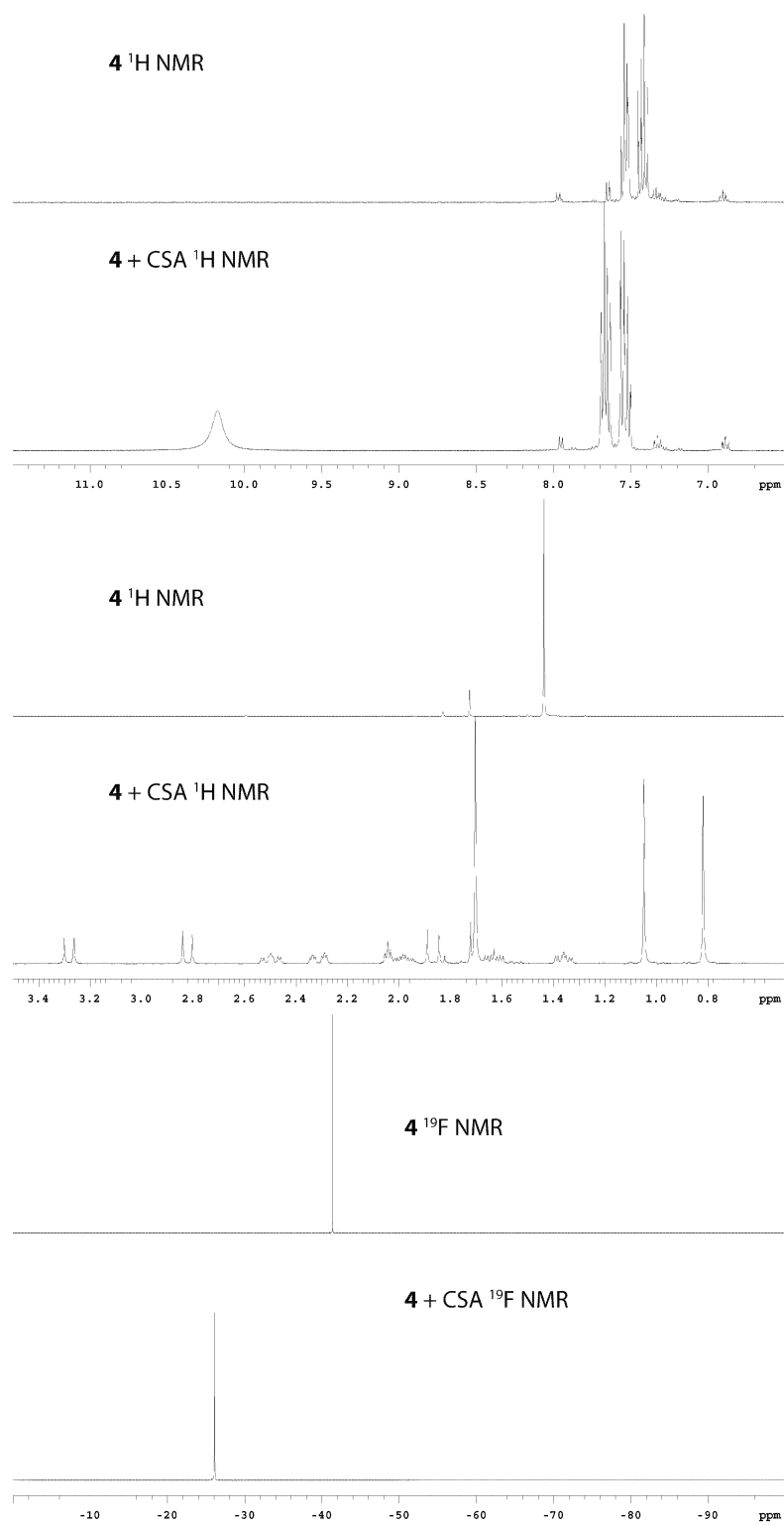
¹H NMR of **8** in CD₂Cl₂ at -10 °C

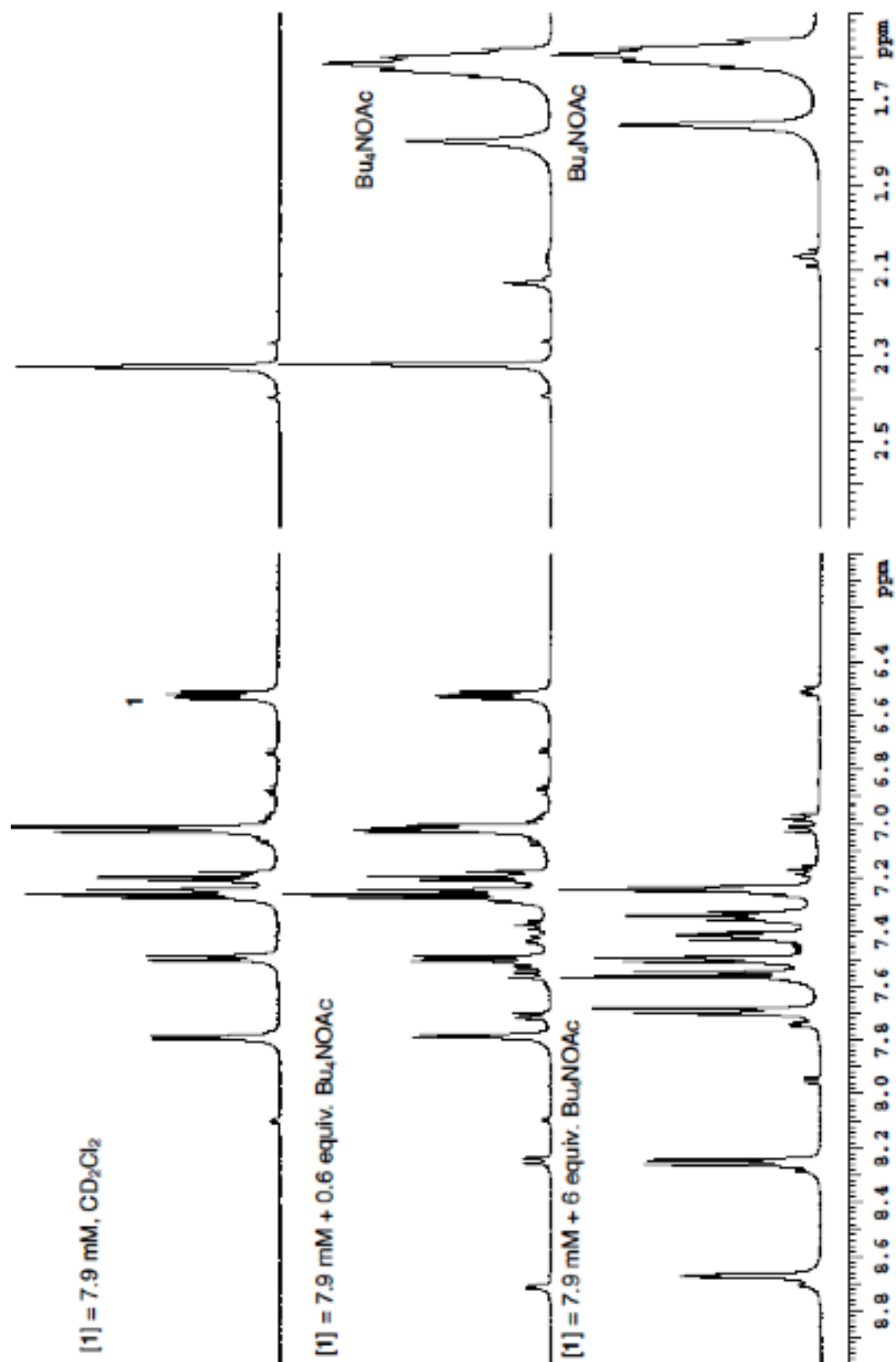


^{19}F NMR of **8** in CD_2Cl_2 at $-10\text{ }^\circ\text{C}$



¹H NMR spectrum of **9** in CD₂Cl₂ at -80 °C.





Computational Results

Cartesian coordinates and electronic energies (E), enthalpies (H) and Gibbs free energies for all of the calculated structures

Structure A

(optimized by M06/BS1)

E (BS1) = -2156.72570336 au

H (BS1) = -2156.220911 au

G(BS1) = -2156.326051 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2159.70179856 au

E(BP86/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2161.14718805 au

E(TPSS/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2161.15063087 au

E(wB97XD/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2160.33723973 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | -0.468393 | -1.279002 | -1.459351 | C | 3.311429 | 2.106494 | 1.676961 |
| Pd | -1.463970 | 0.296426 | 0.559093 | H | 5.551474 | 0.334744 | -0.807808 |
| N | 1.126257 | -0.067933 | -1.954114 | H | 4.319279 | 2.095533 | 2.090003 |
| N | 0.230968 | 0.066013 | 1.704602 | C | 4.554242 | -1.379628 | -0.019604 |
| C | 1.123527 | 1.011542 | -2.726322 | C | 2.901812 | 3.130547 | 0.876124 |
| C | 0.536028 | -0.950043 | 2.502281 | H | 5.444064 | -1.755035 | 0.485882 |
| H | 0.177173 | 1.256838 | -3.206511 | H | 3.582115 | 3.950975 | 0.649050 |
| H | -0.236588 | -1.702191 | 2.649930 | C | 3.342370 | -2.143194 | 0.077738 |
| C | 2.278709 | 1.787058 | -2.897953 | C | 1.579406 | 3.169624 | 0.318785 |
| C | 1.796956 | -1.029720 | 3.106888 | C | 3.218192 | -3.359237 | 0.778524 |
| H | 2.017789 | -1.871786 | 3.756800 | C | 1.086090 | 4.203160 | -0.503236 |
| C | 3.444363 | 1.427250 | -2.248868 | H | 4.088668 | -3.781098 | 1.280149 |
| C | 2.740613 | -0.051952 | 2.855713 | H | 1.726644 | 5.052748 | -0.736923 |
| H | 4.349542 | 2.022958 | -2.365979 | C | 2.006580 | -4.023518 | 0.804051 |
| H | 3.729346 | -0.110681 | 3.310378 | C | -0.204622 | 4.151484 | -0.992178 |
| C | 3.472001 | 0.274955 | -1.441735 | H | 1.929397 | -4.976361 | 1.325761 |
| C | 2.428196 | 1.028169 | 2.010628 | H | -0.579523 | 4.968591 | -1.606043 |
| C | 4.617358 | -0.221455 | -0.736608 | C | 0.857928 | -3.502787 | 0.166384 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | -1.064995 | 3.063896 | -0.714250 | C | -2.959622 | 0.410504 | -1.913360 |
| H | -0.077293 | -4.060408 | 0.200029 | C | -3.364641 | -3.676310 | 0.658044 |
| H | -2.082009 | 3.060154 | -1.102385 | C | -4.179143 | 0.758710 | -2.713487 |
| C | 0.946649 | -2.304294 | -0.510086 | H | -4.357717 | -3.275989 | 0.891022 |
| C | -0.583685 | 2.039534 | 0.062233 | H | -4.838795 | -0.117761 | -2.738640 |
| C | 2.192735 | -1.643439 | -0.568045 | H | -3.438602 | -4.414659 | -0.143381 |
| C | 0.711591 | 2.096539 | 0.605802 | H | -4.732463 | 1.582724 | -2.254610 |
| C | 2.273948 | -0.450189 | -1.329122 | H | -2.991870 | -4.152422 | 1.572730 |
| C | 1.137672 | 1.048385 | 1.457888 | H | -3.897936 | 0.998160 | -3.742655 |
| O | -1.925173 | -2.594855 | -0.873738 | H | 2.238929 | 2.663760 | -3.538747 |
| O | -3.066574 | 0.630315 | -0.650085 | C | -2.421883 | 1.361919 | 2.058901 |
| O | -2.253107 | -1.647045 | 1.142199 | F | -1.550373 | 1.979937 | 2.834887 |
| O | -1.955821 | -0.057813 | -2.488409 | F | -3.254619 | 2.232630 | 1.544011 |
| C | -2.449606 | -2.548027 | 0.281983 | F | -3.073815 | 0.463259 | 2.759569 |

Structure B

(optimized by M06/BS1)

E (BS1) = -2385.25344878 au

H (BS1) = -2384.692743 au

G(BS1) = -2384.809328 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.28981153 au

E(BP86/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2389.87043061 au

E(TPSS/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2389.86983886 au

E(wB97XD/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.97595176 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|----------|-----------|
| Pd | -1.740692 | 0.047163 | 0.319334 | C | 2.044272 | 1.245166 | -3.124271 |
| Pd | 0.284750 | -1.597358 | -0.345126 | H | 1.916534 | 1.527374 | -4.166146 |
| O | -1.998917 | -1.388555 | 1.922974 | C | 1.282255 | 2.987963 | 2.624460 |
| N | 1.315154 | -0.098432 | -1.309853 | C | 3.004935 | 1.844273 | -2.333399 |
| C | -0.152007 | 1.058493 | 2.715778 | H | 2.005045 | 3.660695 | 3.086017 |
| C | 1.204945 | 0.266249 | -2.575833 | H | 3.660298 | 2.613803 | -2.741945 |
| H | -0.572486 | 0.189331 | 3.218112 | C | 0.889326 | 3.203929 | 1.293022 |
| H | 0.425685 | -0.229056 | -3.152458 | C | 3.155731 | 1.441730 | -0.995040 |
| C | 0.752782 | 1.928207 | 3.336221 | C | -0.083129 | 3.505686 | -1.381041 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | 3.407725 | 0.361982 | 1.643630 | H | -3.442294 | -3.580629 | -2.264945 |
| C | -0.616618 | 3.604899 | -2.679932 | H | -3.142907 | -3.482106 | 2.895450 |
| C | 3.516613 | -0.264679 | 2.900627 | H | -4.262233 | -2.082152 | -2.754601 |
| H | -0.303639 | 4.423970 | -3.327072 | H | -1.885813 | -4.623841 | 2.295035 |
| H | 4.277667 | 0.072727 | 3.604549 | H | -2.863581 | -2.720224 | -3.698200 |
| C | -1.540127 | 2.676440 | -3.122490 | H | -1.541075 | -3.514242 | 3.643433 |
| C | 2.685356 | -1.323211 | 3.219940 | H | 1.048435 | 1.734976 | 4.363800 |
| H | -1.960292 | 2.773799 | -4.122801 | O | 1.543508 | -3.339723 | -0.904262 |
| H | 2.800142 | -1.820163 | 4.183039 | C | 2.680725 | -3.150852 | -1.474801 |
| C | -1.962176 | 1.598909 | -2.313817 | C | 3.370512 | -4.456891 | -1.856487 |
| C | 1.697663 | -1.792657 | 2.327127 | H | 3.580090 | -5.041210 | -0.952176 |
| H | -2.700301 | 0.893841 | -2.691461 | H | 2.707146 | -5.064282 | -2.483427 |
| H | 1.083674 | -2.654254 | 2.586515 | H | 4.306167 | -4.255678 | -2.387682 |
| C | -1.433245 | 1.471865 | -1.050174 | O | 3.225337 | -2.071895 | -1.718099 |
| C | 1.544717 | -1.162060 | 1.112011 | C | -3.502626 | 1.107537 | 0.823779 |
| C | -0.522136 | 2.434385 | -0.576038 | F | -4.143914 | 0.443608 | 1.781946 |
| C | 2.410501 | -0.106503 | 0.766076 | F | -4.329789 | 1.233419 | -0.212499 |
| C | -0.038340 | 2.300471 | 0.748496 | F | -3.242144 | 2.338918 | 1.287261 |
| C | 2.287625 | 0.440305 | -0.533036 | C | 1.353202 | 4.264371 | 0.447311 |
| O | -2.881694 | -1.097152 | -0.929889 | H | 2.088513 | 4.961223 | 0.848628 |
| O | -0.765819 | -2.944545 | 0.853274 | C | 0.885508 | 4.406940 | -0.824556 |
| O | -1.105588 | -1.969859 | -2.016694 | H | 1.243997 | 5.226350 | -1.448016 |
| N | -0.525267 | 1.248709 | 1.456728 | C | 4.245324 | 1.434899 | 1.185929 |
| C | -2.328057 | -1.830522 | -1.827769 | H | 5.006666 | 1.821940 | 1.864258 |
| C | -1.585818 | -2.565935 | 1.738812 | C | 4.128082 | 1.948974 | -0.071582 |
| C | -3.292734 | -2.585084 | -2.701039 | H | 4.794604 | 2.743613 | -0.407353 |
| C | -2.077107 | -3.623352 | 2.691240 | | | | |

Structure C

(optimized by M06/BS1)

E (BS1) = -2385.23561626 au

H (BS1) = -2384.675740 au

G(BS1) = -2384.790038 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.26914466 au

E(BP86/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2389.84081703 au

E(TPSS/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2389.86701062 au

E(wB97XD/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.95201030 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | 0.250468 | -1.587650 | 0.407505 | H | 2.648877 | 2.051909 | 1.946095 |
| Pd | 1.464856 | 0.711819 | -0.680206 | C | -1.295203 | -1.767047 | -0.886795 |
| O | 1.555225 | -1.343273 | 2.081858 | C | 0.929870 | 2.028439 | 0.668402 |
| N | -0.419086 | 1.175050 | -1.455817 | C | -2.422062 | -1.070417 | -0.407946 |
| C | -0.946711 | 0.070793 | 2.662522 | C | -0.350050 | 2.568166 | 0.436065 |
| C | -0.911226 | 0.844534 | -2.641214 | C | -2.320837 | -0.395042 | 0.835782 |
| H | 0.034386 | -0.082235 | 3.111214 | C | -1.039097 | 2.138290 | -0.722967 |
| H | -0.352334 | 0.098566 | -3.203433 | O | 1.513080 | -2.668034 | -0.749041 |
| C | -1.963746 | 0.833567 | 3.252029 | O | 3.189621 | -0.779221 | 0.664022 |
| C | -2.103285 | 1.404715 | -3.122331 | O | 1.984214 | -0.912577 | -2.101238 |
| H | -2.477514 | 1.095292 | -4.094845 | N | -1.136451 | -0.513987 | 1.488089 |
| C | -3.173140 | 0.982475 | 2.601132 | C | 2.169602 | -2.066923 | -1.684606 |
| C | -2.799896 | 2.304916 | -2.339534 | C | 2.785728 | -1.082746 | 1.787127 |
| H | -3.968059 | 1.585400 | 3.040209 | C | 3.268288 | -2.900624 | -2.278685 |
| H | -3.747320 | 2.722536 | -2.681192 | C | 3.734129 | -1.160811 | 2.961338 |
| C | -3.386782 | 0.354879 | 1.361111 | H | 4.176255 | -2.667356 | -1.706797 |
| C | -2.267661 | 2.707638 | -1.102705 | H | 3.726002 | -2.172727 | 3.383017 |
| C | -3.625789 | -1.006298 | -1.141058 | H | 3.066019 | -3.971333 | -2.188048 |
| C | -0.930594 | 3.527395 | 1.291729 | H | 4.747869 | -0.892356 | 2.652855 |
| C | -3.679782 | -1.695394 | -2.367698 | H | 3.438489 | -2.615244 | -3.320657 |
| C | -0.197766 | 3.906948 | 2.432386 | H | 3.396821 | -0.480267 | 3.753378 |
| H | -4.597100 | -1.671360 | -2.955719 | H | -1.774093 | 1.315481 | 4.207393 |
| H | -0.615005 | 4.642533 | 3.120508 | O | 3.452467 | 1.621460 | -0.584205 |
| C | -2.579082 | -2.401324 | -2.815619 | C | 3.348575 | 2.602797 | -1.406467 |
| C | 1.055554 | 3.363507 | 2.661996 | C | 4.634878 | 3.375986 | -1.625001 |
| H | -2.636257 | -2.940125 | -3.760641 | H | 5.131892 | 3.572143 | -0.668433 |
| H | 1.618673 | 3.677938 | 3.540576 | H | 5.320695 | 2.768226 | -2.228266 |
| C | -1.375474 | -2.446827 | -2.080031 | H | 4.436050 | 4.315290 | -2.149791 |
| C | 1.642657 | 2.434518 | 1.777384 | O | 2.314372 | 2.918983 | -2.012120 |
| H | -0.531534 | -3.023583 | -2.454165 | C | -0.341399 | -3.435264 | 1.152594 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| F | 0.638932 | -3.919442 | 1.887175 | H | -5.629085 | -0.163346 | -1.173911 |
| F | -0.603847 | -4.300926 | 0.186895 | C | -2.220845 | 4.045095 | 0.934210 |
| F | -1.426803 | -3.303463 | 1.911621 | H | -2.681622 | 4.782342 | 1.592882 |
| C | -4.590180 | 0.429527 | 0.586969 | C | -2.855530 | 3.664715 | -0.211572 |
| H | -5.419143 | 1.020387 | 0.975431 | H | -3.818494 | 4.098919 | -0.480955 |
| C | -4.702644 | -0.225262 | -0.602513 | | | | |

Structure D

(optimized by M06/BS1)

E (BS1) = -2385.2597535 au

H (BS1) = -2384.697839 au

G(BS1) = -2384.809347 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.29265303 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | 0.833199 | -1.196923 | 0.465134 | C | -2.097650 | 3.956603 | 1.580036 |
| Pd | 0.839902 | 1.220944 | -1.024269 | H | -4.033336 | -3.656953 | -1.811765 |
| O | 2.104571 | -0.097895 | 1.714110 | H | -2.808508 | 4.555213 | 2.150256 |
| N | -1.045735 | 0.758142 | -1.795853 | C | -1.887377 | -3.606885 | -1.961523 |
| C | -0.603956 | 0.399258 | 2.630883 | C | -0.739718 | 4.051508 | 1.827657 |
| C | -1.355990 | -0.051441 | -2.798115 | H | -1.860256 | -4.331459 | -2.774790 |
| H | 0.416515 | 0.683579 | 2.891444 | H | -0.385471 | 4.734452 | 2.599840 |
| H | -0.522209 | -0.568739 | -3.270791 | C | -0.671849 | -3.069923 | -1.487515 |
| C | -1.748914 | 0.895756 | 3.269939 | C | 0.205227 | 3.291436 | 1.107717 |
| C | -2.683361 | -0.243136 | -3.206811 | H | 0.276040 | -3.383701 | -1.922848 |
| H | -2.893955 | -0.921440 | -4.029428 | H | 1.268871 | 3.372437 | 1.328504 |
| C | -2.998874 | 0.492030 | 2.845106 | C | -0.698197 | -2.158833 | -0.456137 |
| C | -3.700348 | 0.409098 | -2.537697 | C | -0.227325 | 2.432851 | 0.115750 |
| H | -3.898714 | 0.882269 | 3.321477 | C | -1.932783 | -1.803432 | 0.120160 |
| H | -4.741629 | 0.254654 | -2.822323 | C | -1.612266 | 2.336857 | -0.138392 |
| C | -3.121466 | -0.423079 | 1.784004 | C | -1.929469 | -0.882120 | 1.200080 |
| C | -3.393710 | 1.283783 | -1.480963 | C | -2.034018 | 1.441137 | -1.156685 |
| C | -3.158077 | -2.311037 | -0.362528 | O | 2.143285 | -2.032113 | -0.825159 |
| C | -2.569414 | 3.082867 | 0.581679 | O | 4.044126 | -0.477755 | 0.617919 |
| C | -3.105780 | -3.236711 | -1.422653 | O | 2.012015 | -0.234086 | -2.185371 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| N | -0.712089 | -0.461961 | 1.630769 | H | 5.108258 | 2.162079 | -0.491658 |
| C | 2.542095 | -1.291906 | -1.798358 | H | 5.019344 | 3.577937 | -1.600512 |
| C | 3.384814 | 0.056916 | 1.495284 | O | 2.599509 | 2.942357 | -2.202841 |
| C | 3.765265 | -1.810312 | -2.491547 | C | -4.355640 | -0.926921 | 1.257795 |
| C | 4.008771 | 1.016975 | 2.488873 | H | -5.287802 | -0.568073 | 1.693811 |
| H | 4.617545 | -1.496913 | -1.874906 | C | -4.369650 | -1.835000 | 0.241882 |
| H | 3.734132 | 0.754661 | 3.517572 | H | -5.318926 | -2.215649 | -0.136486 |
| H | 3.766631 | -2.903590 | -2.534953 | C | 1.158838 | -2.900344 | 1.573020 |
| H | 5.097839 | 1.017893 | 2.382207 | F | 2.389388 | -2.866954 | 2.028830 |
| H | 3.857800 | -1.373557 | -3.489478 | F | 0.999856 | -4.001419 | 0.859624 |
| H | 3.621980 | 2.023191 | 2.282700 | F | 0.308394 | -2.925054 | 2.594125 |
| H | -1.632788 | 1.614613 | 4.076442 | C | -3.955107 | 2.887061 | 0.263289 |
| O | 2.552856 | 1.945399 | -0.206348 | H | -4.699189 | 3.453383 | 0.824878 |
| C | 3.133334 | 2.648519 | -1.136299 | C | -4.351651 | 2.029638 | -0.719312 |
| C | 4.537689 | 3.057792 | -0.768018 | H | -5.409197 | 1.902080 | -0.950894 |
| H | 4.518855 | 3.712980 | 0.112215 | | | | |

Structure E

(optimized by M06/BS1)

E (BS1) = -2385.25240435 au

H (BS1) = -2384.692273 au

G(BS1) = -2384.806315 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.28617677 au

| | | | | | | | |
|----|-------------|-------------|-------------|---|-------------|-------------|-------------|
| Pd | 0.83319900 | -1.19692300 | 0.46513400 | H | -2.86548800 | -0.91114900 | -3.87201100 |
| Pd | 0.77919900 | 1.64531800 | -1.08890400 | C | -3.02651900 | 0.52401400 | 2.80037100 |
| O | 2.07016100 | 0.01422400 | 1.63541800 | C | -3.72536200 | 0.50643700 | -2.49300100 |
| N | -1.08348000 | 1.03145900 | -1.80217000 | H | -3.93182400 | 0.90679500 | 3.27183500 |
| C | -0.63602000 | 0.52193600 | 2.52869700 | H | -4.75998900 | 0.28840700 | -2.75980800 |
| C | -1.36370100 | 0.13056800 | -2.73408500 | C | -3.13116900 | -0.47471200 | 1.81426700 |
| H | 0.37573700 | 0.86613100 | 2.74721600 | C | -3.45273900 | 1.46928300 | -1.50577900 |
| H | -0.51032300 | -0.37282000 | -3.18597200 | C | -3.14739300 | -2.36773100 | -0.32630400 |
| C | -1.78876100 | 1.02584100 | 3.14848300 | C | -2.70320500 | 3.34361400 | 0.51976800 |
| C | -2.68351700 | -0.15737500 | -3.11032100 | C | -3.08974400 | -3.26647100 | -1.40965900 |

| | | | | | | | |
|---|-------------|-------------|-------------|---|-------------|-------------|-------------|
| C | -2.26840300 | 4.24412100 | 1.51135900 | H | 3.67872400 | 0.95248700 | 3.41502600 |
| H | -4.01352500 | -3.69956900 | -1.79353100 | H | 3.93128700 | -2.55968600 | -2.50753200 |
| H | -3.00409300 | 4.80859000 | 2.08485700 | H | 4.97849400 | 1.36225300 | 2.24779700 |
| C | -1.87285600 | -3.60028600 | -1.97433400 | H | 3.86337100 | -0.99302700 | -3.40504400 |
| C | -0.91404700 | 4.41672300 | 1.73978900 | H | 3.41859100 | 2.23579400 | 2.21513000 |
| H | -1.84387100 | -4.30281300 | -2.80648500 | H | -1.68660900 | 1.81670500 | 3.88640000 |
| H | -0.58911600 | 5.12153200 | 2.50524900 | O | 2.47327700 | 2.40374300 | -0.26274700 |
| C | -0.66006600 | -3.05890500 | -1.49661500 | C | 3.24126300 | 2.78912500 | -1.24592500 |
| C | 0.06339400 | 3.71556800 | 1.00386900 | C | 4.66938100 | 3.03355500 | -0.82520700 |
| H | 0.28930800 | -3.34710800 | -1.94624500 | H | 4.71092500 | 3.66039800 | 0.07349800 |
| H | 1.12431600 | 3.86972300 | 1.19652800 | H | 5.12226500 | 2.06533100 | -0.57143300 |
| C | -0.69272700 | -2.17264200 | -0.44491600 | H | 5.23112400 | 3.50377000 | -1.63731600 |
| C | -0.33253500 | 2.82769500 | 0.02188700 | O | 2.86053000 | 2.91139500 | -2.40552600 |
| C | -1.92756400 | -1.83728000 | 0.14516900 | C | -4.35626100 | -1.04558800 | 1.33678600 |
| C | -1.71516600 | 2.64301100 | -0.20423400 | H | -5.29007600 | -0.72670200 | 1.79896900 |
| C | -1.93482300 | -0.90430500 | 1.21598600 | C | -4.36045100 | -1.94923400 | 0.31698100 |
| C | -2.10063600 | 1.69832100 | -1.19135000 | H | -5.30296800 | -2.36610900 | -0.03872600 |
| O | 2.17399600 | -1.96395100 | -0.82282100 | C | 1.17718300 | -2.87184100 | 1.56764600 |
| O | 4.00067300 | -0.19106200 | 0.48359400 | F | 2.37999300 | -2.75858100 | 2.07790000 |
| O | 1.92210600 | -0.07911100 | -2.03252000 | F | 1.11441500 | -3.96905000 | 0.84316300 |
| N | -0.72541500 | -0.42530100 | 1.60627600 | F | 0.28070800 | -2.93793700 | 2.54148400 |
| C | 2.53940200 | -1.10936600 | -1.72766000 | C | -4.07939900 | 3.09590100 | 0.19461200 |
| C | 3.32702600 | 0.27660100 | 1.39002100 | H | -4.84637500 | 3.64669600 | 0.74058300 |
| C | 3.81260700 | -1.47502200 | -2.42510100 | C | -4.44018500 | 2.20953700 | -0.77619800 |
| C | 3.89757900 | 1.26371900 | 2.38667200 | H | -5.49130300 | 2.04111600 | -1.01076400 |
| H | 4.61863500 | -1.08994300 | -1.78681400 | | | | |

Structure F

(optimized by M06/BS1)

E (BS1) = -2385.25358776 au

H (BS1) = -2384.691364 au

G(BS1) = -2384.807530 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.28754324 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | -2.007806 | -1.066554 | 0.393992 | C | 3.797583 | 1.650244 | 0.241133 |
| Pd | 2.275160 | -0.607999 | -0.522208 | C | -3.157126 | 1.532179 | 0.711851 |
| O | -1.095000 | -1.941829 | 2.209655 | C | 2.725699 | 2.236310 | -0.480611 |
| N | 1.817876 | 1.365232 | -0.994524 | O | -1.227730 | -2.606747 | -0.650208 |
| C | -2.951552 | 0.542605 | 2.811510 | O | -0.085350 | -0.301624 | 1.158286 |
| C | 0.756918 | 1.833167 | -1.635235 | O | 0.370697 | -1.307441 | -1.517677 |
| H | -2.648703 | -0.343144 | 3.368631 | N | -2.832040 | 0.474414 | 1.493525 |
| H | 0.057212 | 1.085212 | -2.007704 | C | -0.117273 | -2.421760 | -1.293931 |
| C | -3.429035 | 1.707106 | 3.425920 | C | -0.070202 | -1.200440 | 2.055825 |
| C | 0.551646 | 3.208285 | -1.818148 | C | 0.490087 | -3.697889 | -1.804305 |
| H | -0.335373 | 3.544437 | -2.351641 | C | 1.159748 | -1.410773 | 2.873105 |
| C | -3.763457 | 2.800810 | 2.649874 | H | 0.595996 | -4.413356 | -0.981122 |
| C | 1.478024 | 4.105018 | -1.321465 | H | 0.931774 | -1.950111 | 3.797236 |
| H | -4.129594 | 3.716191 | 3.114190 | H | -0.188655 | -4.148566 | -2.538937 |
| H | 1.342879 | 5.178679 | -1.456624 | H | 1.859522 | -2.005320 | 2.263798 |
| C | -3.629946 | 2.740314 | 1.251621 | H | 1.464737 | -3.494373 | -2.258475 |
| C | 2.604665 | 3.631321 | -0.626892 | H | 1.648262 | -0.452803 | 3.080703 |
| C | -3.298722 | 2.407105 | -1.569146 | H | -3.523863 | 1.734800 | 4.507799 |
| C | 4.783792 | 2.476674 | 0.820571 | O | 2.772650 | -2.453920 | 0.242820 |
| C | -3.121742 | 2.175077 | -2.946443 | C | 3.458727 | -3.206944 | -0.566479 |
| C | 5.812919 | 1.852847 | 1.550128 | C | 3.929348 | -4.493672 | 0.084163 |
| H | -3.350032 | 2.968740 | -3.657403 | H | 3.101661 | -4.989750 | 0.605710 |
| H | 6.594799 | 2.460506 | 2.005928 | H | 4.358004 | -5.165542 | -0.664815 |
| C | -2.673265 | 0.945777 | -3.392952 | H | 4.691853 | -4.266532 | 0.840935 |
| C | 5.817744 | 0.476973 | 1.689342 | O | 3.718560 | -2.947831 | -1.735989 |
| H | -2.545343 | 0.777481 | -4.461084 | C | -3.785549 | -1.995087 | 0.088215 |
| H | 6.616303 | 0.002663 | 2.259960 | F | -3.798474 | -2.992263 | 0.964793 |
| C | -2.369822 | -0.106454 | -2.501814 | F | -3.944703 | -2.491341 | -1.126768 |
| C | 4.818450 | -0.335094 | 1.116044 | F | -4.823941 | -1.196317 | 0.346875 |
| H | -2.004567 | -1.057550 | -2.880952 | C | -3.930073 | 3.803095 | 0.337545 |
| H | 4.839712 | -1.414771 | 1.259583 | H | -4.292180 | 4.747721 | 0.741440 |
| C | -2.520946 | 0.112825 | -1.154701 | C | -3.768803 | 3.640675 | -1.005348 |
| C | 3.803324 | 0.241562 | 0.376389 | H | -4.004011 | 4.460122 | -1.684406 |
| C | -2.990418 | 1.351598 | -0.685002 | C | 4.664553 | 3.895799 | 0.641209 |

H 5.430180 4.536562 1.080250
C 3.626570 4.451139 -0.044984

H 3.552562 5.532654 -0.159180

Structure G

(optimized by M06/BS1)

E (BS1) = -2385.25143095 au

H (BS1) = -2384.689759 au

G(BS1) = -2384.804474 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.28138147 au

Pd 1.233962 -1.498816 -0.714669

C -2.998951 3.480674 -2.276379

Pd -3.037614 0.284205 0.621650

H 3.157020 -1.334641 4.156801

O 0.037466 -1.766852 -2.571473

H -3.552049 3.798890 -3.160282

N -1.480211 1.115903 1.707482

C 2.332527 -1.495522 2.172796

C 1.920621 0.707911 -2.731905

C -3.429849 2.327716 -1.583497

C -0.911187 0.625937 2.798118

H 1.880361 -2.463583 2.364391

H 1.384094 0.067264 -3.430142

H -4.294541 1.767701 -1.941901

H -1.338836 -0.292145 3.193881

C 2.210805 -0.883229 0.948284

C 2.420746 1.967406 -3.082925

C -2.746115 1.911961 -0.457943

C 0.204770 1.244738 3.382454

C 2.809715 0.370364 0.729415

H 0.643394 0.811803 4.278078

C -1.635132 2.673527 -0.037116

C 3.082686 2.725318 -2.136111

C 2.713014 0.961142 -0.557469

C 0.742087 2.375336 2.801632

C -0.962298 2.229859 1.126112

H 3.476501 3.708975 -2.391447

O 0.317451 -3.133322 -0.013148

H 1.613589 2.863802 3.240108

O -0.713475 -0.495138 -0.950485

C 3.253719 2.229569 -0.833106

O -0.575821 -2.012471 1.730698

C 0.163495 2.901193 1.632054

N 2.071535 0.232839 -1.502829

C 3.517394 1.041069 1.751078

C -0.535451 -2.968190 0.977306

C -1.181216 3.818525 -0.722237

C -0.884711 -1.043507 -2.081976

C 3.634366 0.398848 2.996307

C -1.488998 -4.136791 1.071885

C -1.898072 4.212593 -1.869277

C -2.156225 -0.816642 -2.835373

H 4.184154 0.886172 3.801722

H -2.168604 -4.107094 0.210806

H -1.583884 5.096368 -2.425147

H -2.181601 -1.424828 -3.743917

C 3.056669 -0.841605 3.190617

H -0.948069 -5.088341 1.026806

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | -3.017952 | -1.041169 | -2.192003 | F | 2.606417 | -3.357059 | -2.085848 |
| H | -2.075864 | -4.061238 | 1.990665 | F | 3.120130 | -3.497647 | -0.000427 |
| H | -2.237064 | 0.247081 | -3.094981 | F | 3.970927 | -1.933774 | -1.212223 |
| H | 2.278380 | 2.331494 | -4.096581 | C | 3.932667 | 2.910239 | 0.229511 |
| O | -4.563394 | -0.733713 | -0.406599 | H | 4.352959 | 3.895533 | 0.029831 |
| C | -4.531060 | -1.715542 | 0.419025 | C | 4.068553 | 2.333126 | 1.455592 |
| C | -5.428033 | -2.888557 | 0.161157 | H | 4.604543 | 2.855857 | 2.248653 |
| H | -6.474298 | -2.561613 | 0.148165 | C | -0.019236 | 4.488187 | -0.208347 |
| H | -5.210606 | -3.311742 | -0.827009 | H | 0.344875 | 5.369850 | -0.738102 |
| H | -5.289229 | -3.653641 | 0.930527 | C | 0.625766 | 4.052471 | 0.911769 |
| O | -3.755348 | -1.691258 | 1.406444 | H | 1.511954 | 4.570768 | 1.281044 |
| C | 2.869800 | -2.655164 | -0.989902 | | | | |

Pd(IV) fragment of Structure G

(optimized by M06/BS1)

E (BS1) = -1475.53269682 au

H (BS1) = -1475.214821 au

G(BS1) = -1475.297780 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -1477.14829983 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | 0.761049 | 0.221420 | 0.151391 | H | 0.826260 | -3.048277 | -0.228995 |
| O | 1.874776 | 2.152072 | 0.164083 | C | -0.477924 | -1.340210 | -0.205002 |
| C | -1.190190 | 2.578521 | 0.333753 | C | -1.800678 | -0.888082 | -0.361929 |
| H | -0.290324 | 3.142323 | 0.576001 | C | -2.083437 | 0.489375 | -0.178912 |
| C | -2.456608 | 3.166681 | 0.232661 | O | 2.533080 | -0.704650 | 0.236621 |
| C | -3.548672 | 2.382543 | -0.087304 | O | 1.280029 | 1.251547 | -1.754474 |
| H | -4.540981 | 2.825072 | -0.173453 | O | 2.262386 | -1.756080 | -1.746120 |
| C | -3.386616 | 1.003739 | -0.303706 | N | -1.026699 | 1.278702 | 0.129157 |
| C | -2.851915 | -1.776684 | -0.678125 | C | 2.937201 | -1.415669 | -0.794419 |
| C | -2.533644 | -3.137654 | -0.830063 | C | 1.877931 | 2.156793 | -1.106965 |
| H | -3.322197 | -3.848312 | -1.075541 | C | 4.398858 | -1.784016 | -0.641966 |
| C | -1.231862 | -3.566327 | -0.660511 | C | 2.589821 | 3.246511 | -1.852604 |
| H | -0.995157 | -4.622691 | -0.777753 | H | 5.010805 | -0.874654 | -0.641518 |
| C | -0.186423 | -2.674977 | -0.340847 | H | 3.054941 | 3.955851 | -1.162992 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | 4.569594 | -2.287437 | 0.316151 | F | 0.919425 | -1.568279 | 2.353820 |
| H | 3.354155 | 2.801132 | -2.499371 | F | -0.648344 | -0.111779 | 2.571542 |
| H | 4.700789 | -2.432475 | -1.468849 | C | -4.436039 | 0.086752 | -0.636781 |
| H | 1.882922 | 3.769108 | -2.507366 | H | -5.448779 | 0.473385 | -0.743582 |
| H | -2.562016 | 4.233807 | 0.408065 | C | -4.174589 | -1.237777 | -0.814072 |
| C | 0.581150 | -0.316374 | 2.093956 | H | -4.983547 | -1.923872 | -1.064905 |
| F | 1.413566 | 0.493261 | 2.738211 | | | | |

Pd(II) fragment of Structure G

(optimized by M06/BS1)

E (BS1) = -909.693380229 au

H (BS1) = -909.452238 au

G(BS1) = -909.514575 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -911.120338273 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | -1.211169 | -0.108619 | 0.000375 | H | -0.958117 | 3.095059 | 0.000656 |
| N | 0.451330 | -1.341284 | 0.000914 | C | 0.192896 | 1.279931 | 0.000466 |
| C | 0.475522 | -2.667691 | 0.000703 | C | 1.501962 | 0.755485 | 0.000205 |
| H | -0.493031 | -3.166326 | 0.001250 | C | 1.624987 | -0.654794 | 0.000291 |
| C | 1.680931 | -3.382548 | -0.000023 | O | -2.975579 | 0.984336 | -0.000751 |
| H | 1.655264 | -4.468881 | -0.000341 | C | -3.696886 | -0.074758 | -0.000737 |
| C | 2.879999 | -2.695066 | -0.000495 | C | -5.185352 | 0.080501 | -0.001044 |
| H | 3.827645 | -3.233882 | -0.001037 | H | -5.496472 | 0.646887 | 0.884438 |
| C | 2.879525 | -1.289788 | -0.000330 | H | -5.495231 | 0.658856 | -0.879138 |
| C | 2.654946 | 1.565090 | -0.000169 | H | -5.675042 | -0.896901 | -0.007661 |
| C | 2.462730 | 2.960123 | -0.000085 | O | -3.151416 | -1.209840 | -0.000150 |
| H | 3.327850 | 3.622990 | -0.000302 | C | 3.931764 | 0.907804 | -0.000728 |
| C | 1.180248 | 3.478270 | 0.000279 | H | 4.830472 | 1.525355 | -0.001067 |
| H | 1.044799 | 4.559549 | 0.000380 | C | 4.042926 | -0.451019 | -0.000861 |
| C | 0.036846 | 2.650471 | 0.000493 | H | 5.024013 | -0.925297 | -0.001405 |

Structure H

(optimized by M06/BS1)

E (BS1) = -1551.95345847 au

H (BS1) = -1551.606365 au

G(BS1) = -1551.689713 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -1553.60037652 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | -0.736070 | 0.110834 | -0.134297 | H | 3.282980 | -3.688457 | 1.816304 |
| N | 1.062350 | 0.995486 | -0.666539 | C | 1.170640 | -3.349465 | 1.616679 |
| O | -1.782533 | 1.860061 | -0.982460 | H | 0.907689 | -4.285851 | 2.106737 |
| H | -2.711532 | 1.543715 | -0.833462 | C | 0.131045 | -2.507969 | 1.163658 |
| H | -1.567401 | 2.496115 | -0.237942 | H | -0.913922 | -2.779719 | 1.295485 |
| O | -2.325095 | -0.951391 | 0.533164 | C | 0.476000 | -1.334173 | 0.549350 |
| O | -3.908973 | 0.482365 | -0.219034 | C | 1.821140 | -0.975493 | 0.375261 |
| O | -0.537899 | 1.050519 | 1.782885 | C | 2.123375 | 0.252785 | -0.263186 |
| O | -0.805618 | 3.171116 | 1.068269 | C | -0.911799 | -0.936935 | -1.871489 |
| C | 1.243908 | 2.158337 | -1.273959 | C | -3.547443 | -0.535206 | 0.364178 |
| H | 0.346653 | 2.699737 | -1.567261 | C | -4.547708 | -1.480303 | 0.986705 |
| C | 2.536156 | 2.644645 | -1.514712 | H | -5.561009 | -1.101807 | 0.830647 |
| H | 2.655264 | 3.602287 | -2.013742 | H | -4.347248 | -1.581642 | 2.059153 |
| C | 3.631801 | 1.905585 | -1.113156 | H | -4.447322 | -2.475702 | 0.539345 |
| H | 4.642003 | 2.273012 | -1.292905 | C | -0.557873 | 2.322404 | 1.942448 |
| C | 3.449176 | 0.670501 | -0.466879 | C | -0.253894 | 2.769464 | 3.355073 |
| C | 4.496333 | -0.191668 | -0.002313 | H | 0.693087 | 2.333965 | 3.693657 |
| H | 5.529070 | 0.120598 | -0.152811 | H | -1.034953 | 2.397795 | 4.029043 |
| C | 4.213211 | -1.373957 | 0.612463 | H | -0.210680 | 3.860424 | 3.413662 |
| H | 5.023701 | -2.015233 | 0.958576 | F | -1.160341 | -2.227647 | -1.667290 |
| C | 2.863635 | -1.812383 | 0.826123 | F | -1.923600 | -0.433617 | -2.570489 |
| C | 2.502712 | -3.018676 | 1.456015 | F | 0.192257 | -0.851218 | -2.619688 |

Structure I

(optimized by M06/BS1)

E (BS1) = -1819.451697 au

H (BS1) = -1818.967087 au

G(BS1) = -1819.063262 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -1822.29296708 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | 1.297863 | -0.746809 | -1.240464 | C | -1.902702 | -1.895012 | 2.604401 |
| Pd | 1.297903 | 0.746788 | 1.240455 | H | -1.994980 | -2.908256 | 2.986769 |
| O | 2.532664 | 0.995739 | -1.679230 | C | -3.018300 | -1.134424 | 2.314035 |
| N | -0.457948 | 0.133923 | -1.906151 | H | -4.020490 | -1.536980 | 2.465258 |
| N | -0.457916 | -0.133906 | 1.906174 | C | -2.863804 | 0.168827 | 1.809981 |
| C | 0.079489 | -2.264360 | -0.883283 | C | -1.548019 | 0.628301 | 1.619667 |
| C | 0.079553 | 2.264366 | 0.883301 | C | -1.275992 | 1.921026 | 1.099123 |
| O | 2.909124 | -1.753903 | -0.420267 | C | -2.344757 | 2.790697 | 0.795849 |
| O | 2.532664 | -0.995793 | 1.679207 | C | -2.024808 | 4.065281 | 0.289928 |
| O | 2.909177 | 1.753843 | 0.420235 | H | -2.825214 | 4.767176 | 0.054283 |
| C | 3.136437 | -1.694306 | 0.827742 | C | -0.700499 | 4.416766 | 0.100667 |
| C | 3.136481 | 1.694224 | -0.827775 | H | -0.462462 | 5.409131 | -0.282625 |
| C | -0.625857 | 1.361113 | -2.379801 | C | 0.354862 | 3.524474 | 0.383164 |
| H | 0.284273 | 1.927592 | -2.571698 | H | 1.386316 | 3.830121 | 0.208832 |
| C | -1.902710 | 1.895045 | -2.604386 | C | 4.259585 | -2.566045 | 1.333742 |
| H | -1.994976 | 2.908288 | -2.986760 | H | 5.086876 | -1.926404 | 1.663814 |
| C | -3.018318 | 1.134467 | -2.314031 | H | 4.617733 | -3.248797 | 0.558794 |
| H | -4.020503 | 1.537035 | -2.465261 | H | 3.921886 | -3.130107 | 2.210423 |
| C | -2.863840 | -0.168784 | -1.809973 | C | 4.259600 | 2.565984 | -1.333803 |
| C | -1.548061 | -0.628273 | -1.619652 | H | 5.086896 | 1.926353 | -1.663880 |
| C | -1.276052 | -1.921002 | -1.099107 | H | 4.617748 | 3.248751 | -0.558868 |
| C | -2.344829 | -2.790658 | -0.795832 | H | 3.921878 | 3.130032 | -2.210486 |
| C | -2.024898 | -4.065244 | -0.289905 | C | -3.683343 | -2.311432 | -0.995334 |
| H | -2.825312 | -4.767128 | -0.054259 | C | -3.934647 | -1.057111 | -1.465778 |
| C | -0.700593 | -4.416742 | -0.100632 | H | -4.958824 | -0.707913 | -1.599325 |
| H | -0.462570 | -5.409108 | 0.282668 | H | -4.511779 | -2.977800 | -0.750973 |
| C | 0.354780 | -3.524466 | -0.383133 | C | -3.934600 | 1.057165 | 1.465776 |
| H | 1.386230 | -3.830123 | -0.208793 | H | -4.958781 | 0.707981 | 1.599322 |
| C | -0.625842 | -1.361091 | 2.379832 | C | -3.683278 | 2.311486 | 0.995338 |
| H | 0.284281 | -1.927581 | 2.571731 | H | -4.511704 | 2.977866 | 0.750981 |

Structure J

(optimized by M06/BS1)

E (BS1) = -2156.69480347 au

H (BS1) = -2156.191520 au

G(BS1) = -2156.293604 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2159.67392680 auE(BP86/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2161.10808469 auE(TPSS/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2161.11094573 auE(wB97XD/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2160.30261025 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | 1.593873 | -0.014880 | -0.594884 | H | 1.424065 | 4.490827 | 2.040042 |
| Pd | 0.170760 | -1.486127 | 1.319698 | H | -2.860313 | -4.418576 | -1.736260 |
| O | 1.987321 | -2.001812 | -1.246329 | C | 1.714210 | 2.751949 | 0.800595 |
| N | -1.166546 | -0.015125 | 1.906429 | C | -1.540721 | -3.267428 | -0.473516 |
| C | -0.566535 | -0.781204 | -2.604422 | H | 2.736427 | 2.589830 | 1.135696 |
| C | -0.960748 | 0.993679 | 2.743394 | H | -0.721567 | -3.979046 | -0.571914 |
| H | 0.061687 | -1.649310 | -2.796222 | C | 1.144555 | 1.926820 | -0.155770 |
| H | 0.031614 | 1.056892 | 3.187817 | C | -1.408806 | -2.139522 | 0.311155 |
| C | -1.842345 | -0.632535 | -3.165814 | C | -0.180912 | 2.172685 | -0.599105 |
| C | -1.969576 | 1.924611 | 3.029382 | C | -2.519053 | -1.276480 | 0.449563 |
| H | -1.763772 | 2.731994 | 3.727389 | C | -0.785160 | 1.258036 | -1.497039 |
| C | -2.605992 | 0.470636 | -2.842867 | C | -2.382253 | -0.156891 | 1.308731 |
| C | -3.205593 | 1.798774 | 2.425296 | O | 3.165567 | -0.091252 | 0.676817 |
| H | -3.611693 | 0.584379 | -3.246985 | O | 1.351782 | -3.038927 | 0.650693 |
| H | -4.001742 | 2.512093 | 2.638707 | O | 1.867704 | -0.664366 | 2.432820 |
| C | -2.091736 | 1.453369 | -1.975260 | N | -0.062520 | 0.147187 | -1.803257 |
| C | -3.445077 | 0.735504 | 1.535580 | C | 2.964354 | -0.368363 | 1.917118 |
| C | -0.919934 | 3.269543 | -0.120568 | C | 1.925696 | -3.002844 | -0.474281 |
| C | -3.750445 | -1.519492 | -0.194375 | C | 4.195321 | -0.332896 | 2.774843 |
| C | -0.305619 | 4.104932 | 0.837831 | C | 2.553966 | -4.276897 | -0.962843 |
| C | -3.847292 | -2.667235 | -1.005495 | H | 4.634021 | -1.338452 | 2.790969 |
| H | -0.850962 | 4.970289 | 1.213479 | H | 1.913990 | -4.707110 | -1.744231 |
| H | -4.786021 | -2.889055 | -1.512505 | H | 4.943741 | 0.356397 | 2.374724 |
| C | 0.970722 | 3.836823 | 1.297959 | H | 3.527713 | -4.070164 | -1.416806 |
| C | -2.765995 | -3.519315 | -1.128937 | H | 3.927905 | -0.069694 | 3.802183 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | 2.651920 | -5.000100 | -0.149981 | H | -2.824544 | 4.311718 | -0.241482 |
| H | -2.218232 | -1.401575 | -3.834703 | C | -2.813635 | 2.595948 | -1.504025 |
| C | 2.509956 | 1.826821 | -1.698851 | H | -3.830962 | 2.749034 | -1.861574 |
| F | 2.697719 | 1.018041 | -2.740431 | C | -4.681446 | 0.484698 | 0.854307 |
| F | 3.656657 | 2.039795 | -1.103940 | H | -5.514583 | 1.165948 | 1.023666 |
| F | 2.034183 | 2.953296 | -2.196797 | C | -4.823737 | -0.592561 | 0.030794 |
| C | -2.255479 | 3.457759 | -0.607570 | H | -5.778470 | -0.777265 | -0.461976 |

Structure K

(optimized by M06/BS1)

E (BS1) = -2156.74358267 au

H (BS1) = -2156.237966 au

G(BS1) = -2156.342807 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2159.72568040 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | 1.892742 | 0.348927 | 0.366758 | C | -0.347553 | -3.424962 | -0.550232 |
| Pd | -0.289122 | 1.147102 | -1.396453 | C | -4.090734 | 1.998620 | 1.396583 |
| O | 2.210335 | 2.377514 | 0.564458 | H | -1.102679 | -4.106324 | -0.942716 |
| N | -1.574426 | -0.407185 | -1.849626 | H | -4.981078 | 2.149032 | 2.006407 |
| C | 0.408364 | 1.329281 | 2.853496 | C | 0.874543 | -3.301995 | -1.199492 |
| C | -1.412823 | -1.353341 | -2.765423 | C | -3.061620 | 2.921400 | 1.418323 |
| H | 1.068345 | 2.194529 | 2.821544 | H | 1.061995 | -3.858000 | -2.115269 |
| H | -0.468071 | -1.337519 | -3.307868 | H | -3.147016 | 3.800429 | 2.056500 |
| C | -0.741923 | 1.284252 | 3.657509 | C | 1.902453 | -2.582479 | -0.603764 |
| C | -2.408770 | -2.309870 | -3.014110 | C | -1.905990 | 2.770255 | 0.620777 |
| H | -2.246965 | -3.059099 | -3.785196 | H | 2.915615 | -2.647205 | -0.999062 |
| C | -1.622128 | 0.231851 | 3.524956 | H | -1.130944 | 3.536641 | 0.644683 |
| C | -3.583827 | -2.276814 | -2.286654 | C | 1.702304 | -1.856871 | 0.596302 |
| H | -2.568311 | 0.227689 | 4.064586 | C | -1.781472 | 1.667503 | -0.200801 |
| H | -4.369867 | -3.009074 | -2.471245 | C | 0.340751 | -1.801601 | 1.099145 |
| C | -1.320643 | -0.824797 | 2.641916 | C | -2.842322 | 0.732436 | -0.232048 |
| C | -3.776726 | -1.278677 | -1.314207 | C | -0.066321 | -0.783678 | 2.008064 |
| C | -0.653111 | -2.661987 | 0.595398 | C | -2.733720 | -0.350259 | -1.138483 |
| C | -4.010865 | 0.879070 | 0.545266 | O | 3.014631 | 0.306476 | -1.312492 |

| | | | | | | | |
|---|----------|-----------|-----------|---|-----------|-----------|-----------|
| O | 0.727161 | 2.929684 | -1.049539 | H | -0.954741 | 2.113145 | 4.327119 |
| O | 1.268120 | 0.407904 | -2.742373 | C | 2.867967 | -2.061110 | 1.573764 |
| N | 0.729933 | 0.319215 | 2.062231 | F | 2.758031 | -1.384268 | 2.711669 |
| C | 2.486967 | 0.319116 | -2.480649 | F | 4.027044 | -1.744386 | 1.000732 |
| C | 1.627010 | 3.196145 | -0.216286 | F | 2.916564 | -3.358219 | 1.896357 |
| C | 3.471098 | 0.232033 | -3.613094 | C | -1.940979 | -2.689903 | 1.228750 |
| C | 2.042678 | 4.634501 | -0.077957 | H | -2.680334 | -3.400084 | 0.859980 |
| H | 3.763721 | 1.250882 | -3.896058 | C | -2.243119 | -1.847825 | 2.253748 |
| H | 1.490361 | 5.083276 | 0.758197 | H | -3.223827 | -1.875598 | 2.726350 |
| H | 4.374931 | -0.307033 | -3.316571 | C | -4.948166 | -1.123607 | -0.502423 |
| H | 3.109744 | 4.707904 | 0.148761 | H | -5.763740 | -1.835202 | -0.625653 |
| H | 3.003360 | -0.235525 | -4.484086 | C | -5.051889 | -0.097939 | 0.389911 |
| H | 1.799104 | 5.189550 | -0.987296 | H | -5.957961 | 0.012786 | 0.985662 |

Structure K'

(optimized by M06/BS1)

E (BS1) = -2156.73939732 au

H (BS1) = -2156.233487 au

G(BS1) = -2156.338741 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2159.71733633 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | 2.286945 | 0.084418 | 0.298244 | H | -0.284800 | 5.281181 | 0.049382 |
| Pd | 0.097119 | -1.028780 | -1.379154 | H | -4.907319 | -3.358711 | 0.735114 |
| O | 2.936022 | 0.900077 | -1.435785 | C | -0.541887 | 3.271264 | 0.778099 |
| N | -1.526846 | -1.916271 | -0.471414 | C | -3.933017 | -1.696094 | -0.250314 |
| C | 2.133306 | 2.948790 | 0.326188 | C | -2.053502 | 1.132862 | 1.775871 |
| C | -1.568696 | -3.090993 | 0.145327 | C | -3.668538 | 0.823406 | -1.578614 |
| H | 3.169306 | 2.749553 | 0.064247 | C | -2.860345 | 0.099308 | 2.292782 |
| H | -0.615639 | -3.604481 | 0.262561 | C | -3.466978 | 2.061644 | -2.218521 |
| C | 1.578362 | 4.212311 | 0.126135 | H | -3.941685 | 0.192829 | 2.194706 |
| C | -2.778581 | -3.637354 | 0.596114 | H | -4.319194 | 2.710943 | -2.416908 |
| H | -2.772519 | -4.606982 | 1.086881 | C | -2.306942 | -0.979515 | 2.937311 |
| C | 0.221117 | 4.347093 | 0.291267 | C | -2.192729 | 2.441982 | -2.593210 |
| C | -3.957493 | -2.944313 | 0.397305 | H | -2.932828 | -1.776701 | 3.331772 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | -2.045232 | 3.403601 | -3.084186 | H | 4.238967 | -3.717283 | -1.471421 |
| C | -0.928507 | -0.991072 | 3.168827 | H | 2.529835 | 1.173963 | -4.585499 |
| C | -1.070564 | 1.611063 | -2.377151 | H | 4.013629 | -4.045698 | 0.245113 |
| H | -0.504094 | -1.760873 | 3.807529 | H | 3.830572 | 1.855202 | -3.541145 |
| H | -0.089347 | 1.944778 | -2.714477 | H | 2.875528 | -4.748993 | -0.954968 |
| C | -0.103205 | -0.001257 | 2.661388 | H | 3.900255 | 0.168693 | -4.092389 |
| C | -1.237157 | 0.384114 | -1.767762 | H | 2.204707 | 5.029955 | -0.218025 |
| C | -0.632306 | 1.041310 | 1.841358 | C | 1.298138 | -0.026500 | 3.193588 |
| C | -2.536783 | 0.012708 | -1.353825 | F | 1.846156 | 1.168150 | 3.336650 |
| C | 0.116892 | 2.067130 | 1.138900 | F | 2.140530 | -0.739386 | 2.337896 |
| C | -2.679586 | -1.223350 | -0.676888 | F | 1.398627 | -0.666380 | 4.344395 |
| O | 3.242448 | -1.606567 | -0.181950 | C | -2.691507 | 2.303889 | 1.260975 |
| O | 1.485552 | -0.243454 | -2.732609 | H | -3.779920 | 2.336669 | 1.261732 |
| O | 1.407641 | -2.714635 | -0.887538 | C | -1.962579 | 3.369950 | 0.859645 |
| N | 1.428088 | 1.910674 | 0.775892 | H | -2.436632 | 4.296935 | 0.541159 |
| C | 2.616266 | -2.653234 | -0.590926 | C | -5.075597 | -0.867049 | -0.505411 |
| C | 2.473483 | 0.497074 | -2.559012 | H | -6.055878 | -1.222661 | -0.190003 |
| C | 3.480423 | -3.876718 | -0.696239 | C | -4.944370 | 0.336284 | -1.133170 |
| C | 3.228074 | 0.972485 | -3.767935 | H | -5.825634 | 0.949779 | -1.320700 |

Structure L

(optimized by M06/BS1)

E (BS1) = -2385.22469071 au

H (BS1) = -2384.665171 au

G(BS1) = -2384.781316 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.25884391 au

E(BP86/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2389.83490402 au

E(TPSS/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2389.86075687 au

E(wB97XD/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.93275954 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | -1.016011 | -1.239614 | 0.467490 | C | -0.629834 | 0.787928 | 2.727989 |
| Pd | 1.522197 | -0.892718 | -0.274551 | C | 0.339603 | 0.674335 | -2.625251 |
| O | 0.051440 | -2.270567 | 2.197588 | H | -0.088068 | -0.026390 | 3.205668 |
| N | 0.854936 | 0.703412 | -1.407949 | H | 0.189086 | -0.312423 | -3.060413 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | -0.734559 | 2.065598 | 3.288277 | N | -1.173405 | 0.509627 | 1.548961 |
| C | 0.007785 | 1.855747 | -3.302089 | C | -0.042298 | -3.129204 | -1.551542 |
| H | -0.429746 | 1.791104 | -4.294936 | C | 1.208971 | -2.707534 | 2.015825 |
| C | -1.390354 | 3.065233 | 2.593278 | C | -0.165422 | -4.398963 | -2.350301 |
| C | 0.232359 | 3.075648 | -2.696341 | C | 1.775916 | -3.673429 | 3.027164 |
| H | -1.445806 | 4.076120 | 2.997183 | H | -1.165541 | -4.832372 | -2.266267 |
| H | -0.021264 | 4.004791 | -3.206970 | H | 0.993699 | -4.352771 | 3.378836 |
| C | -1.982135 | 2.783521 | 1.351723 | H | 0.086647 | -4.202432 | -3.397351 |
| C | 0.805341 | 3.122093 | -1.413215 | H | 2.617855 | -4.231682 | 2.609875 |
| C | -3.038239 | 2.024816 | -1.192719 | H | 0.567292 | -5.120281 | -1.968479 |
| C | 2.031031 | 3.005096 | 1.168146 | H | 2.134756 | -3.101073 | 3.892926 |
| C | -3.506778 | 1.604236 | -2.451073 | H | -0.267952 | 2.260724 | 4.250134 |
| C | 2.678470 | 2.874312 | 2.412517 | C | -3.375970 | -1.481903 | 0.645062 |
| H | -3.964217 | 2.328583 | -3.124216 | O | 3.611000 | -1.033316 | -0.863984 |
| H | 2.933130 | 3.768635 | 2.981535 | C | 4.089729 | -0.175150 | -1.701468 |
| C | -3.382783 | 0.275995 | -2.824953 | C | 5.531885 | -0.493884 | -2.078585 |
| C | 3.020001 | 1.621280 | 2.887484 | H | 5.908232 | 0.244693 | -2.792931 |
| H | -3.737867 | -0.038526 | -3.805610 | H | 6.159523 | -0.495906 | -1.179689 |
| H | 3.547359 | 1.534629 | 3.837209 | H | 5.590311 | -1.498019 | -2.514316 |
| C | -2.842155 | -0.692655 | -1.965453 | O | 3.517118 | 0.801820 | -2.178293 |
| C | 2.719526 | 0.443136 | 2.169208 | F | -3.739103 | -2.547281 | -0.054152 |
| H | -2.812432 | -1.737143 | -2.267557 | F | -3.165958 | -1.883503 | 1.913698 |
| H | 3.035031 | -0.529075 | 2.545095 | F | -4.415485 | -0.645993 | 0.716017 |
| C | -2.394803 | -0.318992 | -0.701699 | C | -2.634149 | 3.738036 | 0.505484 |
| C | 2.045662 | 0.549705 | 0.973868 | H | -2.710640 | 4.768830 | 0.850046 |
| C | -2.449421 | 1.060275 | -0.351165 | C | -3.114865 | 3.377244 | -0.716694 |
| C | 1.725483 | 1.822955 | 0.464837 | H | -3.581154 | 4.122210 | -1.361689 |
| C | -1.874777 | 1.461111 | 0.877441 | C | 1.101641 | 4.314733 | -0.674872 |
| C | 1.108806 | 1.892321 | -0.808445 | H | 0.862218 | 5.276624 | -1.128004 |
| O | -0.947328 | -2.944024 | -0.668416 | C | 1.681913 | 4.256385 | 0.556949 |
| O | 2.004337 | -2.393054 | 1.071057 | H | 1.911688 | 5.175954 | 1.096182 |
| O | 0.918940 | -2.369357 | -1.792320 | | | | |

Structure M

(optimized by M06/BS1)

E (BS1) = -2386.96571235 au

H (BS1) = -2386.403593 au

G(BS1) = -2386.520684 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.30453837 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | -0.642533 | -1.637098 | 0.358563 | C | 2.615819 | 0.832551 | 2.168258 |
| Pd | 1.651576 | -0.614419 | -0.323925 | H | -4.471044 | -1.676367 | -2.018295 |
| O | 0.925995 | -2.464037 | 2.290217 | H | 3.086698 | -0.081677 | 2.524443 |
| N | 0.597427 | 0.841810 | -1.341283 | C | -3.484062 | -0.582028 | -0.471311 |
| C | -0.650732 | 0.113340 | 2.714949 | C | 1.892651 | 0.843643 | 0.995294 |
| C | 0.033658 | 0.745552 | -2.534519 | C | -2.960015 | 0.679171 | -0.063327 |
| H | -0.016695 | -0.716826 | 3.027561 | C | 1.365216 | 2.058805 | 0.518631 |
| H | 0.016124 | -0.248104 | -2.977747 | C | -2.114977 | 0.912680 | 1.087443 |
| C | -0.704246 | 1.318444 | 3.425688 | C | 0.699518 | 2.048525 | -0.733779 |
| C | -0.492272 | 1.870853 | -3.181051 | O | -0.098755 | -3.181640 | -0.845077 |
| H | -0.958627 | 1.752304 | -4.155808 | O | 2.587974 | -2.032001 | 0.813138 |
| C | -1.355561 | 2.384488 | 2.854975 | O | 1.488386 | -2.047510 | -1.954683 |
| C | -0.398851 | 3.109798 | -2.577607 | N | -1.310577 | -0.075251 | 1.574218 |
| H | -1.314504 | 3.377380 | 3.303647 | C | 0.797549 | -3.071591 | -1.740746 |
| H | -0.791252 | 4.000302 | -3.070366 | C | 2.069033 | -2.605181 | 1.844964 |
| C | -2.055894 | 2.210318 | 1.646898 | C | 1.049305 | -4.289404 | -2.585972 |
| C | 0.215848 | 3.229333 | -1.320441 | C | 3.054698 | -3.524679 | 2.537613 |
| C | -3.310576 | 1.815066 | -0.841275 | H | 0.183237 | -4.957019 | -2.589745 |
| C | 1.538131 | 3.273837 | 1.215450 | H | 2.569133 | -4.054071 | 3.361714 |
| C | -3.893337 | 1.641320 | -2.112273 | H | 1.317462 | -3.992848 | -3.604607 |
| C | 2.236949 | 3.230894 | 2.436388 | H | 3.466618 | -4.241677 | 1.818985 |
| H | -4.109290 | 2.527348 | -2.709743 | H | 1.905336 | -4.829907 | -2.163193 |
| H | 2.387627 | 4.151091 | 3.001364 | H | 3.898968 | -2.936798 | 2.918385 |
| C | -4.199865 | 0.385555 | -2.579792 | H | -0.145769 | 1.417184 | 4.352611 |
| C | 2.762368 | 2.034321 | 2.890817 | C | -3.728513 | -1.734868 | 0.479222 |
| H | -4.635814 | 0.250411 | -3.567130 | O | 3.659326 | -0.150258 | -0.924645 |
| H | 3.327149 | 2.019064 | 3.822778 | C | 3.878453 | 0.704785 | -1.869292 |
| C | -4.060797 | -0.713633 | -1.722574 | C | 5.351004 | 0.749286 | -2.255869 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|----------|-----------|
| H | 5.511588 | 1.495665 | -3.039823 | H | -2.512875 | 4.312470 | 1.361306 |
| H | 5.961969 | 0.991504 | -1.378506 | C | -3.122171 | 3.131654 | -0.310784 |
| H | 5.671266 | -0.237532 | -2.609765 | H | -3.447494 | 3.977860 | -0.916138 |
| O | 3.057171 | 1.424256 | -2.431445 | C | 0.386833 | 4.451658 | -0.591230 |
| F | -2.816220 | -2.731180 | 0.387852 | H | 0.013220 | 5.375306 | -1.034046 |
| F | -3.765280 | -1.350291 | 1.752632 | C | 1.011923 | 4.469745 | 0.619481 |
| F | -4.904409 | -2.309808 | 0.209808 | H | 1.144310 | 5.412979 | 1.150795 |
| C | -2.605230 | 3.316903 | 0.928233 | | | | |

Structure N

E (BS1) = -2385.23123197 au

H (BS1) = -2384.672605 au

G(BS1) = -2384.786605 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.25288698 au

E(BP86/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2389.83428484 au

E(TPSS/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2389.85873575 au

E(wB97XD/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.92963629 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | 0.436421 | -1.536464 | -0.619550 | C | -1.689806 | 1.354619 | -0.849516 |
| Pd | -1.649644 | -0.189808 | 0.432044 | C | -2.392986 | 1.501392 | -2.022685 |
| O | -1.234774 | -1.877334 | -2.134616 | C | -0.867152 | 2.401892 | -0.395528 |
| O | -1.522584 | -1.738793 | 1.941679 | C | -2.235124 | 2.689762 | -2.768263 |
| C | -1.028730 | -2.851212 | 1.607231 | H | -3.075397 | 0.730743 | -2.375577 |
| O | -0.339528 | -3.082992 | 0.574113 | C | -0.698637 | 3.590770 | -1.134596 |
| C | -2.408752 | -1.935884 | -1.741655 | C | -1.403477 | 3.709899 | -2.347590 |
| O | -2.884688 | -1.365005 | -0.690129 | H | -2.789735 | 2.799369 | -3.699345 |
| C | -0.203637 | 2.241349 | 0.845926 | H | -1.298055 | 4.617664 | -2.941436 |
| C | 0.118606 | 0.840872 | 2.680527 | C | 2.072061 | -1.244838 | 0.605245 |
| C | 0.615985 | 3.246579 | 1.381527 | C | 2.592622 | 0.079565 | 0.361531 |
| C | 0.920842 | 1.811232 | 3.297288 | C | 2.172375 | -1.703278 | 1.944557 |
| H | -0.079629 | -0.132148 | 3.125452 | C | 3.428366 | 0.745376 | 1.291158 |
| C | 1.175106 | 3.002896 | 2.648809 | C | 2.946467 | -1.006306 | 2.866703 |
| H | 1.352767 | 1.596363 | 4.270466 | H | 1.773148 | -2.684553 | 2.196925 |
| H | 1.814559 | 3.757370 | 3.107317 | C | 3.616500 | 0.178980 | 2.557559 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | 3.056419 | -1.430221 | 3.866312 | H | -3.241824 | -2.597040 | -3.595150 |
| H | 4.255999 | 0.671197 | 3.289595 | C | 3.944180 | -3.916185 | -1.769070 |
| C | 0.934203 | 0.614364 | -2.773333 | H | 4.865191 | -3.329250 | -1.848129 |
| C | 2.245348 | 0.709644 | -0.846008 | H | 4.121990 | -4.702791 | -1.026273 |
| C | 1.508242 | 1.791351 | -3.261006 | H | 3.699594 | -4.374520 | -2.730823 |
| H | 0.155213 | 0.078751 | -3.314461 | N | -0.422202 | 1.067189 | 1.492072 |
| C | 2.827169 | 1.937739 | -1.244974 | N | 1.269683 | 0.111210 | -1.590377 |
| C | 2.433321 | 2.466337 | -2.478907 | C | -3.420559 | 0.601875 | 1.246227 |
| H | 1.180726 | 2.187311 | -4.218806 | F | -3.187081 | 1.711421 | 1.959547 |
| H | 2.855798 | 3.414507 | -2.814378 | F | -4.331694 | 0.895824 | 0.322879 |
| O | 1.713949 | -3.062985 | -1.872449 | F | -3.942438 | -0.306660 | 2.060470 |
| C | 2.805150 | -3.044866 | -1.300476 | C | 0.806942 | 4.431404 | 0.598606 |
| O | 3.111433 | -2.329693 | -0.265140 | C | 0.180604 | 4.591905 | -0.601160 |
| C | -1.240393 | -4.002896 | 2.553712 | H | 1.465517 | 5.206906 | 0.989057 |
| H | -1.095124 | -4.959025 | 2.043782 | H | 0.333387 | 5.504518 | -1.177774 |
| H | -0.500025 | -3.925917 | 3.361441 | C | 4.000383 | 1.999225 | 0.882781 |
| H | -2.235227 | -3.949481 | 3.005736 | C | 3.737604 | 2.559259 | -0.330585 |
| C | -3.412264 | -2.742103 | -2.523392 | H | 4.668319 | 2.504850 | 1.582287 |
| H | -3.244864 | -3.804192 | -2.307130 | H | 4.194236 | 3.507201 | -0.617205 |
| H | -4.440052 | -2.483045 | -2.256029 | | | | |

Structure O

E (BS1) = -2385.26151169 au

H (BS1) = -2384.699852 au

G(BS1) = -2384.816555 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2388.28617677 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | -0.014502 | -1.521478 | 0.674627 | O | 3.309154 | -0.699411 | 0.524070 |
| Pd | 1.744487 | 0.049480 | -0.519921 | C | -0.301882 | 1.980565 | -1.096719 |
| O | 2.246077 | -0.899853 | 2.513061 | C | -0.518391 | 0.197817 | -2.578333 |
| O | 1.903887 | -1.680596 | -1.845372 | C | -1.396730 | 2.664855 | -1.654250 |
| C | 1.732797 | -2.811016 | -1.307279 | C | -1.620815 | 0.811383 | -3.184065 |
| O | 1.092752 | -3.028364 | -0.242184 | H | -0.125367 | -0.767366 | -2.893164 |
| C | 3.208985 | -1.056169 | 1.771833 | C | -2.063496 | 2.036251 | -2.718498 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | -2.125120 | 0.305606 | -4.003122 | C | -1.994016 | -3.777922 | 0.818500 |
| H | -2.928838 | 2.521259 | -3.172009 | O | -2.475288 | -2.499207 | 1.000524 |
| C | 1.509873 | 1.755506 | 0.502750 | C | 2.371929 | -3.992934 | -1.985662 |
| C | 2.261435 | 2.264742 | 1.539299 | H | 1.916566 | -4.931407 | -1.658119 |
| C | 0.436509 | 2.511759 | -0.009550 | H | 2.302479 | -3.889036 | -3.073121 |
| C | 1.921910 | 3.522232 | 2.076982 | H | 3.438293 | -4.004253 | -1.726672 |
| H | 3.109367 | 1.713694 | 1.937829 | C | 4.475983 | -1.735686 | 2.249120 |
| C | 0.088613 | 3.771867 | 0.523446 | H | 4.555977 | -2.719528 | 1.770586 |
| C | 0.860646 | 4.264702 | 1.590290 | H | 5.359574 | -1.159641 | 1.954248 |
| H | 2.520843 | 3.918938 | 2.896092 | H | 4.447586 | -1.864256 | 3.334601 |
| H | 0.622465 | 5.237529 | 2.020817 | C | -1.265164 | -4.202121 | 2.054152 |
| C | -3.159699 | -1.769901 | 0.050972 | H | -0.294856 | -3.682027 | 2.096606 |
| C | -3.206712 | -0.360729 | 0.259866 | H | -1.825962 | -3.928725 | 2.954056 |
| C | -3.898566 | -2.372785 | -0.951721 | H | -1.087552 | -5.279390 | 2.015811 |
| C | -4.198007 | 0.358900 | -0.467903 | N | 0.108626 | 0.773774 | -1.560552 |
| C | -4.755108 | -1.606373 | -1.751019 | N | -1.193759 | -0.085661 | 1.665025 |
| H | -3.828409 | -3.443287 | -1.093568 | C | 3.196564 | 1.118537 | -1.624085 |
| C | -4.933122 | -0.269596 | -1.490382 | F | 2.643091 | 2.086810 | -2.375898 |
| H | -5.321796 | -2.097375 | -2.539915 | F | 4.125782 | 1.692991 | -0.857677 |
| H | -5.660751 | 0.319722 | -2.048137 | F | 3.817861 | 0.279434 | -2.447505 |
| C | -0.552499 | 0.563313 | 2.637124 | C | -1.744827 | 3.934276 | -1.087030 |
| C | -2.387824 | 0.387396 | 1.201501 | C | -1.031780 | 4.460600 | -0.052846 |
| C | -1.026173 | 1.752957 | 3.199553 | H | -2.596001 | 4.470935 | -1.506306 |
| H | 0.410359 | 0.142360 | 2.927537 | H | -1.306639 | 5.431798 | 0.360584 |
| C | -2.815573 | 1.683622 | 1.593801 | C | -4.501258 | 1.715767 | -0.130051 |
| C | -2.126696 | 2.341009 | 2.627863 | C | -3.889386 | 2.328815 | 0.909410 |
| H | -0.468817 | 2.230256 | 4.001138 | H | -5.282950 | 2.219534 | -0.699084 |
| H | -2.472902 | 3.325458 | 2.945704 | H | -4.159892 | 3.340281 | 1.212762 |
| O | -2.142433 | -4.427438 | -0.179554 | | | | |

Acetate

E (BS1) = -228.372381147 au

H (BS1) = -228.318464 au

G(BS1) = -228.350668 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -228.565351316 au

E(BP86/BS2//M06/BS1, Solvent = CH₂Cl₂) = -228.701437827 au

E(TPSS/BS2//M06/BS1, Solvent = CH₂Cl₂) = -228.721606582 au

E(wB97XD/BS2//M06/BS1, Solvent = CH₂Cl₂) = -228.617441167 au

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | -0.219624 | 0.001877 | -0.005648 | H | 1.723657 | -1.079441 | -0.138447 |
| C | 1.342794 | -0.057158 | -0.002116 | O | -0.687501 | 1.162706 | 0.001194 |
| H | 1.751252 | 0.595096 | -0.788730 | O | -0.804754 | -1.102591 | 0.001301 |
| H | 1.724111 | 0.335116 | 0.953796 | | | | |

Water

E (BS1) = -76.3738331110 au

H (BS1) = -76.348480 au

G(BS1) = -76.369910 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -76.4260659962 au

| | | | |
|---|----------|-----------|-----------|
| O | 0.000000 | 0.000000 | 0.118339 |
| H | 0.000000 | 0.760840 | -0.473357 |
| H | 0.000000 | -0.760840 | -0.473357 |

Structure from inflexion on increasing Pd_a···Pd_b in cation A

(optimized by M06/BS1)

E (BS1) = -2156.69969139 au

H (BS1) = -2156.194560 au

G (BS1) = -2156.301071 au

E(M06/BS2//M06/BS1, Solvent = CH₂Cl₂) = -2159.67031263 au

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | 2.004050 | -0.607388 | -0.495913 | C | 4.737115 | 2.642975 | -0.469321 |
| Pd | -1.830983 | -0.796201 | -0.086022 | C | -3.139989 | 2.573587 | 2.078776 |
| N | 2.762527 | 1.285983 | -0.868439 | C | 6.046045 | 2.688874 | 0.113581 |
| N | -2.078209 | 0.482627 | 1.498288 | C | -3.993770 | 3.636609 | 1.634945 |
| C | 2.196355 | 2.296174 | -1.518759 | H | 6.619290 | 3.611172 | 0.029904 |
| C | -1.513294 | 0.395494 | 2.696840 | H | -4.205712 | 4.452866 | 2.323534 |
| H | 1.199601 | 2.117843 | -1.918662 | C | 6.567181 | 1.605383 | 0.754479 |
| H | -0.883386 | -0.475090 | 2.871591 | C | -4.535111 | 3.628964 | 0.384122 |
| C | 2.848777 | 3.524443 | -1.682835 | H | 7.565773 | 1.658395 | 1.187527 |
| C | -1.732878 | 1.394532 | 3.653717 | H | -5.186284 | 4.443237 | 0.068779 |
| H | -1.264529 | 1.301133 | 4.629416 | C | 5.836769 | 0.376111 | 0.878485 |
| C | 4.115565 | 3.698122 | -1.158621 | C | -4.277778 | 2.565941 | -0.545214 |
| C | -2.540614 | 2.474174 | 3.348255 | C | 6.323315 | -0.782013 | 1.515722 |
| H | 4.638518 | 4.646670 | -1.278141 | C | -4.825920 | 2.478289 | -1.841461 |
| H | -2.718118 | 3.253161 | 4.088914 | H | 7.318242 | -0.773246 | 1.959104 |
| | | | | H | -5.491753 | 3.264538 | -2.194182 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | 5.543998 | -1.920976 | 1.568602 | O | -0.032399 | -0.252198 | -1.523011 |
| C | -4.536662 | 1.400110 | -2.653497 | C | 0.388581 | -2.780063 | 0.548761 |
| H | 5.934066 | -2.812782 | 2.057058 | C | -0.435830 | -1.242638 | -2.204744 |
| H | -4.979994 | 1.340226 | -3.645748 | C | -0.088103 | -4.191525 | 0.728336 |
| C | 4.249974 | -1.969829 | 1.002772 | C | 0.299253 | -1.751039 | -3.393314 |
| C | -3.680163 | 0.353271 | -2.233484 | H | -0.938539 | -4.354411 | 0.050007 |
| H | 3.665085 | -2.886170 | 1.050897 | H | 1.039826 | -2.486134 | -3.049515 |
| H | -3.477611 | -0.493375 | -2.886147 | H | 0.691841 | -4.919335 | 0.492610 |
| C | 3.751635 | -0.846478 | 0.383095 | H | -0.380706 | -2.251338 | -4.088733 |
| C | -3.131931 | 0.447511 | -0.982958 | H | -0.459337 | -4.337131 | 1.748211 |
| C | 4.544377 | 0.317270 | 0.318575 | H | 0.834859 | -0.935602 | -3.888901 |
| C | -3.424679 | 1.524096 | -0.130036 | H | 2.349651 | 4.324455 | -2.222882 |
| C | 4.010394 | 1.444873 | -0.349461 | C | -3.427939 | -1.863840 | 0.573105 |
| C | -2.874392 | 1.535036 | 1.173054 | F | -4.404236 | -1.119300 | 1.050097 |
| O | 1.445409 | -2.588383 | -0.111540 | F | -3.859050 | -2.571511 | -0.448174 |
| O | -1.499773 | -1.848053 | -1.826771 | F | -2.986619 | -2.662741 | 1.523503 |
| O | -0.310060 | -1.841732 | 1.048510 | | | | |

Basis Set Comparison for Transition State Energies

Relative energies (kcal mol⁻¹) calculated for four density functionals for reaction coordinate analyses in Schemes 5 and 6; energy (enthalpy).

| | M06 | BP86 | TPSS | wB97XD |
|--|-------------|-------------|-------------|-------------|
| C (TS for fragmentation from B) | 13.7 (13.0) | 19.5 (18.4) | 2.7 (1.6) | 15.9 (14.9) |
| J (TS for C–C from A) | 18.4 (28.3) | 25.3 (35.2) | 10.3 (20.1) | 22.3 (32.1) |
| L (TS for C–C from B) | 18.9 (19.3) | 21.8 (22.1) | 5.2 (5.5) | 26.6 (27.0) |
| N (TS for C–O from B) | 23.5 (22.5) | 23.0 (22.0) | 7.3 (6.26) | 29.4 (28.3) |

Functionals BP86, TPSS and wB97XD were chosen to represent three different classes of functional (rungs 2, 3, and 4, respectively on Jacob's ladder; M06 is rung5). Although the results for TPSS are broadly consistent trends with the other functionals, TPSS is reported to be not as good as M06 for computing reaction barriers (Karton, A.; Tarnopolsky, A.; Lamère, J-F.; Schaltz, G. C.; Martin, J. M. L. *J. Phys. Chem. A* **2008**, *112*, 12868), and that TPSS gives the least accurate bond dissociation energies (Cramer, C. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10757). It seems possible that the poor performance of TPSS might be representative of the “meta generalized gradient approximation” functionals, i.e. the third rung of Jacob's ladder.

Full citation for reference 20

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- ix Treatment of **1** with XeF₂ followed by AcOH and then TMSCF₃ results in the formation of Pd(III) tetraacetate complex **3**; no Pd(IV) complex **5** could be observed when this order of addition was executed. In addition, if binuclear Pd(III) tetraacetate complex **3**, prepared as outlined above, is treated with TMSCF₃, no reaction to produce **5** was observed.
- x Analogous conditions (XeF₂ and TMSX) have been employed in the synthesis of compounds **2** and **3** (see above). Synthesis of **9** by the aforementioned procedure can afford mixtures of compounds **9** and **1**; in some iterations, a 1:1 mixture of **9** and **1** were observed while in others, **9**, free of **1** was observed by ¹H NMR spectroscopy.
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- xii AcOH, not OAc⁻, catalyzes the oxidation of **1** to **5**. No reaction was observed upon treatment of **1** with 3.0 equiv **4** in the presence of 2.0 equiv *n*Bu₄NOAc for 13 h at 23 °C.
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