Supporting Information for:

An Experimentally Derived Model for Stereoselectivity in the Aerobic Oxidative Kinetic Resolution of Secondary Alcohols by (sparteine)$PdCl_2$

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FIGURES AND SCHEMES REPRODUCED FROM THE TEXT

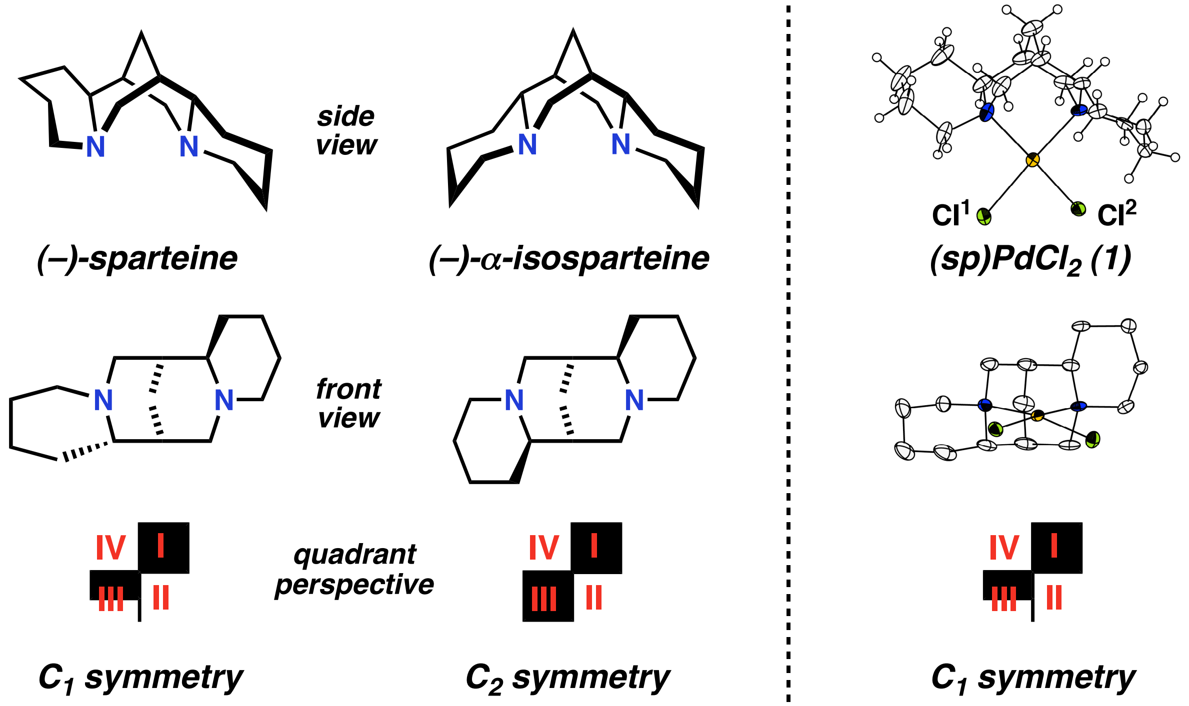
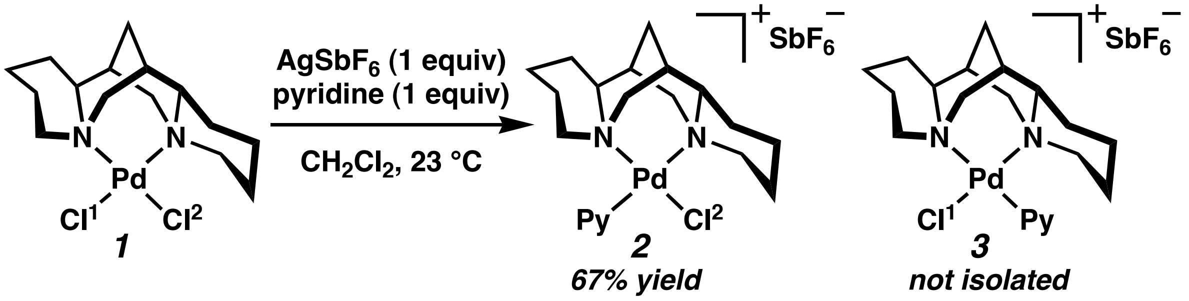
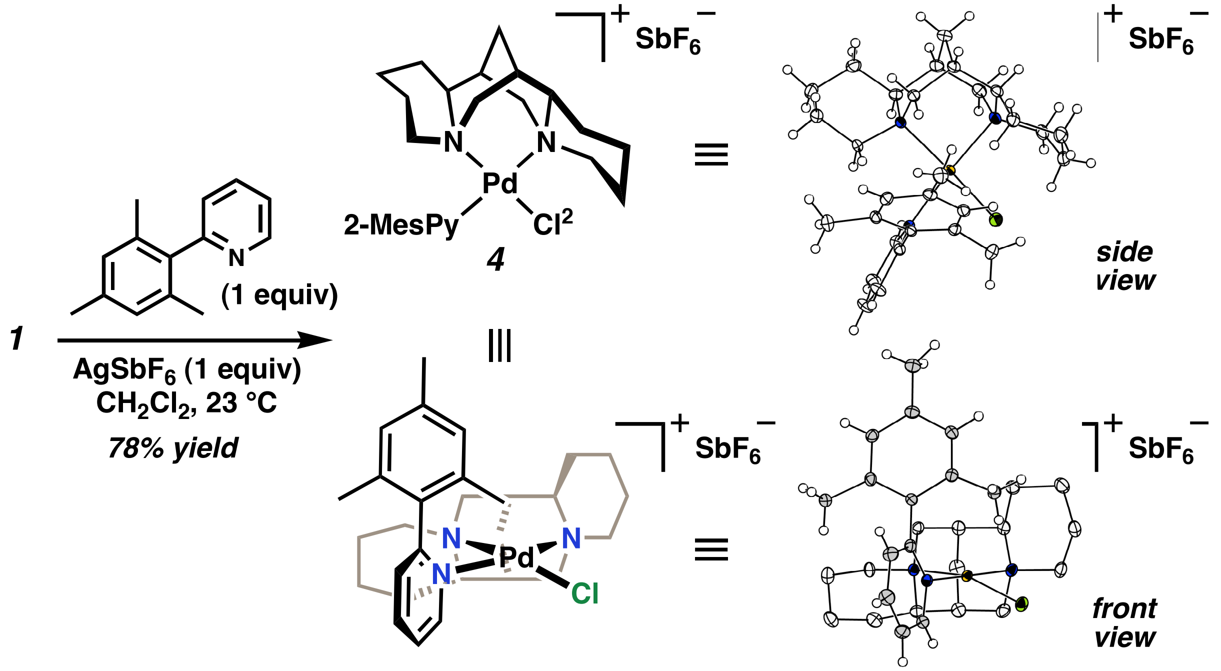


Figure 1. Three perspectives of (–)-sparteine, (–)-α-isosparteine, and (sp)$PdCl_2$ showing the C_1 and C_2 symmetry of these ligands and the quaternization effect around the metal center. Molecular structure of **1** is shown with 50% probability ellipsoids. Hydrogens from the sp framework in the front view have been removed for clarity.

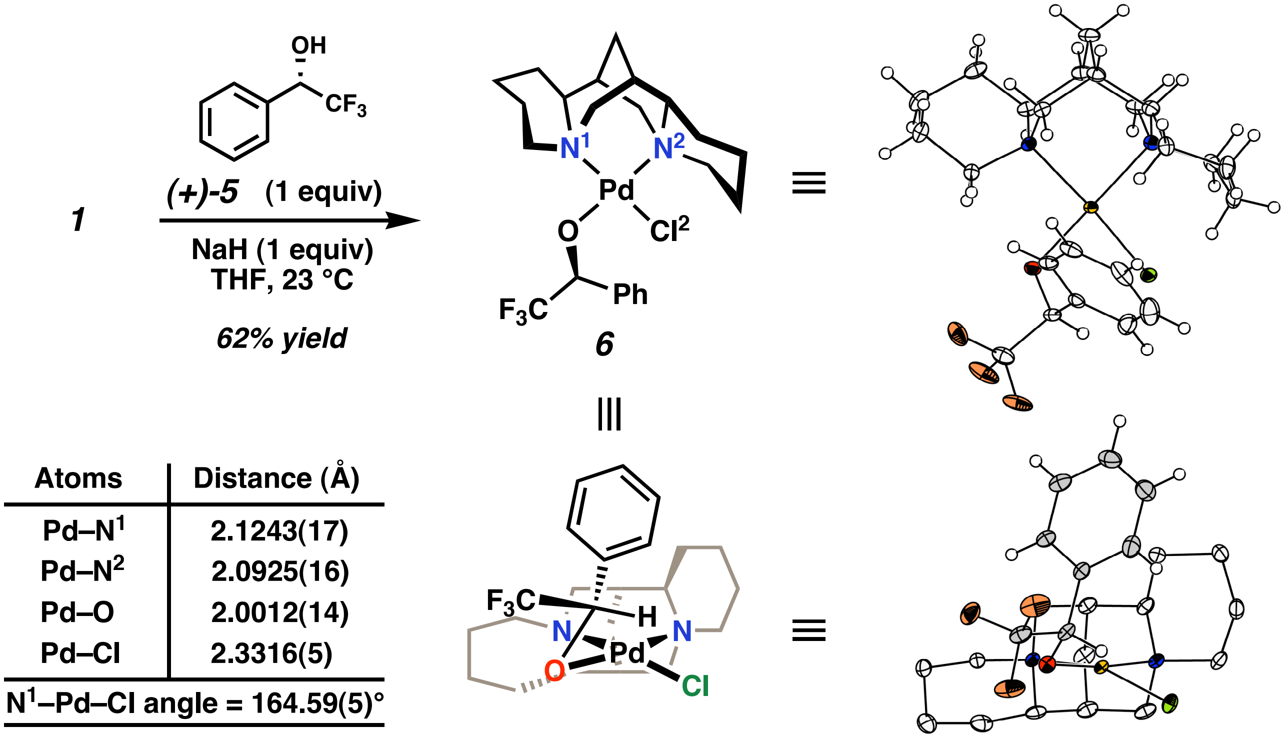
Scheme 1



Scheme 2[1]



Scheme 3[1]



Atoms	Distance (Å)
Pd–N^1	2.1243(17)
Pd–N^2	2.0925(16)
Pd–O	2.0012(14)
Pd–Cl	2.3316(5)
N^1–Pd–Cl angle = 164.59(5)°	

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[1] Molecular structures of **4** and **6** are shown with 50% probability ellipsoids. Hydrogens from the sp framework in the front view and the anion of **4** have been removed for clarity.

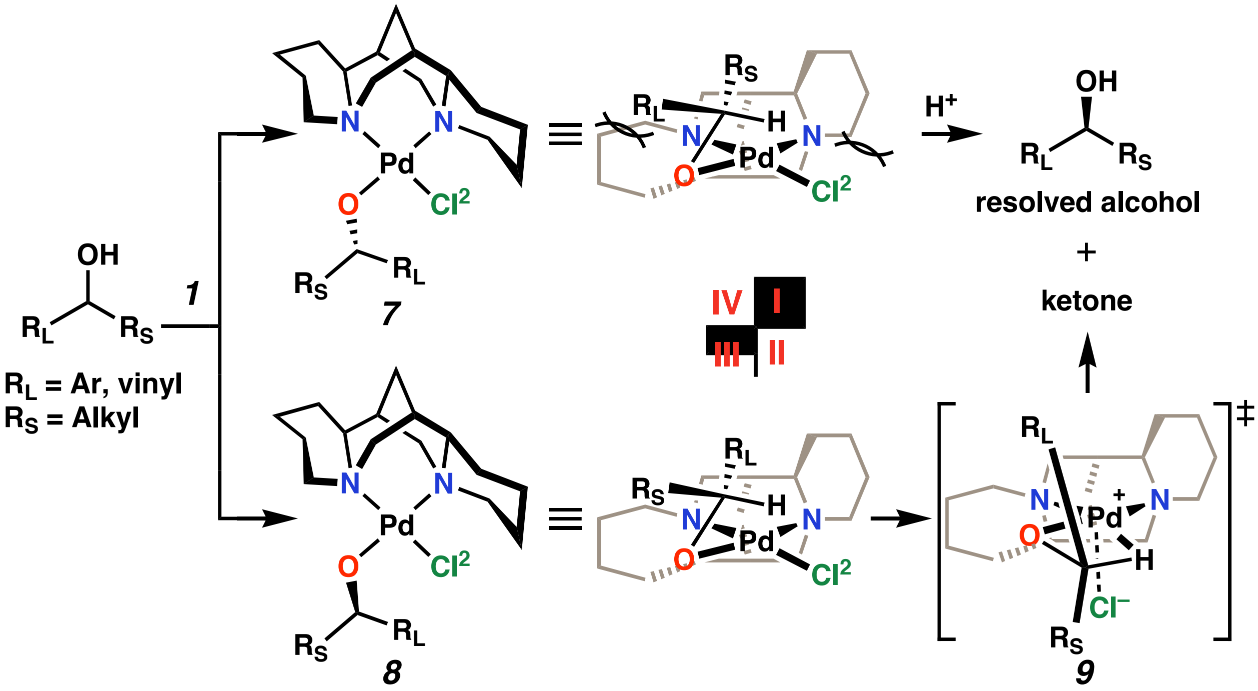


Figure 2. A model for stereoselectivity in the Pd catalyzed aerobic oxidative kinetic resolution using (sp)$PdCl_2$.

STEREO VIEWS OF MOLECULAR STRUCTURES

Figure S01. Stereo side view of (sparteine)$PdCl_2$ (**1**). Molecular structure shown with 50% probability ellipsoids. Solvent molecules ($CDCl_3$) have been omitted for clarity.

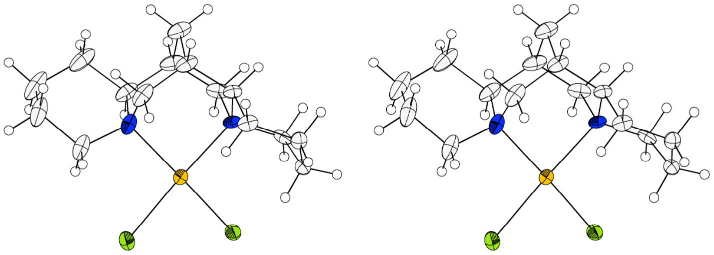
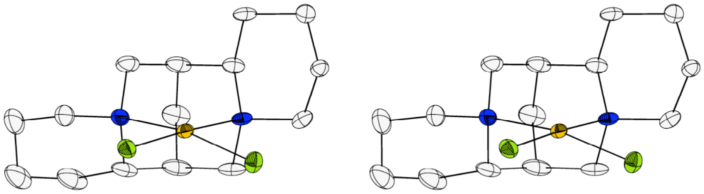


Figure S02. Stereo front view of (sparteine)$PdCl_2$ (**1**). Molecular structure shown with 50% probability ellipsoids. Hydrogen atoms and solvent molecules ($CDCl_3$) have been omitted for clarity.



STEREO VIEWS OF MOLECULAR STRUCTURES, CONT'D

Figure S03. Stereo side view of [(sparteine)Pd(pyridine)Cl]$^+$SbF$_6^-$ (**2**). Molecular structure shown with 50% probability ellipsoids. The anion has been omitted for clarity.

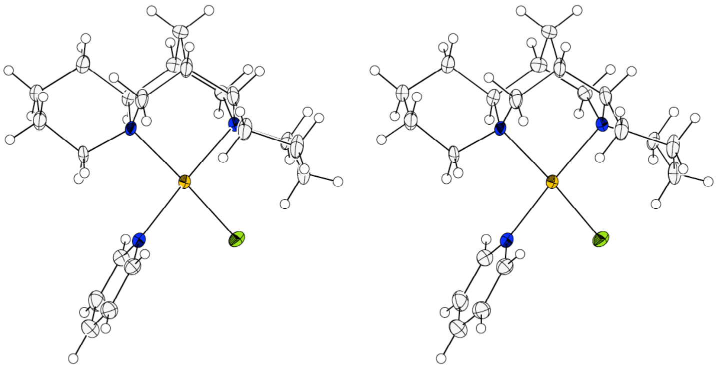
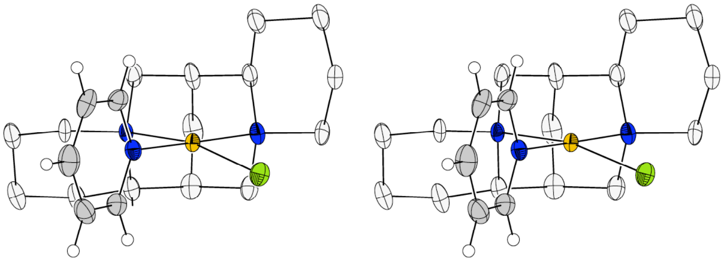


Figure S04. Stereo front view of [(sparteine)Pd(pyridine)Cl]$^+$SbF$_6^-$ (**2**). Molecular structure shown with 50% probability ellipsoids. Hydrogen atoms in the sparteine ligand and the anion have been omitted for clarity.



STEREO VIEWS OF MOLECULAR STRUCTURES, CONT'D

Figure S05. Stereo side view of [(sparteine)Pd(2-mesitylpyridine)Cl]$^+$SbF$_6^-$ (**4**). Molecular structure shown with 50% probability ellipsoids. The anion has been omitted for clarity.

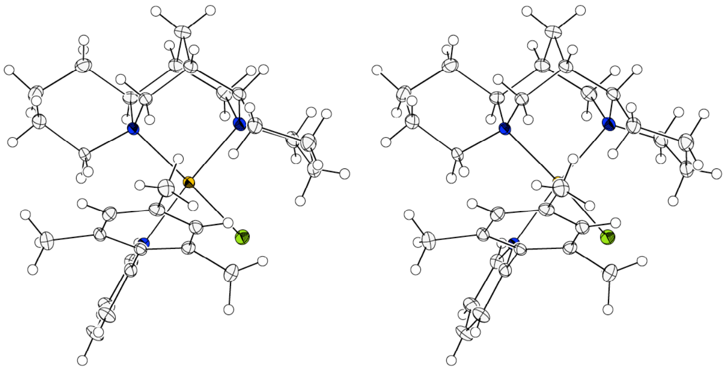
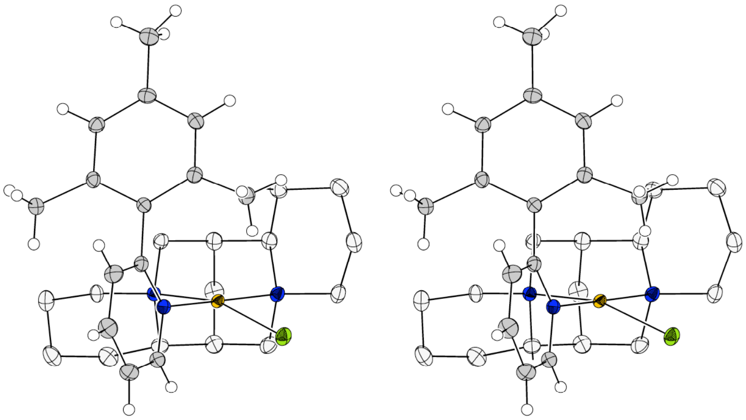


Figure S06. Stereo front view of [(sparteine)Pd(2-mesitylpyridine)Cl]$^+$SbF$_6^-$ (**4**). Molecular structure shown with 50% probability ellipsoids. Hydrogen atoms in the sparteine ligand and the anion have been omitted for clarity.



STEREO VIEWS OF MOLECULAR STRUCTURES, CONT'D

Figure S07. Stereo side view of (sparteine)Pd(OCH(CF_3)C_6H_5)Cl (**6**). Molecular structure shown with 50% probability ellipsoids. Solvent molecules (CH_2Cl_2) have been omitted for clarity.

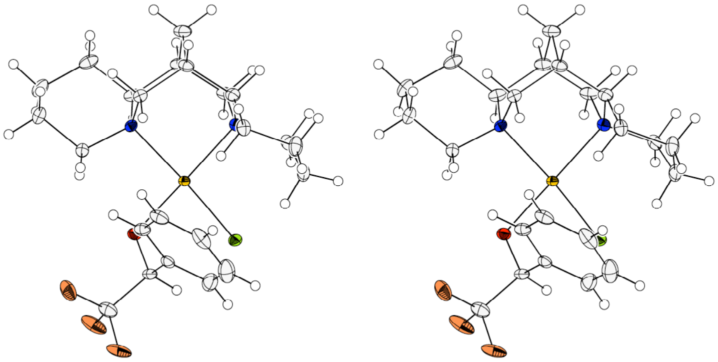
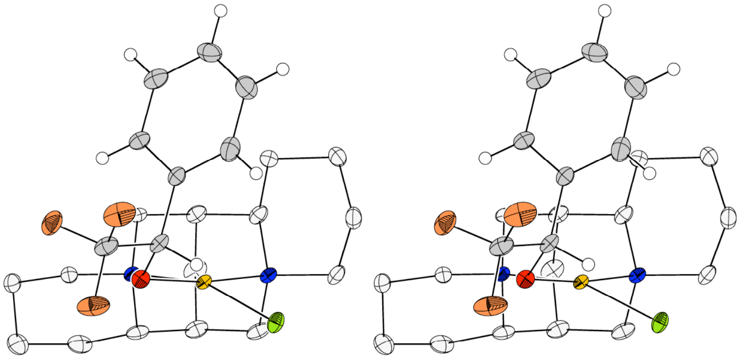


Figure S08. Stereo front view of (sparteine)Pd(OCH(CF_3)C_6H_5)Cl (**6**). Molecular structure shown with 50% probability ellipsoids. Hydrogen atoms in the sparteine ligand and solvent molecules (CH_2Cl_2) have been omitted for clarity.



STEREO VIEWS OF MOLECULAR STRUCTURES, CONT'D

Figure S09. Stereo side view of (α-isosparteine)PdCl$_2$ **(S02)**. Molecular structure shown with 50% probability ellipsoids.

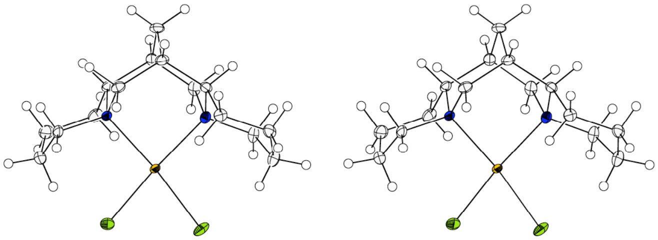
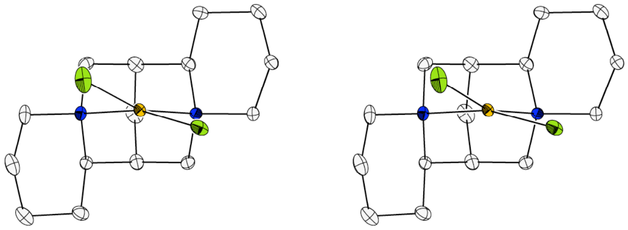
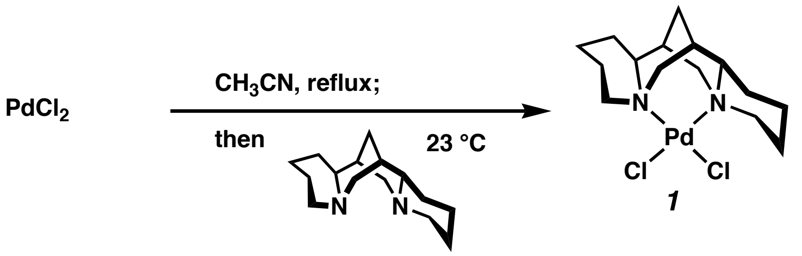


Figure S10. Stereo top view of (α-isosparteine)PdCl$_2$ **(S02)**. Molecular structure shown with 50% probability ellipsoids. Hydrogen atoms in the sparteine ligand have been omitted for clarity.

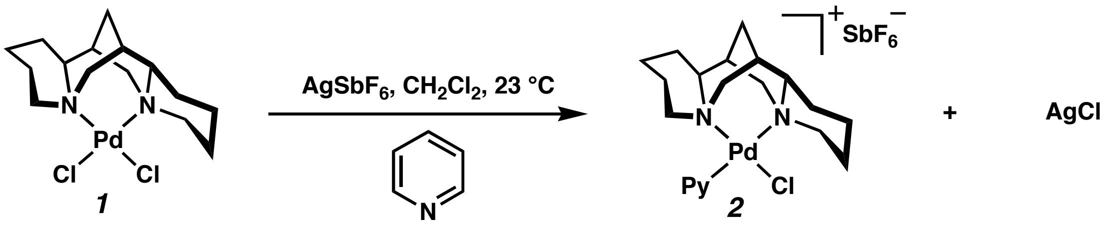


EXPERIMENTAL SECTION

Materials and Methods. Unless stated otherwise, reactions were conducted in oven-dried glassware under an argon atmosphere with freshly distilled solvents using standard Schlenk techniques. Although we have never experienced an accident, all reactions must be performed with appropriate caution in a fume hood due to the flammable nature of mixtures of oxygen and organic solvents. All commercially obtained reagents were used as received. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized via UV and anisaldehyde staining. ICN silica gel (particle size 0.032-0.063 mm) was used for flash column chromatography. Analytical chiral HPLC was performed on a Chiralcel OJ column (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. Analytical achiral GC was carried out on an Agilent DB-WAX column (30.0 m x 0.25 mm) purchased from Bodman Industries. Organic reagents were purchased from the Sigma-Aldrich Chemical Company, Milwaukee, WI and metal salts obtained from Strem Chemicals, Newburyport, MA. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer (at 300 MHz and 75 MHz respectively) and are reported relative to Me$_4$Si (δ 0.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Quantitative analysis was carried out by Desert Analytics Laboratory, Tuscon, AZ. X-ray crystallographic structures were obtained by Mr. Larry M. Henling and Dr. Mike W. Day of the California Institute of Technology Beckman Institute X-Ray Crystallography Laboratory.



(sp)PdCl$_2$ 1. PdCl$_2$ (1.5 g, 8.46 mmol, 1.0 equiv) was suspended in CH$_3$CN (40 mL) and refluxed under N$_2$ until formation of (CH$_3$CN)$_2$PdCl$_2$ was complete, as indicated by the change in color of the suspension form dark purple to yellow-orange. The mixture was allowed to cool to 23 °C at which time (–)-sparteine (1.94 mL, 8.46 mmol, 1.0 equiv) was added. Upon stirring of the dark orange-red solution for 1 h under N$_2$, an orange precipitate formed which was isolated via filtration in air. Trituration of the orange solid from CHCl$_3$ with Et$_2$O resulted in **1** as a pale orange powder (2.89 g, 7.02 mmol, 83% yield) that was identical by NMR to previously published reports.[2] A single crystal suitable for X-ray analysis was grown by slow evaporation from CDCl$_3$.



[(sparteine)Pd(pyridine)Cl]$^+$SbF$_6^-$ 2. A Schlenk flask was charged with AgSbF$_6$ (163 mg, 0.475 mmol, 1.0 equiv) and (sp)PdCl$_2$ (**1**) (196 mg, 0.475 mmol, 1.0 equiv). Addition of pyridine

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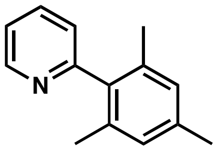
[2] Jensen, D. R.; Pugsley, J. S.; Sigman, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 7475.

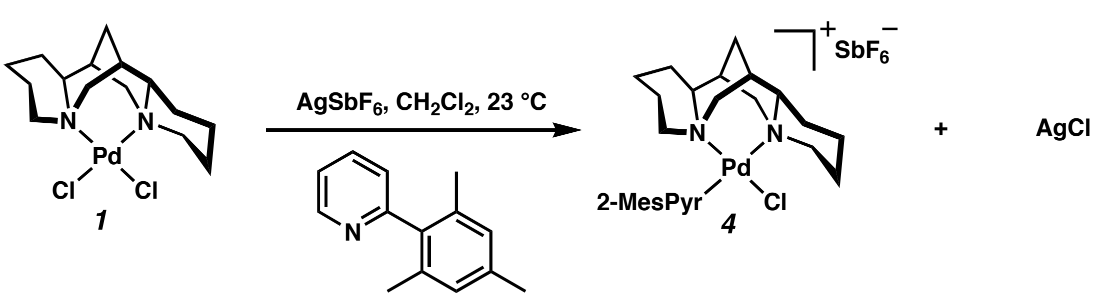
(38 µL, 0.475 mmol, 1.0 equiv) via syringe followed immediately by CH_2Cl_2 (10 mL,) resulted in nearly instantaneous formation of an orange-yellow solution and pale precipitate. After stirring for 30 min, silver chloride was removed by filtration through Celite in air. Concentration of the filtrate under vacuum yielded **2** as a yellow-orange solid (276 mg, 0.399 mmol, 84% yield) of 80% purity. Crystals suitable for x-ray diffraction were grown from acetone layered with pentane. The ^{1}HNMR spectrum of the crystalline material was identical to that of the major compound in the crude product. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.16 (d, J = 4.9 Hz, 1H), 8.89 (d, J = 5.5 Hz, 1H), 8.06 (app.tt, J = 7.7, 1.7 Hz, 1H), 7.67-7.59 (comp m, 2H), 4.69 (dd, J = 12.1, 3.3 Hz, 1H), 4.00 (dt, J = 13.2, 2.2 Hz, 1H), 3.77 (dt, J = 11.5, 1.7 Hz, 1H), 3.24-2.82 (comp m, 2H), 2.81-2.71 (comp m, 2H), 2.48 (m 1H), 2.33-1.48 (comp m, 17H), 1.10 (m, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 153.7, 152.7, 140.3, 127.7, 126.9, 69.9, 66.6, 66.0, 64.8, 63.7, 49.1, 35.4, 35.1, 31.3, 27.2, 27.0, 26.2, 24.8, 24.1, 21.1. Anal. Calcd for $C_{20}H_{31}ClF_6N_3PdSb$: C, 34.76; H, 4.52; N, 6.08. Found: C, 34.90; H, 4.64; N, 5.79. mp 137-130 °C dec.

Attempted thermolysis of [(sparteine)Pd(pyridine)Cl]$^+$SbF$_6^-$ (2). 2 (15.1 mg, 0.022 mmol) was weighed into a sealable NMR tube and dissolved in dichloroethane-d_4 (0.740 mL). A ^{1}HNMR spectrum was acquired. After the tube was heated to 80 °C for 4 h in an oil bath, an ^{1}HNMR spectrum was again acquired. No change was observed.



S01

2-Mesitylpyridine S01. S01 was prepared by the modified procedure of Hermann, et al.[3] A Schlenk tube was charged with nickel(II) acetoacetonate (103 mg, 0.40 mmol, 0.05 mol%), 1,3-bis(2,4,6-trimethylphenyl)-imidazolium chloride (136 mg, 0.40 mmol, 0.05 mol%) and 2-chloropyridine (757 µL, 8.0 mmol, 1.0 equiv) under argon. After addition of THF (8.0 mL), the pale green mixture was stirred for 15 min. Mesityl magnesium bromide (1.83 mL, 2.0 M in THF, 12.0 mmol, 1.5 equiv) was transferred via cannula to the mixture, which immediately became dark brown. After stirring for 45 m, methanol (5 mL) was added and the mixture filtered over Celite and concentrated in vacuo. Flash column chromatography on silica gel (9:1 Hexanes/EtOAc eluent) afforded a pale pink oil (1.42 g, 7.2 mmol, 90% yield), identical by ^{1}H NMR to that reported.



[(sparteine)Pd(2-mesitylpyridine)Cl]$^+$SbF$_6^-$ 4. 4 was prepared according to the method described for **2** which led to a yellow-orange solid (361 mg, 0.446 mmol, 94% yield) of 83% purity. Crystals suitable for x-ray diffraction were grown by slow diffusion of pentane into an

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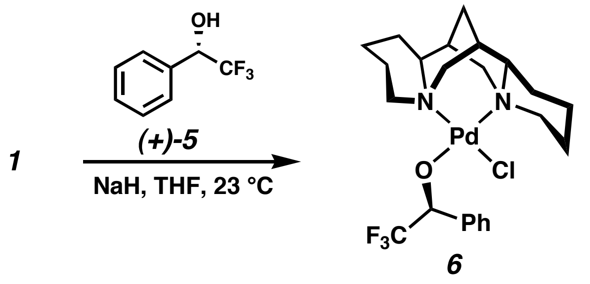
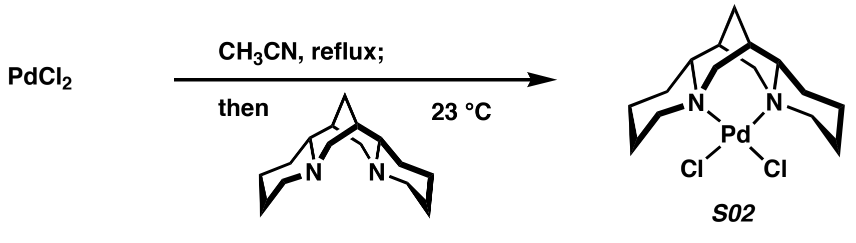
[3] Boehm, V. P. W.; Weskamp, T.; Gstoettmayr, C. W. K.; Hermann, W. A. *Angew. Chem. Int. Ed.* **2000**, *39*, 1602.

acetone solution of **4**. The ^{1}HNMR spectrum of the crystalline material was identical to that of the major compound in the crude product. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.87 (d, *J* = 5.5 Hz, 1H), 7.94 (td, *J* = 7.7, 1.6 Hz, 1H), 7.52 (td, *J* = 6.0, 1.6 Hz, 1H), 7.34 (d, 7.7 Hz, 1H), 7.20 (s, 1H), 7.18 (s, 1H), 4.41 (d, *J* = 11.0 Hz, 1H), 3.79 (d, *J* = 12.1 Hz, 1H), 3.61 (dt, *J* = 12.6, 2.2 Hz, 1H), 2.78-1.13 (comp m, 23H), 2.42 (s, 3H), 2.21 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 162.1, 154.9, 141.2, 139.9, 139.5, 135.5, 134.4, 130.3, 129.6, 129.4, 125.7, 70.1, 67.3, 65.3, 64.8, 64.0, 48.3, 34.8, 34.3, 28.9, 27.3, 27.0, 25.2, 24.6, 23.9, 22.2, 21.4, 21.3, 20.6. Anal. Calcd for $C_{29}H_{41}ClF_6N_3PdSb$: C, 43.04; H, 5.11; N, 5.19. Found: C, 43.08; H, 4.99; N, 5.02. mp 140-145 °C dec.

Attempted thermolysis of [(sparteine)Pd(2-mesitylpyridine)Cl]$^+$SbF$_6^-$ (4). **4** (6.1 mg, 0.0069 mmol) was weighed into a sealable NMR tube and dissolved in dichloroethane-*d*$_4$ (0.750 mL). A ^{1}HNMR spectrum was acquired. After the tube was heated to 80 °C for 2 h in an oil bath, a ^{1}HNMR spectrum was again acquired. No change was observed.



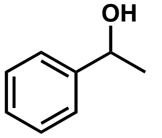
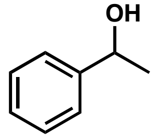
(sparteine)Pd(OCH(CF_3)C_6H_5)Cl 6. (+)-*S*-α-(trifluoromethyl)benzyl alcohol (97 μL, 0.713 mmol, 1.0 equiv) was treated with an excess of sodium hydride (60% dispersion in mineral oil, 57 mg, 1.43 mmol, 2.0 equiv) in THF (5 mL) under argon. After bubbling had ceased, the alkoxide was transferred to a stirring suspension of (sparteine)$PdCl_2$ (**1**) (294 mg, 0.713 mmol, 1.0 equiv) in THF (19 mL) under argon at 23 °C. The yellow-orange suspension gradually became an orange solution with very fine white precipitate. After stirring for 30 min, the orange solution was filtered away from the sodium chloride and the solvents removed under vacuum to afford an orange solid (336 mg, 0.61 mmol, 84% yield) of 74% purity. **6** was obtained after recrystallization from CH_2Cl_2 layered with hexane at -20 °C in a glove box as an unstable dark orange solid (215 mg 0.39 mmol, 64% yield from crude material). The ^{1}HNMR spectrum of the crystalline material corresponded exactly to that of the major species in the crude product. A single crystal suitable for x-ray diffraction was grown from CH_2Cl_2 layered with hexane at -20 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.44-7.34 (comp m, 3H), 5.11 (q, *J* = 8.0 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 3.70-3.52 (comp m, 3H), 2.85-2.72 (comp m, 2H), 2.48-1.15 (comp m, 20H); ^{13}C NMR (75 MHz, CD_2Cl_2) d 129.9, 128.9, 128.8, 128.54, 128.47, 128.2, 78.5 (d, *J* = 27.7), 69.9, 65.7, 65.6, 64.3, 57.4, 49.2, 35.4, 34.9, 29.8, 28.0, 27.4, 25.3, 24.7, 24.2, 20.5.



(α-isosparteine)$PdCl_2$ S02. (–)-α-isosparteine was prepared by the method of Leonard.[4] $(CH_3CN)_2PdCl_2$ (73 mg, 0.28 mmol, 1.0 equiv) and (–)-α-isosparteine (66 mg, 0.28 mmol, 1.0 equiv) were dissolved in CH_3CN (5 mL) and allowed to stir at 23 °C under argon for 1 h. The dark orange solution was filtered through Celite and concentrated in vacuo to afford **S02** as a rust-colored microcrystalline solid (84 mg, 0.20 mmol, 72% yield). A single crystal suitable for x-ray diffraction was grown by slow evaporation from CH_2Cl_2. ^1H NMR (300 MHz, CD_2Cl_2) δ 3.95 (qd, J = 12.4, 3.9 Hz, 2H), 3.72-3.66 (m, 2H), 3.51 (d, J = 12.4 Hz, 2H), 2.98-2.84 (m, 2H), 2.24-2.19 (m, 2H), 2.15-2.10 (m, 2H) 1.94-1.79 (comp m, 10 H), 1.65-1.51 (comp m, 4 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 72.15, 64.6, 60.7, 35.8, 35.5, 30.9, 25.5, 25.0. Anal. Calcd for $C_{15}H_{26}Cl_2N_2Pd$: C, 43.76; H, 6.37; N, 6.80. Found: C, 43.82; H, 6.36; N, 6.68. mp 180-182 °C.

Oxidative Kinetic Resolution of 1-phenylethanol with S02 and 1. A thick-walled oven-dried 10 mL (1 cm OD) tube equipped with magnetic stir bar was charged with powdered molecular sieves (MS3Å, 150 mg, 500 mg/mmol), **S02** or **1** (6.2 mg, 0.015 mmol, 0.05 equiv), and tridecane (29.3 μL, 0.12 mmol, 0.40 equiv) as internal standard, followed by toluene (3.0 mL), 1-phenylethanol (36 μL, 0.30 mmol, 1 equiv), and (–)-α-isosparteine or sparteine (10.5 mg, 0.045 mmol, 0.15 equiv). The tube was evacuated and back-filled with O_2 (3 x, balloon), heated to 80 °C, and allowed to stir under O_2 (1 atm, balloon). To monitor the reaction, aliquots (200 μL) were removed and passed through a pipette plug of silica gel using Et_2O as eluent. Conversion was analyzed by GC; the sample was then concentrated in vacuo and %ee analyzed by chiral HPLC as previously reported[5] (see Table S01).

Table S01. Oxidative Kinetic Resolution with **S02** and **1** using (–)-sparteine and (–)-α-isosparteine as the exogenous base.

entry	substrate	catalyst	time	% conversion	%ee	s[c]
1[a]		(α-isosparteine)$PdCl_2$	72 h	33.6	28.6	4.7
2[b]		(sp)$PdCl_2$	24 h	58.1	93.2	17.3

[a] Data represent an average of two runs. [b] Data represent an average of three runs. [c] The selectivity factor, s, was determined by the following equation: $s = k_{rel} = \ln[(1-C)(1 - ee)]/\ln[(1 - C)(1 + ee)]$ where C is conversion and ee is enantiomeric excess.

Oxidative Kinetic Resolution of 1-phenylethanol with S02 and 1 with Cs_2CO_3 as the Sole Exogenous Base. In order to test whether the difference in s between S02 and 1 in the oxidative kinetic resolution (see table S01) was due to a difference in the activity of the free alkaloids as bases,[6] the resolution was carried out using only Cs_2CO_3 as the base under non-optimized

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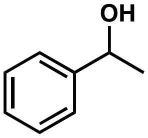
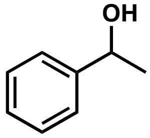
[4] (a) Leonard, N. J.; Beyler, R. E. *J. Am. Chem. Soc.* **1948**, *70*, 2298. (b) Leonard, N. J.; Beyler, R. E. *J. Am. Chem. Soc.* **1950**, *72*, 1316.

[5] (a) Ferreira, E. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2001**, *123*, 7725. (b) Bagdanoff, J. T.; Stoltz, B. M. *Org. Lett.* **2003**, *5*, 835.

[6] We thank a reviewer for raising this issue.

conditions. A thick-walled oven-dried 10 mL (1 cm OD) tube equipped with magnetic stir bar was charged with powdered molecular sieves (MS3Å, 150 mg, 500 mg/mmol), **S02** or **1** (6.2 mg, 0.015 mmol, 0.05 equiv), and tridecane (29.3 μL, 0.12 mmol, 0.40 equiv) as internal standard, followed by toluene (3.0 mL), 1-phenylethanol (36 μL, 0.30 mmol, 1 equiv), and finely ground anhydrous Cs_2CO_3 (98 mg, 0.300 mmol, 1 equiv). The tube was evacuated and back-filled with O_2 (3 x, balloon), heated to 80 °C, and allowed to stir under O_2 (1 atm, balloon). To monitor the reaction, aliquots (100 μL) were removed and passed through a pipette plug of silica gel using Et_2O as eluent. Conversion was analyzed by GC; the sample was then concentrated in vacuo and %ee analyzed by chiral HPLC as previously reported[5] (see Table S02).

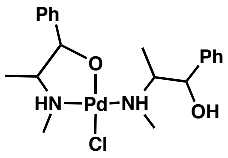
Table S02. Oxidative kinetic resolution with **S02** and **1** using Cs_2CO_3 as the sole exogenous base.

entry	substrate	catalyst	time	% conversion	%ee	s[b]
1[a]		**(α-isosparteine)$PdCl_2$**	**12 h**	**17.3**	**4.96**	**1.7**
2[a]		**(sp)$PdCl_2$**	**12 h**	**36.2**	**35.2**	**6.0**

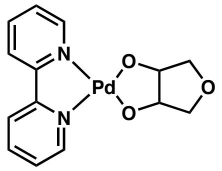
[a] Data represent an average of two runs. [b] The selectivity factor, s, was determined by the following equation: $s = k_{rel} = \ln[(1-C)(1-ee)]/\ln[(1-C)(1+ee)]$ where C is conversion and ee is enantiomeric excess.

Conversion of 6 to 2,2,2-trifluoroacetophenone. 6 (18.8 mg, 0.034 mmol, 1.0 equiv) and bis(trimethylsilyl)benzene (4.4 mg, 0.021 mmol, 0.59 equiv) as internal standard were dissolved in CD_2Cl_2 (700 μL) in an NMR tube in the glove box. A ^{1}HNMR spectrum was acquired and the integration of resonances corresponding to the methine proton of **6** and the methyl resonance of bis(trimethylsilyl)benzene compared. The tube was taken into the glove box, and $AgSbF_6$ (17.5 mg, 0.051 mmol, 1.5 equiv) was added to the orange solution upon which a greenish-black suspension was produced immediately. A ^{1}H NMR spectrum was acquired which showed complete disappearance of resonances corresponding to **6** and the appearance of resonances corresponding to 2,2,2-trifluoroacetophenone (92% yield based on integration of the *ortho*-aryl ^{1}H resonance of 2,2,2-trifluoroacetophenone and the methyl resonance of bis(trimethylsilyl)benzene and comparison with the first spectrum).

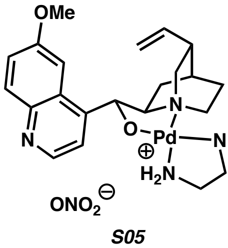
Figure S11. Tabulation of palladium alkoxide structures possessing β-hydrogens reported in the Cambridge Structural Database.[7]



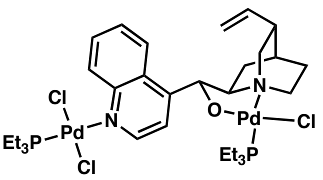
S03



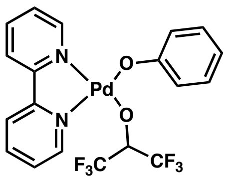
S04



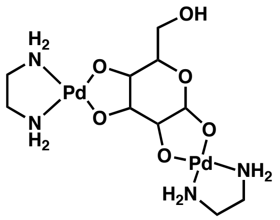
S05



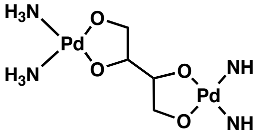
S06



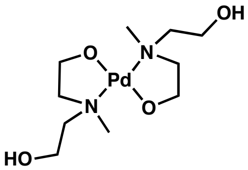
S07



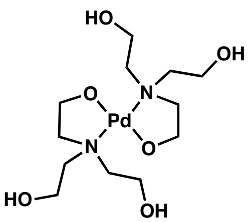
S08



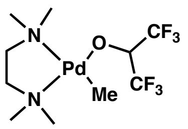
S09



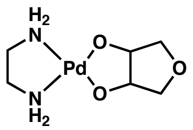
S10



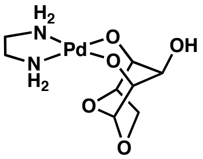
S11



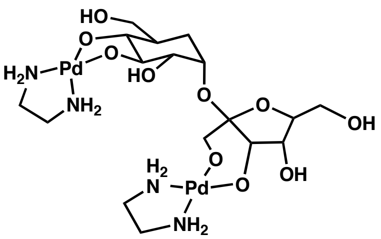
S12



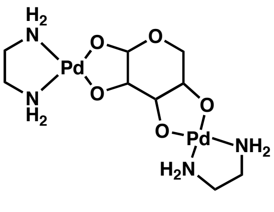
S13



S14



S15



S16

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[7] ***S03***: Bouquillon, S.; du Moullinet d'Hardemare, A.; Averbuch-Pouchot, M.-T.; Henin, F.; Muzart, J.; Durif, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, 2028. ***S04***: Achternbosch, M.; Klufers, P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1994**, *50*, 175. ***S05, S06***: Hubel, R.; Polborn, K.; Beck, W. *Eur. J. Inorg. Chem.* **1999**, 471. ***S07***: Kapteijn, G. M.; Grove, D. M.; van Koten, G.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chim. Acta* **1993**, *207*, 131. ***S08***: Klufers, P.; Kunte, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4210. ***S09***: Kastele, X.; Klufers, P.; Kunte, T. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2042. ***S10, S11***: Kapteijn, G. M.; Baesjou, P.; Alsters, P. L.; Grove, D. M.; Smeets, W. J. J.; Kooijman, H.; Spek, A. L.; van Koten, G. *Chem. Ber.* **1997**, *130*, 35. ***S12***: Kapteijn, G. M.; Dervisi, A.; Grove, D. M.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 10939. ***S13, S14, S15***: Ahlrichs, R.; Ballauff, M.; Eichkorn, K.; Hanemann, O.; Kettenbach, G.; Klufers, P. *Chem.-Eur. J.* **1998**, *4*, 835. ***S15***: Klufers, P.; Kunte, T. *Eur. J. Inorg. Chem.* **2002**, 1285.

MOLECULAR STTRUCTURES AND CRYSTALLOGRAPHIC DATA FOR 1, 2, 4, 6 AND S02

Figure S12. (sparteine)PdCl$_2$ (**1**) shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 203513.

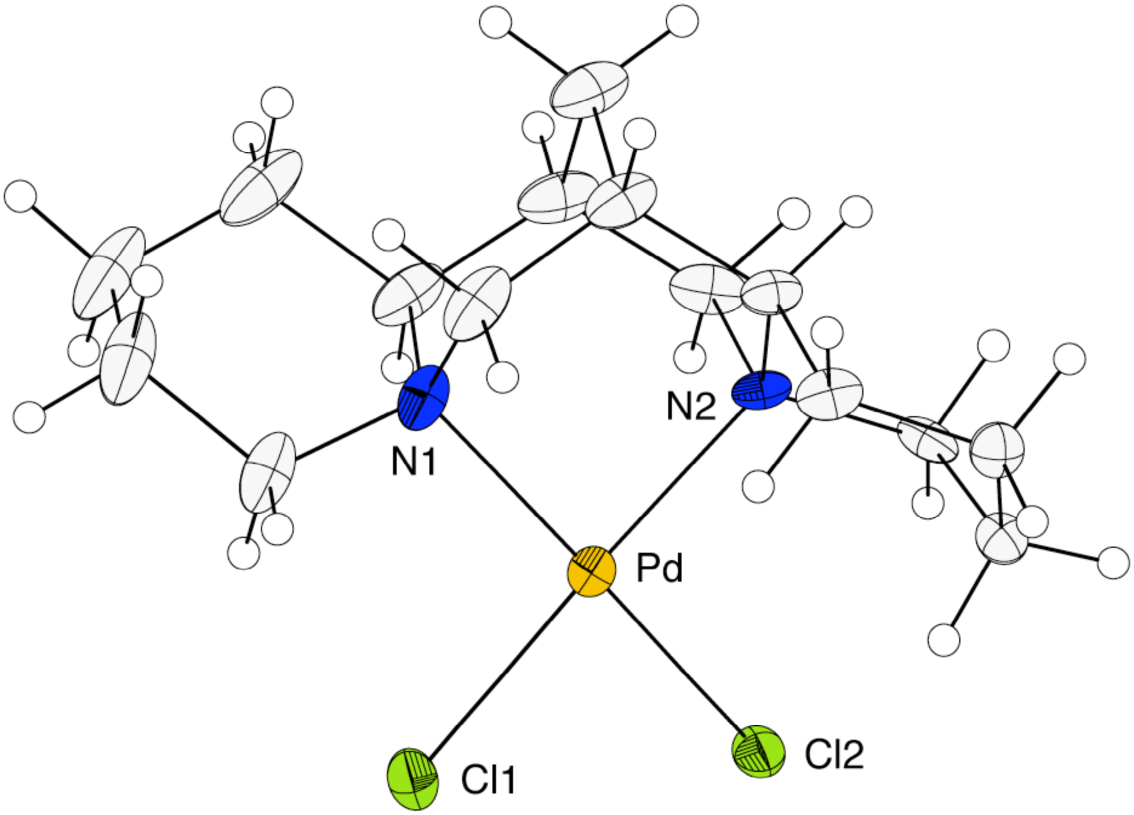

Table S03. Selected bond lengths [Å] and angles for **1** (CCDC 203513)

Pd-N(2)	2.096(3)	N(2)-Pd-N(1)	87.51(10)
Pd-N(1)	2.127(2)	N(2)-Pd-Cl(2)	93.44(7)
Pd-Cl(2)	2.3150(8)	N(1)-Pd-Cl(2)	170.06(8)
Pd-Cl(1)	2.3161(9)	N(2)-Pd-Cl(1)	176.24(7)
		N(1)-Pd-Cl(1)	95.65(8)
		Cl(2)-Pd-Cl(1)	83.09(3)

Table S04. Crystal data and structure refinement for **1** (CCDC 203513).

Empirical formula	$C_{15}H_{26}Cl_2N_2Pd \bullet 2CHCl_3$
Formula weight	650.41
Crystallization Solvent	Chloroform
Crystal Habit	Blade
Crystal size	0.33 x 0.15 x 0.06 mm^3
Crystal color	Orange
Data Collection	
Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 17268 reflections used in lattice determination	2.17 to 28.42°
Unit cell dimensions	a = 10.5805(7) Å b = 12.4401(8) Å c = 18.6906(12) Å
Volume	2460.1(3) Å^3
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.756 Mg/m^3
F(000)	1304
θ range for data collection	1.97 to 28.44°
Completeness to θ = 28.44°	96.7 %
Index ranges	$-13 \leq h \leq 14, -16 \leq k \leq 16, -24 \leq l \leq 24$
Data collection scan type	ω scans at 5 ϕ settings
Reflections collected	43840
Independent reflections	5883 [R_{int}= 0.0794]
Absorption coefficient	1.632 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9084 and 0.6150
Structure solution and Refinement	
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Patterson method
Secondary solution method	Difference Fourier map

Table S04 continued. Crystal data and structure refinement for **1** (CCDC 203513).

Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	5883 / 24 / 329
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.367
Final R indices [$I>2\sigma(I)$, 22793 reflections]	R1 = 0.0332, *w*R2 = 0.0526
R indices (all data)	R1 = 0.0436 *w*R2 = 0.0538
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Absolute structure parameter	-0.04(2)
Largest diff. peak and hole	0.984 and -0.639 e.Å^{-3}

Special Refinement Details

The crystals contain chloroform as a solvent of co-crystallization. Each asymmetric unit contains two molecules of disordered chloroform. The disorder was successfully modeled and all solvent atoms were refined anisotropically. However, the 1,2 and 1,3 distances within the solvents were restrained to be similar and each distance was assigned a free variable so as to not place artificial values in the geometry. All hydrogen atoms were constrained to ride on the corresponding carbon.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Figure S13. [(sparteine)Pd(pyridine)Cl]$^+$SbF$_6^-$ (**2**) shown with 50% probability ellipsoids. The anion has been omitted for clarity. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 213927.

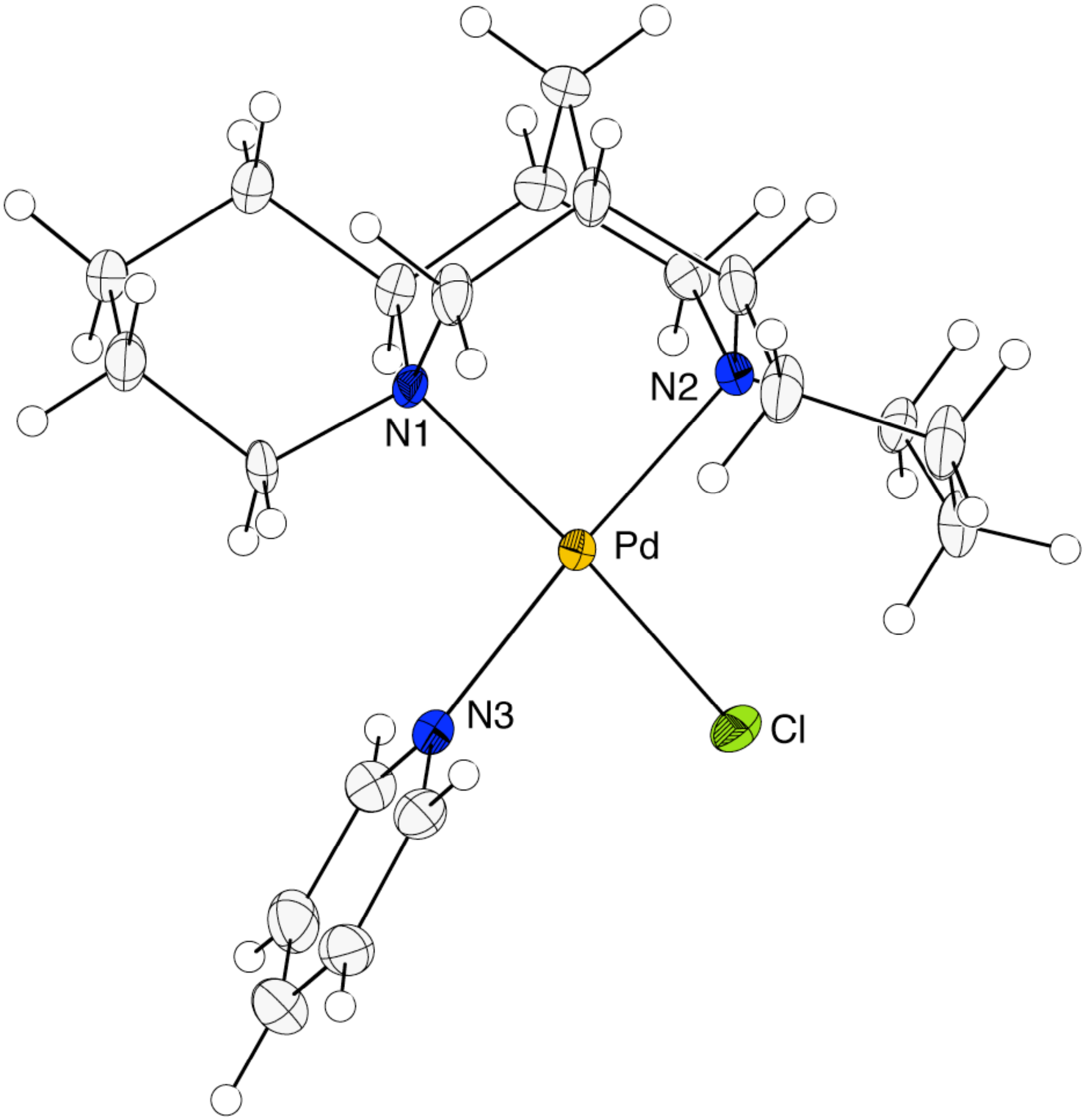

Table S05. Selected bond lengths [Å] and angles for **2** (CCDC 213927).

Pd-N(3)	2.046(3)	N(3)-Pd-N(2)	176.64(10)
Pd-N(2)	2.087(2)	N(3)-Pd-N(1)	95.73(9)
Pd-N(1)	2.122(2)	N(2)-Pd-N(1)	87.39(9)
Pd-Cl	2.3105(7)	N(3)-Pd-Cl	81.52(7)
		N(2)-Pd-Cl	95.67(7)
		N(1)-Pd-Cl	168.52(7)

Table S06. Crystal data and structure refinement for **2** (CCDC 213927).

Empirical formula	$[C_{20}H_{31}ClN_3Pd]^+$ $[SbF_6]^-$
Formula weight	691.08
Crystallization Solvent	Acetone/pentane
Crystal Habit	Block
Crystal size	0.23 x 0.20 x 0.19 mm^3
Crystal color	Yellow

Data Collection

Preliminary Photos	Rotation	
Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 54240 reflections used in lattice determination	2.19 to 39.64°	
Unit cell dimensions	a = 10.3598(2) Å b = 22.2422(3) Å c = 10.8117(2) Å	β= 104.3020(10)°
Volume	2414.07(7) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	$P2_1$	
Density (calculated)	1.901 Mg/m^3	
F(000)	1360	
Data collection program	Bruker SMART v5.054	
θ range for data collection	1.83 to 40.92°	
Completeness to θ = 40.92°	97.6 %	
Index ranges	$-18 \leq h \leq 18$, $-40 \leq k \leq 40$, $-19 \leq l \leq 19$	
Data collection scan type	ω scans at 7 ϕ and 2 2θ settings	
Data reduction program	Bruker SAINT v6.022	
Reflections collected	110239	
Independent reflections	29947 [R_{int}= 0.0717]	
Absorption coefficient	2.034 mm^{-1}	
Absorption correction	Calculated, **NOT** applied	
Max. and min. transmission	0.6986 and 0.6520	

Table S06 continued. Crystal data and structure refinement for **2** (CCDC 213927).

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Patterson method
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	29947 / 1 / 577
Treatment of hydrogen atoms	Constrained
Goodness-of-fit on F^2	1.664
Final R indices [$I>2\sigma(I)$, 22793 reflections]	R1 = 0.0503, *w*R2 = 0.0842
R indices (all data)	R1 = 0.0709, *w*R2 = 0.0864
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(\mathrm{Fo}^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	-0.018(12)
Largest diff. peak and hole	5.743 and -4.948 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Figure S14. [(sparteine)Pd(2-mesitylpyridine)Cl]$^+$SbF$_6^-$ (**4**) shown with 50% probability ellipsoids. The anion has been omitted for clarity. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 215758.

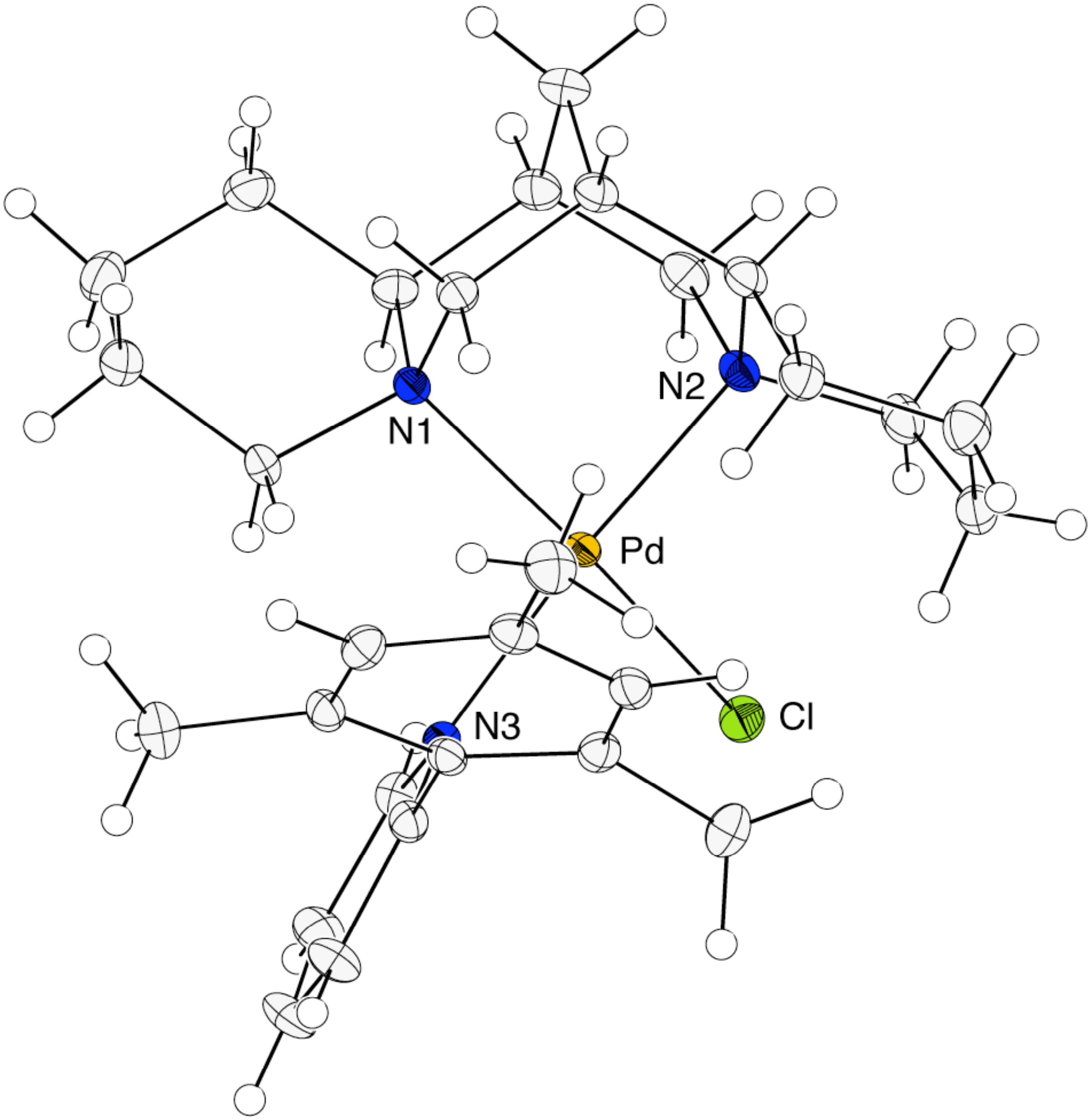

Table S07. Selected bond lengths [Å] and angles for **4** (CCDC 215758).

Pd-N(3)	2.0809(13)	N(3)-Pd-N(2)	175.42(5)
Pd-N(2)	2.0914(14)	N(3)-Pd-N(1)	96.95(5)
Pd-N(1)	2.1326(14)	N(2)-Pd-N(1)	87.48(9)
Pd-Cl	2.3345(4)	N(3)-Pd-Cl	82.53(4)
		N(2)-Pd-Cl	93.56(4)
		N(1)-Pd-Cl	163.51(4)

Table S08. Crystal data and structure refinement for **4** (CCDC 215758).

Empirical formula	$[C_{29}H_{41}N_3ClPd]^+$ $[SbF_6]^-$
Formula weight	809.25
Crystallization Solvent	Acetone/pentane
Crystal Habit	Block
Crystal size	0.30 x 0.30 x 0.26 mm^3
Crystal color	Clear
Data Collection	
Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 41762 reflections used in lattice determination	2.27 to 40.10°
Unit cell dimensions	a = 12.3773(2) Å b = 13.1425(2) Å c = 18.7060(3) Å
Volume	3042.88(8) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.766 Mg/m^3
F(000)	1616
Data collection program	Bruker SMART v5.054
θ range for data collection	1.89 to 40.43°
Completeness to $\theta = 40.43°$	96.5 %
Index ranges	$-22 \le h \le 22$, $-22 \le k \le 23$, $-33 \le l \le 32$
Data collection scan type	ω scans at 3 ϕ settings each for two 2θ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	77220
Independent reflections	18496 [R_{int}= 0.0639]
Absorption coefficient	1.628 mm^{-1}
Absorption correction	None
Max. and min. transmission (predicted)	0.6769 and 0.6409

Table S08 continued. Crystal data and structure refinement for **4** (CCDC 215758).

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	18496 / 0 / 534
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.165
Final R indices [$I>2\sigma(I)$, 15330 reflections]	R1 = 0.0313, *w*R2 = 0.0489
R indices (all data)	R1 = 0.0450, *w*R2 = 0.0507
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.003
Average shift/error	0.000
Absolute structure parameter	-0.036(8)
Largest diff. peak and hole	2.104 and -0.833 e.Å^{-3}

Special Refinement Details

All peaks in the final difference Fourier map greater than 1e$^-$/Å^3 are within 1Å of either Pd or Sb.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Figure S15. (sparteine)Pd(OCH(CF_3)C_6H_5)Cl (**6**) shown with 50% probability ellipsoids. The solvent molecules (CH_2Cl_2) have been omitted for clarity. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 222289.

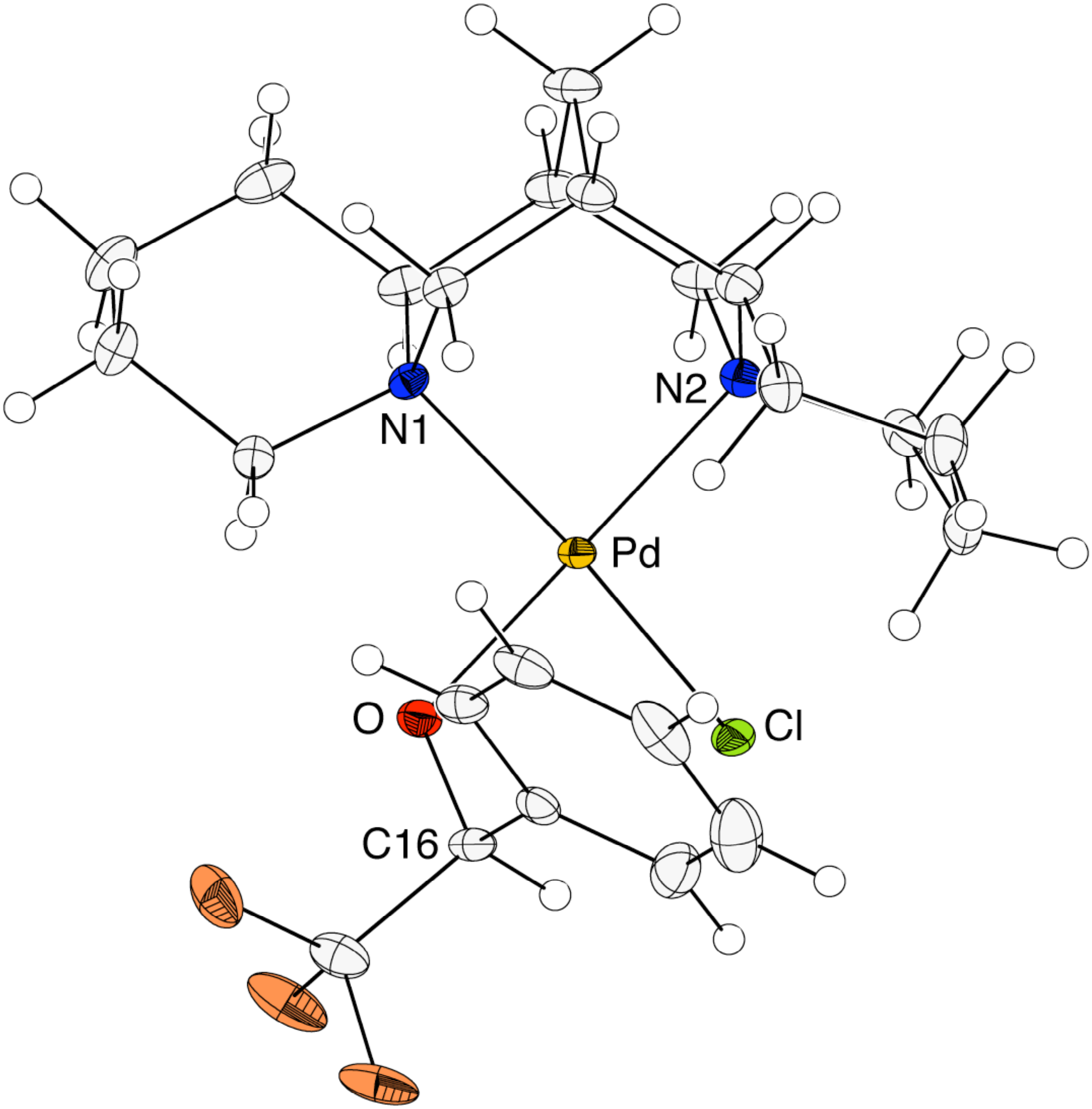

Table S09. Selected bond lengths [Å] and angles for **6** (CCDC 222289).

Pd-O	2.0012(14)	O-Pd-N(2)	176.27(6)
Pd-N(2)	2.0925(16)	O-Pd-N(1)	89.78(6)
Pd-N(1)	2.1243(17)	N(2)-Pd-N(1)	88.07(6)
Pd-Cl	2.3316(5)	O(1)-Pd-Cl	87.71(4)
O-C(16)	1.402(2)	N(2)-Pd-Cl	95.16(4)
		N(1)-Pd-Cl	164.59(5)

Table S10. Crystal data and structure refinement for **6** (CCDC 222289).

Empirical formula	$C_{23}H_{32}ClF_3N_2OPd \cdot 2CH_2Cl_2$	
Formula weight	721.21	
Crystallization Solvent	Dichloromethane/hexane	
Crystal Habit	Block	
Crystal size	0.33 x 0.33 x 0.26 mm^3	
Crystal color	Orange	
	Data Collection	
Preliminary Photos	Rotation	
Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 30297 reflections used in lattice determination	2.35 to 38.68°	
Unit cell dimensions	a = 14.8633(3) Å	
	b = 13.4427(3) Å	β= 98.5410(10)°
	c = 15.0189(3) Å	
Volume	2967.54(11) Å^3	
Z	4	
Crystal system	Monoclinic	
Space group	$P2_1$	
Density (calculated)	1.614 Mg/m^3	
F(000)	1464	
Data collection program	Bruker SMART v5.054	
θ range for data collection	1.80 to 40.44°	
Completeness to θ = 40.44°	93.7 %	
Index ranges	-26 ≤ h ≤ 26, -24 ≤ k ≤ 24, -27 ≤ l ≤ 27	
Data collection scan type	ω scans at 7 ϕ settings	
Data reduction program	Bruker SAINT v6.022	

Table S10 continued. Crystal data and structure refinement for **6** (CCDC 222289).

Reflections collected	79009
Independent reflections	33021 [R_{int}= 0.0654]
Absorption coefficient	1.117 mm^{-1}
Absorption correction	None
Max. and min. transmission (predicted)	0.7600 and 0.7094

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	33021 / 1 / 667
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	0.987
Final R indices [$I>2\sigma(I)$, 21505 reflections]	R1 = 0.0401, *w*R2 = 0.0608
R indices (all data)	R1 = 0.0826, *w*R2 = 0.0669
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.003
Average shift/error	0.000
Absolute structure parameter	-0.036(10)
Largest diff. peak and hole	2.072 and -1.257 e.Å^{-3}

Special Refinement Details

Peaks in the difference Fourier larger than 1e$^-$/Å^3 lie near metal centers or near solvent molecules.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Figure S16. (α-isosparteine)PdCl$_2$ (**S02**) shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 223628.

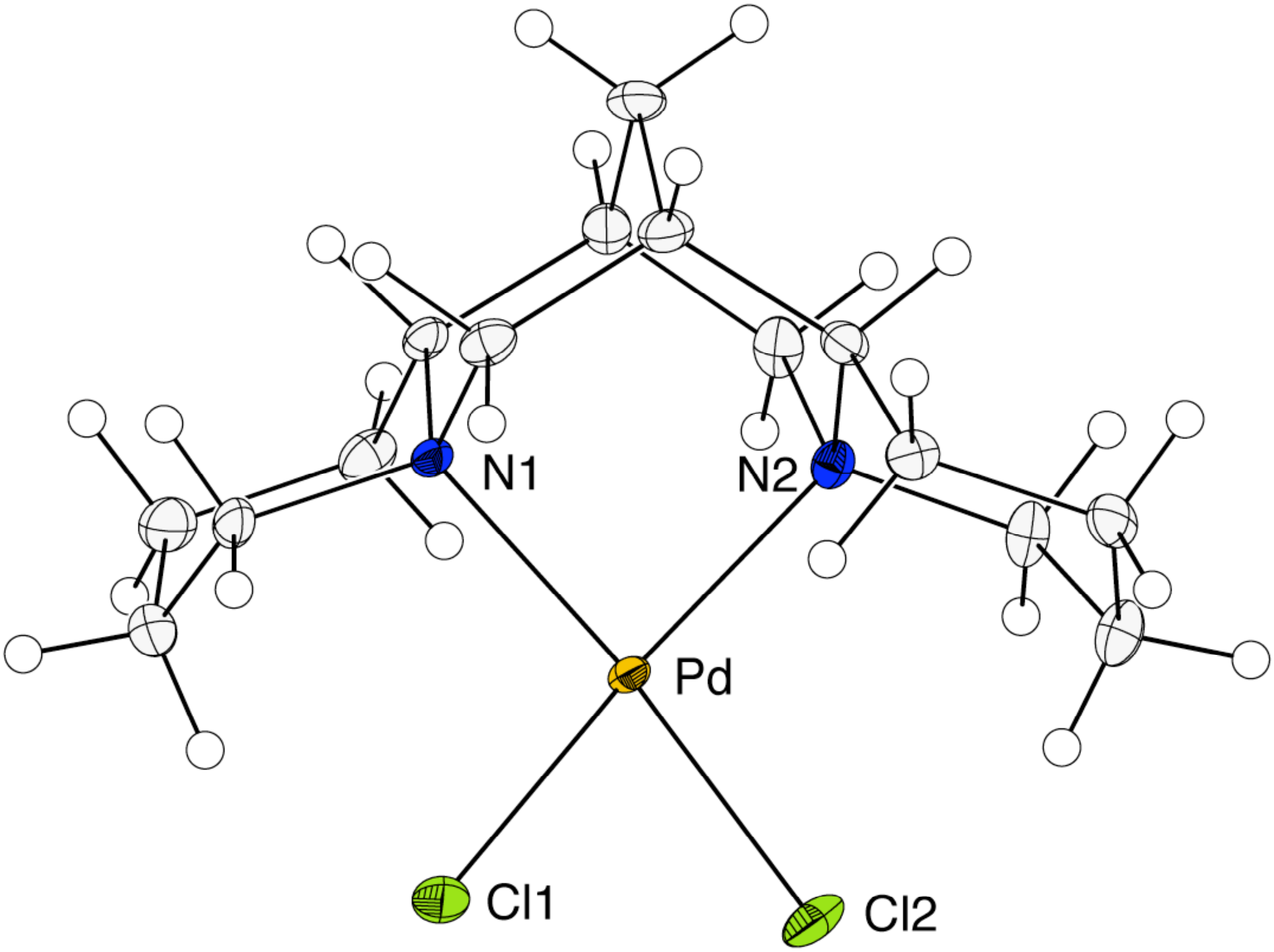

Table S11. Selected bond lengths [Å] and angles for **S02** (CCDC 223628).

Pd-N(1)	2.1091(11)	N(1)-Pd-N(2)	87.23(4)
Pd-N(2)	2.1271(12)	N(1)-Pd-Cl(2)	166.25(4)
Pd-Cl(2)	2.3140(3)	N(2)-Pd-Cl(2)	95.68(3)
Pd-Cl(1)	2.3275(4)	N(1)-Pd-Cl(1)	94.81(3)
		N(2)-Pd-Cl(1)	163.54(3)
		Cl(2)-Pd-Cl(1)	86.205(15)

Table S12. Crystal data and structure refinement for **S02** (CCDC 223628).

Empirical formula	$C_{15}H_{26}Cl_2N_2Pd$
Formula weight	411.68
Crystallization Solvent	Dichloromethane
Crystal Habit	Fragment
Crystal size	0.39 x 0.24 x 0.22 mm^3
Crystal color	Maroon
	Data Collection
Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 24049 reflections used in lattice determination	2.22 to 44.96°
Unit cell dimensions	a = 9.2815(3) Å b = 11.4873(4) Å c = 15.1073(5) Å
Volume	1610.73(9) Å^3
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.698 Mg/m^3
F(000)	840
Data collection program	Bruker SMART v5.054
θ range for data collection	2.23 to 44.97°
Completeness to θ = 44.97°	94.4 %
Index ranges	$-17 \leq h \leq 16, -22 \leq k \leq 20, -28 \leq l \leq 29$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.45
Reflections collected	44470
Independent reflections	11830 [R_{int}= 0.0673]
Absorption coefficient	1.476 mm^{-1}
Absorption correction	None
Max. and min. transmission (predicted)	0.7372 and 0.5968

Table S12 continued. Crystal data and structure refinement for **S02** (CCDC 223628).

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11830 / 0 / 285
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.139
Final R indices [$I>2\sigma(I)$, 9732 reflections]	R1 = 0.0317, *w*R2 = 0.0525
R indices (all data)	R1 = 0.0452, *w*R2 = 0.0542
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.004
Average shift/error	0.000
Absolute structure parameter	-0.042(13)
Largest diff. peak and hole	1.557 and -1.497 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2s(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.