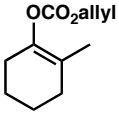
Supporting Information:

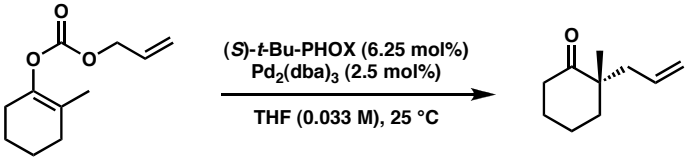
1. Experimental data with stabilized enolates:

General Procedure for Preparation of Allyl Enol Carbonates:



To a solution of potassium *t*-butoxide (5.88 g, 52.5 mmol, 1.05 equiv) in DMF (100 mL) was added 2-methylcyclohexanone (6.13 mL, 50 mmol, 1.0 equiv). After 12 h, the reaction mixture was cooled in an ice bath and allyl chloroformate (6.4 mL, 60 mmol, 1.2 equiv) was added in a dropwise fashion. After an additional 30 min in the ice bath and 15 min at 25 °C, the reaction mixture was quenched into water (250 mL), extracted with DCM/hexanes 2/1 (4 x 125 mL), dried ($MgSO_4$), and evaporated. Chromatography (2.5 to 4 % Et_2O in Hexanes on SiO_2) afforded the allyl enol carbonate[1] (4.49 g, 46% yield) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 5.94 (ddt, J = 17.4, 10.5, 5.6 Hz, 1H), 5.36 (dq, J = 17.1, 1.5 Hz, 1H), 5.26 (dq, J = 10.2, 1.2 Hz, 1H), 4.63 (dt, J = 5.7, 1.4 Hz, 2H), 2.13 (m, 2H), 2.02 (m, 2H), 1.70 (m, 2H), 1.59 (m, 2H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 142.2, 131.5, 120.8, 118.8, 68.5, 30.0, 26.6, 23.1, 22.3, 15.7; IR (Neat Film NaCl) 3936, 1755, 1275, 1239, 1037 cm^{-1}; HRMS *m/z* calc'd for $C_{11}H_{16}O_3$ $[M]^+$: 196.1100, found 196.1092.

General Procedure for 1.0 mmol Preparative Reactions of Allyl Enol Carbonates:



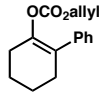
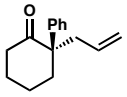
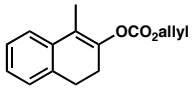
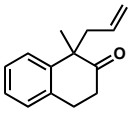
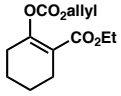
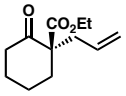
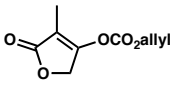
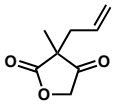
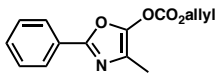
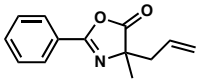
A 50 mL rb flask equipped with a magnetic stir bar was flame dried under vacuum. After cooling under dry argon, $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol, 0.025 equiv) and *(S)-t*-Bu-PHOX (24.2 mg, 0.0625 mmol, 0.0625 equiv) were added. After the flask was flushed with argon, THF (30 mL) was added and the contents were stirred at 25 °C for 30 min, at which time the allyl enol carbonate (196.2 mg, 1.0 mmol, 1.0 equiv) was added by syringe in one portion. When the reaction was complete by TLC, the reaction mixture was evaporated under reduced pressure and the residue chromatographed (2 to 3 % Et_2O in pentane on SiO_2) to afford (*S*)-2-allyl-2-methylcyclohexanone (129.6 mg, 85.1% yield) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 5.75-5.61 (m, 1H), 5.05 (s, 1H), 5.01 (m, 1H), 2.40-2.31 (m, 3H), 2.21 (dd, J = 13.8, 7.5 Hz, 1H), 1.78 (m, 5H), 1.56 (m, 1H), 1.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.4, 133.7, 117.9, 48.4, 41.9, 38.8, 38.5,

27.4, 22.6, 21.0; IR (Neat Film NaCl) 2934, 2865, 1707, 1451, 912 cm^{-1}; HRMS *m/z* calc'd for $C_{10}H_{16}O$ $[M]^+$: 152.1201, found 152.1204; $[\alpha]_D^{28}$ -22.90° (*c* 2.09, hexane, 98% ee).

Asymmetric Allylation with Stabilized Enolates

Table SI1 summarizes results obtained with stabilized enolates with low pK_a values relative to the typical ketone enolates employed in these reactions. Despite the low levels of enantioselectivity, chemical yield is very high. This may imply that an alternate mechanism is accessible with this low pK_a substrates (e.g., an outer sphere mechanism).

Table SI1. Asymmetric Allylation via Stabilized Allyl Enol Carbonates.

entry	substrate[a]	product[b]	time (h)	% yield[c]	% ee[d]
1			2	99	11
2			2	93	0
3			2	89	24
4			2	87	2
5			2	89	2

[a] Reactions were performed using 1.0 mmol of substrate in THF (0.033 M in substrate) at 25 °C with 2.5 mol% $Pd_2(dba)_3$ and 6.25 mol% *(S)-t*-BuPHOX. [b] Absolute stereochemistry of products assigned by analogy. [c] Isolated yields. [d] Measured by chiral GC or HPLC.

Characterization data for compounds in Table SI1:

Products shown in entries 1, 2, and 3 have been reported previously.[2]

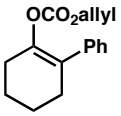


Table SI1, Entry 1: Prepared by the general procedure in 43% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.18 (comp. m, 5H), 5.80 (ddt, *J* = 17.4, 10.5, 5.4 Hz, 1H), 5.20 (ddt, *J* = 17.4, 1.8, 1.2 Hz, 1H), 5.18 (ddt, *J* = 10.5, 1.5, 1.2 Hz, 1H), 5.02 (ddd, *J* = 5.7, 1.5, 1.5 Hz, 2H), 2.46-2.38 (m, 2H), 2.37-2.30 (m, 2H), 1.90-1.72 (comp. m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 143.4, 138.8, 131.3, 128.1, 127.6, 126.8, 125.9, 118.4, 68.4, 30.1, 27.1, 22.8, 22.5; IR (Neat Film NaCl) 3081, 3057, 3024, 2938, 2862,

1753, 1687, 1601, 1492, 1444, 1367, 1238, 1178, 1091, 1036, 941, 784, 760, 700 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{16}H_{18}O_3$ $[M]^+$: 258.1256, found 258.1256.

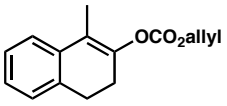


Table SI1, Entry 2: Prepared by the general procedure in 59% yield as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.29-7.11 (comp. m, 4H), 6.00 (ddt, *J* = 17.1, 10.2, 6.0 Hz, 1H), 5.43 (ddt, *J* = 17.1, 1.8, 1.2 Hz, 1H), 5.33 (ddt, *J* = 10.2, 1.5, 1.2 Hz, 1H), 4.72 (ddd, *J* = 6.0, 1.5, 1.2 Hz, 2H), 2.97 (t, *J* = 7.8 Hz, 2H), 2.55 (tq, *J* = 8.1, 1.5 Hz, 2H), 2.00 (t, *J* = 1.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 145.9, 135.0, 134.1, 131.2, 127.1, 126.6, 126.5, 123.4, 119.7, 119.2, 68.9, 28.7, 26.0, 10.9; IR (Neat Film NaCl) 3021, 2993, 2944, 2891, 2836, 1757, 1674, 1488, 1451, 1365, 1304, 1279, 1246, 1217, 1181, 1157, 1031, 1018, 986, 943, 782, 760 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{15}H_{16}O_3$ $[M]^+$: 244.1100, found 244.1095.

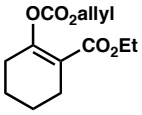


Table SI1, Entry 3: Prepared by the general procedure in 78% yield as a light yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 5.96 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.39 (ddt, *J* = 17.1, 1.5, 1.5 Hz, 1H), 5.28 (ddt, *J* = 10.5, 1.5, 1.2 Hz, 1H), 4.67 (ddd, *J* = 5.7, 1.2, 1.2 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.44-2.34 (m, 2H), 2.32-2.24 (m, 2H), 1.80-1.58 (comp. m, 4H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 154.8, 152.2, 131.2, 119.2, 118.3, 69.0, 60.5, 28.6, 25.1, 21.9, 21.5, 14.0; IR (Neat Film NaCl) 3087, 1983, 2942, 2866, 1760, 1715, 1666, 1449, 1368, 1233, 1189, 1081, 1056, 1035, 994, 946, 767 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{18}O_5$ $[M]^+$: 254.1154, found 254.1153.

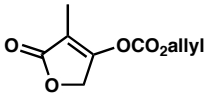


Table SI1, Entry 4: Prepared by a modification of the general procedure using TEA as the base and THF as solvent in 79% yield as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 17.1, 10.2, 6.0 Hz, 1H), 4.93 (ddt, *J* = 17.1, 2.7, 1.2 Hz, 1H), 5.37 (ddt, *J* = 10.2, 2.1, 0.9 Hz, 1H), 5.07 (q, *J* = 1.8 Hz, 2H), 4.74 (ddd, *J* = 6.0, 1.2, 0.9 Hz, 2H), 1.81 (t, *J* = 1.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 163.4, 150.2, 130.0, 120.8, 109.4, 70.3, 67.5, 6.9; IR (Neat Film NaCl) 3089, 2958, 2931, 1774, 1702, 1446, 1392, 1360, 1330, 1240, 1132, 1079, 1025, 945, 889, 775, 754 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_9H_{11}O_5$ $[M + H]^+$: 199.0606, found 199.0600.

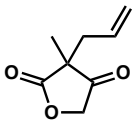


Table SI1, Entry 4: Prepared by the general procedure. Purified by flash chromatography (SiO_2, 2 →12% EtOAc in hexanes). 87% yield, 2% ee. R_f = 0.20 (10%

EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.62 (dddd, *J* = 17.7, 9.6, 7.5, 7.2 Hz, 1H), 5.13 (app. ddd, *J* = 9.6, 1.8, 0.9 Hz, 1H), 5.12 (app. ddd, *J* = 17.1, 1.5, 0.9 Hz, 1H), 4.59 (d, *J* = 17.1 Hz, 1H), 4.44 (d, *J* = 17.4 Hz, 1H), 2.53-2.37 (m, 2H), 1.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.9, 176.6, 130.1, 121.1, 72.5, 45.6, 40.2, 19.0; IR (Neat Film NaCl) 3543, 3083, 2983, 2939, 2877, 1803, 1758, 1642, 1454, 1436, 1378, 1341, 1231, 1122, 1065, 1043, 998, 912, 664 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{10}O_3$ $[M]^+$: 154.0630, found 154.0626.

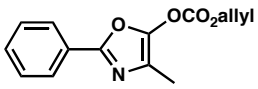


Table SI1, Entry 5: Prepared by a modification of Leplawy's procedure[3] in 96% yield as a colorless oil that solidifies on standing; Mp 37.5-39 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.90 (m, 2H), 7.45-7.38 (comp. m, 3H), 5.99 (ddt, *J* = 17.4, 10.5, 5.7 Hz, 1H), 5.45 (ddt, *J* = 17.4, 1.5, 1.2 Hz, 1H), 5.36 (ddt, *J* = 10.5, 1.2, 1.2 Hz, 1H), 4.78 (ddd, *J* = 6.0, 1.2, 1.2 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 155.0, 151.6, 146.2, 130.5 (2C), 128.9, 127.3, 126.1, 120.6, 70.7, 10.5; IR (Neat Film NaCl) 3066, 2930, 1786, 1669, 1554, 1490, 1450, 1367, 1213, 1082, 1069, 1026, 992, 939, 774, 711, 692 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{14}H_{13}O_4N$ $[M]^+$: 259.0845, found 259.0855.

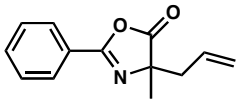
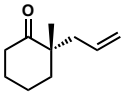
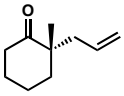
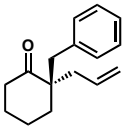
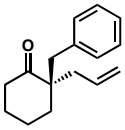
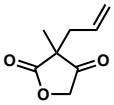
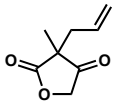
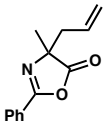
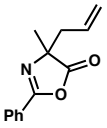
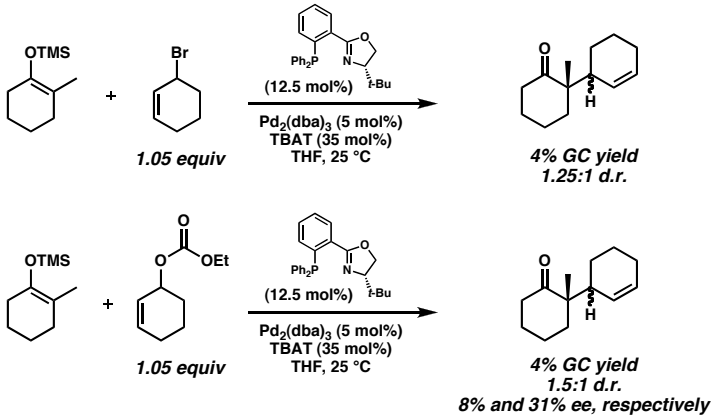


Table SI1, Entry 5: Prepared by the general procedure. Purified by flash chromatography (SiO_2, 4 →7% Et_2O in hexanes). 89% yield, 2% ee. R_f = 0.39 (25% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (ddd, *J* = 7.2, 1.5, 1.2 Hz, 2H), 7.57 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.48 (ddd, *J* = 7.8, 6.9, 1.5 Hz, 2H), 5.67 (dddd, *J* = 17.1, 9.9, 7.5, 6.9 Hz, 1H), 5.18 (dddd, *J* = 17.1, 1.5, 1.5, 1.5 Hz, 1H), 5.11 (dddd, *J* = 10.2, 1.5, 0.9, 0.9 Hz, 1H), 2.64 (dddd, *J* = 13.8, 6.9, 0.9, 0.9 Hz, 1H), 2.57 (dddd, *J* = 13.8, 7.5, 1.2, 1.2 Hz, 1H), 1.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.2, 159.8, 132.7, 130.8, 128.7, 127.9, 125.9, 120.4, 69.7, 42.3, 23.2; IR (Neat Film NaCl) 3078, 2982, 2934, 1819, 1655, 1581, 1493, 1451, 1321, 1293, 1177, 1094, 1071, 1005, 930, 889, 780, 700 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{13}O_2N$ $[M]^+$: 215.0946, found 215.0938.

Table SI2. Methods for the Determination of Enantiomeric Excess.

entry	product	compound assayed	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
1			GC, G-TA 100 °C isotherm	11.13	12.74	88
2			HPLC Chiracel OJ 2% EtOH in hexane isocratic, 1.0 mL/min	19.81	13.82	85
3			GC, G-TA 100 °C isotherm	19.67	21.64	2
4			HPLC Chiracel OD-H 2% IPA in hexane isocratic, 1.0 mL/min	6.61	5.40	2

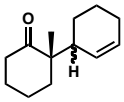
Tsuji Allylation with cyclohexenyl substrates



Sample Procedure

In a flame dried 1-dram vial, $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), (*S*)-*t*-BuPHOX (4.7 mg, 0.0625 mmol), and TBAT (18.9 mg, 0.035 mmol) were combined. The vial was evacuated for 10 minutes prior to addition of THF (3 mL). The mixture was allowed to stir at 25 °C for 30 min prior to addition of tridecane (10 μL, 0.4 mmol), silyl enol ether (18.4 mg, 0.1 mmol), and bromocyclohexene (16.1 mg, 0.105 mmol) via syringe. GC yield was determined by a GC assay with tridecane as the internal standard. (Isothermal at 80 °C for 5 min, then ramp from 80 °C to 115 °C at 10 °C/min, then isothermal at 115°C for 75 min. Silyl enol ether: 5.759 min, tridecane: 7.329 min, bromocyclohexene: 8.426 min, minor product diastereomer: 72.223 min, major product diastereomer: 73.434 min). Enantiomeric excess was determined by an Agilent 6850 GC utilizing a G-TA column (30 mm x 0.25 cm) with 1.0 mL/min carrier gas flow. The method utilized for enantiomeric excess determination was isothermal at 110°C for 60 min (major product diastereomer: 47.504 min and 53.594 min (major enantiomer), minor product diastereomer: 48.282 min (major enantiomer) and 55.842 min). Isolation of products as a

mixture of diastereomers was accomplished by flash chromatography (1 cm x 20 cm SiO_2, 2% ether in pentane).



^{1}H NMR (300 MHz) δ 5.74 (complex multiplet, 1H), 5.49 (dddd, 0.7H, *J* = 11.0, 1.9, 1.9, 1.9 Hz), 5.20 (dddd, 0.3H, *J* = 10.1, 2.1, 2.1, 2.1 Hz), 2.84-2.29 (complex multiplet, 3H), 2.01-1.22 (complex multiplet, 12H), 0.90 (s, 2.1 H), 0.89 (s, 0.9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.7, 216.1, 129.6, 129.5, 128.0, 127.3, 52.0, 51.7, 39.5, 39.0, 38.6, 37.0, 36.0, 28.0, 27.7, 25.4, 24.0, 23.1, 23.0, 22.9, 21.1, 21.0, 19.4, 18.6; IR (Neat Film, NaCl) 3023, 2934, 2862, 1705, 1452, 1313, 1121 cm^{-1}; HRMS *m/z* calc'd for $C_{13}H_{24}O$ [M^+]: 192.1514, found 192.1519.

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(1) Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett*. **1983**, *24*, 1793-1796.

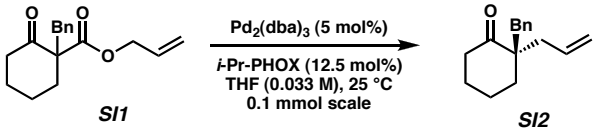
(2) (a) Trost, B. M.; Schroeder, G .M.; Kristensen, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3492-3495. (b) Trost, B. M.; Radinov, R.; Grenzer, E. M. *J. Am. Chem. Soc*. **1997**, *119*, 7879-7880.

(3) Slomczynska, U.; Kaminski, Z. J.; Leplawy, M. T. *Bull. Pol. Acad. Sci. Chem.* **1991**, *39*, 85-88.

2. Non-linear experiments:

Material and Methods. Unless otherwise stated, reactions were performed in flame-dried glassware under argon atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) was purchased from Strem and stored in a dessicator under argon atmosphere prior to use. (*S*)-*t*-Bu-PHOX, (*S*)-*i*-Pr-PHOX, (*R*)-*i*-Pr-PHOX, and all substrates were prepared by our previously reported methods.[4,5] Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed by using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching or anisaldehyde. ICN silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC, utilizing a Chiracel OJ column (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd with visualization at 254 nm. Analytical achiral GC was performed with an Agilent 6850 GC utilizing a DB-WAX column (30 mm x 0.24 mm with 1.0 mL/min carrier gas flow). Temperature controlled ^{1}H NMR kinetic experiments were performed on a Varian Inova 500 MHz.

General Procedures for Nonlinear Experiments



SI1 *SI2*

THF stock solutions with the desired enantiomeric excess of *i*-Pr-PHOX were freshly prepared prior to each experiment. The enantiomeric excess of the *i*-Pr-PHOX delivered was confirmed by subsequent chiral HPLC with a Chiracel OJ column using 1% ethanol in hexanes (1.0 mL/min) as an eluent on the remaining stock solution ((*S*)-*i*-Pr-PHOX: 13.16 min and (*R*)-*i*-Pr-PHOX: 7.60 min).

A 1-dram vial equipped with a stirbar was flame dried twice under vacuum. After cooling under nitrogen, $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol) was added. The vial was evacuated for 5 minutes. THF (3 mL total) was added and then *i*-Pr-PHOX (4.8 mg, 0.0125 mmol) in THF was added via syringe. Contents were allowed to stir for 30 minutes at 25 °C prior to addition of benzyl β-ketoester **SI1** (27.2 mg, 0.1 mmol) via syringe. The reaction progress was monitored by TLC. Upon completion, the reaction, was concentrated and purified via column chromatography (1 cm x 11.5 cm SiO_2, 20% ether in pentane). Subsequently, the enantiomeric excess of product was determined by chiral HPLC with a Chiracel OJ column using 1% ethanol in hexanes (1.0 mL/min) as an eluent (**SI2**: 15.942 min and 24.345 min).

Comparison of the enantiomeric excess of the product versus the enantiomeric excess of the *i*-Pr-PHOX revealed a linear relationship (Figure 1). The absence of a nonlinear effect suggests that the active catalyst in our Tsuji allylation system involves one molecule of *i*-Pr-PHOX, thus one palladium metal center. Furthermore, the absence

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[4] Behenna, D. C.; Stoltz, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 15044-15045.
[5] Mohr, J. T.; Behenna, D. C.; Harned. A. M.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6924-6927.

of a nonlinear effect suggests that the rate determining step does not involve a bimetallic system, such as a palladium-enolate and a palladium π-allyl complex.

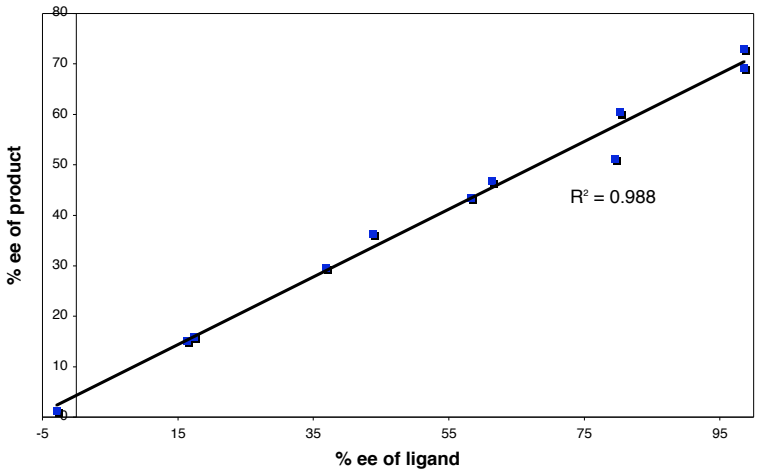
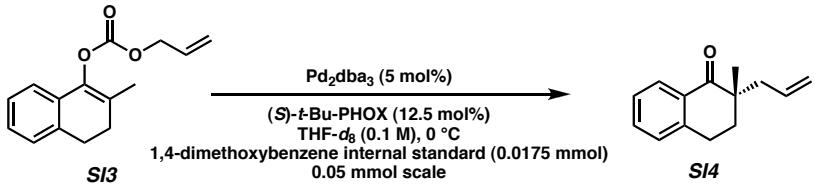


Figure 1. Plot of Enantiomeric Excess of β-Ketoester SI2 versus Enantiomeric Excess of *i*-Pr-PHOX

3. Kinetic Data:

General Procedures for Kinetic Experiments

Determination of Substrate Order



Solid $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol) and (*S*)-*t*-Bu-PHOX (2.4 mg, 0.00625 mmol) were placed in a NMR tube equipped with a screw cap and a Teflon septum. The NMR tube was then placed under vacuum and backfilled with argon (3 x 1 min). THF-d_8 (0.2 mL, dried over sodium benzophenone ketyl) was added to the NMR tube via syringe under a positive pressure of argon. The mixture was heated at 40 °C for 30 min. The mixture was then cooled to –78 °C using a CO_2/acetone bath. A THF-d_8 solution (0.3 mL, 0.1 M in substrate total) of allyl enol carbonate **SI3** (12.2 mg, 0.05 mmol) and 1,4-dimethoxybenzene (2.4 mg, 0.0175 mmol) were added to the reaction mixture under argon. Before recording the ^{1}H NMR spectrum, the sample was allowed to warm for 5 - 10 seconds and mixed. Reaction progress was monitored by ^{1}H NMR spectroscopy at 0 ºC, where integral areas of the allylic protons of **SI3** (dt, 2H, δ = 4.677 ppm, J = 5.5, 1.0 Hz) relative to the phenyl protons of the dimethoxybenzene internal standard (s, 4H, δ = 6.795 ppm) were obtained at 5 minute intervals. The experiment was concluded upon complete conversion of **SI3**, which was determined by the disappearance of the allylic protons of **SI3**.

Analysis of consumption of **SI3** over time is consistent with a zero-order dependence in allyl enol carbonate (Figure 2).

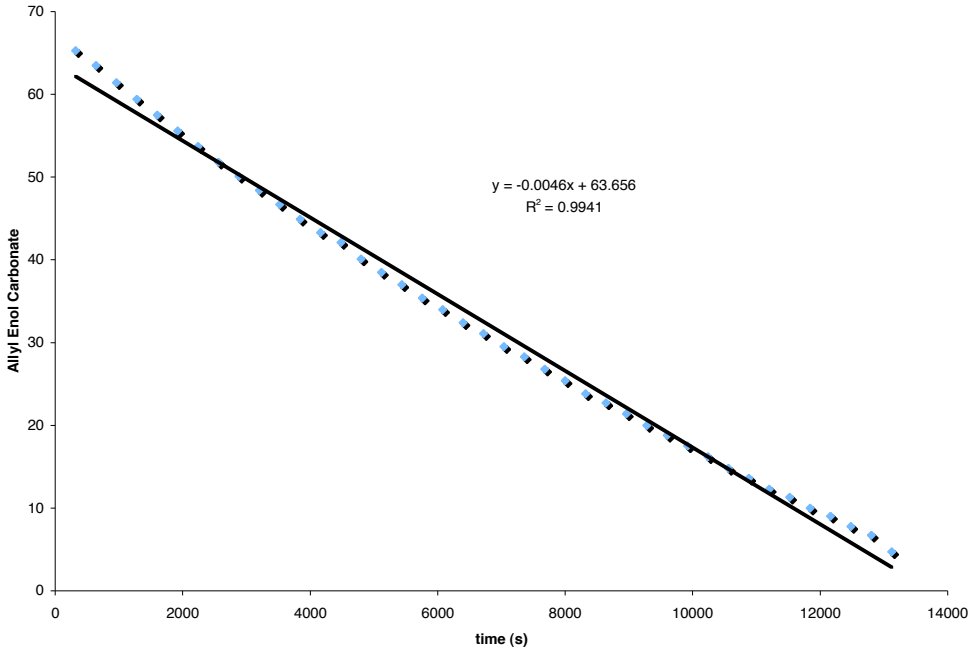
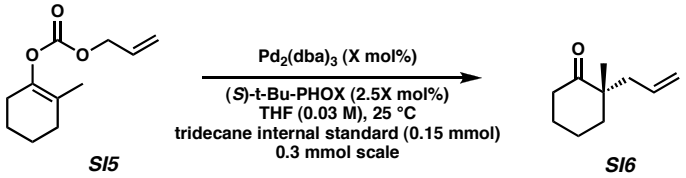


Figure 2. Plot of Consumption of Allyl Enol Carbonate SI3 versus Time as Observed by ^{1}H NMR Spectroscopy

Determination of Palladium(PHOX) Order



Asymmetric Tsuji allylation of enol carbonate **SI5** was carried out in an identical manner to those previously reported at different concentrations of the in situ generated Pd(PHOX) complex.[1] Reaction progress was monitored by an achiral GC equipped with a DB-WAX column with tridecane as the internal standard. GC yield was determined by using an acquisition method that ramped the temperature from 70 °C to 175 °C at a rate of 5 °C/min (tridecane: 6.915 min, cycloalkanone **SI6**: 12.185 min, and enol carbonate **SI5**: 17.697 min).

Rate constants (k_{obs}) were determined at 25 °C by GC analysis. The dependence of reaction rate on the concentration of the in situ generated Pd(PHOX) was measured at a constant concentration of **SI15** (0.03 M) and a constant concentration of tridecane (0.015M). Figure 3 shows that the reaction is first-order in Pd(PHOX) complex.

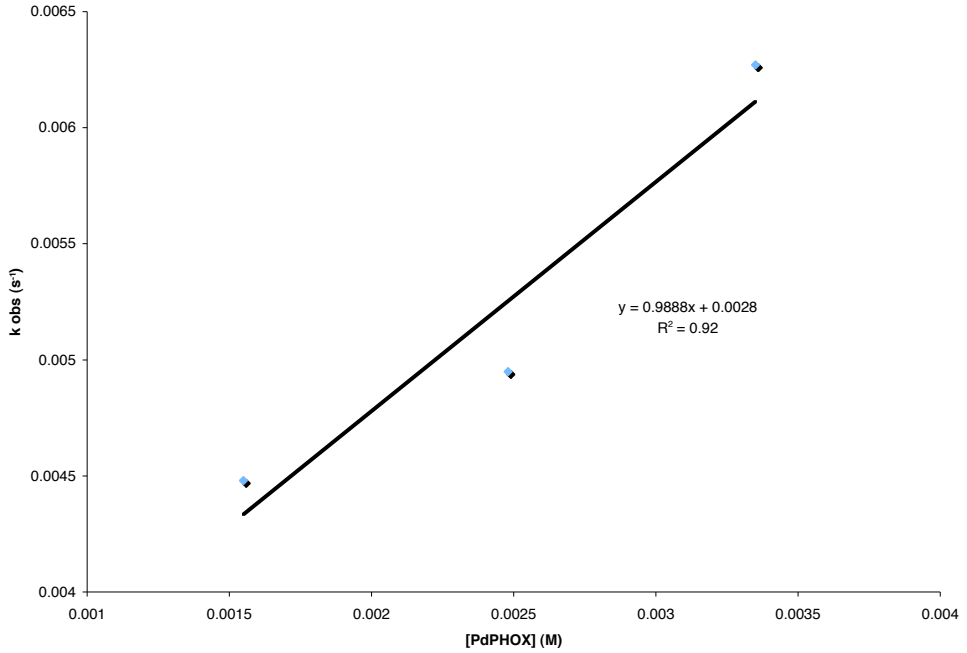


Figure 3. Plot of k_{obs} versus [PdPHOX]

Based on these preliminary kinetic experiments, we believe that our asymmetric Tsuji allylation is zero-order in substrate and first-order in *in situ* palladium(PHOX) complex.

4. Calculated Data:

Calculation details:
All calculations were run using Jaguar 6.5

Geometry optimization was done with a mixed basis set (MIDI! on all atoms except N, P, Pd, the six atoms from the allyl fragment and enolate component which were treated with LACVP or 6-31G*).

"Gas Phase Energy" was calculated as single point energy calculations from the above geometries with the LACV3P**++ basis set with both B3LYP and PBE.

"Solvent Phase Energy" was calculated with B3LYP and the LACV3P** basis set. Diffuse functions were omitted, as they appear to have adverse effects on Jaguar's solvation model. Solvent = THF (probe radius = 2.527Å, ε = 7.52)

"Zero Point Energy" was calculated from analytic vibrational frequencies.

All transition states were reported were fully optimized and yielded one imaginary frequency.

Contact John Keith for other calculation details (johnk@wag.caltech.edu)

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Complex 1

(B3LYP)

Gas Phase Energy = -654.64331885491 = Eh
Solvent Phase Energy = -0.01095745854 = Eh
Zero Point Energy = 159.985 = kcal/mol

(PBE)

Gas Phase Energy = -653.82932310282 = Eh

Geometry Coordinates

C1	0.0113083798	0.0124257236	-0.0061783496
C2	-0.0013818048	0.0086824472	1.3267454073
C3	1.2339260089	0.0153211569	2.1717260330
O4	1.1429594509	-1.0908202308	3.1072486300
C5	2.1186404294	-1.1171196145	4.0385647212
O6	3.0180904838	-0.3191945640	4.1324261749
O7	2.0035448532	-2.1647199625	4.8809113190
C8	0.8991992312	-3.0435401244	4.8363028339
C9	1.0771331487	-4.2973061924	4.4017656946
H10	-0.9133147377	0.0566512194	-0.5891741503
H11	0.9476871255	-0.0189251237	-0.5744052870
H12	-0.9534029285	0.0384538672	1.8713083079
H13	2.1474818658	-0.0980871386	1.5652816886
H14	1.3285573872	0.9488691482	2.7535568736
C15	-1.5746866876	-3.4044541922	5.1922740477
C16	-0.3551976806	-2.4877409835	5.4538668734
C17	-0.0529567564	-5.3043896563	4.4860652339
C18	-1.1917306988	-4.8771957822	5.4433840026
H19	-1.9051008295	-3.2856823628	4.1486577507
H20	-2.4102397826	-3.1039696803	5.8392585659
H21	-0.2035478549	-2.3634255284	6.5406674169
H22	-0.5522573151	-1.4841068032	5.0483581460
H23	-0.4659570753	-5.4740200848	3.4748151872
H24	0.3551672995	-6.2753897821	4.8132244080
H25	-0.8589056652	-4.9939727985	6.4867831715
H26	-2.0626868838	-5.5322187705	5.3021157953
C27	2.3661026241	-4.7966479686	3.8064196230
H28	2.7491463200	-5.6575604840	4.3802683709
H29	2.2066227425	-5.1482417926	2.7722771430
H30	3.1442248494	-4.0244807837	3.7932077238

Complex 2

(B3LYP)

Gas Phase Energy = -466.03738555019 = Eh
Solvent Phase Energy = -0.00763066733 = Eh
Zero Point Energy = 151.022 = kcal/mol

(PBE)

Gas Phase Energy = -465.41294401844 = Eh

Geometry Coordinates

C1	-0.0109108095	-0.0090913358	-0.0039725405
C2	-0.0019377287	0.0036042017	1.3311872844
C3	1.2380737348	-0.0031750635	2.1857876305
C4	1.4287766106	-1.2691160917	3.0695595585
C5	2.7189398847	-1.0964231308	3.9031287517
O6	3.5264703528	-0.2162058183	3.6688334943
C7	0.2197252134	-1.4655974661	4.0267158875
C8	0.4425853342	-2.5256322103	5.1342095225
C9	1.6991627758	-2.1908086263	5.9645485923
C10	2.9434642135	-2.0867930224	5.0391924948
H11	-0.0056320434	-0.5013459258	4.5157686164
H12	-0.6675204448	-1.7358556422	3.4339196855
H13	0.5474941665	-3.5277876176	4.6914167333
H14	-0.4422202193	-2.5569111685	5.7863780637
H15	1.5517832876	-1.2318804997	6.4865076425
H16	1.8737722150	-2.9553599127	6.7343017634
H17	3.8338193270	-1.7655138907	5.5946626836
H18	3.1533849642	-3.0833841603	4.6143920855
C19	1.6086725483	-2.5137696692	2.1667783431
H20	2.4990070331	-2.4061609466	1.5279721473
H21	1.7168858220	-3.4408988269	2.7458276242
H22	0.7345201419	-2.6209798584	1.5084046329
H23	1.2232556197	0.8767106710	2.8575081124
H24	-0.9639896574	0.0470791753	1.8593952008
H25	0.9176493118	-0.0351836527	-0.5858169872
H26	-0.9443975068	0.0188140773	-0.5750236071
H27	2.1318023368	0.1153535642	1.5506968142

Complex CO2

(B3LYP)

Gas Phase Energy = -188.64660127352 = Eh
Zero Point Energy = 7.282 = kcal/mol

(PBE)

Gas Phase Energy = -188.45726211825 = Eh

Geometry Coordinates

C1	-0.8753363139	0.6870813764	3.6403431163
O2	0.0327656439	1.4194127886	3.5572223432
O3	-1.7834484094	-0.0452538213	3.7234453188

Complex Pd(PHOX)

(B3LYP)

Gas Phase Energy = -1566.71636231574 = Eh
Solvent Phase Energy = -0.01365948285 = Eh
Zero Point Energy = 282.286 = kcal/mol

(PBE)

Gas Phase Energy = -1565.11360608546 = Eh

Geometry Coordinates

Pd1	0.1771925079	0.0303972044	-0.4792913529
N2	0.3026055938	-0.1410796128	2.7832384005
P3	2.2198705967	0.1131084513	0.4386177259
C4	-1.0038182842	-0.4993172805	3.3625614198
C5	-1.3695267186	0.7361541683	4.2307918808
O6	-0.3882895714	1.7308207778	3.8622197991
C7	0.5365601358	1.0775218072	3.0867538636
C8	1.7119479275	1.8758559013	2.6970712247
C9	2.5690975521	1.5236726441	1.6174755080
H10	-1.2808860521	0.5535120633	5.3074731832
H11	-2.3613727745	1.1431853758	4.0214715692
H12	-1.7172300412	-0.5928340006	2.5308864595
C13	-0.9841978369	-1.8701715435	4.0945009747
C14	-2.3648552261	-2.1070062927	4.7373306520
H15	-2.5902874904	-1.3712288252	5.5181278530
H16	-3.1649458690	-2.0598774342	3.9887377476
H17	-2.4051576939	-3.0976292088	5.2029555345
C18	0.1177154570	-1.9123891038	5.1697106313
H19	-0.0286262495	-1.1533905905	5.9471385087
H20	0.1230764126	-2.8888419941	5.6667758799
H21	1.1022823775	-1.7536811771	4.7207186916
C22	-0.7141035645	-2.9721399418	3.0521117944
H23	-0.6925443510	-3.9577358762	3.5312475708
H24	-1.4991625169	-2.9905243568	2.2864005629
H25	0.2426939315	-2.8105282874	2.5505088026
C26	3.8406411180	-3.7385110338	2.5048718642
C27	4.1074926647	-2.4953066171	3.0804314492
C28	3.6158390117	-1.3260446596	2.4942467370
C29	2.8405525532	-1.3857520540	1.3280198613
C30	2.5686003340	-2.6405304324	0.7628757974
C31	3.0698671727	-3.8065787580	1.3421728173
H32	4.2263028740	-4.6465171258	2.9601381937
H33	4.7048511534	-2.4314405374	3.9864012030
H34	3.8388033638	-0.3655148675	2.9489214760
H35	1.9555010794	-2.6973239457	-0.1333013057
H36	2.8521177860	-4.7695353786	0.8877957053
C37	5.4861173515	0.6665806808	-2.8578378957
C38	4.2062548075	1.2036606991	-3.0082511302
C39	3.2507099574	1.0247192022	-2.0079837737
C40	3.5613462203	0.3211578322	-0.8338278752
C41	4.8523299578	-0.2141929668	-0.6939888728
C42	5.8049371963	-0.0441991918	-1.7000423116
H43	6.2285709031	0.7952972902	-3.6409822040
H44	3.9476943978	1.7523924171	-3.9099742196
H45	2.2440352795	1.4175481875	-2.1322906313
H46	5.1159062955	-0.7705053528	0.1999946198
H47	6.7974292943	-0.4705309077	-1.5784051954
C48	3.6692839902	2.3615463383	1.3687018727
H49	4.3411402151	2.1287397114	0.5515794144
C50	1.9763230183	3.0296087707	3.4539024330
H51	1.3009806790	3.2790098495	4.2642189791
C52	3.9287604198	3.4947888886	2.1392257713
H53	4.7973722597	4.1073788890	1.9123437951
C54	3.0767496909	3.8370912632	3.1861609677
H55	3.2645320738	4.7206656803	3.7890262267

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Complex Enolate

(B3LYP)

Gas Phase Energy = -348.71065236365 = Eh
Solvent Phase Energy = -0.08425259124 = Eh
Zero Point Energy = 102.902 = kcal/mol

(PBE)

Gas Phase Energy = -348.25500040654 = Eh

Geometry Coordinates

O1	-0.0003410345	0.0018492883	-0.0018906891
C2	-0.0012930859	-0.0008335598	1.2724903838
C3	1.1061593054	-0.0010872893	2.1166904574
C4	-1.4104526170	-0.0319872575	1.9233471036
C5	2.4818715361	0.0739164076	1.5196859652
C6	-1.4515514456	0.3591684973	3.4170181569
C7	-0.3527287552	-0.4105932402	4.1753994277
C8	1.0376837131	-0.0101397774	3.6211509483
H9	-1.2650581487	1.4419209104	3.5240176167
H10	-2.4459585505	0.1554018823	3.8553292856
H11	-0.5098798273	-1.4922663929	4.0247324928
H12	-0.4093491028	-0.2110971796	5.2604028648
H13	1.3059029375	0.9803472051	4.0738041013
H14	1.7916277693	-0.7143291969	4.0427607809
H15	-1.8367868734	-1.0464439177	1.7975540590
H16	-2.0494777870	0.6403990799	1.3261341092
H17	2.3821126706	0.0632008815	0.4232794062
H18	3.0422779241	0.9968736269	1.8062482500
H19	3.1410928032	-0.7749511975	1.8204725621

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Complex 3

(B3LYP)

Gas Phase Energy = -1683.90795339188 = Eh
Solvent Phase Energy = -0.05367430515 = Eh
Zero Point Energy = 330.264 = kcal/mol

(PBE)

Gas Phase Energy = -1682.15272185669 = Eh

Geometry Coordinates

Pd1	0.0179829299	-0.0676708739	-0.0340612533
C2	0.5050195355	-1.1692203769	1.8489587378
C3	-0.8985553714	-1.0206510966	1.6545794544
C4	1.3163391626	-0.0389784858	1.8956242167
H5	-1.5090774567	-1.9019537550	1.4854221069
H6	2.3957602772	-0.1371207332	1.8535746508
H7	-1.4192523527	-0.1889278914	2.1262357489
H8	0.9276249187	0.9130875980	2.2504672281

H9	0.9636611927	-2.1435452811	1.6917623608
N10	1.1511428117	1.0692029511	-1.4617307199
P11	-1.7174002497	-0.1717162380	-1.5812161704
C12	2.6446626690	1.1016133800	-1.4946703082
C13	2.9128829823	2.4582786137	-2.1982793762
O14	1.6458038779	2.7356867692	-2.8905046568
C15	0.7042142647	1.9499153489	-2.3012413409
H16	3.6970106065	2.4401837791	-2.9562777418
C17	-1.0801338212	-3.5570386762	-4.6791348973
C18	-0.9045469272	-3.7929162060	-3.3142014391
C19	-1.0864813043	-2.7594305492	-2.3980923311
C20	-1.4620964696	-1.4768035670	-2.8390164366
C21	-1.6366193894	-1.2479218533	-4.2131459744
C22	-1.4431481568	-2.2866855522	-5.1253184971
H23	-0.9335313877	-4.3634376384	-5.3934074944
H24	-0.6224696672	-4.7828988999	-2.9639494457
H25	-0.9402425784	-2.9505439510	-1.3367592315
H26	-1.9276546004	-0.2655093506	-4.5751408796
H27	-1.5807296881	-2.1020685290	-6.1880005070
C28	-6.0108222495	-0.6827395226	0.0847630174
C29	-5.5822308034	-1.5014328706	-0.9587416830
C30	-4.2929564870	-1.3649872842	-1.4782699849
C31	-3.4198230169	-0.4035262947	-0.9472616242
C32	-3.8571442232	0.4141129064	0.1112558776
C33	-5.1470706008	0.2775924727	0.6174870591
H34	-7.0156694884	-0.7918028681	0.4852892341
H35	-6.2527440211	-2.2501124139	-1.3737276006
H36	-3.9715041448	-2.0086007331	-2.2926869648
H37	-3.1922296286	1.1650736918	0.5348615338
H38	-5.4801222065	0.9178646759	1.4308987877
C39	-2.0917909438	3.8288111183	-3.9397626248
C40	-3.1955760773	3.0087813541	-3.7309847663
C41	-3.0479854883	1.8169764747	-3.0216946696
C42	-1.8029857361	1.4161325566	-2.5147376653
C43	-0.6774653169	2.2487612543	-2.7363715505
C44	-0.8484695501	3.4481733444	-3.4474833487
H45	-2.1943350346	4.7645713961	-4.4827813227
H46	-4.1734051120	3.2929850556	-4.1118290136
H47	-3.9204699432	1.1932225546	-2.8516287667
H48	0.0149971016	4.0830108962	-3.6095204853
H49	3.0945447092	3.2781428195	-1.4921063989
C50	3.2673196683	-0.1322099069	-2.2290481406
C51	4.8097960218	0.0355752320	-2.2321692566
H52	5.1372215469	0.8949872402	-2.8338522574
H53	5.1986577741	0.1574569696	-1.2094740686
H54	5.2753864147	-0.8611778049	-2.6646233451
C55	2.7466860750	-0.2452939683	-3.6796940074
H56	2.9375390805	0.6699273619	-4.2584065984
H57	3.2584862794	-1.0737003009	-4.1902023908
H58	1.6679877242	-0.4548105081	-3.7011281686
C59	2.9295243491	-1.4292044742	-1.4578823501
H60	3.3997035260	-2.2895861753	-1.9559421718
H61	3.3142422646	-1.3859212143	-0.4274744391
H62	1.8451801419	-1.6056103459	-1.4248356794
H63	3.0184804616	1.1146049470	-0.4645288410

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Complex 4

(B3LYP)

Gas Phase Energy = -2032.73911500101 = Eh
Solvent Phase Energy = -0.01784563176 = Eh
Zero Point Energy = 434.031 = kcal/mol

(PBE)

Gas Phase Energy = -2030.53944632755 = Eh

Geometry Coordinates

Pd1	0.1522421755	-0.1116392671	-0.0014489177
C2	0.3201673009	-0.1796904055	2.2760129712
O3	2.7683828369	-0.1292058406	-0.0509452580
C4	-0.3089759399	1.0020591816	1.8725967702
C5	0.3572462693	1.8198794116	0.9189059555
C6	3.6231836400	-1.0320514691	-0.4454565077
C7	4.5645342779	-0.6017701382	-1.5790101993
C8	3.7319944213	-2.2986969229	0.0963151434
C9	2.9319355116	-2.6638738931	1.3176139803
C10	4.7627721980	-3.3113686164	-0.3585935803
H11	-0.1635796499	2.6681043577	0.4843450687
H12	-0.2222383097	-0.9166488314	2.8606049645
H13	1.4435092171	1.8793455997	0.9323271725
H14	1.4035149507	-0.2611482144	2.2437892374
H15	-1.3662592386	1.1559400314	2.0796270765
N16	-0.0964120286	-2.1721913229	-0.6248671759
P17	0.1746800925	0.4526738241	-2.2431717911
H18	3.9999458625	-0.5790651765	-2.5330843392
H19	4.8626842027	0.4444461070	-1.3794720165
H20	2.9495855916	-3.7566841867	1.4997009411
H21	3.3236753121	-2.1850991038	2.2432746779
H22	1.8783429227	-2.3407749381	1.2329248766
H23	4.3030634936	-4.3222079238	-0.4201911164
H24	5.5694359641	-3.4207278375	0.4055290059
C25	-0.7350831020	-3.2196094825	0.2145874496
C26	0.0253384366	-4.4963013059	-0.2322589823
O27	0.5646050655	-4.1275435673	-1.5433923246
C28	0.5490572057	-2.7557291926	-1.5872860900
H29	-0.5979310895	-5.3814233610	-0.3767989277
C30	1.0751352456	-0.8356551795	-3.2059721504
C31	1.1800742899	-2.1879310773	-2.7905657485
H32	0.8671385414	-4.7299403361	0.4300132078
C33	-2.2861720057	-3.2868486983	0.0078957052
C34	-2.8503553237	-4.4322244334	0.8875736219
H35	-2.4968156257	-5.4213090582	0.5626847308
H36	-2.5704486745	-4.2925639033	1.9434975890
H37	-3.9486254196	-4.4383230060	0.8269120766
C38	-2.6429574335	-3.5374779809	-1.4747726814
H39	-2.1569173063	-4.4433254395	-1.8650556956
H40	-3.7310120313	-3.6646211075	-1.5783460509
H41	-2.3418826533	-2.6849977453	-2.0990721550
C42	-2.9326790960	-1.9607299977	0.4721737948
H43	-4.0245459550	-2.0136723051	0.3421425130
H44	-2.7256056999	-1.7760957874	1.5377230994

H45	-2.5505778966	-1.1091203781	-0.1060660246
H46	-0.5403211568	-2.9996832719	1.2703192523
C47	2.3860184274	4.3928572056	-3.2837949551
C48	1.1849262514	4.1040696560	-3.9307794581
C49	0.4990063076	2.9223334720	-3.6431855483
C50	1.0156992509	2.0222375547	-2.6982728271
C51	2.2242796977	2.3187630128	-2.0406796476
C52	2.9016472517	3.4996854342	-2.3422000820
H53	2.9179077889	5.3148280951	-3.5105141300
H54	0.7783647615	4.7996636351	-4.6623478042
H55	-0.4393082329	2.7098002870	-4.1494234414
H56	2.6195443006	1.6088146650	-1.3055510017
H57	3.8379878854	3.7243131230	-1.8353142604
C58	-4.0140849884	0.8486431113	-4.2294907723
C59	-3.0426757843	0.0654841238	-4.8504161246
C60	-1.7758545288	-0.0722575192	-4.2781553383
C61	-1.4704573260	0.5697076485	-3.0683288784
C62	-2.4649169194	1.3419170502	-2.4406972350
C63	-3.7217207787	1.4881266566	-3.0229061547
H64	-4.9979071726	0.9582920145	-4.6804358217
H65	-3.2670363641	-0.4380494793	-5.7884578786
H66	-1.0232965470	-0.6749349737	-4.7796770291
H67	-2.2502441947	1.8272918150	-1.4903614712
H68	-4.4779273956	2.0969750059	-2.5318640115
C69	1.6776467046	-0.4539878202	-4.4182651942
H70	1.6202426167	0.5839995041	-4.7339037256
C71	1.8801960366	-3.0948204178	-3.6107465389
H72	1.9634346085	-4.1239615571	-3.2816818655
C73	2.3570314890	-1.3677921209	-5.2172415639
H74	2.8120335257	-1.0408065248	-6.1494141375
C75	2.4586284413	-2.6978214199	-4.8070394514
H76	2.9941504587	-3.4227225064	-5.4152182616
C77	5.8108451629	-1.4802030793	-1.7353239197
H78	6.5162215574	-1.2846717852	-0.9091958086
H79	6.3415542060	-1.2405257562	-2.6715555184
C80	5.4125045433	-2.9724497525	-1.7051510232
H81	6.2936522790	-3.6113461306	-1.8783039381
H82	4.7016915621	-3.1642056614	-2.5260393040

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Complex 5

(B3LYP)

Gas Phase Energy = -2032.73488137273 = Eh

Solvent Phase Energy = -0.01873037575 = Eh

Zero Point Energy = 434.098 = kcal/mol

Frequency = -34.91

(PBE)

Gas Phase Energy = -2030.53248097952 = Eh

Geometry Coordinates

Pd1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	2.4803720451
C3	2.3476054165	0.0000000000	0.7367316679
P4	-1.8800020861	-0.5618249390	-1.1806220877

N5	-0.7195656370	2.0597627224	0.0137173621
C6	0.9064332782	-1.8840233523	0.2142974169
C7	2.0445691690	-1.0617588596	-0.0915735806
C8	-0.7922314100	0.6676829591	3.2821701313
C9	-2.2509241518	0.1857639555	3.2879022041
C10	-0.4063556970	1.7062882460	4.1018820247
C11	1.0425569704	2.0837572704	4.2713044757
C12	-1.3793764863	2.4634873294	4.9843006402
C13	-3.1383462101	0.7776325158	4.3901106130
C14	-2.8397718715	2.2847274286	4.5576714445
H15	-2.9358046298	0.2743380753	5.3511223962
H16	-4.2047722555	0.6135394931	4.1628775917
H17	-3.5217147132	2.7350407823	5.2969811729
H18	-3.0092349046	2.7942325503	3.5925930708
H19	-2.7000559021	0.3900064897	2.2954888901
H20	-2.2191406357	-0.9177934332	3.3776356079
H21	1.2619118657	3.1338681065	3.9709727183
H22	1.3566809869	2.0156057803	5.3358840075
H23	1.6974826371	1.4175034753	3.6882268715
H24	-1.1277811425	3.5473387431	4.9780721229
H25	-1.2778659160	2.1626772194	6.0543878341
H26	0.6299523797	-2.6735728266	-0.4795275726
H27	3.0728822401	0.7458542597	0.4238115325
H28	0.6660856868	-2.0624677761	1.2615306105
H29	1.9397681570	0.0474465421	1.7466374505
H30	2.5138443074	-1.1399840470	-1.0713262590
C31	0.1812309612	3.1604316961	0.4629063979
C32	-0.7452405288	3.9527408768	1.4154757460
O33	-2.0914874689	3.6008132210	0.9327958474
C34	-1.9379362622	2.4149678241	0.2662991991
H35	-0.6577173350	5.0398267895	1.3699702015
C36	-3.3331200492	0.4700475481	-0.6838786444
C37	-3.2113039348	1.7446025095	-0.0738916922
H38	-0.6625795277	3.5742926563	2.4425828016
C39	0.7450457047	3.9829183995	-0.7415342329
C40	1.6788928218	5.0867728182	-0.1831908470
H41	1.1333993955	5.8178336242	0.4308846595
H42	2.4818338428	4.6497621426	0.4300802510
H43	2.1453981695	5.6346533982	-1.0152001957
C44	-0.3906385962	4.6292424156	-1.5676040534
H45	-1.0344233910	5.2700520102	-0.9488046425
H46	0.0405812648	5.2509039584	-2.3665418098
H47	-1.0170744416	3.8597922931	-2.0401356505
C48	1.5760122526	3.0579503875	-1.6615697933
H49	1.9939656734	3.6413559812	-2.4962698698
H50	2.4117096252	2.6038245279	-1.1088845448
H51	0.9573327549	2.2498820850	-2.0736224508
H52	1.0163878771	2.7227230956	1.0184537406
C53	-3.4086102107	-4.9030843740	-0.5674705694
C54	-3.3279831636	-4.3939449216	-1.8624661290
C55	-2.8845741818	-3.0871164255	-2.0789992967
C56	-2.5132856862	-2.2791085131	-0.9942049296
C57	-2.5818701933	-2.8056336904	0.3091561554
C58	-3.0355866321	-4.1061042413	0.5169557627
H59	-3.7541665409	-5.9212640420	-0.4019386526
H60	-3.6090571493	-5.0145894062	-2.7102397005

H61	-2.8244554032	-2.7014474119	-3.0935496837
H62	-2.2712339676	-2.1974572829	1.1576893747
H63	-3.0889145554	-4.5027041241	1.5287555954
C64	-1.4395461626	0.0044342230	-5.7793216043
C65	-2.6908340590	0.1962592220	-5.1932725625
C66	-2.8553650403	0.0399216749	-3.8163992255
C67	-1.7630296496	-0.3100851497	-3.0062840665
C68	-0.5044470040	-0.4853757023	-3.6055647271
C69	-0.3463340711	-0.3368857458	-4.9827212123
H70	-1.3153088822	0.1284774518	-6.8528320453
H71	-3.5436197597	0.4722026535	-5.8099053953
H72	-3.8341496035	0.2030161266	-3.3744114483
H73	0.3526202106	-0.7246791946	-2.9792211061
H74	0.6334966583	-0.4780263819	-5.4328751065
C75	-4.6206080175	-0.0498147446	-0.9005027928
H76	-4.7270762954	-1.0440822164	-1.3251947583
C77	-4.3817107142	2.4461824658	0.2675069522
H78	-4.2784088137	3.4157065455	0.7403735308
C79	-5.7665363634	0.6634457911	-0.5578048907
H80	-6.7482084736	0.2304573169	-0.7366032364
C81	-5.6440672192	1.9221918765	0.0236956770
H82	-6.5282403983	2.4903939387	0.3019617665

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Complex 6

(B3LYP)

Gas Phase Energy = -2032.72926163396 = Eh
Solvent Phase Energy = -0.02182969499 = Eh
Zero Point Energy = 434.068 = kcal/mol
Frequency = -30.63

(PBE)

Gas Phase Energy = -2030.52840672257 = Eh

Geometry Coordinates

Pd1	0.0000000000	0.0000000000	0.0000000000
C2	0.0000000000	0.0000000000	2.4380822781
C3	0.6432168078	0.0000000000	5.2288898795
C4	-0.9577996270	0.8242757005	1.8292527455
C5	-1.9333911447	0.3010441896	0.9393466568
C6	1.3920387959	-1.0411775719	4.6521739538
O7	2.4038882128	-0.8626009024	3.8926831343
C8	0.9582318422	-2.4964169892	4.8908529369
C9	1.1490531325	1.4175118987	5.1694290282
C10	-0.5291132928	-0.2378446570	6.1606933875
H11	-2.6383125028	0.9742306191	0.4606679979
H12	-2.2888799627	-0.7201752021	1.0704217078
H13	-0.8301103775	1.9037677609	1.8923316849
H14	0.9290103527	0.3785585874	2.8291907710
H15	-0.1499539666	-1.0723479593	2.4991565056
H16	1.0755042597	-3.0454280781	3.9377318532
H17	1.6900573488	-2.9549284256	5.5873659314
H18	0.3709363831	2.1387011460	4.8407575547
H19	1.4785716180	1.7684365765	6.1722558610
H20	2.0158725557	1.4938857868	4.4933295049

H21	-0.4306748395	0.4183825616	7.0521528150
H22	-1.4820690508	0.0839987822	5.6819176663
N23	2.2012755411	-0.1770214513	-0.2701657118
P24	-0.0746830027	-0.1706195745	-2.3497321554
C25	3.1417415294	-0.7281884090	0.7519737679
C26	4.3768076860	0.1876453930	0.5678148220
O27	4.1972964798	0.7472717266	-0.7857698346
C28	2.8740324098	0.5651857183	-1.0812655715
C29	2.4219869655	1.2718017843	-2.3027869054
C30	1.1917621682	1.0385633280	-2.9727103546
H31	5.3405861920	-0.3246122924	0.5811828515
H32	4.3875997254	1.0240633226	1.2786452064
H33	2.7148545860	-0.6192644112	1.7585164888
C34	3.4375695046	-2.2484693420	0.5347891135
C35	4.3907486126	-2.6996420717	1.6737633360
H36	5.3864747323	-2.2393179696	1.5824731914
H37	3.9597180661	-2.4271499633	2.6491859319
H38	4.5280525539	-3.7907324593	1.6299833012
C39	4.0695216000	-2.5273875995	-0.8464098140
H40	4.9965819577	-1.9542667694	-0.9971420737
H41	4.3206008154	-3.5959200446	-0.9286627601
H42	3.3723668218	-2.2834327564	-1.6610162573
C43	2.1196406902	-3.0445101136	0.6744536143
H44	2.3253943365	-4.1224262846	0.5863410312
H45	1.6726112849	-2.8563674501	1.6605266346
H46	1.4006668427	-2.7668136954	-0.1079690935
C47	-3.9164397725	1.0237571877	-4.6834959146
C48	-3.1101506713	0.0008040066	-5.1816198066
C49	-1.9486547064	-0.3737647815	-4.5042330557
C50	-1.5839113122	0.2712736866	-3.3110678713
C51	-2.4103528689	1.2928404124	-2.8118376405
C52	-3.5634403651	1.6698713517	-3.4973505416
H53	-4.8211297859	1.3126888881	-5.2138114521
H54	-3.3846515179	-0.5092779083	-6.1026847695
H55	-1.3291652504	-1.1724067821	-4.9036477189
H56	-2.1491921337	1.7870732624	-1.8782323947
H57	-4.1931451028	2.4637717511	-3.1015363532
C58	1.0991936356	-4.2519871459	-4.2399010222
C59	1.7062582256	-3.0882490547	-4.7107716932
C60	1.3797715802	-1.8494949096	-4.1550951219
C61	0.4425787059	-1.7645983729	-3.1129760199
C62	-0.1530088040	-2.9457673083	-2.6361437772
C63	0.1677128116	-4.1780335204	-3.2029527657
H64	1.3542028781	-5.2150802439	-4.6763391844
H65	2.4354538428	-3.1416090041	-5.5165096608
H66	1.8537370634	-0.9495705283	-4.5385949304
H67	-0.8712756638	-2.8985923454	-1.8196670867
H68	-0.3040158359	-5.0837941180	-2.8285858033
C69	3.0096058630	2.9563150416	-3.9655288892
C70	3.3081916232	2.2303795607	-2.8181216893
C71	0.9155798386	1.7771799082	-4.1331398154
C72	1.8088181324	2.7271029623	-4.6278451081
H73	3.7131767993	3.6979080775	-4.3358575125
H74	4.2418481011	2.3973850102	-2.2929354265
H75	-0.0206353150	1.6132140828	-4.6575701994
H76	1.5595325253	3.2848774661	-5.5278170572

C77	-0.6739835636	-1.6916908541	6.6302127243
H78	-1.6635797548	-1.8512185521	7.0878784722
H79	0.0799410992	-1.9102276847	7.4059672475
C80	-0.4583710845	-2.6651725868	5.4495242864
H81	-1.2066190791	-2.4485879632	4.6667337224
H82	-0.6270041583	-3.7050178951	5.7739204697

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Complex 7

(B3LYP)

Gas Phase Energy = -2032.72448663528 = Eh
Solvent Phase Energy = -0.02524726980 = Eh
Zero Point Energy = 433.361 = kcal/mol
Frequency = -15.07

(PBE)

Gas Phase Energy = -2030.52549546915 = Eh

Geometry Coordinates

Pd1	0.0000000000	0.0000000000	0.0000000000
C2	0.0000000000	0.0000000000	2.3211968669
C3	0.8424999870	0.0000000000	5.2512512366
C4	-0.6604120923	-1.9348412135	0.9595233626
C5	2.0348324454	-0.2310662807	4.5376139376
O6	2.6348456752	0.6466958488	3.8354158531
C7	2.6662417406	-1.6330421228	4.5701704904
C8	0.2961210408	1.3961934591	5.3680717406
C9	0.1728499396	-1.0508920472	6.1098325762
H10	0.7948244678	0.5765149642	2.7720940497
H11	-1.0279369486	0.3229104883	2.4686154440
H12	1.2858408351	-1.6542438342	1.8480005605
H13	-0.3944955452	-2.8749897192	0.4852676950
H14	-1.7244022252	-1.7326377282	1.0634760359
H15	3.5597004710	-1.5853182383	5.2270714149
H16	3.0593542203	-1.8489673429	3.5582365913
H17	-0.7921611092	1.4502644686	5.1542871484
H18	0.4156091570	1.7923032950	6.4009815514
H19	0.8276757331	2.0791754177	4.6873643011
H20	-0.1086039186	-0.6061760141	7.0889316396
H21	-0.7975838993	-1.3648843601	5.6603378580
N22	-0.2745441670	-0.2905545527	-2.1920555215
P23	0.8648308863	2.1113477013	-0.6693151461
C24	-1.2509872732	-1.2571523956	-2.7626386475
C25	-0.4420654562	-1.9002773930	-3.9231160958
O26	0.6345547654	-0.9384740923	-4.1632467737
C27	0.6946263401	-0.1464163899	-3.0415768310
C28	1.8728726616	0.7334422716	-2.9853464257
C29	2.0761494729	1.7610679965	-2.0218505857
H30	-0.9906321073	-2.0177097100	-4.8602362182
H31	0.0126772887	-2.8586026226	-3.6381708761
H32	-1.4950380278	-2.0010319604	-1.9954775416
C33	2.4241038645	2.7233170959	1.5561167438
C34	1.7400677103	3.2648340468	0.4560900697
C35	1.7305566879	4.6604610113	0.2713410300
H36	2.4342950681	1.6572310425	1.7657888990

C37	-0.1744459942	3.8005104158	-2.7353763444
C38	-0.3842402897	3.1941069380	-1.4871547730
C39	-1.5873254814	3.4462197271	-0.8046222505
H40	0.7497590375	3.6229391528	-3.2795306915
C41	-2.5829048012	-0.5723812117	-3.2115703309
C42	-3.5226457050	-1.6611799856	-3.7906283054
H43	-3.1206050633	-2.1126142666	-4.7095296194
H44	-3.6984259948	-2.4631779990	-3.0568533627
H45	-4.4954173395	-1.2140115013	-4.0424949399
C46	-2.3236751391	0.5166456810	-4.2766675801
H47	-1.7994590868	0.1136099881	-5.1557923258
H48	-3.2821669514	0.9339498639	-4.6198067842
H49	-1.7273284056	1.3400238101	-3.8615835900
C50	-3.2711894530	0.0620790727	-1.9813446505
H51	-4.2359934795	0.5002592874	-2.2786198113
H52	-3.4654380926	-0.6960811123	-1.2072950761
H53	-2.6515770794	0.8562591986	-1.5472490587
C54	3.0863060738	3.5602725378	2.4558857286
C55	2.4027650897	5.4884113118	1.1684566451
H56	-1.7673404030	2.9824138821	0.1636368688
C57	3.0798840591	4.9403968382	2.2615620909
H58	3.5686606868	3.1019120375	3.3147293051
H59	3.5894325554	5.5940185150	2.9665952082
H60	2.3898130592	6.5665337320	1.0198503902
H61	1.1923191041	5.0998890573	-0.5650727955
C62	3.2639293977	2.5054802833	-2.0831420359
H63	3.4376797169	3.2834967942	-1.3462185188
C64	2.8582121102	0.5133783170	-3.9652365103
H65	2.6930188108	-0.2734663361	-4.6926562066
C66	4.2268004642	2.2702537433	-3.0626286700
H67	5.1353855670	2.8677815670	-3.0804999502
C68	4.0213668206	1.2695081458	-4.0094654907
H69	4.7664559798	1.0728666145	-4.7766134510
C70	-1.1435577183	4.6448497973	-3.2830470551
H71	-0.9667010913	5.1117833019	-4.2499459543
C72	-2.5469733724	4.2973968449	-1.3506503759
H73	-3.4690537648	4.4911595023	-0.8068178154
C74	-2.3280888886	4.8971398964	-2.5920592894
H75	-3.0784118973	5.5595794610	-3.0183503598
C76	1.7313693390	-2.7447299319	5.0553938736
H77	2.2909677741	-3.6804210814	5.2200821173
H78	0.9637938530	-2.9596843707	4.2909866494
C79	1.0289212136	-2.3009106400	6.3589482287
H80	0.4080627879	-3.1172395038	6.7609951908
H81	1.8016646973	-2.0804973041	7.1152871298
C82	0.2694098235	-1.2734770317	1.7771592089

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Complex 8

(B3LYP)

Gas Phase Energy = -2032.75792237478 = Eh
Solvent Phase Energy = -0.01322731344 = Eh
Zero Point Energy = 434.122 = kcal/mol

(PBE)

Gas Phase Energy = -2030.55097086362 = Eh

Geometry Coordinates

Pd1	0.1915648604	-0.0578528428	-0.0045695048
C2	0.7380779138	0.2487995492	1.9995464524
C3	0.9177841207	-1.0073451258	2.7347292550
C4	2.1009685961	-1.5430077692	3.0837744176
C5	2.4878983867	-3.6194572433	0.6346249865
O6	1.0583871202	-1.9540125174	-0.2257736421
C7	2.2726742622	-2.3890021033	0.0776056574
C8	3.4297966073	-1.4751329042	-0.3067694587
C9	1.3453136245	-4.5030156999	1.0554435136
C10	3.8735081920	-4.2179363732	0.7748355573
H11	1.6597711792	0.8380857605	1.9368195007
H12	-0.0661278683	0.8647676841	2.4088914371
H13	0.0075837368	-1.5471634442	2.9999230666
H14	2.1666842094	-2.4793286188	3.6288899558
H15	3.0398243445	-1.0476341725	2.8491588813
N16	-0.3151411952	-0.2210320715	-2.2673198189
P17	-1.0099909164	1.8893277359	-0.2353169597
H18	1.2026386203	-5.3564874568	0.3580888722
H19	1.5340795723	-4.9528330440	2.0514005731
H20	0.4021506133	-3.9378683602	1.0961707804
H21	3.4558833885	-1.3843806675	-1.4135071228
H22	3.2005713018	-0.4583710791	0.0668447451
H23	4.1612766875	-4.2676650211	1.8487845849
H24	3.8539533942	-5.2762285658	0.4391254461
C25	-0.1707710001	-1.5388970127	-2.9376804206
C26	0.5848833580	-1.1678773667	-4.2428486570
O27	0.3965718734	0.2867028847	-4.3570544158
C28	-0.0234016542	0.6990763044	-3.1184031584
C29	-0.0901801771	2.1649562186	-2.9507016808
C30	-0.5336065898	2.8158246961	-1.7713310450
H31	0.1849787453	-1.6192735173	-5.1539130856
H32	1.6635538895	-1.3603616856	-4.1744656024
H33	0.4335428166	-2.1672215716	-2.2734206758
C34	-1.5507008039	-2.2342628594	-3.1622908909
C35	-1.3000056189	-3.5938690621	-3.8631928080
H36	-0.8746059321	-3.4698997206	-4.8704068576
H37	-0.6150941371	-4.2177932248	-3.2693802954
H38	-2.2505255673	-4.1371046791	-3.9707983782
C39	-2.4955577412	-1.3642139207	-4.0210720513
H40	-2.0550758561	-1.1204001307	-4.9998245432
H41	-3.4376912446	-1.9035547547	-4.2023374903
H42	-2.7378972057	-0.4251752261	-3.5037520189
C43	-2.2033919921	-2.5068433753	-1.7866159330
H44	-3.1236858616	-3.0968506834	-1.9199341474
H45	-1.5148537869	-3.0636939639	-1.1349875996
H46	-2.4641750329	-1.5673286597	-1.2833208377
C47	-0.7351988819	5.1428542117	3.0777342034
C48	-1.9902940587	4.7276393083	2.6361133318
C49	-2.1006118621	3.7627045552	1.6327710106
C50	-0.9499837117	3.1987892116	1.0607850552
C51	0.3118483935	3.6159099203	1.5230068995
C52	0.4159497924	4.5860115161	2.5170725798
H53	-0.6524707600	5.8936163832	3.8605807615

H54	-2.8904676073	5.1553437529	3.0726229093
H55	-3.0854016586	3.4503657429	1.2964933333
H56	1.2147396958	3.1780202374	1.1024854807
H57	1.3977544977	4.9010793435	2.8635438565
C58	-5.5721822676	1.0976674868	-0.6537203254
C59	-4.9793523413	2.0817837082	-1.4447955083
C60	-3.6099851672	2.3339098202	-1.3456845603
C61	-2.8160674451	1.5952320583	-0.4544319317
C62	-3.4200745858	0.5953567211	0.3276738616
C63	-4.7910605004	0.3570153269	0.2342728769
H64	-6.6399550725	0.9052587831	-0.7322854924
H65	-5.5846466717	2.6582142658	-2.1414020266
H66	-3.1622611951	3.1085298952	-1.9630976861
H67	-2.8092648528	0.0016576511	1.0050616425
H68	-5.2473410856	-0.4162861624	0.8481598024
C69	-0.5766164268	4.2191986417	-1.7623943464
H70	-0.9095791948	4.7354282688	-0.8675032058
C71	0.3066134829	2.9389340228	-4.0524075135
H72	0.6546991590	2.4236847708	-4.9406427424
C73	-0.1888534396	4.9709030312	-2.8705946740
H74	-0.2348239360	6.0568682123	-2.8287902764
C75	0.2606249955	4.3274412581	-4.0192348967
H76	0.5763238190	4.9016115004	-4.8869892838
C77	4.9562887125	-3.4610120967	-0.0033264612
H78	4.8661386095	-3.6803287843	-1.0812050486
H79	5.9587135159	-3.7919330880	0.3110557758
C80	4.7963226149	-1.9385504327	0.2112779548
H81	5.6071565314	-1.3895053766	-0.2934912805
H82	4.8835268496	-1.7225425270	1.2893223041

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Complex 9

(B3LYP)

Gas Phase Energy = -2032.74615186694 = Eh
Solvent Phase Energy = -0.01150958455 = Eh
Zero Point Energy = 434.278 = kcal/mol
Frequency = -310.74

(PBE)

Gas Phase Energy = -2030.54481985386 = Eh

Geometry Coordinates

Pd1	-0.0043666097	0.0634387862	0.0584997996
C2	0.0070301491	0.1093603823	2.2104800572
C3	1.3809836889	0.0923046314	2.5751574707
C4	2.1337719483	1.2231012929	2.9104985345
C5	3.2615043957	2.1293264681	1.3058756248
O6	1.6508404679	1.4960421691	-0.2819578274
C7	2.1093206112	2.3759665974	0.5197675089
C8	1.2867406393	3.6483812887	0.7117120749
C9	4.1528897960	0.9682068027	0.9203252161
C10	3.9828945429	3.2963699640	1.9819053361
H11	-0.5402218720	1.0258575014	2.4494500813
H12	-0.5664594077	-0.7887870614	2.4359080111
H13	1.8911886327	-0.8702890690	2.5576346448

H14	3.0695012544	1.0739744176	3.4420746077
H15	1.5994052343	2.1238049488	3.2026376188
N16	0.0598027013	-0.1507606747	-2.3652811753
P17	-1.8988267118	-1.1875206227	-0.3477454845
H18	4.8116316350	1.2485030675	0.0735001053
H19	4.8134459789	0.6793548089	1.7587925662
H20	3.5634789877	0.0919793950	0.6127374514
H21	1.2084237611	4.1364644156	-0.2796986047
H22	0.2541749651	3.3496393037	0.9756055892
H23	3.9873328709	3.1615714475	3.0835539236
H24	5.0493474817	3.2771056818	1.6831225435
C25	1.3309108023	0.1810614157	-3.0550807095
C26	0.8910225442	1.2580287268	-4.0897827309
O27	-0.5680682715	1.1190895635	-4.1437226055
C28	-0.9058379715	0.3663336690	-3.0417826594
C29	-2.3556196621	0.2503022358	-2.8003711737
C30	-2.9294723790	-0.4275592628	-1.6914924094
H31	1.2716436199	1.1104281738	-5.1038867802
H32	1.1212299331	2.2758671052	-3.7497625271
H33	2.0131888195	0.6092412024	-2.3126094410
C34	1.9944710527	-1.0877589318	-3.6779034594
C35	3.2954968468	-0.6618860827	-4.4036098376
H36	3.0945550658	-0.0098999411	-5.2665946508
H37	3.9712282665	-0.1305765168	-3.7158460289
H38	3.8216624034	-1.5526772970	-4.7781852931
C39	1.0427151133	-1.7914018068	-4.6709814172
H40	0.7079690166	-1.1106221418	-5.4682127999
H41	1.5575815230	-2.6401635697	-5.1462692117
H42	0.1565372175	-2.1790632194	-4.1497984629
C43	2.3663733904	-2.0656736741	-2.5393859493
H44	2.8776872764	-2.9478889243	-2.9550727816
H45	3.0424607685	-1.5817340672	-1.8185428345
H46	1.4711677153	-2.4015219368	-2.0023770477
C47	-4.9857758571	-1.8215422525	3.0822534802
C48	-4.6702699354	-2.8969135612	2.2525319378
C49	-3.7572341243	-2.7377091227	1.2083770539
C50	-3.1437451996	-1.4952556675	0.9828513043
C51	-3.4608629400	-0.4212893720	1.8344622973
C52	-4.3797126106	-0.5822574108	2.8696882541
H53	-5.6966301602	-1.9495905712	3.8958736944
H54	-5.1374082326	-3.8659337610	2.4167936563
H55	-3.5227954964	-3.5838104971	0.5681301190
H56	-2.9803705094	0.5434447887	1.6830382378
H57	-4.6170652447	0.2585608854	3.5180215106
C58	-1.0423446840	-5.5146784482	-1.8369275927
C59	-2.0652162923	-4.7811237959	-2.4378130859
C60	-2.3378093279	-3.4776209438	-2.0172885838
C61	-1.5817596932	-2.8888154214	-0.9916794829
C62	-0.5435110064	-3.6317485021	-0.4041155969
C63	-0.2836971483	-4.9382818293	-0.8171342513
H64	-0.8345014604	-6.5311394994	-2.1646302183
H65	-2.6572510971	-5.2253558197	-3.2355813982
H66	-3.1436769655	-2.9204076742	-2.4882240108
H67	0.0643119259	-3.1770472487	0.3757621197
H68	0.5194360829	-5.5035453497	-0.3491395012
C69	-4.3309567383	-0.4629720977	-1.5913714220

H70	-4.7900339729	-0.9696964429	-0.7484630146
C71	-3.1991766733	0.8608780164	-3.7429400764
H72	-2.7407847681	1.3829060717	-4.5756876027
C73	-5.1507369355	0.1403645374	-2.5425295950
H74	-6.2320589425	0.0880192955	-2.4339354764
C75	-4.5818586235	0.8083042804	-3.6235973487
H76	-5.2103802919	1.2895048275	-4.3693208260
C77	3.3935843916	4.6746888398	1.6482914839
H78	3.6828770373	4.9697891388	0.6253733622
H79	3.8019437690	5.4363281057	2.3301100420
C80	1.8507165035	4.6395234511	1.7395643891
H81	1.4323039335	5.6436565142	1.5706238144
H82	1.5613964410	4.3467043411	2.7621993770

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Complex 10

(B3LYP)

Gas Phase Energy = -2032.79265164845 = Eh
Solvent Phase Energy = -0.01320247828 = Eh
Zero Point Energy = 436.003 = kcal/mol

(PBE)

Gas Phase Energy = -2030.58452882899 = Eh

Geometry Coordinates

Pd1	0.0720538868	0.0428463229	0.0099922639
C2	0.1823952393	0.0807276368	3.1441744177
C3	0.9868244414	-0.0413482100	4.4706878791
C4	1.0117446381	0.4512350308	1.9246127186
C5	0.8479732080	1.6552857713	1.2186102544
C6	1.9459401444	-1.2505665304	4.3933555328
O7	1.7797394260	-2.1590009219	3.5946976409
C8	3.0834756682	-1.3205780504	5.4113248468
C9	-0.0108204601	-0.3537065252	5.6196570138
C10	1.7656846439	1.2674364822	4.7784009153
H11	1.6760690159	2.0855625627	0.6590397637
H12	0.0702612855	2.3606437920	1.5081520885
H13	1.9744286139	-0.0554575430	1.8517660042
H14	-0.3256968273	-0.8772717915	2.9927053433
H15	-0.6035676672	0.8337681560	3.2886683122
N16	0.0484820169	-2.2853000136	-0.3976119107
P17	-0.7102341132	0.0214395134	-2.2148560190
H18	3.7706645397	-2.1220425249	5.0937819529
H19	2.6427740306	-1.6388325815	6.3782108942
H20	0.4849699728	-0.4715208688	6.5985465661
H21	-0.7381239401	0.4726328396	5.7119503953
H22	-0.5731314347	-1.2806682257	5.4109840625
H23	2.2926459144	1.5902870483	3.8618999508
H24	1.0323602254	2.0635735350	5.0074200204
C25	0.0609439448	-3.2580504675	0.7255767213
C26	1.2631248171	-4.1793755031	0.3705211187
O27	1.5050457660	-3.9039475631	-1.0474204185
C28	0.8256728704	-2.7365105650	-1.3214621184
C29	1.1008358857	-2.1782701010	-2.6615948386
C30	0.4890408738	-1.0109593988	-3.1967527048

H31	1.0716161971	-5.2510148996	0.4680682596
H32	2.1650133576	-3.9099959040	0.9350579742
H33	0.2646088251	-2.7222304050	1.6595664200
C34	-1.3072661327	-3.9997669336	0.8635278086
C35	-1.2098812150	-4.9996551446	2.0435941864
H36	-0.4866097167	-5.8042555496	1.8447936330
H37	-0.9092094092	-4.4848574196	2.9689330704
H38	-2.1899178524	-5.4701321508	2.2140042606
C39	-1.6726280358	-4.7520967625	-0.4362427854
H40	-0.8854136775	-5.4613605143	-0.7329157546
H41	-2.6021536753	-5.3227565150	-0.2879394314
H42	-1.8358339521	-4.0468267949	-1.2624684923
C43	-2.4121125123	-2.9666683809	1.1845480490
H44	-3.3744282653	-3.4814873145	1.3314558084
H45	-2.1726515138	-2.4156799195	2.1068399847
H46	-2.5240247405	-2.2441332382	0.3673154852
C47	-4.8363112980	-2.0144593546	-2.9723984437
C48	-3.7513922214	-2.3705730274	-3.7726248755
C49	-2.5015840574	-1.7803920205	-3.5680641511
C50	-2.3200197983	-0.8286844618	-2.5522219347
C51	-3.4185615847	-0.4875286143	-1.7442527129
C52	-4.6674240007	-1.0694183139	-1.9590789706
H53	-5.8093280350	-2.4731173374	-3.1356856461
H54	-3.8765619927	-3.1077399192	-4.5635379229
H55	-1.6666922446	-2.0622871319	-4.2047590342
H56	-3.2887940948	0.2376267572	-0.9428108291
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C60	-0.0645545666	2.6401959335	-2.9237900966
C61	-0.8753936666	1.5430660785	-3.2587200675
C62	-1.7745918263	1.6692103634	-4.3306614785
C63	-1.8479227101	2.8591134108	-5.0561857332
H64	-1.0842297636	4.8625131638	-5.2926029702
H65	0.5033051520	4.6649184764	-3.3890527821
H66	0.6078759339	2.5615382272	-2.0710561244
H67	-2.4238350807	0.8383667700	-4.5961507454
H68	-2.5518526350	2.9460398511	-5.8818049236
C69	0.8634098162	-0.6036993693	-4.4874960931
H70	0.4144613913	0.2885664182	-4.9115175531
C71	2.0446382301	-2.8727927175	-3.4370646676
H72	2.5050639468	-3.7562853405	-3.0096107953
C73	1.8006810884	-1.3079279906	-5.2410127888
H74	2.0638814782	-0.9595474772	-6.2377039883
C75	2.3948084026	-2.4497335188	-4.7128787974
H76	3.1313153560	-3.0074737718	-5.2868418177
C77	3.8063600601	0.0213914446	5.6105285093
H78	4.5404854526	-0.0664440798	6.4252479976
H79	4.3696318528	0.2801472431	4.6984207991
C80	2.7902258113	1.1494348280	5.9139507169
H81	2.2935087270	0.9442125103	6.8766427542
H82	3.3219781402	2.1059402224	6.0322366545

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CALIFORNIA INSTITUTE OF TECHNOLOGY

BECKMAN INSTITUTE

X-RAY CRYSTALLOGRAPHY LABORATORY

Date 20 July 2004

Crystal Structure Analysis of:

DCB24

(shown below)

For Investigator: Doug Behenna ext. 2116

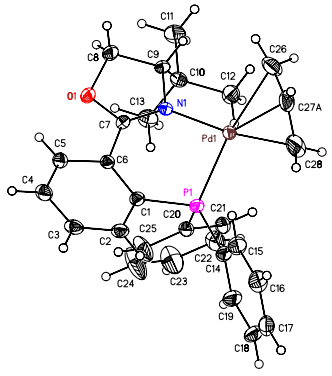
Advisor: B. M. Stoltz ext. 6064

Account Number: BMS.JandJ-2.11-GRANT.000006

By Michael W. Day 116 Beckman ext. 2734

e-mail: mikeday@caltech.edu

Contents



DCB24

Note: The crystallographic data have been deposited in the Cambridge Database (CCDC) and has been placed on hold pending further instructions from me. The deposition number is 245187. Ideally the CCDC would like the publication to contain a footnote of the type: "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 245187."

Table 1. Crystal data and structure refinement for DCB24 (CCDC 245187).

Empirical formula	$[C_{28}H_{31}NOPPd]^{+}\ PF_6^{-} \bullet \frac{1}{2}C_2H_5OH$
Formula weight	702.91
Crystallization Solvent	Ethanol
Crystal Habit	Fragment
Crystal size	0.35 x 0.34 x 0.23 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 15322 reflections used in lattice determination	2.31 to 41.00°
Unit cell dimensions	a = 17.5183(6) Å b = 15.7792(5) Å β= 107.0990(10)° c = 11.3736(4) Å
Volume	3004.98(18) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	C2
Density (calculated)	1.554 Mg/m^3
F(000)	1428
θ range for data collection	1.77 to 42.31°
Completeness to θ = 42.31°	85.0 %
Index ranges	$-32 \le h \le 32, -28 \le k \le 29, -20 \le l \le 15$
Data collection scan type	ω scans at 3 ϕ settings of 2θ=-28º and 2 at 2θ=-59º
Reflections collected	28501
Independent reflections	15572 [R_{int}= 0.0351]
Absorption coefficient	0.787 mm^{-1}
Absorption correction	SADABS
Max. and min. transmission	0.8397 and 0.7702

Table 1 (cont.)

Structure solution and Refinement

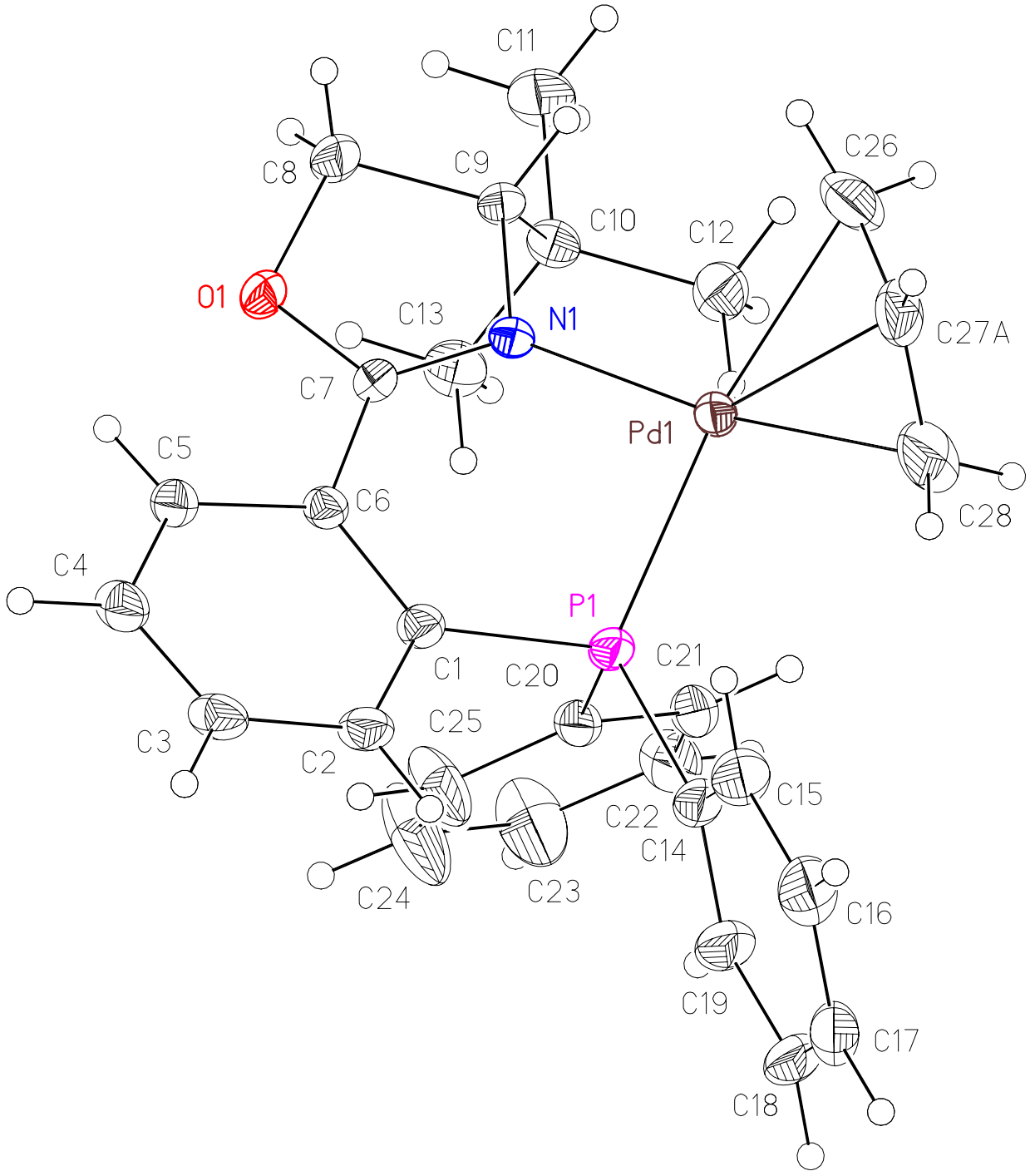
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	15572 / 1 / 408
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.343
Final R indices [$I>2\sigma(I)$, 13582 reflections]	R1 = 0.0373, *w*R2 = 0.0725
R indices (all data)	R1 = 0.0459, *w*R2 = 0.0748
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	-0.019(13)
Largest diff. peak and hole	1.422 and -0.710 e.Å^{-3}

Special Refinement Details

The propyl ligand, C26-C27-C28, is disordered in two alternate orientations, differing by "up-down" positions for C27. Additional disorder is observed in one PF_6 counterion and an included solvent molecule, modeled as ethanol hydrogen bonded to a fluorine of one counterion.

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.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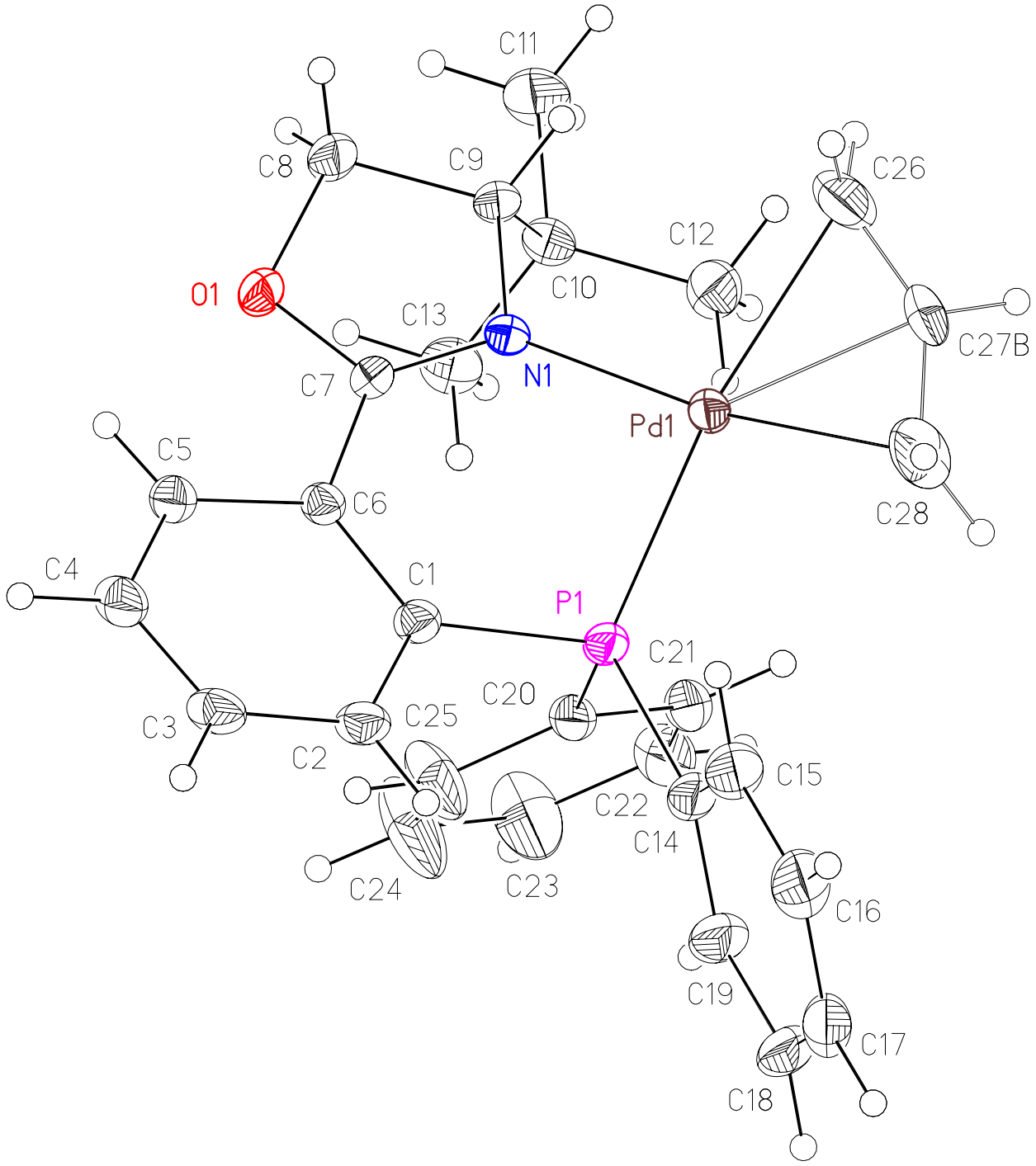
C9
C10
C12
C26
O1
C13
N1
C27A
C7
Pd1
C5
C6
C28
C4
P1
C1
C20
C21
C25
C3
C2
C22
C15
C14
C24
C23
C16
C19
C17
C18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C8
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C26
C12
O1
C10
C13
C27B
N1
C7
Pd1
C5
C6
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C1
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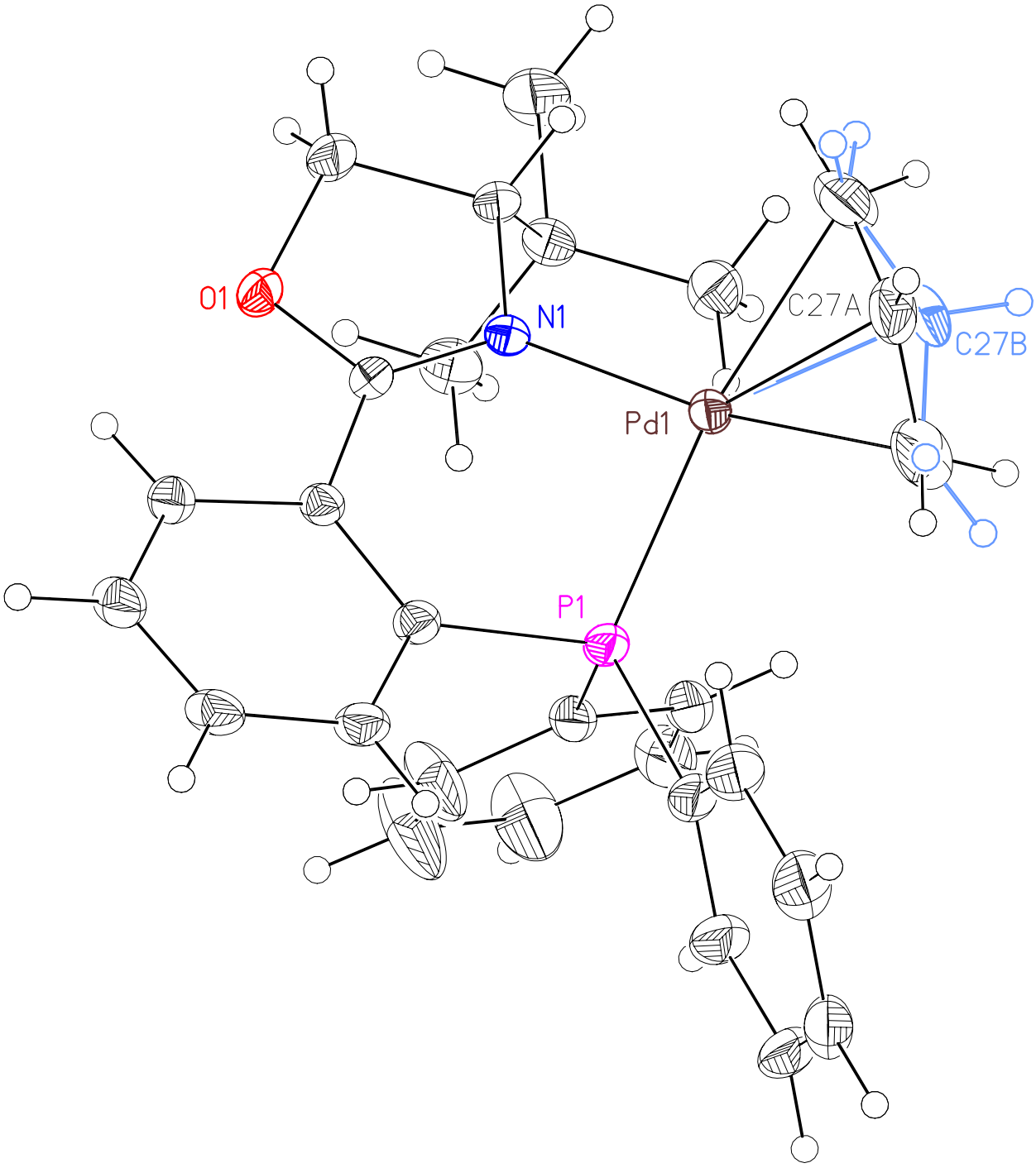
C24
C23
C16
C19
C17
C18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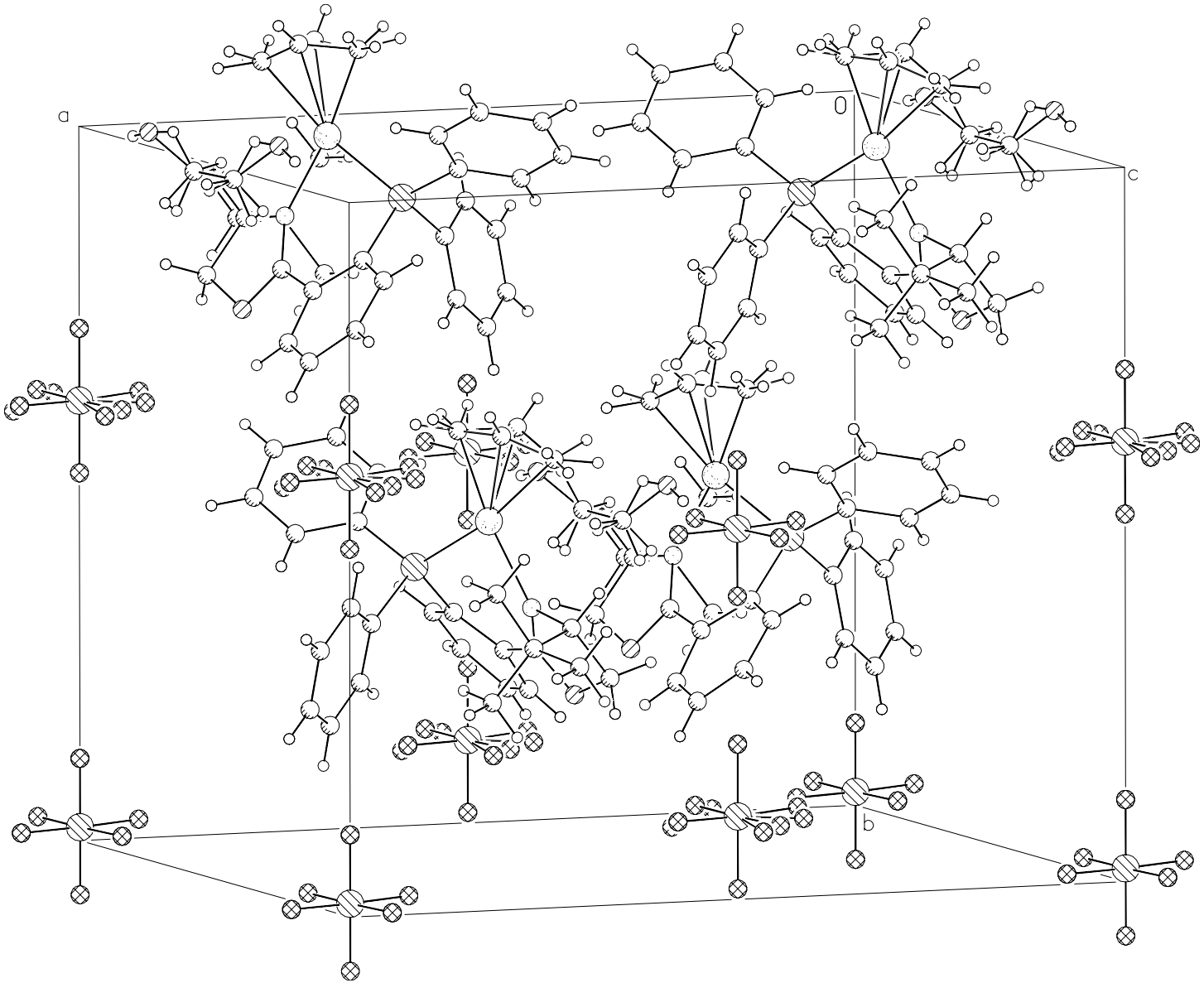
C27B
Pd1
P1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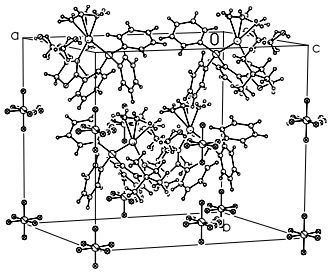
c
b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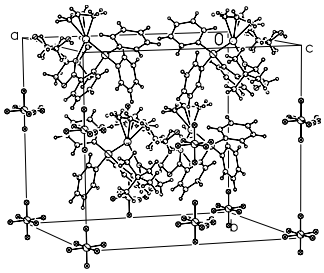
a
c

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for DCB24 (CCDC 245187). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Pd(1)	2838(1)	4922(1)	2994(1)	18(1)	1
P(1)	2327(1)	5673(1)	4282(1)	19(1)	1
O(1)	3784(1)	7349(1)	2545(1)	22(1)	1
N(1)	3187(1)	6087(1)	2419(2)	17(1)	1
C(1)	3099(1)	6431(1)	5056(2)	18(1)	1
C(2)	3275(1)	6569(1)	6320(2)	23(1)	1
C(3)	3845(1)	7170(1)	6920(2)	24(1)	1
C(4)	4208(1)	7669(1)	6242(2)	25(1)	1
C(5)	4040(1)	7544(1)	4982(2)	21(1)	1
C(6)	3512(1)	6903(1)	4381(2)	17(1)	1
C(7)	3458(1)	6748(1)	3074(2)	17(1)	1
C(8)	3836(1)	6994(1)	1381(2)	25(1)	1
C(9)	3264(1)	6242(1)	1155(2)	20(1)	1
C(10)	2441(1)	6383(1)	190(2)	23(1)	1
C(11)	2594(2)	6514(2)	-1064(2)	33(1)	1
C(12)	1931(1)	5586(2)	100(2)	29(1)	1
C(13)	2015(1)	7156(1)	510(2)	28(1)	1
C(14)	2024(1)	5153(1)	5500(2)	26(1)	1
C(15)	2543(2)	4578(2)	6254(2)	33(1)	1
C(16)	2337(2)	4162(2)	7193(2)	41(1)	1
C(17)	1591(2)	4315(2)	7372(3)	45(1)	1
C(18)	1070(2)	4884(2)	6615(2)	43(1)	1
C(19)	1277(2)	5303(2)	5676(2)	35(1)	1
C(20)	1492(1)	6337(1)	3474(2)	22(1)	1
C(21)	888(1)	5982(1)	2497(2)	24(1)	1
C(22)	256(1)	6481(2)	1823(2)	33(1)	1
C(23)	218(2)	7332(2)	2102(3)	50(1)	1
C(24)	812(2)	7686(2)	3061(4)	63(1)	1
C(25)	1439(1)	7192(2)	3747(3)	44(1)	1
C(26)	3314(2)	3965(2)	1935(3)	41(1)	1
C(27A)	3201(3)	3620(2)	2979(5)	30(1)	0.563(11)
C(27B)	2776(4)	3655(3)	2334(7)	32(2)	0.437(11)
C(28)	2576(3)	3683(2)	3388(3)	56(1)	1
P(2)	0	3840(1)	0	18(1)	1
F(1)	0	2828(1)	0	36(1)	1
F(2)	0	4853(2)	0	32(1)	1
F(3)	955(3)	3812(3)	530(5)	49(1)	0.77(3)
F(4)	-75(4)	3827(4)	1359(6)	51(1)	0.77(3)
F(3B)	900(13)	3927(11)	140(50)	100(9)	0.23(3)
F(4B)	170(30)	3897(16)	1430(20)	94(10)	0.23(3)
P(3)	5000	4813(1)	0	36(1)	1
F(5)	5000	3850(3)	0	210(4)	1
F(6)	5000	5758(3)	0	223(5)	1
F(7)	4919(1)	4802(3)	1329(2)	120(2)	1
F(8)	4076(1)	4798(4)	-481(2)	120(1)	1

C(30)	4962(4)	5145(5)	5617(6)	55(4)	0.50
C(31)	5035(8)	5160(5)	4359(7)	106(8)	0.50
O(30)	5453(3)	4644(3)	3892(5)	68(2)	0.50

Table 3. Selected bond lengths [Å] and angles [°] for DCB24 (CCDC 245187).

Pd(1)-C(28)	2.087(2)	C(28)-Pd(1)-N(1)	171.47(9)
Pd(1)-N(1)	2.1020(15)	C(28)-Pd(1)-C(27B)	37.19(19)
Pd(1)-C(27B)	2.127(4)	N(1)-Pd(1)-C(27B)	134.59(17)
Pd(1)-C(27A)	2.153(4)	C(28)-Pd(1)-C(27A)	36.07(16)
Pd(1)-C(26)	2.239(2)	N(1)-Pd(1)-C(27A)	135.98(13)
Pd(1)-P(1)	2.2639(5)	C(27B)-Pd(1)-C(27A)	23.7(2)
		C(28)-Pd(1)-C(26)	67.92(10)
		N(1)-Pd(1)-C(26)	103.55(9)
		C(27B)-Pd(1)-C(26)	33.40(17)
		C(27A)-Pd(1)-C(26)	36.35(15)
		C(28)-Pd(1)-P(1)	101.37(8)
		N(1)-Pd(1)-P(1)	87.15(5)
		C(27B)-Pd(1)-P(1)	136.98(16)
		C(27A)-Pd(1)-P(1)	132.75(14)
		C(26)-Pd(1)-P(1)	168.99(7)

Table 4. Bond lengths [Å] and angles [°] for DCB24 (CCDC 245187).

Pd(1)-C(28)	2.087(2)	P(3)-F(6)	1.492(5)
Pd(1)-N(1)	2.1020(15)	P(3)-F(5)	1.520(5)
Pd(1)-C(27B)	2.127(4)	P(3)-F(8)	1.549(2)
Pd(1)-C(27A)	2.153(4)	P(3)-F(8)#2	1.549(2)
Pd(1)-C(26)	2.239(2)	P(3)-F(7)#2	1.5592(19)
Pd(1)-P(1)	2.2639(5)	P(3)-F(7)	1.5592(19)
P(1)-C(20)	1.814(2)	C(30)-C(31)	1.4740
P(1)-C(14)	1.8179(19)	C(31)-O(30)	1.3080
P(1)-C(1)	1.8262(18)		
O(1)-C(7)	1.337(2)	C(28)-Pd(1)-N(1)	171.47(9)
O(1)-C(8)	1.465(2)	C(28)-Pd(1)-C(27B)	37.19(19)
N(1)-C(7)	1.287(2)	N(1)-Pd(1)-C(27B)	134.59(17)
N(1)-C(9)	1.502(2)	C(28)-Pd(1)-C(27A)	36.07(16)
C(1)-C(2)	1.397(3)	N(1)-Pd(1)-C(27A)	135.98(13)
C(1)-C(6)	1.412(2)	C(27B)-Pd(1)-C(27A)	23.7(2)
C(2)-C(3)	1.399(3)	C(28)-Pd(1)-C(26)	67.92(10)
C(3)-C(4)	1.382(3)	N(1)-Pd(1)-C(26)	103.55(9)
C(4)-C(5)	1.390(3)	C(27B)-Pd(1)-C(26)	33.40(17)
C(5)-C(6)	1.406(2)	C(27A)-Pd(1)-C(26)	36.35(15)
C(6)-C(7)	1.482(3)	C(28)-Pd(1)-P(1)	101.37(8)
C(8)-C(9)	1.526(3)	N(1)-Pd(1)-P(1)	87.15(5)
C(9)-C(10)	1.549(3)	C(27B)-Pd(1)-P(1)	136.98(16)
C(10)-C(13)	1.529(3)	C(27A)-Pd(1)-P(1)	132.75(14)
C(10)-C(12)	1.529(3)	C(26)-Pd(1)-P(1)	168.99(7)
C(10)-C(11)	1.541(3)	C(20)-P(1)-C(14)	105.92(10)
C(14)-C(15)	1.388(3)	C(20)-P(1)-C(1)	103.80(8)
C(14)-C(19)	1.401(3)	C(14)-P(1)-C(1)	105.63(9)
C(15)-C(16)	1.388(3)	C(20)-P(1)-Pd(1)	112.83(6)
C(16)-C(17)	1.401(4)	C(14)-P(1)-Pd(1)	121.10(7)
C(17)-C(18)	1.386(5)	C(1)-P(1)-Pd(1)	106.03(6)
C(18)-C(19)	1.391(3)	C(7)-O(1)-C(8)	106.45(14)
C(20)-C(25)	1.394(3)	C(7)-N(1)-C(9)	107.51(15)
C(20)-C(21)	1.407(3)	C(7)-N(1)-Pd(1)	128.28(14)
C(21)-C(22)	1.391(3)	C(9)-N(1)-Pd(1)	123.75(12)
C(22)-C(23)	1.386(4)	C(2)-C(1)-C(6)	118.94(16)
C(23)-C(24)	1.385(4)	C(2)-C(1)-P(1)	120.43(14)
C(24)-C(25)	1.385(4)	C(6)-C(1)-P(1)	120.61(14)
C(26)-C(27B)	1.259(6)	C(1)-C(2)-C(3)	121.19(18)
C(26)-C(27A)	1.372(6)	C(4)-C(3)-C(2)	119.57(19)
C(27A)-C(28)	1.314(6)	C(3)-C(4)-C(5)	120.13(18)
C(27B)-C(28)	1.345(7)	C(4)-C(5)-C(6)	120.84(18)
P(2)-F(3B)	1.543(18)	C(5)-C(6)-C(1)	119.03(17)
P(2)-F(3B)#1	1.543(18)	C(5)-C(6)-C(7)	116.43(15)
P(2)-F(4B)	1.57(2)	C(1)-C(6)-C(7)	124.49(15)
P(2)-F(4B)#1	1.57(2)	N(1)-C(7)-O(1)	116.61(16)
P(2)-F(4)	1.590(5)	N(1)-C(7)-C(6)	128.16(16)
P(2)-F(4)#1	1.590(5)	O(1)-C(7)-C(6)	115.06(14)
P(2)-F(2)	1.598(2)	O(1)-C(8)-C(9)	103.71(14)
P(2)-F(1)	1.5982(18)	N(1)-C(9)-C(8)	101.78(15)
P(2)-F(3)	1.603(4)	N(1)-C(9)-C(10)	112.07(15)
P(2)-F(3)#1	1.603(4)	C(8)-C(9)-C(10)	115.76(17)

C(13)-C(10)-C(12)	110.76(17)	F(4)-P(2)-F(2)	90.8(3)
C(13)-C(10)-C(11)	110.13(18)	F(4)#1-P(2)-F(2)	90.8(3)
C(12)-C(10)-C(11)	107.80(17)	F(3B)-P(2)-F(1)	95.1(7)
C(13)-C(10)-C(9)	111.34(16)	F(3B)#1-P(2)-F(1)	95.1(7)
C(12)-C(10)-C(9)	109.42(17)	F(4B)-P(2)-F(1)	93.2(9)
C(11)-C(10)-C(9)	107.27(17)	F(4B)#1-P(2)-F(1)	93.2(9)
C(15)-C(14)-C(19)	119.5(2)	F(4)-P(2)-F(1)	89.2(3)
C(15)-C(14)-P(1)	118.74(16)	F(4)#1-P(2)-F(1)	89.2(3)
C(19)-C(14)-P(1)	121.78(19)	F(2)-P(2)-F(1)	180.0
C(14)-C(15)-C(16)	120.8(2)	F(3B)#1-P(2)-F(3)	164.4(18)
C(15)-C(16)-C(17)	119.7(3)	F(4B)-P(2)-F(3)	75.9(19)
C(18)-C(17)-C(16)	119.5(2)	F(4B)#1-P(2)-F(3)	104.3(19)
C(17)-C(18)-C(19)	120.8(2)	F(4)-P(2)-F(3)	90.6(3)
C(18)-C(19)-C(14)	119.7(3)	F(4)#1-P(2)-F(3)	89.4(3)
C(25)-C(20)-C(21)	118.5(2)	F(2)-P(2)-F(3)	91.6(2)
C(25)-C(20)-P(1)	122.91(16)	F(1)-P(2)-F(3)	88.4(2)
C(21)-C(20)-P(1)	118.53(15)	F(3B)-P(2)-F(3)#1	164.4(18)
C(22)-C(21)-C(20)	120.12(19)	F(4B)-P(2)-F(3)#1	104.3(19)
C(23)-C(22)-C(21)	120.4(2)	F(4B)#1-P(2)-F(3)#1	75.9(19)
C(24)-C(23)-C(22)	119.8(2)	F(4)-P(2)-F(3)#1	89.4(4)
C(25)-C(24)-C(23)	120.2(3)	F(4)#1-P(2)-F(3)#1	90.6(3)
C(24)-C(25)-C(20)	120.9(2)	F(2)-P(2)-F(3)#1	91.6(2)
C(28)-C(27A)-C(26)	128.5(5)	F(1)-P(2)-F(3)#1	88.4(2)
C(26)-C(27B)-C(28)	136.7(6)	F(3)-P(2)-F(3)#1	176.8(4)
F(3B)-P(2)-F(3B)#1	169.8(13)	F(6)-P(3)-F(5)	180.000(1)
F(3B)-P(2)-F(4B)	90.7(14)	F(6)-P(3)-F(8)	90.9(2)
F(3B)#1-P(2)-F(4B)	88.7(14)	F(5)-P(3)-F(8)	89.1(2)
F(3B)-P(2)-F(4B)#1	88.7(14)	F(6)-P(3)-F(8)#2	90.9(2)
F(3B)#1-P(2)-F(4B)#1	90.7(14)	F(5)-P(3)-F(8)#2	89.1(2)
F(4B)-P(2)-F(4B)#1	173.5(18)	F(8)-P(3)-F(8)#2	178.3(4)
F(3B)-P(2)-F(4)	105.8(18)	F(6)-P(3)-F(7)#2	90.64(19)
F(3B)#1-P(2)-F(4)	74.3(18)	F(5)-P(3)-F(7)#2	89.36(19)
F(4B)#1-P(2)-F(4)	165(2)	F(8)-P(3)-F(7)#2	92.36(12)
F(3B)-P(2)-F(4)#1	74.3(18)	F(8)#2-P(3)-F(7)#2	87.63(12)
F(3B)#1-P(2)-F(4)#1	105.8(18)	F(6)-P(3)-F(7)	90.64(19)
F(4)-P(2)-F(4)#1	178.4(5)	F(5)-P(3)-F(7)	89.36(19)
F(3B)-P(2)-F(2)	84.9(7)	F(8)-P(3)-F(7)	87.63(12)
F(3B)#1-P(2)-F(2)	84.9(7)	F(8)#2-P(3)-F(7)	92.36(12)
F(4B)-P(2)-F(2)	86.8(9)	F(7)#2-P(3)-F(7)	178.7(4)
F(4B)#1-P(2)-F(2)	86.8(9)	O(30)-C(31)-C(30)	127.1

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z #2 -x+1,y,-z

Table 5. Anisotropic displacement parameters ($Å^2 x 10^4$) for DCB24 (CCDC 245187). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	249(1)	152(1)	169(1)	-17(1)	102(1)	-31(1)
P(1)	209(2)	217(2)	157(2)	-38(2)	86(2)	-57(2)
O(1)	270(6)	206(6)	201(7)	-11(5)	116(5)	-71(5)
N(1)	204(7)	184(6)	156(8)	-27(5)	87(6)	-26(5)
C(1)	165(7)	215(7)	168(9)	-20(6)	54(6)	-17(5)
C(2)	219(8)	303(9)	177(9)	-41(7)	90(6)	-23(6)
C(3)	205(8)	354(10)	166(9)	-79(7)	51(7)	-6(7)
C(4)	184(8)	309(9)	235(10)	-102(7)	43(6)	-28(6)
C(5)	183(7)	219(7)	217(9)	-44(6)	61(6)	-25(5)
C(6)	152(6)	186(6)	157(8)	-25(5)	45(5)	-7(5)
C(7)	156(6)	171(6)	187(8)	0(5)	69(5)	-16(5)
C(8)	339(10)	257(9)	205(10)	-22(7)	156(8)	-94(7)
C(9)	261(8)	209(7)	169(9)	-16(6)	122(6)	-43(6)
C(10)	297(9)	266(8)	146(9)	-36(6)	90(7)	-33(7)
C(11)	459(13)	381(12)	182(11)	8(8)	141(9)	-24(9)
C(12)	310(10)	332(10)	208(10)	-58(8)	62(7)	-86(8)
C(13)	301(10)	319(10)	203(10)	15(8)	67(7)	20(7)
C(14)	351(10)	292(9)	196(10)	-70(6)	156(8)	-132(7)
C(15)	479(13)	311(10)	261(12)	-10(8)	201(10)	-86(9)
C(16)	698(18)	313(11)	271(13)	-1(9)	233(12)	-136(11)
C(17)	830(20)	342(12)	308(13)	-148(10)	375(14)	-305(13)
C(18)	540(13)	487(13)	403(12)	-178(16)	351(11)	-278(15)
C(19)	403(12)	419(12)	300(12)	-104(9)	225(10)	-149(9)
C(20)	172(7)	261(8)	228(10)	-94(7)	67(6)	-52(6)
C(21)	232(8)	267(8)	226(10)	-87(7)	70(7)	-72(6)
C(22)	221(9)	419(12)	325(13)	-131(9)	26(8)	-40(8)
C(23)	261(11)	445(14)	680(20)	-170(14)	-48(11)	86(10)
C(24)	311(13)	421(15)	980(30)	-389(17)	-102(15)	122(11)
C(25)	221(10)	410(13)	591(18)	-309(12)	-44(10)	35(8)
C(26)	668(17)	230(10)	422(16)	-52(9)	325(14)	39(10)
C(27A)	400(30)	150(14)	370(30)	4(14)	120(20)	-16(13)
C(27B)	440(40)	154(18)	410(40)	-103(18)	190(30)	-37(18)
C(28)	1130(30)	165(9)	595(19)	10(10)	600(20)	-74(12)
P(2)	208(3)	164(2)	159(3)	0	52(2)	0
F(1)	453(11)	158(7)	586(14)	0	334(10)	0
F(2)	458(9)	159(8)	316(9)	0	61(7)	0
F(3)	201(11)	356(18)	770(30)	35(16)	-63(14)	-7(11)
F(4)	890(30)	440(20)	310(20)	47(14)	357(19)	125(16)
F(3B)	390(70)	340(50)	2400(300)	500(110)	640(110)	170(50)
F(4B)	2200(300)	320(60)	120(60)	130(40)	150(120)	130(130)
P(3)	413(4)	349(6)	402(5)	0	235(3)	0
F(5)	2790(100)	370(20)	3230(110)	0	1010(80)	0
F(6)	4250(130)	290(20)	3080(100)	0	2540(100)	0
F(7)	772(14)	2450(40)	439(11)	130(20)	293(10)	-630(20)
F(8)	562(12)	2360(50)	671(14)	-350(30)	185(11)	-300(20)

C(30)	250(30)	870(110)	530(50)	330(50)	120(30)	250(40)
C(31)	890(100)	540(90)	1800(200)	-350(90)	380(130)	-80(80)
O(30)	770(30)	560(30)	640(30)	-10(20)	130(30)	380(20)

Table 6. Hydrogen bonds for DCB24 (CCDC 245187) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(30)-H(30)...F(7)	0.85	1.99	2.799(6)	157.8

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z #2 -x+1,y,-z