Synthesis, Characterization, and Reactivity of Arylpalladium Cyanoalkyl Complexes. Selection of Catalysts for the α-Arylation of Nitriles.

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Supporting Information

General Methods. All reactions were performed in a drybox or with Schlenk techniques under N_2. All solvents were dried over Na/benzophenone. All aryl halides, nitriles and bases were purchased from Aldrich Chemical Co. and used without further purification. 1,2-bis(diphenylphosphino)benzene (DPPBz), 1,1'-bis(di-*i*-propylphosphino)ferrocene (D^{i}PrPF), ethyldiphenylphosphine (PPh_2Et), racemic-2,2'-bis(diphenylphosphino)-1-1'-binaphthyl (BINAP), tri-*t*-butylphosphine (P^{t}Bu$_3$), and $Pd_2dba_3{}^{\bullet}CHCl_3$ were purchased from Strem Chemical Company and used without further purification. $Pd[P(o\text{-tol})_3]_2$ was prepared by a literature procedure.[1] Dimeric arylpalladium halide complexes that were ligated by P(*o*-tol)$_3$ and used as synthetic intermediates were prepared by a procedure based on literature methods.[1] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 400 or 500 MHz spectrometer, with shifts reported in parts per million downfield from tetramethylsilane and referenced to residual protiated (^1H) or deuterated solvent (^{13}C). $^{31}P\{^1H\}$ NMR spectra were obtained on an Omega 500 MHz spectrometer with shifts reported relative to an external 85% H_3PO_4 standard; resonances downfield of the standard are reported as positive. IR spectra were recorded on a MIDAC Fourier Transform spectrometer. GC analyses were performed on a HP-6890 instrument using a DB-1301 narrow bore column for high temperature ramp applications (max. 120 °C /min). Elemental Analyses were performed by Robertson Microlit Labortatories, Inc., Madison, NJ 07940.

General Procedure for the Synthesis of [Pd(DPPBz)(Ar)(Br)]. $Pd[P(o\text{-tol})_3]_2$ was combined with 2.5 equiv of ArBr in benzene. The solution was filtered through Celite, and $\{Pd[P(o\text{-tol})_3](Ar)(\mu\text{-Br})\}_2$ was isolated by precipitation after addition of pentane and used without further purification. This solid was combined with 2 equiv of 1,2-bis(diphenylphosphino)benzene (DPPBz) in benzene and stirred at room temperature for 3 h, and [Pd(DPPBz)(Ar)(Br)] was isolated by precipitation after addition of pentane and used without further purification. The ^1H and $^{31}P\{^1H\}$ spectra for [Pd(DPPBz)(Ar)(Br)] are as follows: [Pd(DPPBz)(C_6H_4-4-*t*-Bu)(Br)]: ^1H NMR (CD_2Cl_2) δ 1.21 (s, 9H), 6.82 (m, 4H), 7.27 (m, 8H), 7.41-7.65 (m, 12H), 7.72 (m, 4H); $^{31}P\{^1H\}$ NMR (toluene) δ 41.3 (d, 27.0 Hz), 52.8 (d, 27.0 Hz); [Pd(DPPBz)(C_6H_4-4-Me)(Br)]:

^{1}H NMR (CD_2Cl_2) δ 2.15 (s, 3H), 6.62 (dd, 7.6 Hz, 2.0 Hz), 6.83 (td, 8.1 Hz, 2.4 Hz, 2H), 7.32 (m, 8H), 7.47 (m, 9H), 7.73 (m, 5H); ^{31}P{^{1}H} NMR (toluene) δ 41.0 (d, 27.5 Hz), 52.6 (d, 27.5 Hz).

Synthesis of [Pd(D^{i}PrPF)(C_6H_4-4-*t*-Bu)(Br)] A solution of 436 mg (1.04 mmol) of 1,1'-bis(di-*i*-propylphenylphosphino)ferrocene in 5 mL of benzene was added dropwise by pipet to a stirred solution of 650 mg (0.521 mmol) of {Pd[P(*o*-tol)$_3$](C_6H_4-4-*t*-Bu)(μ-Br)}$_2$ in 50 mL of benzene. The solution changed from cloudy yellow to cloudy orange immediately. The solution was stirred at room temperature for 2 h. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the solution was concentrated. After the addition of pentane, the product precipitated and the orange solid was isolated in 82.7% yield (636 mg). The product was filtered, washed with pentane and used without further purification. ^{1}H NMR (C_6D_6) δ 0.85 (dd, 15.0 Hz, 7.0 Hz, 6Hz), 1.09 (m, 12H), 1.34 (s, 9H), 1.72 (dd, 15.8 Hz, 7.3 Hz, 6H), 2.13 (m, 2H), 2.91 (m, 2H), 3.95 (m, 4H), 4.08 (m, 4H), 7.28 (dd, 8.0 Hz, 2.5 Hz, 2H), 7.72 (virtual t, 8.0 Hz, 2H); ^{31}P{^{1}H} NMR (toluene) δ 27.6 (d, 21.9 Hz), 38.1 (d, 21.9 Hz).

Synthesis of [Pd(*rac*-BINAP)(C_6H_4-4-*t*-Bu)(Br)][2] A suspension of 649 mg (1.04 mmol) of racemic-2,2'-bis(diphenylphosphino)-1-1'-binaphthyl in 50 mL of benzene was added by pipet to a stirred solution of 650 mg (0.521 mmol) of {Pd[P(*o*-tol)$_3$](C_6H_4-4-*t*-Bu)(μ-Br)}$_2$ in 200 mL of benzene. The solution changed from cloudy yellow to cloudy green immediately. The solution was stirred at room temperature for 2 h. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the solvent was removed *in vacuo*. The remaining solid was dissolved in toluene, and the yellow product was obtained in 84.0% yield (825 mg) by layering the toluene solution with ether and cooling at -35 °C. ^{1}H NMR (CD_2Cl_2) δ 1.25 (s, 9H), 6.69 (m, 4H), 6.91-6.99 (m, 8H), 7.18 (m, 2H), 7.30-7.41 (m, 10 H), 7.50-7.61 (m, 8H), 7.78 (m, 4H); ^{31}P{^{1}H} NMR (toluene) δ 11.6 (d, 39.0 Hz), 28.1 (d, 39.0 Hz).

Synthesis of *trans*-[Pd(PPh_2Et)$_2$(C_6H_4-4-Me)(Br)] Ethyldiphenylphosphine (0.46 mL, 2.2 mmol) was added dropwise by syringe to a stirred solution of 645 mg (0.554 mmol) of {Pd[P(*o*-tol)$_3$](C_6H_4-4-Me)(μ-Br)}$_2$ in 50 mL of benzene. The solution changed from cloudy to clear yellow immediately. The solution was stirred at room temperature for 2 h. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the clear yellow solution was concentrated. After addition the addition of pentane, the product precipitated and the pale yellow solid was isolated in 90.0% yield (705 mg). The product was filtered, washed with pentane and used without further purification. ^{1}H NMR (C_6D_6) δ 0.82 (m, 6H), 2.03 (s, 3H), 2.08 (m, 4H), 6.48 (d, 2.0 Hz, 2H), 6.82 (dt, 2.0 Hz, < 1Hz, 2H), 7.01 (m, 12 H), 7.64 (m, 8H); ^{31}P{^{1}H} NMR (toluene) δ 18.9 (s).

General Procedure for the Preparation of Deprotonated Nitriles. The potassium salts of acetonitrile, isovaleronitrile, benzyl cyanide, and isobutyronitrile were formed by the addition of one equiv of the corresponding nitrile to a solution of $KN(SiMe_3)_2$ in a 1:50 mixture of toluene and pentane. After 1 h of reaction time, the mixture was concentrated, and the solid potassium salt was filtered, washed with pentane and used without further purification. The salts were stored in the drybox at –35 °C.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$CN)(C$_6$H$_4$-4-*t*-Bu)] (1). To a 20 mL vial was added 200 mg (0.261 mmol) of [Pd(DPPBz)(C$_6$H$_4$-4-*t*-Bu)(Br)] and 165 mg (2.09 mmol) of KN(C)CH$_2$ as solids. The mixture was suspended in 5 mL of toluene and stirred at room temperature for 1 h. When the reaction was complete, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy, the mixture was filtered through Celite to remove residual salts. The resulting clear yellow solution was then concentrated, and the white product was obtained in 61.2% (116 mg) yield by layering the concentrated toluene solution with pentane and cooling at -35 °C. The compound was recrystallized as colorless needles from a THF solution of the product layered with pentane at -35 °C. ^1H NMR (C$_6$D$_6$) δ 1.23 (s, 9H), 1.93 (virtual t, 8.8 Hz, 2H), 6.81 (m, 2H), 6.88-6.94 (m, 6H), 7.00-7.05 (m, 6H), 7.07 (dd, 8.3 Hz, 1.8 Hz, 2H), 7.25 (m, 4H), 7.34 (m, 2H), 7.51 (dd, 8.3 Hz, 7.3 Hz, 2H), 7.63 (m, 4H) ; $^{31}P\{^1H\}$ NMR (C$_6$D$_6$) δ 44.6 (d, 17.1 Hz), 47.2 (d, 17.1 Hz); $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$): δ -7.76 (dd, 92.8 Hz, 7.4 Hz), 31.93 (s), 34.31 (s), 124.33 (d, 7.0 Hz), 128.82 (dd, 7.1 Hz, 2.5 Hz), 128.98 (d, 10.8 Hz), 129.54 (d, 10.2 Hz), 130.87 (d, 1.6 Hz), 131.27 (d, 2.3 Hz), 131.47 (d, 43.9 Hz), 132.01 (d, 36.5 Hz), 132.29-132.37 (overlapping doublets), 133.90 (d, 12.6 Hz), 134.00 (d, 12.6 Hz), 134.44 (d, 15.3 Hz), 134.61 (d, 16.4 Hz), 136.07 (virtual t, 3.6 Hz), 143.43 (virtual t, 40.7 Hz), 144.26 (dd, 41.4 Hz, 43.0 Hz), 145.25 (s), 160.47 (dd, 124.8 Hz, 7.5 Hz); IR (KBr, cm^{-1}) ν(CN) 2184; Anal. Calc'd for C$_{42}$H$_{39}$NP$_2$Pd: C, 69.47; H, 5.41; N, 1.93. Found: C, 69.28; H, 5.37; N, 1.95.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH(CHMe$_2$)CN)C$_6$H$_5$)(C$_6$H$_4$-4-Me)] (2). Following the procedure for the preparation of **1**, reaction of 200 mg (0.276 mmol) of [Pd(DPPBz)(C$_6$H$_4$-4-Me)(Br)] and 37 mg (0.31 mmol) of KN(C)CH(CHMe$_2$) in 5 mL of toluene gave 138 mg (68.7%) of the product as a slightly yellow solid after crystallization from toluene layered with pentane at -35 °C. The compound was recrystallized as colorless needles from a THF solution of the product layered with pentane at –35 °C. ^1H NMR (C$_6$D$_6$) δ 0.90 (d, 6.5Hz, 3H), 1.06 (d, 6.5 Hz, 3H), 1.99 (m, 1H), 2.17 (s, 3H), 2.52 (ddd, 8.8 Hz, 3.8 Hz, 1.5 Hz, 1H), 6.81 (m, 2H), 6.89-6.94 (m, 8H), 7.00-7.03 (m, 4H), 7.12 (m, 2H), 7.23 (m, 2H), 7.29 (virtual t, 7.0 Hz, 1H), 7.33-7.41 (m, 3H), 7.47 (m, 2H), 7.70 (broad s, 2H), 7.87 (dd, 8.3 Hz, 1 Hz, 2H); $^{31}P\{^1H\}$ NMR (C$_6$D$_6$) δ 45.8 (d, 14.6 Hz), 47.3 (d, 14.6 Hz); $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$): δ 19.32 (dd, 90.4 Hz, 6.1 Hz), 21.13 (s), 24.93

(d, 10.3 Hz), 25.71 (s), 31.75 (dd, 4.7 Hz, 1.9 Hz), 125.81 (s), 127.77 (d, 8.2 Hz), 128.96 (d, 10.4 Hz), 128.98 (d, 9.9 Hz), 129.35 (d, 9.1 Hz), 129.61 (d, 9.7 Hz), 130.80 (d, 3.1 Hz), 130.89 (d, 2.9 Hz), 130.95 (d, 2.3 Hz), 131.08-132.66 (4 overlapping doublets), 131.64 (d, 2.0 Hz), 132.22 (dd, 5.5 Hz, 2.0 Hz), 132.36 (dd, 4.7 Hz, 1.8 Hz), 133.63 (d, 13.1 Hz), 133.81 (d, 12.6 Hz), 134.07 (d, 12.6 Hz), 134.20(d, 14.3 Hz), 134.60 (d, 15.3 Hz), 134.74 (d, 15.1 Hz), 136.34 (virtual t, 3.3 Hz), 138.54 (s), 144.14 (dd, 69.2 Hz, 40.2 Hz), 144.61 (virtual t, 36.7 Hz), 161.48 (dd, 120.8 Hz, 9.2 Hz); IR (KBr, cm^{-1}) ν(CN) 2171; Anal. Calc'd for $C_{42}H_{39}NP_2Pd \cdot C_4H_8O$: C, 69.21; H, 5.93; N, 1.75. Found: C, 69.52; H, 5.93; N, 1.49.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CHPhCN)(C$_6$H$_4$-4-Me)] (3). Following the procedure for the preparation of **1**, reaction of 200 mg (0.276 mmol) of [Pd(DPPBz)(C$_6$H$_4$-4-Me)(Br)] and 49 mg (0.32 mmol) of KN(C)CHPh in 10 mL of toluene gave 171 mg (81.3%) of the product as a yellow solid after crystallization from toluene layered with pentane at -35 °C. ^{1}H NMR (C_6D_6) δ 2.16 (s, 3H), 4.40 (dd, 11.3 Hz, 9.8 Hz, 1H), 6.75-6.85 (m, 9H), 6.88-6.91 (m, 6H), 6.98 (m, 4H), 7.08-7.13 (m, 4H), 7.17-7.27 (m, 6H), 7.34 (broad s, 2H), 7.66 (ddd, 11.0 Hz, 8.5 Hz, 1.5 Hz, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 42.3 (d, 17.1 Hz), 47.3(d, 17.1 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 17.25 (dd, 81.4 Hz, 5.2 Hz), 21.08 (s), 122.35 (d, 2.1 Hz), 125.87 (d, 3.5 Hz), 127.38 (dd, 7.2 Hz, 2 Hz), 127.96 (s), 128.07 (d, 6.8 Hz), 128.86 (d, 10.6 Hz), 128.97 (d, 10.4 Hz), 129.42 (d, 4.2 Hz), 129.49 (d, 4.3 Hz), 130.82 (d, 2.3 Hz), 131.02 (d, 1.8 Hz), 131.18 (d, 1 Hz), 131.28 (d, 2.4 Hz), 130.86-131.75 (4 overlapping doublets), 132.24 (dd, 4.2 Hz, 2.0 Hz), 132.38 (dd, 4.5 Hz, 2.1 Hz), 133.84 (d, 12.6 Hz,), 134.10 (d, 12.8 Hz), 134.30 (d, 12.3 Hz), 134.38 (d, 14.1 Hz), 134.05-134.44 (2 obscured doublets), 136.40 (virtual t, 3.6 Hz), 138.53 (s), 143.86 (virtual t, 42.3 Hz), 144.26 (dd, 39.7 Hz, 39.2 Hz), 144.70 (dd, 5.7 Hz, 3.1 Hz), 161.29 (dd, 118.4 Hz, 9.4 Hz); IR (KBr, cm^{-1}) ν(CN) 2180; Anal. Calc'd for $C_{45}H_{37}NP_2Pd$: C, 71.10; H, 4.91; N, 1.84. Found: C, 71.07; H, 4.94; N, 1.77.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CMe$_2$CN)(C$_6$H$_4$-4-Me)] (4). Following the procedure for the preparation of **1**, reaction of 190 mg (0.262 mmol) of [Pd(DPPBz)(C$_6$H$_4$-4-Me)(Br)] and 56 mg (0.53 mmol) of KN(C)CMe$_2$ in 5 mL of toluene gave 104 mg (55.6%) of the product as pale yellow crystals after layering a toluene solution with pentane at -35 °C. Recrystallization by vapor diffusion of pentane into a toluene solution at -35 °C gave crystals that were suitable for X-ray structural analysis. ^{1}H NMR (C_6D_6); δ 1.51 (d, 7.0Hz, 6H), 2.14 (s, 3H), 6.76 (m, 4H), 6.88-6.96 (m, 6H), 7.00-7.11 (m, 7H), 7.25 (ddd, 10.6 Hz, 8.3 Hz, 1.0 Hz, 4H), 7.33 (m, 1H), 7.38 (dd, 7.3 Hz, 6.5 Hz, 2H), 7.91 (ddd, 11.0 Hz, 8.0 Hz, 1.5 Hz, 4H); ^{31}P{^{1}H} NMR (C_6D_6) δ 43.7 (d, 12.2 Hz), 45.5 (d, 12.2 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 12.45 (dd, 100.8 Hz, 4.1 Hz), 21.06 (s), 30.27 (virtual t, 4.0 Hz), 125.81 (s), 127.95 (d, 7.8 Hz), 128.79 (d, 10.1 Hz), 129.27 (d, 9.8 Hz), 131.07 (d, 2.9 Hz), 131.24 (d, 2.1 Hz), 131.43 (d, 46.7 Hz), 131.92 (dd, 3.0 Hz, 1.8 Hz), 132.16 (d, 49.4 Hz),

132.19 (dd, 3.5 Hz, 1 Hz), 134.03 (d, 11.2 Hz), 134.07 (d, 14.3 Hz), 134.31 (d, 15.6 Hz), 134.71 (d, 13.6 Hz), 136.67 (virtual t, 3.3 Hz), 138.52 (s), 143.67 (virtual t, 39.9 Hz), 146.25 (virtual t, 40.9 Hz), 163.55 (dd, 114.5, 12.5 Hz); IR (KBr, cm^{-1}) ν(CN) 2170; Anal. Calc'd for $C_{41}H_{37}NP_2Pd \cdot C_7H_8$: C, 71.68; H, 5.64; N, 1.74. Found: C, 71.45; H, 5.83; N, 1.63.

[Pd(D^{i}PrPF)(CHPhCN)(C$_6$H$_4$-4-*t*-Bu)] (5). Following the procedure for the preparation of **1**, reaction of 215 mg (0.291 mmol) of [Pd(D^{i}PrPF)(C$_6$H$_4$-4-*t*-Bu)(Br)] and 59 mg (0.38 mmol) of KN(C)CHPh in 6 mL of toluene gave 124 mg (55.0%) of the product as a bright yellow solid after crystallization from toluene layered with pentane at -35 °C. ^{1}H NMR (C_6D_6) δ 0.73 (dd, 12.8 Hz, 6.8 Hz, 3H), 0.83 (dd, 14.8 Hz, 7.3 Hz, 6H), 0.94 (dd, 11.8 Hz, 6.3 Hz, 3H), 1.17 (dd, 13.8 Hz, 6.8 Hz, 3H), 1.28 (dd, 16.0 Hz, 7.0 Hz, 3H), 1.35 (s, 9H), 1.43 (dd, 14.5 Hz, 7.5 Hz, 3H), 1.56 (dd, 14.3 Hz, 7.3 Hz, 3H), 1.99 (m, 1H), 2.10 (m, 1H), 2.23 (m, 2H), 3.92 (m, 1H), 3.95 (m, 2H), 3.97 (m, 1H), 3.99 (m, 1H), 4.05 (m, 2H), 4.10 (m, 1H), 4.35 (dd, 14.5 Hz, 9.5 Hz, 1H), 6.69 (m, 1H), 6.75 (dt, 7.5 Hz, 2.3 Hz, 1H), 6.90 (td, 7.0 Hz, 1.0 Hz, 1H), 7.03 (m, 4H), 7.30 (dt, 7.5 Hz, 2.0 Hz, 1H), 8.09 (m, 1H); ^{31}P{^{1}H} NMR (C_6D_6) δ 25.5 (d, 22.0 Hz), 32.7 (d, 22.0 Hz); ^{13}C NMR (C_4D_8O): δ 15.25 (dd, 82.9 Hz, 7.5 Hz), 18.57 (s), 19.23 (s), 19.33 (s), 19.45 (broad s), 19.96 (s), 20.45 (d, 6.0 Hz), 21.01 (d, 5.3 Hz), 21.54 (d, 6.8 Hz), 25.44 (d, 23.1 Hz), 25.70 (d, 22.3 Hz), 25.80 (d, 15.5 Hz), 26.07 (d, 15.8 Hz), 32.13 (s), 34.39 (s), 71.38 (d, 3.5 Hz), 71.87 (d, 4.0 Hz), 71.97 (d, 3.6 Hz), 72.41 (d, 5.0 Hz), 73.73 (d, 4.8 Hz), 74.04 (d, 5.3 Hz), 74.12 (d, 7.3 Hz), 74.20 (d, 8.4 Hz), 76.07 (dd, 27.4 Hz, 4.8 Hz), 79.98 (dd, 23.7 Hz, 8.4 Hz), 121.84 (s), 123.82 (d, 7.8 Hz), 124.57 (d, 7.7 Hz), 125.15 (d, 8.4 Hz), 126.09 (s), 127.62 (s), 135.36 (virtual t, 3.2 Hz), 137.68 (virtual t, 3.6 Hz), 145.19 (s), 145.74 (dd, 4.0 Hz, 4.0 Hz), 158.25 (dd, 110.9 Hz, 16.5 Hz); IR (KBr, cm^{-1}) ν(CN) 2176; Anal. Calc'd for $C_{37}H_{57}FeNP_2Pd$: C, 62.06; H, 7.16; N, 1.81. Found: C, 62.01; H, 7.21; N, 1.78.

[Pd(D^{i}PrPF)(N(C)CMe$_2$)(C$_6$H$_4$-4-*t*-Bu)] (6). Following the procedure for the preparation of **1**, reaction of 152 mg (0.206 mmol) of [Pd(D^{i}PrPF)(C$_6$H$_4$-4-*t*-Bu)(Br)] and 42 mg (0.39 mmol) of KN(C)CMe$_2$ in 7 mL of toluene gave 62 mg (41%) of the product as red crystals after crystallization from toluene layered with pentane at -35 °C. These crystals were suitable for X-ray structural analysis. ^{1}H NMR (C_6D_6) δ 0.88 (dd, 14.0 Hz, 7.0 Hz, 6H), 1.12 (m, 12H), 1.41 (s, 9H), 1.62 (dd, 15.8 Hz, 7.3 Hz, 6H), 1.71 (d, 6.5 Hz, 6H), 2.05 (m, 2H), 2.46 (m, 2H), 3.94 (m, 2H), 3.98 (m, 2H), 4.07 (m, 2H), 4.10 (m, 2H), 7.32 (dd, 8.3 Hz, 1.8 Hz, 2H), 7.76 (dd, 8.0 Hz, 7.0 Hz, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 28.2 (d, 31.7 Hz), 36.7 (d, 31.7 Hz); ^{13}C{^{1}H} NMR (C_4D_8O, -10 °C): δ 18.39 (d, 4.8 Hz), 19.37 (broad s), 19.89 (d, 4.15 Hz), 20.02 (broad s), 20.81 (d, 7.0 Hz), 25.13 (d, 17.0 Hz), 26.14 (d, 26.7 Hz), 32.31 (s), 33.52 (d, 12.6 Hz), 34.71 (s), 71.53 (d, 5.4 Hz), 72.23 (d, 4.8 Hz), 74.01 (d, 7.8 Hz), 74.16 (d, 6.4 Hz), 75.46 (dd, 24.5 Hz, 3.2 Hz), 81.99 (dd, 29.5 Hz, 9.9 Hz), 123.68 (d, 8.6 Hz), 137.48 (s), 145.32 (s), 159.99 (dd, 116.5 Hz,

16.7 Hz) 175.45 (d, 8.2 Hz); IR (KBr, cm^{-1}) ν(N=C=C) 2186, 1997; Anal. Calc'd for $C_{36}H_{55}FeNP_2Pd$: C, 59.55; H, 7.64; N, 1.93. Found: C, 59.09; H, 7.61; N, 1.73.

[Pd(BINAP)(CH(CHMe$_2$)CN)(C$_6$H$_4$-4-*t*-Bu)] (7). Following the procedure for the preparation of **1**, reaction of 190 mg (0.202 mmol) of [Pd(BINAP)(C_6H_4-4-*t*-Bu)(Br)] and 28 mg (0.23 mmol) of KN(C)CH($CHMe_2$) in 5 mL of toluene gave 119 mg (62.4%) of the product as a pink solid or a mixture of white and red crystals after cooling a toluene solution layered with pentane at -35 °C. The bulk material obtained from this crystallization consistently contained about 10% $Pd(BINAP)_2$, which was the red crystals. ^{1}H NMR (C_6D_6) (ratio = 1:1) δ 0.87 (d, 6.5 Hz, 3H), 1.21 (d, 7.0 Hz, 3H), 1.27 (s, 4.5H), 1.31 (s, 4.5H), 1.80 (m, 0.5H), 1.90 (m, 1.5H), 6.23 (broad, 1H), 6.31 (m, 2H), 6.40 (m, 1.5H), 6.46 (m, 2H), 6.54 (m, 1.5H), 6.67 (m, 0.5H), 6.76 (m, 1H), 6.81-6.89 (m, 3H), 6.91 (m, 0.5H), 6.99 (m, 2.5H), 7.01 (m, 1.5H), 7.07-7.15 (m, 3H), 7.17-7.26 (m, 6H), 7.38-7.50 (m, 4H), 7.60 (broad, 2H), 7.67 (m, 1H), 7.76 (m, 1H), 7.98-8.07 (m, 2H); ^{31}P{^{1}H} NMR (C_6D_6) (ratio = 1:1) δ 18.3 (d, 24.2 Hz), 19.3 (d, 24.2 Hz), 20.3 (d, 22.2 Hz), 22.5 (d, 24.2 Hz); IR (KBr, cm^{-1}) ν(CN) 2176.

[Pd(BINAP)(CHPhCN)(C$_6$H$_4$-4-*t*-Bu)] (8). Following the procedure for the preparation of **1**, reaction of 190 mg (0.202 mmol) of [Pd(BINAP)(C_6H_4-4-*t*-Bu)(Br)] and 63 mg (0.40 mmol) of KN(C)CHPh in 7 mL of toluene gave 111 mg (56.1%) of the product as a yellow solid after cooling a toluene solution layered with pentane at -35 °C. The compound was recrystallized as a pale yellow powder from a THF solution of the product layered with ether at –35 °C ^{1}H NMR (C_6D_6) (ratio = 2:1) δ 1.31 (s, 3H), 1.32 (s, 6H), 3.71 (dd, 15.3 Hz, 9.3 Hz, 0.67H), 3.85 (dd, 15.3 Hz, 9.8 Hz, 0.33H), 6.22 (m, 2H), 6.31-6.38 (m, 2.33H), 6.45-6.60 (m, 5H), 6.72-6.82 (m, 5H), 6.87-7.12 (m, 11.67H), 7.20-7.31 (m, 4H), 7.36-7.52 (m, 5H), 7.61 (broad, 2H), 7.83 (m, 2H), 8.04-8.12 (m, 2H); ^{31}P{^{1}H} NMR (C_6D_6) (ratio = 2:1) δ 19.9 (d, 29.3 Hz), 23.2 (d, 29.3 Hz); 16.2 (d, 29.3 Hz), 23.0 (d, 29.3 Hz); IR (KBr, cm^{-1}) ν(CN) 2183; Anal. Calc'd for $C_{62}H_{51}NP_2Pd{\cdot}C_4H_{10}O$: C, 75.31; H, 5.84; N, 1.33. Found: C, 75.01; H, 5.85; N, 1.20.

{Pd(PPh$_2$Et)(C$_6$H$_4$-4-Me)(μ-CMe$_2$CN)}$_2$ (9) Following the procedure for the preparation of **1**, reaction of 160 mg (0.227 mmol) of *trans*-[$Pd(PPh_2Et)_2$(C_6H_4-4-Me)(Br)] and 49 mg (0.45 mmol) of KN(C)CMe_2 in 5 mL of toluene gave 77 mg (70%) of the product as a pale yellow crystals after crystallization from toluene layered with pentane at -35 °C. Recrystallization by vapor diffusion of pentane into a toluene solution at -35 °C gave crystals that were suitable for X-ray structural analysis. ^{1}H NMR (C_6D_6) δ 0.74 (m, 6H), 1.38 (d, 5.5 Hz, 12H), 1.55 (m, 4H), 2.19 (s, 6H), 6.85 (d, 7.5 Hz, 4H), 7.01 (m, 12H), 7.32 (d, 8.0 Hz, 4H), 7.47 (m, 8H); ^{31}P{^{1}H} NMR (C_6D_6) δ 19.4 (s), 21.1; ^{13}C{^{1}H} NMR (C_4D_8O, -10 °C): δ 8.42 (s), 15.38 (d, 97.7 Hz), 19.97 (broad d, 26.0 Hz), 21.04 (s), 25.66 (broad virtual t, 20.2 Hz), 128.11 (s), 128.82 (m),

130.41 (s), 130.93 (s), 134.05 (dd, 36.3 Hz, 1.8 Hz), 135.35 (m), 135.62 (broad s), 138.78 (broad s), 156.7 (m); IR (KBr, cm^{-1}) ν(CN) 2195 (broad); Anal. Calc'd for $C_{50}H_{56}N_2P_2Pd_2$: C, 62.57; H, 5.88; N, 2.92. Found: C, 62.51; H, 5.96; N, 2.86.

Reductive Elimination Reactions: Representative Procedure.
Into an NMR tube with a Teflon-lined screw-cap was placed 0.6 mL of a C_6D_6 solution containing 8.0 mg (0.011 mmol) of complex **1**, 11.6 mg (0.0441 mmol) of PPh_3, and 1.9 mg (0.011 mmol) of 1,3,5-trimethoxybenzene as an internal standard. A ^1H NMR spectrum was obtained of this initial mixture. The tube was then placed in an oil bath at 110 °C for 2 d, after which time ^1H NMR spectroscopy showed the formation of coupled product in 63% yield. The yield of coupled product was determined by integrating the methylene resonances of the palladium complex and the methylene protons of the aryl nitrile with respect to the internal standard. The yield of α-aryl nitrile from thermolysis of complexes **2-9** was determined in a similar manner and on the same scale.

General Procedure for the Reaction of Nitrile with Arylbromide.
The reaction conditions and average yields for each reaction are shown in Table 2. A typical procedure is given for the reaction in Entry 1.

2-(4-*tert*-Butyl-phenyl)-2-methyl-propionitrile. Isobutyronitrile (79.5 mg, 1.15 mmol) was added to a vial containing a stirred solution of $NaN(SiMe_3)_2$ (239 mg, 1.30 mmol) in toluene (1 mL). The solution was stirred for 10 min before it was transferred to a screw-capped vial containing a stirred suspension of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), BINAP (6.2 mg, 0.010 mmol), and 1-bromo-4-*tert*-butylbenzene (213 mg, 1.00 mmol) in toluene (1 mL). The vial was sealed with a cap containing a PTFE septum and removed from the drybox. The reaction mixture was stirred under the conditions indicated in Table 2 and monitored by GC analysis. Upon consumption of the aryl halide, the reaction mixture was cooled to room temperature, poured into DI water and extracted with ether. The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was chromatographed on silica gel (hexane/ethyl acetate = 90/10) to give 180 mg (89.6%) of 2-(4-*tert*-butyl-phenyl)-2-methyl-propionitrile. ^1H NMR ($CDCl_3$) δ 1.33 (s, 9H), 1.73 (s, 6H), 7.41 (s, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 29.13, 31.25, 34.48, 36.71, 124.72, 124.76, 125.79, 138.34, 150.74; IR (KBr, cm^{-1}) ν(CN) 2233; Anal. Calc'd for $C_{14}H_{19}N$: C, 85.53; H, 9.51; N, 6.96. Found: C, 83.36; H, 9.36; N, 6.77.

2-(4-Methoxy-phenyl)-2-methyl-propionitrile.[3] 4-Bromoanisole (187 mg, 1.00 mmol), isobutyronitrile (79.5 mg, 1.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), BINAP (6.2 mg, 0.010 mmol), and $NaN(SiMe_3)_2$ (239 mg, 1.30 mmol) were used. Purified by chromatography on silica

gel (hexane/ethyl acetate = 80/20) to give 150 mg (85.7%) of 2-(4-methoxy-phenyl)-2-methyl-propionitrile. ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 6H), 3.81 (s, 3H), 6.91 (d, 8.8 Hz, 2H), 7.39 (d, 8.8 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 29.24, 36.39, 55.31, 114.12, 124,76, 126.21, 133.45, 158.95.

4-(1-Cyano-1-methyl-ethyl)-benzonitrile.[3] 4-Bromobenzonitrile (182 mg, 1.00 mmol), isobutyronitrile (79.5 mg, 1.15 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), BINAP (3.1 mg, 0.005 mmol), and $NaN(SiMe_3)_2$ (239 mg, 1.30 mmol) were used. Purified by filtration on a pad of silica gel eluting with ethyl acetate to give 168 mg (99%) of 4-(1-cyano-1-methyl-ethyl)-benzonitrile. ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 6H), 7.61 (d, 8.0 Hz, 2H), 7.71 (d, 8.5 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) 28.80, 37.43, 111.99, 118.15, 123.29, 126.03, 132.79, 146.43.

2-Methyl-2-*o*-tolyl-propionitrile.[4] 2-Bromotoleune (171 mg, 1.00 mmol), isobutyronitrile (79.5 mg, 1.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), BINAP (6.2 mg, 0.010 mmol), and $NaN(SiMe_3)_2$ (239 mg, 1.30 mmol) were used. Purified by Kugelrohr distillation to give 116 mg (73.1%) of 2-methyl-2-*o*-tolyl-propionitrile. ^{1}H NMR ($CDCl_3$) δ 1.79 (s, 6H), 2.65 (s, 3H), 7.21-7.24 (m, 3H), 7.31 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 21.10, 28.19, 34.92, 124.54, 124.65, 126.41, 127.97, 132.69, 136.31, 137.94.

2-(4-*tert*-Butyl-phenyl)-bicyclo[2.2.1]heptane-2-carbonitrile. 1-Bromo-4-*tert*-butylbenzene (213 mg, 1.00 mmol), 2-norbornanecarbonitrile (139 mg, 1.15 mmol), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol), BINAP (12.5 mg, 0.020 mmol), and $NaN(SiMe_3)_2$ (239 mg, 1.30 mmol) were used. Purified by chromatography on silica gel (hexane/ethyl acetate = 90/10) to give 179 mg (70.5%) of 2-(4-*tert*-butyl-phenyl)-bicyclo[2.2.1]heptane-2-carbonitrile. ^{1}H NMR ($CDCl_3$) (two isomers in a 2:1 ratio) δ 1.18 (m, 1H), 1.33 (s, 6H), 1.34 (s, 3H), 1.37 (m, 0.33H), 1.47 (m, 0.67), 1.55 (m, 1H) 1.61-1.74 (m, 2H), 2.03-2.15 (m, 2H), 2.34 (m, 1H), 2.43 (m, 0.67H), 2.49 (m, 0.33H), 2.78 (d, 4.0 Hz, 0.67H), 2.84 (d, 3.5 Hz, 0.33H), 7.32-7.41 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) (two isomers) δ 23.15, 26.48, 28.63, 28.69, 31.24 (two coincident singlets), 34.14, 34.47, 36.62, 36.88, 37.35, 39.39, 40.65, 45.23, 46.10, 46.25, 46.85, 48.38, 125.14, 125.63, 125.69, 126.07, 126.24, 127.14, 134.48, 138.34, 150.38, 150.68; IR (KBr, cm^{-1}) ν(CN) 2224; Anal. Calc'd for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.53. Found: C, 85.34; H, 9.14; N, 5.36.

(4-*tert*-Butyl-phenyl)-phenyl-acetonitrile. 1-Bromo-4-*tert*-butylbenzene (213 mg, 1.00 mmol), benzyl cyanide (141 mg, 1.20 mmol), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol), BINAP (12.5 mg, 0.020 mmol), and KO^{t}Bu (146 mg, 1.30 mmol) were used. Purified by chromatography on silica gel (hexane/ethyl acetate = 90/10) to give 239 mg (96.0%) of (4-*tert*-butyl-phenyl)-phenyl-acetonitrile. ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 9H), 5.02 (s, 1H), 7.17-7.30 (m, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.22, 34.53, 42.17, 119.82, 126.08, 127.32, 127.69, 128.11, 129.10, 132.83, 136.03,

151.25; IR (KBr, cm^{-1}) ν(CN) 2245; Anal. Calc'd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.47; H, 7.80; N, 5.62.

2,2-Diphenyl-butyronitrile. Bromobenzene (157 mg, 1.00 mmol), 2-phenylbutyronitrile (167 mg, 1.15 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (10.4 mg, 0.010 mmol), P^tBu_3 (8.1 mg, 0.040 mmol), and $LiN(SiMe_3)_2$ (209 mg, 1.25 mmol) were used. Purified by chromatography on silica gel (hexane/ethyl acetate = 90/10) to give 208 mg (94.0%) of 2,2-diphenyl-butyronitrile. ^1H NMR ($CDCl_3$) δ 1.06 (t, 7.5 Hz, 3H), 2.43 (q, 7.5 Hz, 2H), 7.31 (m, 2H), 7.34-7.40 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 10.03, 32.73, 52.50, 122.18, 126.88, 127.73, 128.75, 140.07; IR (neat, cm^{-1}) ν(CN) 2234; Anal. Calc'd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.63; H, 6.84; N, 6.32.

2,2-Diphenyl-butyronitrile. Bromobenzene (157 mg, 1.00 mmol), butyronitrile (76.7 mg, 1.11 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (10.4 mg, 0.010 mmol), P^tBu_3 (8.1 mg, 0.040 mmol), and $LiN(SiMe_3)_2$ (385 mg, 2.30 mmol) were used. Purified by chromatography on silica gel (hexane/ethyl acetate = 90/10) to give 134 mg (60.6%) of 2,2-diphenyl-butyronitrile. ^1H NMR ($CDCl_3$) δ 1.06 (t, 7.5 Hz, 3H), 2.43 (q, 7.5 Hz, 2H), 7.31 (m, 2H), 7.34-7.40 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 10.03, 32.73, 52.50, 122.18, 126.88, 127.73, 128.75, 140.07.

Diphenyl-acetonitrile.[5] Bromobenzene (157 mg, 1.00 mmol), acetonitrile (47.2 mg, 1.15 mmol), $Pd(OAc)_2$ (11.2 mg, 0.050 mmol), BINAP (31.1 mg, 0.050 mmol), and $NaN(SiMe_3)_2$ (239 mg, 1.30 mmol) were used. Purified by chromatography on silica gel (hexane/ethyl acetate = 85/15) to give 66.1 mg (68.4%) of diphenyl-acetonitrile. ^1H NMR ($CDCl_3$) δ 5.15 (s, 1H), 7.32-7.41 (m, 10H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 42.57, 119.64, 127.70, 128.21, 129.16, 135.86.

Di-*o*-tolyl-acetonitrile. 2-Bromotoluene (171 mg, 1.00 mmol), acetonitrile (47.2 mg, 1.15 mmol), $Pd(OAc)_2$ (11.2 mg, 0.050 mmol), BINAP (31.1 mg, 0.050 mmol), and $NaN(SiMe_3)_2$ (239 mg, 1.30 mmol) were used. Purified by chromatography on silica gel (hexane/ethyl acetate = 90/10) to give 68.3 mg (61.7 %) of di-*o*-tolyl-acetonitrile. ^1H NMR ($CDCl_3$) δ 2.31 (s, 6H), 5.36 (s, 1H), 7.24-7.29 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 19.22, 36.91, 119.11, 126.74, 128.14, 128.41, 130.98, 132.96, 135.85; IR (KBr, cm^{-1}) ν(CN) 2235; Anal. Calc'd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.89; H, 6.79; N, 6.21.

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Experimental details for the crystal structure determination of **4**.

Data Collection

A colorless prism crystal of $C_{55}H_{53}NP_2Pd$ having approximate dimensions of 0.12 x 0.13 x 0.19 mm was mounted on a glass fiber. All measurements were made on an unknown diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1° in ω, 10s exposure, de-zingered) data frames, corresponded to a primitive triclinic cell with dimensions:

a = 15.452(1) Å	α = 104.686(2)^o
b = 16.887(1) Å	β = 108.412(1)^o
c = 10.5491(3) Å	γ = 62.816(1)
V = 2303.7(2) Å^3	

For Z = 2 and F.W. = 896.38, the calculated density is 1.29 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: P_{-1} (#2).

The data were collected at a temperature of -90 ± 1°C to a maximum 2θ value of 55.0 °. Four omega scans consisting of 57, 51, 35, and 45 data frames, respectively, were collected with a scan width of 2.0° and a detector-to-crystal distance, Dx, of 33mm. Each frame was exposed twice (for the purpose of de-zingering) for 180s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, "Processing of X-Ray Diffraction Data Collected in Oscillation Mode," Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

A total of 10459 reflections was collected. No decay correction was applied.
The linear absorption coefficient, μ, for Mo-Kα radiation is 5.1 cm^{-1} and no absorption correction was applied. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by the Patterson Method and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. In the case of the methyl group hydrogen atoms, one hydrogen was located in the difference map and included at an idealized distance to set the orientation of the other two hydrogen atoms. The final cycle of full-matrix least-squares refinement[3] was based on 7212 observed reflections ($I > 5.00\sigma(I)$) and 532 variable parameters and converged (largest parameter shift was 0.43 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.034$$

$$R_w = [(\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2)]^{1/2} = 0.041$$

The standard deviation of an observation of unit weight[4] was 2.00. The weighting scheme was based on counting statistics and included a factor (p = 0.010) to downweight the intense reflections. Plots of $\Sigma \, w \, (|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.63 and -0.62 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous

dispersion effects were included in Fcalc[6]; the values for Δf' and Δf" were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

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(3) Least-Squares:

Function minimized $S w(|F_o|-|F_c|)^2$

where $w = 4F_o^2/2(F_o^2) = [s^2(F_o) + (pF_o/2)^2]^{-1}$

$F_o^2 = S(C-RB)/Lp$

and $s^2(F_o^2) = [S^2(C+R^2B) + (pF_o^2)^2]/Lp^2$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count

Lp = Lorentz-polarization factor

p = p-factor

(4) Standard deviation of an observation of unit weight:

$[S w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$

where N_o = number of observations

N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

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(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

Experimental details for the crystal structure determination of **4**.

A. Crystal Data

Empirical Formula	$C_{55}H_{53}NP_2Pd$
Formula Weight	896.38
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.12 X 0.13 X 0.19 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 15.452(1)Å b = 16.887(1) Å c = 10.5491(3) Å α = 104.686(2)^o β = 108.412(1)^o γ = 62.816(1)^o V = 2303.7(2) Å^3
Space Group	P_{-1} (#2)
Z value	2
D_{calc}	1.292 g/cm^3
F_{000}	932.00
μ(MoKα)	5.09 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Take-off Angle	2.8^{o}
Crystal to Detector Distance	33 mm
Temperature	-90.0^{o}C
Scan Rate	180s/frame
Scan Width	2.0 °
$2\theta_{max}$	55.0^{o}
No. of Reflections Measured	Total: 10459
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Patterson Method
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	$1/^2\sigma$(Fo)

p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>5.00sigma(I))	7212
No. Variables	532
Reflection/Parameter Ratio	13.56
Residuals: R; Rw	0.034 ; 0.041
Goodness of Fit Indicator	2.00
Max Shift/Error in Final Cycle	0.43
Maximum peak in Final Diff. Map	0.63 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.62 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq} for **4**.

atom	x	y	z	B_{eq}
Pd(1)	-0.14956(2)	-0.22962(1)	0.18861(2)	2.109(5)
P(1)	0.01861(6)	-0.25384(5)	0.26941(7)	2.23(2)
P(2)	-0.14164(5)	-0.24667(5)	0.39986(6)	2.07(2)
N(1)	-0.0056(2)	-0.3117(2)	-0.0879(2)	3.99(7)
C(1)	-0.1704(2)	-0.2027(2)	-0.0120(2)	2.54(6)
C(2)	-0.0784(3)	-0.2628(2)	-0.0534(3)	2.91(7)
C(3)	-0.2558(3)	-0.2185(2)	-0.1226(3)	3.60(8)
C(4)	-0.1852(3)	-0.1048(2)	0.0006(3)	3.68(8)
C(5)	-0.2976(2)	-0.2036(2)	0.1453(2)	2.30(6)
C(6)	-0.3724(2)	-0.1158(2)	0.1424(3)	2.97(7)
C(7)	-0.4728(2)	-0.0967(2)	0.1135(3)	3.28(7)
C(8)	-0.5058(2)	-0.1638(2)	0.0886(3)	3.28(7)
C(9)	-0.4331(2)	-0.2511(2)	0.0926(3)	3.36(8)
C(10)	-0.3321(2)	-0.2704(2)	0.1196(3)	2.83(7)
C(11)	-0.6153(3)	-0.1440(2)	0.0598(4)	4.84(10)
C(12)	0.0526(2)	-0.1696(2)	0.2433(3)	2.61(7)
C(13)	0.0134(2)	-0.0834(2)	0.3108(3)	3.28(7)
C(14)	0.0235(3)	-0.0132(2)	0.2807(3)	4.14(9)
C(15)	0.0727(3)	-0.0293(3)	0.1821(3)	4.59(10)
C(16)	0.1128(3)	-0.1143(3)	0.1155(3)	4.27(10)
C(17)	0.1029(2)	-0.1850(2)	0.1450(3)	3.21(7)
C(18)	0.1151(2)	-0.3630(2)	0.2256(3)	2.41(6)
C(19)	0.2168(3)	-0.3827(2)	0.2680(3)	3.68(8)
C(20)	0.2870(3)	-0.4682(2)	0.2365(3)	4.31(9)
C(21)	0.2567(3)	-0.5342(2)	0.1621(3)	4.02(8)
C(22)	0.1566(3)	-0.5158(2)	0.1176(3)	3.51(8)
C(23)	0.0859(2)	-0.4306(2)	0.1494(3)	2.90(7)
C(24)	0.0461(2)	-0.2446(2)	0.4541(2)	2.21(6)
C(25)	0.1352(2)	-0.2424(2)	0.5377(3)	2.81(7)
C(26)	0.1558(2)	-0.2432(2)	0.6746(3)	3.21(7)
C(27)	0.0876(2)	-0.2463(2)	0.7305(3)	2.96(7)
C(28)	-0.0014(2)	-0.2466(2)	0.6503(3)	2.70(7)
C(29)	-0.0243(2)	-0.2454(2)	0.5110(2)	2.13(6)
C(30)	-0.1393(2)	-0.3521(2)	0.4189(2)	2.17(6)
C(31)	-0.1127(2)	-0.4245(2)	0.3198(3)	2.61(7)

C(32)	-0.1056(2)	-0.5074(2)	0.3323(3)	3.26(7)
C(33)	-0.1273(2)	-0.5166(2)	0.4429(3)	3.43(8)
C(34)	-0.1545(2)	-0.4452(2)	0.5418(3)	3.44(8)
C(35)	-0.1607(2)	-0.3629(2)	0.5305(3)	2.82(7)
C(36)	-0.2349(2)	-0.1600(2)	0.4878(2)	2.39(6)
C(37)	-0.2196(2)	-0.0857(2)	0.5648(3)	3.02(7)
C(38)	-0.2904(3)	-0.0203(2)	0.6316(3)	3.73(8)
C(39)	-0.3772(3)	-0.0272(2)	0.6223(3)	3.78(8)
C(40)	-0.3947(2)	-0.0996(2)	0.5441(3)	3.62(8)
C(41)	-0.3243(2)	-0.1658(2)	0.4755(3)	2.82(7)
C(42)	-0.3679(3)	-0.5523(3)	0.1583(5)	6.3(1)
C(43)	-0.3617(4)	-0.5061(4)	0.2874(5)	7.5(2)
C(44)	-0.3919(4)	-0.5287(4)	0.3813(5)	8.4(2)
C(45)	-0.4263(4)	-0.5944(4)	0.3454(6)	7.1(1)
C(46)	-0.4348(4)	-0.6366(3)	0.2186(6)	7.5(2)
C(47)	-0.4068(4)	-0.6152(3)	0.1275(5)	7.0(1)
C(48)	-0.3343(4)	-0.5331(4)	0.0607(6)	10.2(2)
C(49)	-0.3455(5)	-0.8526(3)	0.4050(5)	6.8(2)
C(50)	-0.3297(4)	-0.8169(3)	0.5368(5)	6.1(1)
C(51)	-0.4055(7)	-0.7535(5)	0.5931(8)	10.6(3)
C(52)	-0.504(1)	-0.7203(7)	0.518(2)	17.7(6)
C(53)	-0.5155(7)	-0.7576(7)	0.383(2)	15.4(5)
C(54)	-0.4407(7)	-0.8250(5)	0.3232(7)	11.1(2)
C(55)	-0.2587(6)	-0.9232(5)	0.3507(6)	11.1(2)
H(1)	-0.2491	-0.2778	-0.1259	4.3237
H(2)	-0.3182	-0.1766	-0.1031	4.3237
H(3)	-0.2528	-0.2111	-0.2072	4.3237
H(4)	-0.1308	-0.0959	0.0660	4.4140
H(5)	-0.1883	-0.0923	-0.0839	4.4140
H(6)	-0.2459	-0.0657	0.0276	4.4140
H(7)	-0.3529	-0.0674	0.1611	3.5687
H(8)	-0.5203	-0.0361	0.1107	3.9349
H(9)	-0.4530	-0.2990	0.0765	4.0369
H(10)	-0.2849	-0.3312	0.1205	3.3971
H(11)	-0.6354	-0.1710	-0.0285	5.8070
H(12)	-0.6259	-0.1677	0.1235	5.8070
H(13)	-0.6536	-0.0809	0.0661	5.8070
H(14)	-0.0208	-0.0724	0.3784	3.9334

H(15)	-0.0033	0.0454	0.3275	4.9720
H(16)	0.0788	0.0188	0.1600	5.5080
H(17)	0.1476	-0.1248	0.0489	5.1282
H(18)	0.1304	-0.2435	0.0983	3.8536
H(19)	0.2384	-0.3372	0.3190	4.4190
H(20)	0.3563	-0.4811	0.2667	5.1676
H(21)	0.3050	-0.5927	0.1412	4.8217
H(22)	0.1358	-0.5615	0.0651	4.2109
H(23)	0.0167	-0.4183	0.1186	3.4846
H(24)	0.1824	-0.2403	0.5001	3.3685
H(25)	0.2168	-0.2416	0.7307	3.8569
H(26)	0.1026	-0.2482	0.8245	3.5464
H(27)	-0.0483	-0.2476	0.6897	3.2424
H(28)	-0.0991	-0.4174	0.2426	3.1303
H(29)	-0.0860	-0.5571	0.2650	3.9156
H(30)	-0.1235	-0.5729	0.4513	4.1179
H(31)	-0.1690	-0.4525	0.6180	4.1239
H(32)	-0.1795	-0.3138	0.5988	3.3864
H(33)	-0.1599	-0.0799	0.5716	3.6259
H(34)	-0.2789	0.0301	0.6845	4.4803
H(35)	-0.4252	0.0178	0.6695	4.5367
H(36)	-0.4550	-0.1043	0.5371	4.3361
H(37)	-0.3373	-0.2149	0.4202	3.3889
H(38)	-0.3378	-0.4602	0.3120	9.0202
H(39)	-0.3882	-0.4978	0.4703	10.0204
H(40)	-0.4442	-0.6105	0.4103	8.5740
H(41)	-0.4604	-0.6814	0.1932	8.9504
H(42)	-0.4146	-0.6450	0.0380	8.3774
H(43)	-0.3450	-0.5692	-0.0228	12.2036
H(44)	-0.3708	-0.4715	0.0486	12.2036
H(45)	-0.2650	-0.5461	0.0922	12.2036
H(46)	-0.2633	-0.8370	0.5911	7.3211
H(47)	-0.3916	-0.7307	0.6865	12.5726
H(48)	-0.5581	-0.6770	0.5541	20.0983
H(49)	-0.5813	-0.7352	0.3256	18.1790
H(50)	-0.4532	-0.8510	0.2317	13.2746
H(51)	-0.2812	-0.9416	0.2581	13.2738
H(52)	-0.2112	-0.8997	0.3604	13.2738

H(53)	-0.2283	-0.9734	0.3992	13.2738

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Anisotropic Displacement Parameters for **4**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	0.0328(2)	0.0266(1)	0.0202(1)	-0.0092(1)	0.00802(9)	0.00515(8)
P(1)	0.0353(5)	0.0292(4)	0.0229(3)	-0.0123(4)	0.0102(3)	0.0045(3)
P(2)	0.0310(5)	0.0273(4)	0.0213(3)	-0.0099(4)	0.0089(3)	0.0045(3)
N(1)	0.058(2)	0.060(2)	0.032(1)	-0.014(2)	0.020(1)	0.011(1)
C(1)	0.042(2)	0.035(2)	0.020(1)	-0.013(2)	0.008(1)	0.008(1)
C(2)	0.054(2)	0.042(2)	0.019(1)	-0.019(2)	0.011(1)	0.008(1)
C(3)	0.053(2)	0.052(2)	0.027(2)	-0.016(2)	0.007(1)	0.011(1)
C(4)	0.062(2)	0.038(2)	0.038(2)	-0.012(2)	0.014(2)	0.014(1)
C(5)	0.036(2)	0.031(2)	0.019(1)	-0.013(1)	0.007(1)	0.003(1)
C(6)	0.041(2)	0.037(2)	0.037(2)	-0.014(2)	0.013(1)	0.007(1)
C(7)	0.038(2)	0.037(2)	0.039(2)	-0.003(2)	0.012(1)	0.007(1)
C(8)	0.032(2)	0.048(2)	0.037(2)	-0.009(2)	0.009(1)	0.004(1)
C(9)	0.037(2)	0.042(2)	0.045(2)	-0.016(2)	0.007(1)	0.001(1)
C(10)	0.032(2)	0.034(2)	0.031(2)	-0.005(2)	0.006(1)	0.004(1)
C(11)	0.039(2)	0.067(2)	0.068(2)	-0.014(2)	0.010(2)	0.008(2)
C(12)	0.039(2)	0.037(2)	0.027(1)	-0.019(2)	0.004(1)	0.008(1)
C(13)	0.052(2)	0.040(2)	0.038(2)	-0.020(2)	0.012(2)	0.007(1)
C(14)	0.068(3)	0.040(2)	0.052(2)	-0.027(2)	0.007(2)	0.009(2)
C(15)	0.079(3)	0.065(3)	0.052(2)	-0.051(2)	-0.003(2)	0.022(2)
C(16)	0.071(3)	0.077(3)	0.040(2)	-0.049(2)	0.014(2)	0.011(2)
C(17)	0.050(2)	0.051(2)	0.031(2)	-0.027(2)	0.011(1)	0.006(1)
C(18)	0.034(2)	0.032(2)	0.026(1)	-0.009(1)	0.012(1)	0.006(1)
C(19)	0.045(2)	0.045(2)	0.044(2)	-0.016(2)	0.012(2)	-0.003(2)
C(20)	0.036(2)	0.058(2)	0.052(2)	-0.002(2)	0.016(2)	0.003(2)
C(21)	0.056(3)	0.038(2)	0.044(2)	-0.001(2)	0.020(2)	0.004(2)
C(22)	0.062(3)	0.032(2)	0.037(2)	-0.013(2)	0.020(2)	0.001(1)
C(23)	0.044(2)	0.036(2)	0.032(2)	-0.013(2)	0.015(1)	0.007(1)
C(24)	0.033(2)	0.027(1)	0.024(1)	-0.011(1)	0.007(1)	0.004(1)
C(25)	0.034(2)	0.040(2)	0.035(2)	-0.016(2)	0.009(1)	0.006(1)

C(26)	0.041(2)	0.050(2)	0.030(2)	-0.021(2)	0.000(1)	0.007(1)
C(27)	0.048(2)	0.043(2)	0.022(1)	-0.020(2)	0.004(1)	0.006(1)
C(28)	0.042(2)	0.035(2)	0.028(1)	-0.014(2)	0.012(1)	0.006(1)
C(29)	0.035(2)	0.024(1)	0.022(1)	-0.009(1)	0.008(1)	0.005(1)
C(30)	0.027(2)	0.029(1)	0.027(1)	-0.010(1)	0.005(1)	0.008(1)
C(31)	0.033(2)	0.032(2)	0.036(2)	-0.011(1)	0.013(1)	0.005(1)
C(32)	0.040(2)	0.030(2)	0.051(2)	-0.011(2)	0.015(2)	0.001(1)
C(33)	0.044(2)	0.031(2)	0.057(2)	-0.013(2)	0.009(2)	0.017(2)
C(34)	0.048(2)	0.044(2)	0.044(2)	-0.015(2)	0.012(2)	0.020(2)
C(35)	0.043(2)	0.035(2)	0.030(2)	-0.012(2)	0.010(1)	0.010(1)
C(36)	0.036(2)	0.029(2)	0.022(1)	-0.006(1)	0.009(1)	0.008(1)
C(37)	0.044(2)	0.031(2)	0.039(2)	-0.013(2)	0.013(1)	0.003(1)
C(38)	0.057(3)	0.034(2)	0.041(2)	-0.009(2)	0.018(2)	-0.002(1)
C(39)	0.046(2)	0.042(2)	0.035(2)	0.006(2)	0.019(2)	0.007(1)
C(40)	0.032(2)	0.056(2)	0.045(2)	-0.006(2)	0.012(2)	0.017(2)
C(41)	0.035(2)	0.036(2)	0.032(2)	-0.009(2)	0.009(1)	0.006(1)
C(42)	0.053(3)	0.111(4)	0.074(3)	-0.025(3)	0.006(2)	0.036(3)
C(43)	0.081(4)	0.125(4)	0.088(4)	-0.060(3)	0.010(3)	0.002(3)
C(44)	0.091(4)	0.136(5)	0.073(3)	-0.042(4)	0.022(3)	-0.010(3)
C(45)	0.062(3)	0.112(4)	0.088(4)	-0.020(3)	0.020(3)	0.025(3)
C(46)	0.072(4)	0.095(4)	0.115(4)	-0.025(3)	0.017(3)	0.031(3)
C(47)	0.065(3)	0.083(3)	0.101(4)	-0.033(3)	-0.005(3)	0.008(3)
C(48)	0.125(5)	0.156(5)	0.130(5)	-0.066(5)	0.013(4)	0.060(4)
C(49)	0.126(5)	0.090(4)	0.075(3)	-0.075(4)	0.003(3)	0.025(3)
C(50)	0.098(4)	0.081(3)	0.079(3)	-0.058(3)	0.012(3)	0.022(3)
C(51)	0.169(7)	0.105(6)	0.191(7)	-0.075(6)	0.090(7)	0.020(5)
C(52)	0.21(1)	0.107(7)	0.45(2)	-0.059(8)	0.19(2)	0.039(10)
C(53)	0.072(6)	0.135(9)	0.40(2)	-0.038(6)	-0.002(9)	0.14(1)
C(54)	0.164(7)	0.156(6)	0.137(5)	-0.131(6)	-0.076(6)	0.085(5)
C(55)	0.226(8)	0.133(5)	0.121(5)	-0.116(6)	0.069(5)	-0.009(4)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond Lengths(Å) for **4**.

atom	atom	distance	atom	atom	distance
Pd(1)	P(1)	2.3351(8)	Pd(1)	P(2)	2.2771(6)
Pd(1)	C(1)	2.171(2)	Pd(1)	C(5)	2.039(3)
P(1)	C(12)	1.830(3)	P(1)	C(18)	1.824(3)
P(1)	C(24)	1.840(3)	P(2)	C(29)	1.828(3)
P(2)	C(30)	1.825(3)	P(2)	C(36)	1.819(3)
N(1)	C(2)	1.156(4)	C(1)	C(2)	1.446(4)
C(1)	C(3)	1.538(4)	C(1)	C(4)	1.538(4)
C(5)	C(6)	1.404(4)	C(5)	C(10)	1.389(4)
C(6)	C(7)	1.377(4)	C(7)	C(8)	1.380(4)
C(8)	C(9)	1.388(4)	C(8)	C(11)	1.510(5)
C(9)	C(10)	1.387(4)	C(12)	C(13)	1.391(4)
C(12)	C(17)	1.391(4)	C(13)	C(14)	1.385(4)
C(14)	C(15)	1.379(5)	C(15)	C(16)	1.374(5)
C(16)	C(17)	1.390(4)	C(18)	C(19)	1.390(4)
C(18)	C(23)	1.389(4)	C(19)	C(20)	1.388(4)
C(20)	C(21)	1.370(4)	C(21)	C(22)	1.373(5)
C(22)	C(23)	1.389(4)	C(24)	C(25)	1.392(4)
C(24)	C(29)	1.405(4)	C(25)	C(26)	1.380(4)
C(26)	C(27)	1.385(4)	C(27)	C(28)	1.370(4)
C(28)	C(29)	1.402(3)	C(30)	C(31)	1.386(4)
C(30)	C(35)	1.392(3)	C(31)	C(32)	1.390(4)
C(32)	C(33)	1.374(4)	C(33)	C(34)	1.376(4)
C(34)	C(35)	1.381(4)	C(36)	C(37)	1.386(4)
C(36)	C(41)	1.392(4)	C(37)	C(38)	1.379(4)
C(38)	C(39)	1.370(4)	C(39)	C(40)	1.377(4)

C(40)	C(41)	1.390(4)	C(42)	C(43)	1.385(6)
C(42)	C(47)	1.371(6)	C(42)	C(48)	1.448(6)
C(43)	C(44)	1.411(6)	C(44)	C(45)	1.362(7)
C(45)	C(46)	1.344(7)	C(46)	C(47)	1.349(6)
C(49)	C(50)	1.362(6)	C(49)	C(54)	1.379(8)
C(49)	C(55)	1.491(8)	C(50)	C(51)	1.357(9)
C(51)	C(52)	1.39(1)	C(52)	C(53)	1.39(2)
C(53)	C(54)	1.39(1)			

Table 4. Bond Angles(°) of **4**.

atom	atom	atom	angle	atom	atom	atom	angle
P(1)	Pd(1)	P(2)	85.66(2)	P(1)	Pd(1)	C(1)	98.19(8)
P(1)	Pd(1)	C(5)	172.06(7)	P(2)	Pd(1)	C(1)	174.63(8)
P(2)	Pd(1)	C(5)	86.94(7)	C(1)	Pd(1)	C(5)	89.0(1)
Pd(1)	P(1)	C(12)	116.20(10)	Pd(1)	P(1)	C(18)	119.48(10)
Pd(1)	P(1)	C(24)	107.09(9)	C(12)	P(1)	C(18)	106.4(1)
C(12)	P(1)	C(24)	103.0(1)	C(18)	P(1)	C(24)	102.6(1)
Pd(1)	P(2)	C(29)	108.81(8)	Pd(1)	P(2)	C(30)	116.40(8)
Pd(1)	P(2)	C(36)	118.26(8)	C(29)	P(2)	C(30)	104.1(1)
C(29)	P(2)	C(36)	102.7(1)	C(30)	P(2)	C(36)	104.8(1)
Pd(1)	C(1)	C(2)	105.9(2)	Pd(1)	C(1)	C(3)	117.3(2)
Pd(1)	C(1)	C(4)	107.1(2)	C(2)	C(1)	C(3)	106.8(2)
C(2)	C(1)	C(4)	109.9(2)	C(3)	C(1)	C(4)	109.6(2)
N(1)	C(2)	C(1)	178.9(3)	Pd(1)	C(5)	C(6)	121.9(2)
Pd(1)	C(5)	C(10)	123.0(2)	C(6)	C(5)	C(10)	115.0(3)
C(5)	C(6)	C(7)	122.9(3)	C(6)	C(7)	C(8)	121.4(3)
C(7)	C(8)	C(9)	116.8(3)	C(7)	C(8)	C(11)	122.2(3)
C(9)	C(8)	C(11)	121.1(3)	C(8)	C(9)	C(10)	121.8(3)
C(5)	C(10)	C(9)	122.1(3)	P(1)	C(12)	C(13)	117.8(2)
P(1)	C(12)	C(17)	122.3(2)	C(13)	C(12)	C(17)	119.2(2)
C(12)	C(13)	C(14)	120.8(3)	C(13)	C(14)	C(15)	119.4(3)
C(14)	C(15)	C(16)	120.5(3)	C(15)	C(16)	C(17)	120.4(3)
C(12)	C(17)	C(16)	119.7(3)	P(1)	C(18)	C(19)	123.2(2)
P(1)	C(18)	C(23)	118.5(2)	C(19)	C(18)	C(23)	118.3(3)

C(18)	C(19)	C(20)	120.6(3)	C(19)	C(20)	C(21)	120.2(3)
C(20)	C(21)	C(22)	120.1(3)	C(21)	C(22)	C(23)	120.1(3)
C(18)	C(23)	C(22)	120.7(3)	P(1)	C(24)	C(25)	123.0(2)
P(1)	C(24)	C(29)	117.6(2)	C(25)	C(24)	C(29)	119.3(2)
C(24)	C(25)	C(26)	120.7(2)	C(25)	C(26)	C(27)	120.1(3)
C(26)	C(27)	C(28)	120.1(2)	C(27)	C(28)	C(29)	120.9(2)
P(2)	C(29)	C(24)	118.7(2)	P(2)	C(29)	C(28)	122.4(2)
C(24)	C(29)	C(28)	118.9(2)	P(2)	C(30)	C(31)	118.4(2)
P(2)	C(30)	C(35)	122.5(2)	C(31)	C(30)	C(35)	119.1(2)
C(30)	C(31)	C(32)	120.7(2)	C(31)	C(32)	C(33)	119.3(3)
C(32)	C(33)	C(34)	120.7(2)	C(33)	C(34)	C(35)	120.2(3)
C(30)	C(35)	C(34)	120.0(3)	P(2)	C(36)	C(37)	120.6(2)
P(2)	C(36)	C(41)	120.5(2)	C(37)	C(36)	C(41)	118.8(3)
C(36)	C(37)	C(38)	120.5(3)	C(37)	C(38)	C(39)	120.6(3)
C(38)	C(39)	C(40)	119.8(3)	C(39)	C(40)	C(41)	120.2(3)
C(36)	C(41)	C(40)	120.0(3)	C(43)	C(42)	C(47)	117.9(4)
C(43)	C(42)	C(48)	119.9(5)	C(47)	C(42)	C(48)	122.1(5)
C(42)	C(43)	C(44)	118.4(4)	C(43)	C(44)	C(45)	120.6(5)
C(44)	C(45)	C(46)	120.2(5)	C(45)	C(46)	C(47)	119.8(5)
C(42)	C(47)	C(46)	123.0(5)	C(50)	C(49)	C(54)	120.4(6)
C(50)	C(49)	C(55)	119.1(5)	C(54)	C(49)	C(55)	120.4(6)
C(49)	C(50)	C(51)	122.1(6)	C(50)	C(51)	C(52)	121.7(10)
C(51)	C(52)	C(53)	113(1)	C(52)	C(53)	C(54)	126(1)
C(49)	C(54)	C(53)	115.5(8)				

Table 5. Torsion Angles(°) of **4**.

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Pd(1)	P(1)	C(12)	C(13)	65.9(2)	Pd(1)	P(1)	C(12)	C(17)	-104.4(2)
Pd(1)	P(1)	C(18)	C(19)	179.2(2)	Pd(1)	P(1)	C(18)	C(23)	-2.7(2)
Pd(1)	P(1)	C(24)	C(25)	-170.5(2)	Pd(1)	P(1)	C(24)	C(29)	13.4(2)
Pd(1)	P(2)	C(29)	C(24)	-6.8(2)	Pd(1)	P(2)	C(29)	C(28)	174.3(2)
Pd(1)	P(2)	C(30)	C(31)	18.9(3)	Pd(1)	P(2)	C(30)	C(35)	-162.8(2)
Pd(1)	P(2)	C(36)	C(37)	-87.8(2)	Pd(1)	P(2)	C(36)	C(41)	90.2(2)
Pd(1)	C(1)	C(2)	N(1)	109(14)	Pd(1)	C(5)	C(6)	C(7)	-179.9(2)
Pd(1)	C(5)	C(10)	C(9)	178.9(2)	P(1)	Pd(1)	P(2)	C(29)	11.30(9)
P(1)	Pd(1)	P(2)	C(30)	-105.9(1)	P(1)	Pd(1)	P(2)	C(36)	127.9(1)
P(1)	Pd(1)	C(1)	C(2)	37.6(2)	P(1)	Pd(1)	C(1)	C(3)	156.6(2)
P(1)	Pd(1)	C(1)	C(4)	-79.7(2)	P(1)	Pd(1)	C(5)	C(6)	79.6(6)
P(1)	Pd(1)	C(5)	C(10)	-98.9(6)	P(1)	C(12)	C(13)	C(14)	-170.3(2)
P(1)	C(12)	C(17)	C(16)	169.9(2)	P(1)	C(18)	C(19)	C(20)	177.1(2)
P(1)	C(18)	C(23)	C(22)	-177.6(2)	P(1)	C(24)	C(25)	C(26)	-174.4(2)
P(1)	C(24)	C(29)	P(2)	-4.7(3)	P(1)	C(24)	C(29)	C(28)	174.3(2)
P(2)	Pd(1)	P(1)	C(12)	-127.5(1)	P(2)	Pd(1)	P(1)	C(18)	102.75(9)
P(2)	Pd(1)	P(1)	C(24)	-13.13(9)	P(2)	Pd(1)	C(1)	C(2)	173.2(7)
P(2)	Pd(1)	C(1)	C(3)	-67.7(8)	P(2)	Pd(1)	C(1)	C(4)	55.9(9)
P(2)	Pd(1)	C(5)	C(6)	101.0(2)	P(2)	Pd(1)	C(5)	C(10)	-77.5(2)
P(2)	C(29)	C(24)	C(25)	179.1(2)	P(2)	C(29)	C(28)	C(27)	179.5(2)
P(2)	C(30)	C(31)	C(32)	177.2(2)	P(2)	C(30)	C(35)	C(34)	-177.8(2)
P(2)	C(36)	C(37)	C(38)	-179.9(2)	P(2)	C(36)	C(41)	C(40)	179.4(2)
N(1)	C(2)	C(1)	C(3)	-16(14)	N(1)	C(2)	C(1)	C(4)	-135(14)
C(1)	Pd(1)	P(1)	C(12)	48.7(1)	C(1)	Pd(1)	P(1)	C(18)	-81.0(1)
C(1)	Pd(1)	P(1)	C(24)	163.1(1)	C(1)	Pd(1)	P(2)	C(29)	-124.7(8)
C(1)	Pd(1)	P(2)	C(30)	118.1(8)	C(1)	Pd(1)	P(2)	C(36)	-8.1(8)
C(1)	Pd(1)	C(5)	C(6)	-75.5(2)	C(1)	Pd(1)	C(5)	C(10)	106.0(2)
C(2)	C(1)	Pd(1)	C(5)	-145.8(2)	C(3)	C(1)	Pd(1)	C(5)	-26.8(2)
C(4)	C(1)	Pd(1)	C(5)	96.9(2)	C(5)	Pd(1)	P(1)	C(12)	-106.1(5)
C(5)	Pd(1)	P(1)	C(18)	124.2(5)	C(5)	Pd(1)	P(1)	C(24)	8.3(5)
C(5)	Pd(1)	P(2)	C(29)	-165.8(1)	C(5)	Pd(1)	P(2)	C(30)	77.0(1)
C(5)	Pd(1)	P(2)	C(36)	-49.2(1)	C(5)	C(6)	C(7)	C(8)	1.6(4)
C(5)	C(10)	C(9)	C(8)	0.6(4)	C(6)	C(5)	C(10)	C(9)	0.2(4)

C(6)	C(7)	C(8)	C(9)	-0.7(4)	C(6)	C(7)	C(8)	C(11)	178.6(3)
C(7)	C(6)	C(5)	C(10)	-1.3(4)	C(7)	C(8)	C(9)	C(10)	-0.4(4)
C(10)	C(9)	C(8)	C(11)	-179.7(3)	C(12)	P(1)	C(18)	C(19)	45.2(2)
C(12)	P(1)	C(18)	C(23)	-136.7(2)	C(12)	P(1)	C(24)	C(25)	-47.5(3)
C(12)	P(1)	C(24)	C(29)	136.5(2)	C(12)	C(13)	C(14)	C(15)	0.3(5)
C(12)	C(17)	C(16)	C(15)	-0.4(5)	C(13)	C(12)	P(1)	C(18)	-158.3(2)
C(13)	C(12)	P(1)	C(24)	-50.8(3)	C(13)	C(12)	C(17)	C(16)	-0.3(4)
C(13)	C(14)	C(15)	C(16)	-1.0(5)	C(14)	C(13)	C(12)	C(17)	0.4(5)
C(14)	C(15)	C(16)	C(17)	1.1(5)	C(17)	C(12)	P(1)	C(18)	31.3(3)
C(17)	C(12)	P(1)	C(24)	138.9(2)	C(18)	P(1)	C(24)	C(25)	62.9(2)
C(18)	P(1)	C(24)	C(29)	-113.2(2)	C(18)	C(19)	C(20)	C(21)	0.6(5)
C(18)	C(23)	C(22)	C(21)	0.3(4)	C(19)	C(18)	P(1)	C(24)	-62.6(2)
C(19)	C(18)	C(23)	C(22)	0.6(4)	C(19)	C(20)	C(21)	C(22)	0.3(5)
C(20)	C(19)	C(18)	C(23)	-1.0(4)	C(20)	C(21)	C(22)	C(23)	-0.7(4)
C(23)	C(18)	P(1)	C(24)	115.5(2)	C(24)	C(25)	C(26)	C(27)	0.1(4)
C(24)	C(29)	P(2)	C(30)	118.0(2)	C(24)	C(29)	P(2)	C(36)	-132.9(2)
C(24)	C(29)	C(28)	C(27)	0.5(4)	C(25)	C(24)	C(29)	C(28)	-1.8(4)
C(25)	C(26)	C(27)	C(28)	-1.5(5)	C(26)	C(25)	C(24)	C(29)	1.6(4)
C(26)	C(27)	C(28)	C(29)	1.1(4)	C(28)	C(29)	P(2)	C(30)	-61.0(2)
C(28)	C(29)	P(2)	C(36)	48.1(2)	C(29)	P(2)	C(30)	C(31)	-100.8()
C(29)	P(2)	C(30)	C(35)	77.5(3)	C(29)	P(2)	C(36)	C(37)	32.0(2)
C(29)	P(2)	C(36)	C(41)	-150.0(2)	C(30)	P(2)	C(36)	C(37)	140.6(2)
C(30)	P(2)	C(36)	C(41)	-41.5(2)	C(30)	C(31)	C(32)	C(33)	1.3(5)
C(30)	C(35)	C(34)	C(33)	0.0(5)	C(31)	C(30)	P(2)	C(36)	151.6(2)
C(31)	C(30)	C(35)	C(34)	0.5(4)	C(31)	C(32)	C(33)	C(34)	-0.9(5)
C(32)	C(31)	C(30)	C(35)	-1.1(4)	C(32)	C(33)	C(34)	C(35)	0.3(5)
C(35)	C(30)	P(2)	C(36)	-30.1(3)	C(36)	C(37)	C(38)	C(39)	-0.4(4)
C(36)	C(41)	C(40)	C(39)	1.3(4)	C(37)	C(36)	C(41)	C(40)	-2.6(4)
C(37)	C(38)	C(39)	C(40)	-0.9(5)	C(38)	C(37)	C(36)	C(41)	2.2(4)
C(38)	C(39)	C(40)	C(41)	0.4(4)	C(42)	C(43)	C(44)	C(45)	-0.1(8)
C(42)	C(47)	C(46)	C(45)	1.1(8)	C(43)	C(42)	C(47)	C(46)	-3.2(7)
C(43)	C(44)	C(45)	C(46)	-2.1(8)	C(44)	C(43)	C(42)	C(47)	2.6(7)
C(44)	C(43)	C(42)	C(48)	-177.8(5)	C(44)	C(45)	C(46)	C(47)	1.6(8)
C(46)	C(47)	C(42)	C(48)	177.2(5)	C(49)	C(50)	C(51)	C(52)	-1.0(9)
C(49)	C(54)	C(53)	C(52)	-4(1)	C(50)	C(49)	C(54)	C(53)	2.4(8)
C(50)	C(51)	C(52)	C(53)	0(1)	C(51)	C(50)	C(49)	C(54)	0.0(6)
C(51)	C(50)	C(49)	C(55)	-178.9(4)	C(51)	C(52)	C(53)	C(54)	3(1)
C(53)	C(54)	C(49)	C(55)	-178.7(6)					

Table 6. Non-bonded Contacts out to 3.60 Å for **4**.

atom	atom	distance	ADC	atom	atom	distance	ADC
N(1)	C(28)	3.249(3)	55401	N(1)	C(27)	3.352(4)	55401
N(1)	C(32)	3.597(4)	54502	C(20)	C(48)	3.445(7)	54502
C(21)	C(48)	3.554(6)	54502	C(28)	C(33)	3.590(4)	54602
C(32)	C(34)	3.576(5)	54602	C(33)	C(43)	3.413(6)	1
C(38)	C(50)	3.552(5)	56501	C(39)	C(40)	3.346(4)	45602
C(40)	C(40)	3.528(6)	45602				

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus $\pm$4 lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure are given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

(1) X, Y, Z (2) -X, -Y, -Z

Experimental details for the crystal structure determination of **6**.

Data Collection

A red plate crystal of $C_{36}H_{55}NP_2FePd$ having approximate dimensions of 0.12 x 0.21 x 0.24 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1^o in ω, 10s exposure, de-zingered) data frames, corresponded to a primitive monoclinic cell with dimensions: a = 14.3398(5) Å, b = 16.7219(4) Å, β = 97.737(1)^o, c = 14.9078(4) Å, V = 3542.2(2) Å^3. For Z = 4 and F.W. = 726.03, the calculated density is 1.36 g/cm^3. The systematic absences of: h0l: h+l = 2n+1; 0k0: k = 2n+1; uniquely determine the space group to be: $P2_1/n$ (#14).

The data were collected at a temperature of -90 ± 1^{o}C to a maximum 2θ value of 60.2^o. Three omega scans consisting of 51, 45, and 25 data frames, respectively, were collected with a scan width of 1.9^o and a detector-to-crystal distance, Dx, of 33mm. Each frame was exposed twice (for the purpose of de-zingering) for 171s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, "Processing of X-Ray Diffraction Data Collected in Oscillation Mode," Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

A total of 10619 reflections was collected. No decay correction was applied. The linear absorption coefficient, μ, for Mo-Kα radiation is 10.3 cm^{-1} and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. In the case of the methyl group hydrogen atoms, one hydrogen was located in the difference map and included at an idealized distance to set the orientation of the other two hydrogen atoms. The final cycle of full-matrix least-squares refinement[3] was based on 6951 observed reflections ($I > 5.00\sigma(I)$) and 370 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.037$$

$$R_W = [(\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2)]^{1/2} = 0.048$$

The standard deviation of an observation of unit weight[4] was 2.30. The weighting scheme was based on counting statistics and included a factor ($p = 0.010$) to downweight the intense reflections. Plots of $\Sigma \, w \, (|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.09 and -0.87 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., & Polidori, G.; *J. Appl. Cryst.*, 27, 435-436 (1994).

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized $Sw(|Fo|-|Fc|)^2$

where $w = 4F_o^2/2(F_o^2)$

and $s^2(F_o^2) = [S^2(C+R^2B) + (pF_o^2)^2]/Lp^2$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count

Lp = Lorentz-polarization factor

p = p-factor

(4) Standard deviation of an observation of unit weight:

$[Sw(|Fo|-|Fc|)^2/(No-Nv)]^{1/2}$

where N_o = number of observations

N_V = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr.*, 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

Experimental details for **6**.

A. Crystal Data

Empirical Formula	$C_{36}H_{55}NP_2FePd$
Formula Weight	726.03
Crystal Color, Habit	red, plate
Crystal Dimensions	0.12 X 0.21 X 0.24 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 14.3398(5)Å b = 16.7219(4) Å c = 14.9078(4) Å β = 97.737(1)° V = 3542.2(2) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.361 g/cm^3
F000	1520.00
μ(MoK_)	10.32 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD

Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Take-off Angle	2.8°
Crystal to Detector Distance	33 mm
Temperature	-90.0°C
Scan Rate	171s/frame
Scan Width	1.9°/frame
2_max	60.2°
No. of Reflections Measured	Total: 10619
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	$1/\sigma^2$(Fo)
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>5.00_(I))	6951
No. Variables	370
Reflection/Parameter Ratio	18.79

Residuals: R; Rw	0.037 ; 0.048
Goodness of Fit Indicator	2.30
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	1.09 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.87 $e^-/Å^3$

Table 7. Atomic coordinates and B_{iso}/B_{eq} for **6**.

atom	x	y	z	Beq
Pd(1)	0.17422(2)	0.18298(1)	0.50037(1)	1.997(5)
Fe(1)	0.01179(3)	0.28885(2)	0.26141(3)	2.490(9)
P(1)	0.20094(6)	0.17574(4)	0.34582(5)	2.10(2)
P(2)	0.04275(5)	0.26185(4)	0.49520(4)	1.99(1)
N(1)	0.2995(2)	0.1216(1)	0.5320(2)	3.13(6)
C(1)	0.3143(2)	0.0518(2)	0.5448(2)	3.50(8)
C(2)	0.3365(3)	-0.0256(2)	0.5625(2)	5.04(10)
C(3)	0.3682(4)	-0.0788(3)	0.4910(3)	9.2(2)
C(4)	0.3349(3)	-0.0624(2)	0.6530(3)	5.8(1)
C(5)	0.1585(2)	0.1595(2)	0.6326(2)	2.28(6)
C(6)	0.1329(2)	0.0817(2)	0.6525(2)	2.73(6)
C(7)	0.1239(2)	0.0575(2)	0.7399(2)	2.73(6)
C(8)	0.1402(2)	0.1096(2)	0.8128(2)	2.38(6)
C(9)	0.1672(2)	0.1869(2)	0.7940(2)	2.52(6)
C(10)	0.1775(2)	0.2114(1)	0.7064(2)	2.36(6)
C(11)	0.1345(2)	0.0836(2)	0.9103(2)	2.85(7)
C(12)	0.1093(3)	-0.0054(2)	0.9182(3)	6.2(1)
C(13)	0.2321(3)	0.0903(3)	0.9645(2)	5.9(1)
C(14)	0.0645(4)	0.1309(3)	0.9517(3)	7.7(1)
C(15)	0.3047(2)	0.2294(2)	0.3141(2)	2.90(7)
C(16)	0.3027(3)	0.3174(2)	0.3383(3)	4.42(9)
C(17)	0.3982(3)	0.1918(2)	0.3559(3)	4.30(9)
C(18)	0.2258(2)	0.0702(2)	0.3197(2)	2.76(7)
C(19)	0.1520(3)	0.0139(2)	0.3475(2)	3.98(8)
C(20)	0.2401(3)	0.0560(2)	0.2210(2)	4.26(9)
C(21)	0.1088(2)	0.2018(2)	0.2539(2)	2.36(6)
C(22)	0.1116(2)	0.2585(2)	0.1821(2)	3.03(7)
C(23)	0.0222(3)	0.2604(2)	0.1293(2)	3.78(8)
C(24)	-0.0368(2)	0.2057(2)	0.1662(2)	3.77(8)
C(25)	0.0161(2)	0.1694(2)	0.2427(2)	2.85(7)
C(26)	0.0576(2)	0.3759(1)	0.3514(2)	2.74(6)
C(27)	-0.0008(3)	0.4096(2)	0.2764(2)	3.34(7)
C(28)	-0.0890(3)	0.3743(2)	0.2694(2)	3.65(8)
C(29)	-0.0884(2)	0.3179(2)	0.3402(2)	2.95(7)

C(30)	0.0031(2)	0.3177(1)	0.3923(2)	2.24(6)
C(31)	-0.0672(2)	0.2113(2)	0.5172(2)	2.63(6)
C(32)	-0.0812(2)	0.1328(2)	0.4650(2)	3.65(8)
C(33)	-0.0760(2)	0.1981(2)	0.6173(2)	3.28(8)
C(34)	0.0561(2)	0.3449(1)	0.5793(2)	2.55(6)
C(35)	0.1471(2)	0.3910(2)	0.5754(2)	3.27(7)
C(36)	-0.0285(2)	0.4013(2)	0.5710(2)	3.67(8)
H(1)	0.4292	-0.0989	0.5117	11.0542
H(2)	0.3254	-0.1221	0.4792	11.0542
H(3)	0.3698	-0.0489	0.4371	11.0542
H(4)	0.3224	-0.0223	0.6950	6.9258
H(5)	0.2871	-0.1020	0.6492	6.9258
H(6)	0.3942	-0.0864	0.6727	6.9258
H(7)	0.1212	0.0441	0.6046	3.2764
H(8)	0.1062	0.0038	0.7502	3.2753
H(9)	0.1791	0.2242	0.8422	3.0268
H(10)	0.1977	0.2645	0.6967	2.8291
H(11)	0.1500	-0.0369	0.8874	7.4845
H(12)	0.0460	-0.0139	0.8919	7.4845
H(13)	0.1163	-0.0203	0.9803	7.4845
H(14)	0.2775	0.0691	0.9301	7.0836
H(15)	0.2338	0.0612	1.0194	7.0836
H(16)	0.2460	0.1450	0.9778	7.0836
H(17)	0.0048	0.1264	0.9158	9.2123
H(18)	0.0832	0.1854	0.9551	9.2123
H(19)	0.0605	0.1113	1.0109	9.2123
H(20)	0.3019	0.2259	0.2502	3.4841
H(21)	0.2429	0.3392	0.3157	5.3035
H(22)	0.3135	0.3233	0.4022	5.3035
H(23)	0.3503	0.3449	0.3121	5.3035
H(24)	0.4006	0.1898	0.4198	5.1617
H(25)	0.4490	0.2231	0.3407	5.1617
H(26)	0.4028	0.1391	0.3329	5.1617
H(27)	0.2835	0.0567	0.3555	3.3097
H(28)	0.1691	-0.0397	0.3366	4.7768
H(29)	0.1478	0.0208	0.4101	4.7768
H(30)	0.0928	0.0255	0.3133	4.7768
H(31)	0.2887	0.0900	0.2059	5.1161

H(32)	0.2570	0.0018	0.2133	5.1161
H(33)	0.1833	0.0676	0.1826	5.1161
H(34)	0.1647	0.2895	0.1718	3.6352
H(35)	0.0048	0.2931	0.0776	4.5306
H(36)	-0.1007	0.1950	0.1438	4.5260
H(37)	-0.0066	0.1300	0.2802	3.4254
H(38)	0.1214	0.3894	0.3710	3.2840
H(39)	0.0176	0.4499	0.2374	4.0122
H(40)	-0.1409	0.3859	0.2247	4.3748
H(41)	-0.1400	0.2856	0.3514	3.5404
H(42)	-0.1177	0.2454	0.4938	3.1603
H(43)	-0.0312	0.0972	0.4856	4.3760
H(44)	-0.0816	0.1428	0.4022	4.3760
H(45)	-0.1394	0.1094	0.4747	4.3760
H(46)	-0.1387	0.1830	0.6233	3.9380
H(47)	-0.0606	0.2461	0.6500	3.9380
H(48)	-0.0340	0.1568	0.6407	3.9380
H(49)	0.0608	0.3211	0.6376	3.0650
H(50)	0.1399	0.4249	0.5238	3.9206
H(51)	0.1970	0.3544	0.5714	3.9206
H(52)	0.1610	0.4224	0.6286	3.9206
H(53)	-0.0177	0.4422	0.6154	4.4089
H(54)	-0.0833	0.3721	0.5800	4.4089
H(55)	-0.0372	0.4247	0.5124	4.4089

$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 8. Anisotropic Displacement Parameters for **6**.

atom	U11	U22	U33	U12	U13	U23
Pd(1)	0.0337(1)	0.0250(1)	0.0174(1)	0.00114(8)	0.00400(9)	-0.00005(8)
Fe(1)	0.0399(3)	0.0326(2)	0.0212(2)	0.0011(2)	0.0006(2)	0.0012(2)
P(1)	0.0337(5)	0.0265(3)	0.0204(4)	-0.0022(3)	0.0063(3)	0.0005(3)
P(2)	0.0330(4)	0.0224(3)	0.0204(4)	-0.0004(3)	0.0047(3)	-0.0004(3)
N(1)	0.043(2)	0.050(2)	0.025(1)	0.014(1)	0.003(1)	0.004(1)
C(1)	0.053(2)	0.054(2)	0.024(2)	0.021(2)	-0.003(1)	-0.006(1)
C(2)	0.084(3)	0.057(2)	0.044(2)	0.032(2)	-0.016(2)	-0.014(2)
C(3)	0.150(5)	0.105(4)	0.085(3)	0.089(4)	-0.022(3)	-0.038(3)
C(4)	0.089(3)	0.042(2)	0.077(3)	0.007(2)	-0.031(2)	0.003(2)
C(5)	0.036(2)	0.033(1)	0.017(1)	0.002(1)	0.003(1)	0.001(1)
C(6)	0.048(2)	0.032(1)	0.024(2)	0.000(1)	0.004(1)	-0.002(1)
C(7)	0.040(2)	0.034(1)	0.030(2)	-0.001(1)	0.005(1)	0.004(1)
C(8)	0.029(2)	0.038(1)	0.023(1)	0.003(1)	0.004(1)	0.005(1)
C(9)	0.032(2)	0.041(2)	0.022(2)	0.004(1)	0.000(1)	-0.003(1)
C(10)	0.038(2)	0.028(1)	0.023(2)	0.001(1)	0.002(1)	0.000(1)
C(11)	0.040(2)	0.045(2)	0.025(2)	-0.002(1)	0.011(1)	0.005(1)
C(12)	0.115(4)	0.070(2)	0.054(2)	-0.009(2)	0.018(2)	0.019(2)
C(13)	0.067(3)	0.112(3)	0.043(2)	-0.011(2)	-0.002(2)	0.032(2)
C(14)	0.134(5)	0.104(3)	0.067(3)	0.058(3)	0.061(3)	0.041(3)
C(15)	0.035(2)	0.042(2)	0.035(2)	-0.004(1)	0.009(1)	0.006(1)
C(16)	0.049(2)	0.048(2)	0.071(3)	-0.018(2)	0.009(2)	0.009(2)
C(17)	0.037(2)	0.065(2)	0.063(3)	-0.006(2)	0.012(2)	0.011(2)
C(18)	0.051(2)	0.029(1)	0.026(2)	0.003(1)	0.007(1)	-0.002(1)
C(19)	0.071(3)	0.029(1)	0.054(2)	-0.006(2)	0.015(2)	0.002(1)
C(20)	0.082(3)	0.046(2)	0.037(2)	0.006(2)	0.019(2)	-0.010(1)
C(21)	0.040(2)	0.033(1)	0.018(1)	0.004(1)	0.007(1)	-0.002(1)
C(22)	0.049(2)	0.044(2)	0.024(2)	0.002(1)	0.009(1)	0.004(1)
C(23)	0.067(3)	0.054(2)	0.021(2)	0.011(2)	0.000(2)	-0.001(1)
C(24)	0.048(2)	0.054(2)	0.037(2)	0.002(2)	-0.013(2)	-0.015(2)
C(25)	0.044(2)	0.033(1)	0.031(2)	-0.005(1)	0.003(1)	-0.008(1)
C(26)	0.051(2)	0.026(1)	0.027(2)	-0.003(1)	0.006(1)	-0.001(1)
C(27)	0.067(3)	0.028(1)	0.032(2)	0.005(1)	0.008(2)	0.006(1)
C(28)	0.059(2)	0.047(2)	0.030(2)	0.024(2)	0.000(2)	0.001(1)
C(29)	0.034(2)	0.044(2)	0.034(2)	0.007(1)	0.004(1)	-0.001(1)
C(30)	0.036(2)	0.026(1)	0.023(1)	0.002(1)	0.003(1)	-0.003(1)

C(31)	0.034(2)	0.033(1)	0.035(2)	-0.001(1)	0.010(1)	0.000(1)
C(32)	0.051(2)	0.041(2)	0.049(2)	-0.016(2)	0.015(2)	-0.009(1)
C(33)	0.049(2)	0.041(2)	0.039(2)	-0.003(1)	0.024(2)	0.002(1)
C(34)	0.049(2)	0.025(1)	0.022(1)	0.002(1)	0.002(1)	-0.004(1)
C(35)	0.060(2)	0.032(1)	0.030(2)	-0.010(1)	-0.001(1)	-0.007(1)
C(36)	0.069(3)	0.030(1)	0.041(2)	0.014(2)	0.008(2)	-0.010(1)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 9. Bond Lengths(Å) for **6**.

atom	atom	distance	atom	atom	distance
Pd(1)	P(1)	2.3890(8)	Pd(1)	P(2)	2.2936(7)
Pd(1)	N(1)	2.067(2)	Pd(1)	C(5)	2.052(3)
Fe(1)	C(21)	2.026(3)	Fe(1)	C(22)	2.040(3)
Fe(1)	C(23)	2.051(3)	Fe(1)	C(24)	2.041(3)
Fe(1)	C(25)	2.018(3)	Fe(1)	C(26)	2.028(3)
Fe(1)	C(27)	2.043(3)	Fe(1)	C(28)	2.047(3)
Fe(1)	C(29)	2.033(3)	Fe(1)	C(30)	2.030(3)
P(1)	C(15)	1.852(3)	P(1)	C(18)	1.853(3)
P(1)	C(21)	1.824(3)	P(2)	C(30)	1.821(3)
P(2)	C(31)	1.857(3)	P(2)	C(34)	1.864(3)
N(1)	C(1)	1.197(4)	C(1)	C(2)	1.351(4)
C(2)	C(3)	1.504(5)	C(2)	C(4)	1.486(5)
C(5)	C(6)	1.394(4)	C(5)	C(10)	1.401(4)
C(6)	C(7)	1.388(4)	C(7)	C(8)	1.389(4)
C(8)	C(9)	1.388(4)	C(8)	C(11)	1.530(4)
C(9)	C(10)	1.395(4)	C(11)	C(12)	1.540(4)
C(11)	C(13)	1.524(5)	C(11)	C(14)	1.477(5)
C(15)	C(16)	1.517(4)	C(15)	C(17)	1.535(4)
C(18)	C(19)	1.515(4)	C(18)	C(20)	1.530(4)
C(21)	C(22)	1.435(4)	C(21)	C(25)	1.425(4)
C(22)	C(23)	1.412(4)	C(23)	C(24)	1.407(5)
C(24)	C(25)	1.417(4)	C(26)	C(27)	1.419(4)
C(26)	C(30)	1.434(4)	C(27)	C(28)	1.388(4)
C(28)	C(29)	1.414(4)	C(29)	C(30)	1.431(4)
C(31)	C(32)	1.527(4)	C(31)	C(33)	1.530(4)
C(34)	C(35)	1.522(4)	C(34)	C(36)	1.528(4)

Table 10. Bond Angles(°) of **6**.

atom	atom	atom	angle	atom	atom	atom	angle
P(1)	Pd(1)	P(2)	103.57(3)	P(1)	Pd(1)	N(1)	87.01(7)
P(1)	Pd(1)	C(5)	165.79(8)	P(2)	Pd(1)	N(1)	167.97(7)
P(2)	Pd(1)	C(5)	86.90(8)	N(1)	Pd(1)	C(5)	83.7(1)
C(21)	Fe(1)	C(22)	41.3(1)	C(21)	Fe(1)	C(23)	69.0(1)
C(21)	Fe(1)	C(24)	69.2(1)	C(21)	Fe(1)	C(25)	41.3(1)
C(21)	Fe(1)	C(26)	112.8(1)	C(21)	Fe(1)	C(27)	141.9(1)
C(21)	Fe(1)	C(28)	178.4(1)	C(21)	Fe(1)	C(29)	138.3(1)
C(21)	Fe(1)	C(30)	110.8(1)	C(22)	Fe(1)	C(23)	40.4(1)
C(22)	Fe(1)	C(24)	68.2(1)	C(22)	Fe(1)	C(25)	68.7(1)
C(22)	Fe(1)	C(26)	111.8(1)	C(22)	Fe(1)	C(27)	112.9(1)
C(22)	Fe(1)	C(28)	139.8(1)	C(22)	Fe(1)	C(29)	179.4(1)
C(22)	Fe(1)	C(30)	139.0(1)	C(23)	Fe(1)	C(24)	40.2(1)
C(23)	Fe(1)	C(25)	68.3(1)	C(23)	Fe(1)	C(26)	138.0(1)
C(23)	Fe(1)	C(27)	110.7(1)	C(23)	Fe(1)	C(28)	111.1(1)
C(23)	Fe(1)	C(29)	139.4(1)	C(23)	Fe(1)	C(30)	179.3(1)
C(24)	Fe(1)	C(25)	40.9(1)	C(24)	Fe(1)	C(26)	177.1(1)
C(24)	Fe(1)	C(27)	136.3(1)	C(24)	Fe(1)	C(28)	109.8(1)
C(24)	Fe(1)	C(29)	111.3(1)	C(24)	Fe(1)	C(30)	140.4(1)
C(25)	Fe(1)	C(26)	142.0(1)	C(25)	Fe(1)	C(27)	176.5(1)
C(25)	Fe(1)	C(28)	137.2(1)	C(25)	Fe(1)	C(29)	110.7(1)
C(25)	Fe(1)	C(30)	112.0(1)	C(26)	Fe(1)	C(27)	40.8(1)
C(26)	Fe(1)	C(28)	68.2(1)	C(26)	Fe(1)	C(29)	68.7(1)
C(26)	Fe(1)	C(30)	41.4(1)	C(27)	Fe(1)	C(28)	39.7(1)
C(27)	Fe(1)	C(29)	67.7(1)	C(27)	Fe(1)	C(30)	69.0(1)
C(28)	Fe(1)	C(29)	40.6(1)	C(28)	Fe(1)	C(30)	69.1(1)
C(29)	Fe(1)	C(30)	41.2(1)	Pd(1)	P(1)	C(15)	117.41(9)
Pd(1)	P(1)	C(18)	108.16(9)	Pd(1)	P(1)	C(21)	121.2(1)
C(15)	P(1)	C(18)	102.9(1)	C(15)	P(1)	C(21)	102.6(1)
C(18)	P(1)	C(21)	102.2(1)	Pd(1)	P(2)	C(30)	119.1(1)
Pd(1)	P(2)	C(31)	116.51(9)	Pd(1)	P(2)	C(34)	113.36(10)
C(30)	P(2)	C(31)	101.9(1)	C(30)	P(2)	C(34)	100.2(1)
C(31)	P(2)	C(34)	103.5(1)	Pd(1)	N(1)	C(1)	130.5(3)
N(1)	C(1)	C(2)	176.2(4)	C(1)	C(2)	C(3)	120.9(4)

C(1)	C(2)	C(4)	122.8(3)	C(3)	C(2)	C(4)	116.2(3)
Pd(1)	C(5)	C(6)	116.7(2)	Pd(1)	C(5)	C(10)	127.0(2)
C(6)	C(5)	C(10)	116.1(2)	C(5)	C(6)	C(7)	122.2(2)
C(6)	C(7)	C(8)	121.6(2)	C(7)	C(8)	C(9)	116.7(2)
C(7)	C(8)	C(11)	122.6(2)	C(9)	C(8)	C(11)	120.6(2)
C(8)	C(9)	C(10)	122.1(2)	C(5)	C(10)	C(9)	121.3(2)
C(8)	C(11)	C(12)	113.0(2)	C(8)	C(11)	C(13)	108.6(3)
C(8)	C(11)	C(14)	111.8(3)	C(12)	C(11)	C(13)	103.8(3)
C(12)	C(11)	C(14)	107.8(3)	C(13)	C(11)	C(14)	111.5(3)
P(1)	C(15)	C(16)	111.6(2)	P(1)	C(15)	C(17)	112.7(2)
C(16)	C(15)	C(17)	110.2(3)	P(1)	C(18)	C(19)	111.8(2)
P(1)	C(18)	C(20)	113.8(2)	C(19)	C(18)	C(20)	110.9(2)
Fe(1)	C(21)	P(1)	124.3(1)	Fe(1)	C(21)	C(22)	69.8(2)
Fe(1)	C(21)	C(25)	69.1(2)	P(1)	C(21)	C(22)	128.9(2)
P(1)	C(21)	C(25)	124.6(2)	C(22)	C(21)	C(25)	106.5(2)
Fe(1)	C(22)	C(21)	68.8(2)	Fe(1)	C(22)	C(23)	70.2(2)
C(21)	C(22)	C(23)	108.4(3)	Fe(1)	C(23)	C(22)	69.4(2)
Fe(1)	C(23)	C(24)	69.5(2)	C(22)	C(23)	C(24)	108.4(3)
Fe(1)	C(24)	C(23)	70.3(2)	Fe(1)	C(24)	C(25)	68.7(2)
C(23)	C(24)	C(25)	108.0(3)	Fe(1)	C(25)	C(21)	69.7(2)
Fe(1)	C(25)	C(24)	70.4(2)	C(21)	C(25)	C(24)	108.7(3)
Fe(1)	C(26)	C(27)	70.2(2)	Fe(1)	C(26)	C(30)	69.4(1)
C(27)	C(26)	C(30)	107.9(3)	Fe(1)	C(27)	C(26)	69.0(1)
Fe(1)	C(27)	C(28)	70.3(2)	C(26)	C(27)	C(28)	108.9(3)
Fe(1)	C(28)	C(27)	70.0(2)	Fe(1)	C(28)	C(29)	69.2(2)
C(27)	C(28)	C(29)	108.2(3)	Fe(1)	C(29)	C(28)	70.2(2)
Fe(1)	C(29)	C(30)	69.3(2)	C(28)	C(29)	C(30)	108.7(3)
Fe(1)	C(30)	P(2)	129.4(1)	Fe(1)	C(30)	C(26)	69.2(2)
Fe(1)	C(30)	C(29)	69.5(2)	P(2)	C(30)	C(26)	125.4(2)
P(2)	C(30)	C(29)	128.1(2)	C(26)	C(30)	C(29)	106.3(2)
P(2)	C(31)	C(32)	110.9(2)	P(2)	C(31)	C(33)	114.9(2)
C(32)	C(31)	C(33)	110.5(2)	P(2)	C(34)	C(35)	111.2(2)
P(2)	C(34)	C(36)	113.4(2)	C(35)	C(34)	C(36)	111.1(2)

Table 11. Torsion Angles(°) of **6**.

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Pd(1)	P(1)	C(15)	C(16)	-56.3(2)	Pd(1)	P(1)	C(15)	C(17)	68.3(2)
Pd(1)	P(1)	C(18)	C(19)	50.8(2)	Pd(1)	P(1)	C(18)	C(20)	177.4(2)
Pd(1)	P(1)	C(21)	Fe(1)	34.5(2)	Pd(1)	P(1)	C(21)	C(22)	125.4(2)
Pd(1)	P(1)	C(21)	C(25)	-52.4(3)	Pd(1)	P(2)	C(30)	Fe(1)	32.5(2)
Pd(1)	P(2)	C(30)	C(26)	-58.7(2)	Pd(1)	P(2)	C(30)	C(29)	126.5(2)
Pd(1)	P(2)	C(31)	C(32)	-45.4(2)	Pd(1)	P(2)	C(31)	C(33)	80.8(2)
Pd(1)	P(2)	C(34)	C(35)	49.5(2)	Pd(1)	P(2)	C(34)	C(36)	175.5(2)
Pd(1)	N(1)	C(1)	C(2)	-155(5)	Pd(1)	C(5)	C(6)	C(7)	177.2(2)
Pd(1)	C(5)	C(10)	C(9)	-177.4(2)	Fe(1)	C(21)	P(1)	C(15)	-98.9(2)
Fe(1)	C(21)	P(1)	C(18)	154.7(2)	Fe(1)	C(21)	C(22)	C(23)	-59.2(2)
Fe(1)	C(21)	C(25)	C(24)	59.8(2)	Fe(1)	C(22)	C(21)	P(1)	-118.4(2)
Fe(1)	C(22)	C(21)	C(25)	59.7(2)	Fe(1)	C(22)	C(23)	C(24)	-58.7(2)
Fe(1)	C(23)	C(22)	C(21)	58.4(2)	Fe(1)	C(23)	C(24)	C(25)	-58.5(2)
Fe(1)	C(24)	C(23)	C(22)	58.6(2)	Fe(1)	C(24)	C(25)	C(21)	-59.3(2)
Fe(1)	C(25)	C(21)	P(1)	118.0(2)	Fe(1)	C(25)	C(21)	C(22)	-60.2(2)
Fe(1)	C(25)	C(24)	C(23)	59.5(2)	Fe(1)	C(26)	C(27)	C(28)	59.1(2)
Fe(1)	C(26)	C(30)	P(2)	124.3(2)	Fe(1)	C(26)	C(30)	C(29)	-60.0(2)
Fe(1)	C(27)	C(26)	C(30)	-59.4(2)	Fe(1)	C(27)	C(28)	C(29)	58.8(2)
Fe(1)	C(28)	C(27)	C(26)	-58.3(2)	Fe(1)	C(28)	C(29)	C(30)	58.8(2)
Fe(1)	C(29)	C(28)	C(27)	-59.3(2)	Fe(1)	C(29)	C(30)	P(2)	-124.6(2)
Fe(1)	C(29)	C(30)	C(26)	59.8(2)	Fe(1)	C(30)	P(2)	C(31)	-97.2(2)
Fe(1)	C(30)	P(2)	C(34)	156.6(2)	Fe(1)	C(30)	C(26)	C(27)	59.9(2)
Fe(1)	C(30)	C(29)	C(28)	-59.4(2)	P(1)	Pd(1)	P(2)	C(30)	-13.0(1)
P(1)	Pd(1)	P(2)	C(31)	109.7(1)	P(1)	Pd(1)	P(2)	C(34)	-130.4(1)
P(1)	Pd(1)	N(1)	C(1)	-96.8(3)	P(1)	Pd(1)	C(5)	C(6)	-26.3(5)
P(1)	Pd(1)	C(5)	C(10)	148.4(2)	P(1)	C(21)	Fe(1)	C(22)	124.0(3)
P(1)	C(21)	Fe(1)	C(23)	161.0(2)	P(1)	C(21)	Fe(1)	C(24)	-155.8(2)
P(1)	C(21)	Fe(1)	C(25)	-118.3(3)	P(1)	C(21)	Fe(1)	C(26)	26.5(2)
P(1)	C(21)	Fe(1)	C(27)	63.9(3)	P(1)	C(21)	Fe(1)	C(28)	-103(3)
P(1)	C(21)	Fe(1)	C(29)	-56.7(3)	P(1)	C(21)	Fe(1)	C(30)	-18.2(2)
P(1)	C(21)	C(22)	C(23)	-177.6(2)	P(1)	C(21)	C(25)	C(24)	177.8(2)
P(2)	Pd(1)	P(1)	C(15)	109.6(1)	P(2)	Pd(1)	P(1)	C(18)	-134.6(1)
P(2)	Pd(1)	P(1)	C(21)	-17.3(1)	P(2)	Pd(1)	N(1)	C(1)	111.3(4)

P(2)	Pd(1)	C(5)	C(6)	111.7(2)	P(2)	Pd(1)	C(5)	C(10)	-73.6(3)
P(2)	C(30)	Fe(1)	C(21)	-18.0(2)	P(2)	C(30)	Fe(1)	C(22)	-56.1(3)
P(2)	C(30)	Fe(1)	C(23)	-93(8)	P(2)	C(30)	Fe(1)	C(24)	64.2(3)
P(2)	C(30)	Fe(1)	C(25)	26.4(2)	P(2)	C(30)	Fe(1)	C(26)	-119.4(3)
P(2)	C(30)	Fe(1)	C(27)	-157.2(2)	P(2)	C(30)	Fe(1)	C(28)	160.2(2)
P(2)	C(30)	Fe(1)	C(29)	123.1(3)	P(2)	C(30)	C(26)	C(27)	-175.9(2)
P(2)	C(30)	C(29)	C(28)	176.0(2)	N(1)	Pd(1)	P(1)	C(15)	-64.6(1)
N(1)	Pd(1)	P(1)	C(18)	51.2(1)	N(1)	Pd(1)	P(1)	C(21)	168.5(1)
N(1)	Pd(1)	P(2)	C(30)	138.1(4)	N(1)	Pd(1)	P(2)	C(31)	-99.2(4)
N(1)	Pd(1)	P(2)	C(34)	20.7(4)	N(1)	Pd(1)	C(5)	C(6)	-75.9(2)
N(1)	Pd(1)	C(5)	C(10)	98.9(3)	N(1)	C(1)	C(2)	C(3)	-105(5)
N(1)	C(1)	C(2)	C(4)	72(5)	C(1)	N(1)	Pd(1)	C(5)	72.5(3)
C(5)	Pd(1)	P(1)	C(15)	-113.8(3)	C(5)	Pd(1)	P(1)	C(18)	2.0(3)
C(5)	Pd(1)	P(1)	C(21)	119.2(3)	C(5)	Pd(1)	P(2)	C(30)	176.7(1)
C(5)	Pd(1)	P(2)	C(31)	-60.6(1)	C(5)	Pd(1)	P(2)	C(34)	59.3(1)
C(5)	C(6)	C(7)	C(8)	-0.1(5)	C(5)	C(10)	C(9)	C(8)	1.7(5)
C(6)	C(5)	C(10)	C(9)	-2.6(4)	C(6)	C(7)	C(8)	C(9)	-0.9(4)
C(6)	C(7)	C(8)	C(11)	-177.6(3)	C(7)	C(6)	C(5)	C(10)	1.8(4)
C(7)	C(8)	C(9)	C(10)	0.1(4)	C(7)	C(8)	C(11)	C(12)	0.2(4)
C(7)	C(8)	C(11)	C(13)	114.8(3)	C(7)	C(8)	C(11)	C(14)	-121.7(4)
C(9)	C(8)	C(11)	C(12)	-176.4(3)	C(9)	C(8)	C(11)	C(13)	-61.8(4)
C(9)	C(8)	C(11)	C(14)	61.7(4)	C(10)	C(9)	C(8)	C(11)	176.9(3)
C(15)	P(1)	C(18)	C(19)	175.7(2)	C(15)	P(1)	C(18)	C(20)	-57.7(2)
C(15)	P(1)	C(21)	C(22)	-8.0(3)	C(15)	P(1)	C(21)	C(25)	174.2(2)
C(16)	C(15)	P(1)	C(18)	-174.9(2)	C(16)	C(15)	P(1)	C(21)	79.3(2)
C(17)	C(15)	P(1)	C(18)	-50.4(2)	C(17)	C(15)	P(1)	C(21)	-156.2(2)
C(18)	P(1)	C(21)	C(22)	-114.4(3)	C(18)	P(1)	C(21)	C(25)	67.9(3)
C(19)	C(18)	P(1)	C(21)	-78.2(2)	C(20)	C(18)	P(1)	C(21)	48.4(3)
C(21)	Fe(1)	C(22)	C(23)	120.0(2)	C(21)	Fe(1)	C(23)	C(22)	-37.8(2)
C(21)	Fe(1)	C(23)	C(24)	82.3(2)	C(21)	Fe(1)	C(24)	C(23)	-81.7(2)
C(21)	Fe(1)	C(24)	C(25)	37.8(2)	C(21)	Fe(1)	C(25)	C(24)	-119.7(3)
C(21)	Fe(1)	C(26)	C(27)	145.0(2)	C(21)	Fe(1)	C(26)	C(30)	-96.0(2)
C(21)	Fe(1)	C(27)	C(26)	-59.0(3)	C(21)	Fe(1)	C(27)	C(28)	-179.4(2)
C(21)	Fe(1)	C(28)	C(27)	168(3)	C(21)	Fe(1)	C(28)	C(29)	48(3)
C(21)	Fe(1)	C(29)	C(28)	-178.2(2)	C(21)	Fe(1)	C(29)	C(30)	61.9(2)
C(21)	Fe(1)	C(30)	C(26)	101.4(2)	C(21)	Fe(1)	C(30)	C(29)	-141.2(2)
C(21)	C(22)	Fe(1)	C(23)	-120.0(2)	C(21)	C(22)	Fe(1)	C(24)	-82.9(2)
C(21)	C(22)	Fe(1)	C(25)	-38.8(2)	C(21)	C(22)	Fe(1)	C(26)	100.2(2)

C(21)	C(22)	Fe(1)	C(27)	144.5(2)	C(21)	C(22)	Fe(1)	C(28)	-178.1(2)
C(21)	C(22)	Fe(1)	C(29)	-54(11)	C(21)	C(22)	Fe(1)	C(30)	60.7(2)
C(21)	C(22)	C(23)	C(24)	-0.3(3)	C(21)	C(25)	Fe(1)	C(22)	38.9(2)
C(21)	C(25)	Fe(1)	C(23)	82.4(2)	C(21)	C(25)	Fe(1)	C(24)	119.7(3)
C(21)	C(25)	Fe(1)	C(26)	-59.7(3)	C(21)	C(25)	Fe(1)	C(27)	156(2)
C(21)	C(25)	Fe(1)	C(28)	-179.4(2)	C(21)	C(25)	Fe(1)	C(29)	-141.3(2)
C(21)	C(25)	Fe(1)	C(30)	-96.9(2)	C(21)	C(25)	C(24)	C(23)	0.1(4)
C(22)	Fe(1)	C(21)	C(25)	-117.6(2)	C(22)	Fe(1)	C(23)	C(24)	120.0(3)
C(22)	Fe(1)	C(24)	C(23)	-37.2(2)	C(22)	Fe(1)	C(24)	C(25)	82.3(2)
C(22)	Fe(1)	C(25)	C(24)	-80.8(2)	C(22)	Fe(1)	C(26)	C(27)	100.2(2)
C(22)	Fe(1)	C(26)	C(30)	-140.9(2)	C(22)	Fe(1)	C(27)	C(26)	-97.4(2)
C(22)	Fe(1)	C(27)	C(28)	142.1(2)	C(22)	Fe(1)	C(28)	C(27)	-61.1(2)
C(22)	Fe(1)	C(28)	C(29)	179.2(2)	C(22)	Fe(1)	C(29)	C(28)	-123(11)
C(22)	Fe(1)	C(29)	C(30)	116(11)	C(22)	Fe(1)	C(30)	C(26)	63.3(2)
C(22)	Fe(1)	C(30)	C(29)	-179.2(2)	C(22)	C(21)	Fe(1)	C(23)	37.0(2)
C(22)	C(21)	Fe(1)	C(24)	80.2(2)	C(22)	C(21)	Fe(1)	C(25)	117.6(2)
C(22)	C(21)	Fe(1)	C(26)	-97.6(2)	C(22)	C(21)	Fe(1)	C(27)	-60.1(2)
C(22)	C(21)	Fe(1)	C(28)	132(3)	C(22)	C(21)	Fe(1)	C(29)	179.3(2)
C(22)	C(21)	Fe(1)	C(30)	-142.3(2)	C(22)	C(21)	C(25)	C(24)	-0.3(3)
C(22)	C(23)	Fe(1)	C(24)	-120.0(3)	C(22)	C(23)	Fe(1)	C(25)	-82.2(2)
C(22)	C(23)	Fe(1)	C(26)	63.5(2)	C(22)	C(23)	Fe(1)	C(27)	101.4(2)
C(22)	C(23)	Fe(1)	C(28)	144.0(2)	C(22)	C(23)	Fe(1)	C(29)	-179.2(2)
C(22)	C(23)	Fe(1)	C(30)	37(8)	C(22)	C(23)	C(24)	C(25)	0.1(4)
C(23)	Fe(1)	C(21)	C(25)	-80.6(2)	C(23)	Fe(1)	C(24)	C(25)	119.5(3)
C(23)	Fe(1)	C(25)	C(24)	-37.2(2)	C(23)	Fe(1)	C(26)	C(27)	61.5(3)
C(23)	Fe(1)	C(26)	C(30)	-179.5(2)	C(23)	Fe(1)	C(27)	C(26)	-141.0(2)
C(23)	Fe(1)	C(27)	C(28)	98.5(2)	C(23)	Fe(1)	C(28)	C(27)	-97.3(2)
C(23)	Fe(1)	C(28)	C(29)	143.1(2)	C(23)	Fe(1)	C(29)	C(28)	-59.4(3)
C(23)	Fe(1)	C(29)	C(30)	-179.3(2)	C(23)	Fe(1)	C(30)	C(26)	25(8)
C(23)	Fe(1)	C(30)	C(29)	143(8)	C(23)	C(22)	Fe(1)	C(24)	37.0(2)
C(23)	C(22)	Fe(1)	C(25)	81.1(2)	C(23)	C(22)	Fe(1)	C(26)	-139.8(2)
C(23)	C(22)	Fe(1)	C(27)	-95.5(2)	C(23)	C(22)	Fe(1)	C(28)	-58.2(3)
C(23)	C(22)	Fe(1)	C(29)	65(11)	C(23)	C(22)	Fe(1)	C(30)	-179.3(2)
C(23)	C(22)	C(21)	C(25)	0.4(3)	C(23)	C(24)	Fe(1)	C(25)	-119.5(3)
C(23)	C(24)	Fe(1)	C(26)	53(2)	C(23)	C(24)	Fe(1)	C(27)	63.6(3)
C(23)	C(24)	Fe(1)	C(28)	99.7(2)	C(23)	C(24)	Fe(1)	C(29)	143.1(2)
C(23)	C(24)	Fe(1)	C(30)	-179.6(2)	C(24)	Fe(1)	C(21)	C(25)	-37.4(2)
C(24)	Fe(1)	C(26)	C(27)	10(2)	C(24)	Fe(1)	C(26)	C(30)	129(2)

C(24)	Fe(1)	C(27)	C(26)	-179.2(2)	C(24)	Fe(1)	C(27)	C(28)	60.4(3)
C(24)	Fe(1)	C(28)	C(27)	-140.3(2)	C(24)	Fe(1)	C(28)	C(29)	100.0(2)
C(24)	Fe(1)	C(29)	C(28)	-95.9(2)	C(24)	Fe(1)	C(29)	C(30)	144.1(2)
C(24)	Fe(1)	C(30)	C(26)	-176.5(2)	C(24)	Fe(1)	C(30)	C(29)	-59.0(2)
C(24)	C(23)	Fe(1)	C(25)	37.8(2)	C(24)	C(23)	Fe(1)	C(26)	-176.5(2)
C(24)	C(23)	Fe(1)	C(27)	-138.6(2)	C(24)	C(23)	Fe(1)	C(28)	-96.0(2)
C(24)	C(23)	Fe(1)	C(29)	-59.1(3)	C(24)	C(23)	Fe(1)	C(30)	157(8)
C(24)	C(25)	Fe(1)	C(26)	-179.4(2)	C(24)	C(25)	Fe(1)	C(27)	36(2)
C(24)	C(25)	Fe(1)	C(28)	60.9(3)	C(24)	C(25)	Fe(1)	C(29)	99.0(2)
C(24)	C(25)	Fe(1)	C(30)	143.4(2)	C(25)	Fe(1)	C(26)	C(27)	-176.8(2)
C(25)	Fe(1)	C(26)	C(30)	-57.9(3)	C(25)	Fe(1)	C(27)	C(26)	146(2)
C(25)	Fe(1)	C(27)	C(28)	25(2)	C(25)	Fe(1)	C(28)	C(27)	-177.8(2)
C(25)	Fe(1)	C(28)	C(29)	62.6(2)	C(25)	Fe(1)	C(29)	C(28)	-139.8(2)
C(25)	Fe(1)	C(29)	C(30)	100.2(2)	C(25)	Fe(1)	C(30)	C(26)	145.8(2)
C(25)	Fe(1)	C(30)	C(29)	-96.7(2)	C(25)	C(21)	Fe(1)	C(26)	144.8(2)
C(25)	C(21)	Fe(1)	C(27)	-177.7(2)	C(25)	C(21)	Fe(1)	C(28)	14(3)
C(25)	C(21)	Fe(1)	C(29)	61.7(2)	C(25)	C(21)	Fe(1)	C(30)	100.1(2)
C(25)	C(24)	Fe(1)	C(26)	172(2)	C(25)	C(24)	Fe(1)	C(27)	-177.0(2)
C(25)	C(24)	Fe(1)	C(28)	-140.8(2)	C(25)	C(24)	Fe(1)	C(29)	-97.4(2)
C(25)	C(24)	Fe(1)	C(30)	-60.1(3)	C(26)	Fe(1)	C(27)	C(28)	-120.4(3)
C(26)	Fe(1)	C(28)	C(27)	37.4(2)	C(26)	Fe(1)	C(28)	C(29)	-82.3(2)
C(26)	Fe(1)	C(29)	C(28)	81.0(2)	C(26)	Fe(1)	C(29)	C(30)	-39.0(1)
C(26)	Fe(1)	C(30)	C(29)	117.5(2)	C(26)	C(27)	Fe(1)	C(28)	120.4(3)
C(26)	C(27)	Fe(1)	C(29)	82.8(2)	C(26)	C(27)	Fe(1)	C(30)	38.3(2)
C(26)	C(27)	C(28)	C(29)	0.5(3)	C(26)	C(30)	Fe(1)	C(27)	-37.8(2)
C(26)	C(30)	Fe(1)	C(28)	-80.4(2)	C(26)	C(30)	Fe(1)	C(29)	-117.5(2)
C(26)	C(30)	P(2)	C(31)	171.6(2)	C(26)	C(30)	P(2)	C(34)	65.4(3)
C(26)	C(30)	C(29)	C(28)	0.4(3)	C(27)	Fe(1)	C(26)	C(30)	119.0(3)
C(27)	Fe(1)	C(28)	C(29)	-119.6(2)	C(27)	Fe(1)	C(29)	C(28)	36.9(2)
C(27)	Fe(1)	C(29)	C(30)	-83.1(2)	C(27)	Fe(1)	C(30)	C(29)	79.7(2)
C(27)	C(26)	Fe(1)	C(28)	-36.4(2)	C(27)	C(26)	Fe(1)	C(29)	-80.1(2)
C(27)	C(26)	Fe(1)	C(30)	-119.0(3)	C(27)	C(26)	C(30)	C(29)	-0.1(3)
C(27)	C(28)	Fe(1)	C(29)	119.6(2)	C(27)	C(28)	Fe(1)	C(30)	82.0(2)
C(27)	C(28)	C(29)	C(30)	-0.6(3)	C(28)	Fe(1)	C(26)	C(30)	82.6(2)
C(28)	Fe(1)	C(29)	C(30)	-120.0(2)	C(28)	Fe(1)	C(30)	C(29)	37.1(2)
C(28)	C(27)	Fe(1)	C(29)	-37.6(2)	C(28)	C(27)	Fe(1)	C(30)	-82.1(2)
C(28)	C(27)	C(26)	C(30)	-0.2(3)	C(28)	C(29)	Fe(1)	C(30)	120.0(2)
C(29)	Fe(1)	C(26)	C(30)	38.9(2)	C(29)	C(28)	Fe(1)	C(30)	-37.7(2)

C(29)	C(30)	P(2)	C(31)	-3.2(3)	C(29)	C(30)	P(2)	C(34)	-109.4(3)
C(30)	P(2)	C(31)	C(32)	85.8(2)	C(30)	P(2)	C(31)	C(33)	-147.9(2)
C(30)	P(2)	C(34)	C(35)	-78.5(2)	C(30)	P(2)	C(34)	C(36)	47.5(2)
C(31)	P(2)	C(34)	C(35)	176.6(2)	C(31)	P(2)	C(34)	C(36)	-57.4(2)
C(32)	C(31)	P(2)	C(34)	-170.5(2)	C(33)	C(31)	P(2)	C(34)	-44.3(2)

Table 12. Non-bonded Contacts out to 3.60 Å for **6**.

atom	atom	distance	ADC	atom	atom	distance	ADC
C(9)	C(29)	3.481(4)	4	C(13)	C(36)	3.585(5)	4
C(14)	C(23)	3.535(6)	55601				

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus $\pm$4 lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure are given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

(1)	X,	Y,	Z	(2)	1/2-X, 1/2+Y, 1/2-Z
(3)	-X,	-Y,	-Z	(4)	1/2+X, 1/2-Y, 1/2+Z

Experimental details for the crystal structure determination of **9**.

Data Collection

A colorless plate crystal of $C_{25}H_{28}NPPd$ having approximate dimensions of 0.08 x 0.12 x 0.17 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1^o in ω, 10s exposure, de-zingered) data frames, corresponded to a C-centered monoclinic cell with dimensions: a = 29.992(1) Å, b = 8.6350(3) Å, β = 94.839(2)^o, c = 17.599(1) Å, and V = 4541.5(3) Å^3. For Z = 8 and F.W. = 479.88, the calculated density is 1.40 g/cm^3. Based on the systematic absences of: hkl: h+k = 2n+1; h0l: l = 2n+1; packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of thestructure, the space group was determined to be: C2/c (#15). The molecule is dimeric and located on a crystallographic inversion center.

The data were collected at a temperature of -90 ± 1^{o}C to a maximum 2θ value of 55.0^o. Four omega scans consisting of 66, 55, 66, and 66 data frames, respectively, were collected with a scan width of 1.9^o and a detector-to-crystal distance, Dx, of 40mm. Each frame was exposed twice (for the purpose of de-zingering) for 228s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, "Processing of X-Ray Diffraction Data Collected in Oscillation Mode," Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

A total of 5562 reflections was collected. No decay correction was applied. The linear absorption coefficient, μ, for Mo-Kα radiation is 9.0 cm^{-1} and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not

refined. In the case of the methyl group hydrogen atoms, one hydrogen was located in the difference map and included at an idealized distance to set the orientation of the other two hydrogen atoms. The final cycle of full-matrix least-squares refinement[3] was based on 2796 observed reflections ($I > 5.00\sigma(I)$) and 253 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.031$$

$$R_W = [(\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2)]^{1/2} = 0.031$$

The standard deviation of an observation of unit weight[4] was 1.57. The weighting scheme was based on counting statistics and included a factor ($p = 0.010$) to downweight the intense reflections. Plots of $\Sigma \, w \, (|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.40 and -0.33 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., & Polidori, G.; *J. Appl. Cryst.*, 27, 435-436 (1994).

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized $Sw(|F_O|-|F_C|)^2$

where $w = 4F_O^2/2(F_O^2)$

and $s^2(F_O^2) = [S^2(C+R^2B) + (pF_O^2)^2]/Lp^2$

S = Scan rate

C = Total integrated peak count
R = Ratio of scan time to background counting time
B = Total background count
Lp = Lorentz-polarization factor
p = p-factor

(4) Standard deviation of an observation of unit weight:

$$[S w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$$

where N_o = number of observations
N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr.*, 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

Experimental details for **9**.

A. Crystal Data

Empirical Formula	$C_{25}H_{28}NPPd$
Formula Weight	479.88
Crystal Color, Habit	colorless, plate
Crystal Dimensions	0.08 X 0.12 X 0.17 mm
Crystal System	monoclinic
Lattice Type	C-centered
Lattice Parameters	a = 29.992(1)Å b = 8.6350(3) Å c = 17.599(1) Å β = 94.839(2)° V = 4541.5(3) Å^3
Space Group	C2/c (#15)
Z value	8
D_{calc}	1.404 g/cm^3
F_{000}	1968.00
μ(MoK_)	8.98 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD

Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Take-off Angle	2.8°
Crystal to Detector Distance	40 mm
Temperature	-90.0°C
Scan Type	ω
Scan Rate	228s/frame
Scan Width	1.9°/frame
2_max	55.0°
No. of Reflections Measured	Total: 5562
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	$1/\sigma^2$(Fo)
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>5.00_(I))	2796

No. Variables	253
Reflection/Parameter Ratio	11.05
Residuals: R; Rw	0.031 ; 0.031
Goodness of Fit Indicator	1.57
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.40 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.33 $e^-/Å^3$

Table 13. Atomic coordinates and B_{iso}/B_{eq} for **9**.

atom	x	y	z	Beq
Pd(1)	0.834629(9)	0.18040(4)	-0.01529(2)	1.869(7)
P(1)	0.87858(3)	0.0379(1)	0.07309(5)	1.90(2)
N(1)	0.7218(1)	0.3624(4)	-0.0455(2)	2.25(8)
C(1)	0.7953(1)	0.2992(5)	-0.1072(2)	2.14(9)
C(2)	0.7543(1)	0.3357(4)	-0.0737(2)	1.91(9)
C(3)	0.8140(1)	0.4463(5)	-0.1395(2)	3.2(1)
C(4)	0.7858(1)	0.1784(5)	-0.1706(2)	3.4(1)
C(5)	0.8895(1)	0.2501(5)	-0.0625(2)	1.82(9)
C(6)	0.9118(1)	0.3797(4)	-0.0325(2)	2.03(9)
C(7)	0.9509(1)	0.4327(4)	-0.0602(2)	2.15(9)
C(8)	0.9702(1)	0.3581(4)	-0.1180(2)	2.06(10)
C(9)	0.9481(1)	0.2303(5)	-0.1495(2)	2.31(10)
C(10)	0.9081(1)	0.1785(5)	-0.1235(2)	2.15(9)
C(11)	1.0141(1)	0.4124(5)	-0.1439(2)	3.1(1)
C(12)	0.8846(1)	0.1291(4)	0.1669(2)	2.00(9)
C(13)	0.9236(1)	0.2040(5)	0.1946(2)	3.4(1)
C(14)	0.9263(2)	0.2753(5)	0.2647(3)	4.2(1)
C(15)	0.8910(2)	0.2748(5)	0.3080(2)	3.6(1)
C(16)	0.8516(2)	0.2029(5)	0.2821(2)	3.4(1)
C(17)	0.8485(1)	0.1296(5)	0.2115(2)	2.8(1)
C(18)	0.8552(1)	-0.1523(4)	0.0925(2)	1.88(9)
C(19)	0.8729(1)	-0.2411(5)	0.1539(2)	2.6(1)
C(20)	0.8578(2)	-0.3896(6)	0.1648(3)	3.6(1)
C(21)	0.8247(2)	-0.4498(5)	0.1160(3)	4.3(1)
C(22)	0.8066(1)	-0.3633(6)	0.0558(3)	4.3(1)
C(23)	0.8218(1)	-0.2155(5)	0.0432(2)	2.9(1)
C(24)	0.9365(1)	-0.0081(5)	0.0557(2)	2.58(10)
C(25)	0.9394(1)	-0.1311(5)	-0.0062(2)	3.5(1)
H(1)	0.8195	0.5203	-0.0998	3.8807
H(2)	0.8413	0.4234	-0.1611	3.8807
H(3)	0.7931	0.4873	-0.1778	3.8807
H(4)	0.7710	0.0918	-0.1510	4.0961
H(5)	0.7674	0.2230	-0.2114	4.0961
H(6)	0.8133	0.1457	-0.1888	4.0961

H(7)	0.9000	0.4337	0.0083	2.4397
H(8)	0.9648	0.5233	-0.0385	2.5825
H(9)	0.9604	0.1765	-0.1900	2.7754
H(10)	0.8932	0.0924	-0.1477	2.5823
H(11)	1.0142	0.5223	-0.1466	3.7627
H(12)	1.0378	0.3786	-0.1087	3.7627
H(13)	1.0179	0.3706	-0.1929	3.7627
H(14)	0.9487	0.2058	0.1650	4.1092
H(15)	0.9532	0.3256	0.2830	5.0683
H(16)	0.8934	0.3243	0.3564	4.3414
H(17)	0.8267	0.2035	0.3122	4.1338
H(18)	0.8215	0.0794	0.1936	3.3028
H(19)	0.8957	-0.1988	0.1887	3.0935
H(20)	0.8704	-0.4497	0.2063	4.3441
H(21)	0.8142	-0.5520	0.1235	5.1582
H(22)	0.7832	-0.4056	0.0223	5.1155
H(23)	0.8094	-0.1573	0.0008	3.4972
H(24)	0.9507	0.0837	0.0401	3.0970
H(25)	0.9517	-0.0451	0.1017	3.0970
H(26)	0.9257	-0.2239	0.0090	4.1726
H(27)	0.9245	-0.0952	-0.0526	4.1726
H(28)	0.9699	-0.1508	-0.0135	4.1726

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 14. Anisotropic Displacement Parameters for **9**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	0.0191(2)	0.0268(2)	0.0253(2)	-0.0014(2)	0.0030(1)	0.0034(2)
P(1)	0.0210(6)	0.0247(6)	0.0265(6)	0.0001(5)	0.0011(5)	0.0006(5)
N(1)	0.022(2)	0.031(2)	0.032(2)	-0.002(2)	0.002(2)	0.011(2)
C(1)	0.021(2)	0.035(3)	0.026(2)	0.000(2)	0.005(2)	0.007(2)
C(2)	0.024(2)	0.022(2)	0.025(2)	-0.007(2)	-0.007(2)	0.011(2)
C(3)	0.030(2)	0.051(3)	0.043(3)	0.002(2)	0.009(2)	0.023(2)
C(4)	0.034(2)	0.062(3)	0.032(2)	0.005(2)	-0.002(2)	-0.004(2)
C(5)	0.019(2)	0.027(2)	0.024(2)	0.002(2)	0.001(2)	0.004(2)
C(6)	0.022(2)	0.026(2)	0.030(2)	0.001(2)	0.005(2)	-0.002(2)
C(7)	0.020(2)	0.023(2)	0.037(2)	-0.003(2)	-0.004(2)	0.003(2)
C(8)	0.021(2)	0.030(3)	0.027(2)	-0.001(2)	0.000(2)	0.011(2)
C(9)	0.030(2)	0.040(3)	0.019(2)	0.008(2)	0.004(2)	0.002(2)
C(10)	0.025(2)	0.031(2)	0.025(2)	-0.002(2)	-0.002(2)	-0.002(2)
C(11)	0.033(2)	0.049(3)	0.038(3)	-0.002(2)	0.008(2)	0.008(2)
C(12)	0.029(2)	0.021(2)	0.024(2)	0.004(2)	-0.005(2)	0.005(2)
C(13)	0.049(3)	0.040(3)	0.041(3)	-0.013(2)	0.000(2)	-0.007(2)
C(14)	0.057(3)	0.053(4)	0.049(3)	-0.018(3)	-0.006(3)	-0.009(3)
C(15)	0.076(4)	0.028(3)	0.029(3)	0.008(3)	-0.019(3)	-0.009(2)
C(16)	0.059(3)	0.039(3)	0.033(3)	0.019(3)	0.009(2)	-0.005(2)
C(17)	0.037(3)	0.031(3)	0.035(3)	0.004(2)	-0.003(2)	-0.001(2)
C(18)	0.021(2)	0.022(3)	0.030(2)	0.000(2)	0.009(2)	-0.003(2)
C(19)	0.035(3)	0.031(3)	0.032(3)	0.003(2)	0.006(2)	0.000(2)
C(20)	0.056(3)	0.035(3)	0.050(3)	0.012(3)	0.026(3)	0.016(2)
C(21)	0.053(3)	0.024(3)	0.091(4)	-0.006(3)	0.033(3)	-0.003(3)
C(22)	0.041(3)	0.045(4)	0.076(4)	-0.013(3)	0.007(3)	-0.019(3)
C(23)	0.038(3)	0.035(3)	0.037(3)	-0.004(2)	-0.002(2)	-0.003(2)
C(24)	0.025(2)	0.036(3)	0.038(2)	0.001(2)	0.005(2)	0.004(2)
C(25)	0.038(3)	0.046(3)	0.050(3)	0.014(2)	0.014(2)	0.009(2)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 15. Bond Lengths(Å) for **9**.

atom	atom	distance	atom	atom	distance
Pd(1)	P(1)	2.308(1)	Pd(1)	N(1)	2.111(3)
Pd(1)	C(1)	2.177(4)	Pd(1)	C(5)	1.998(3)
P(1)	C(12)	1.824(4)	P(1)	C(18)	1.829(4)
P(1)	C(24)	1.834(4)	N(1)	C(2)	1.152(4)
C(1)	C(2)	1.443(5)	C(1)	C(3)	1.519(5)
C(1)	C(4)	1.537(5)	C(5)	C(6)	1.386(5)
C(5)	C(10)	1.396(5)	C(6)	C(7)	1.385(5)
C(7)	C(8)	1.373(5)	C(8)	C(9)	1.380(5)
C(8)	C(11)	1.503(5)	C(9)	C(10)	1.392(5)
C(12)	C(13)	1.390(5)	C(12)	C(17)	1.390(5)
C(13)	C(14)	1.374(5)	C(14)	C(15)	1.356(6)
C(15)	C(16)	1.378(6)	C(16)	C(17)	1.390(5)
C(18)	C(19)	1.394(5)	C(18)	C(23)	1.379(5)
C(19)	C(20)	1.379(6)	C(20)	C(21)	1.358(6)
C(21)	C(22)	1.371(6)	C(22)	C(23)	1.380(6)
C(24)	C(25)	1.529(5)			

Table 16. Bond Angles(°) for **9**.

atom	atom	atom	angle	atom	atom	atom	angle
P(1)	Pd(1)	N(1)	90.10(8)	P(1)	Pd(1)	C(1)	174.3(1)
P(1)	Pd(1)	C(5)	89.9(1)	N(1)	Pd(1)	C(1)	92.9(1)
N(1)	Pd(1)	C(5)	171.0(1)	C(1)	Pd(1)	C(5)	87.9(1)
Pd(1)	P(1)	C(12)	112.7(1)	Pd(1)	P(1)	C(18)	113.5(1)
Pd(1)	P(1)	C(24)	119.9(1)	C(12)	P(1)	C(18)	103.3(2)
C(12)	P(1)	C(24)	102.8(2)	C(18)	P(1)	C(24)	102.8(2)
Pd(1)	N(1)	C(2)	157.8(3)	Pd(1)	C(1)	C(2)	103.1(2)
Pd(1)	C(1)	C(3)	118.5(2)	Pd(1)	C(1)	C(4)	106.0(2)
C(2)	C(1)	C(3)	109.0(3)	C(2)	C(1)	C(4)	109.5(3)
C(3)	C(1)	C(4)	110.3(3)	N(1)	C(2)	C(1)	178.4(4)
Pd(1)	C(5)	C(6)	118.2(3)	Pd(1)	C(5)	C(10)	125.7(3)
C(6)	C(5)	C(10)	116.1(3)	C(5)	C(6)	C(7)	121.9(3)
C(6)	C(7)	C(8)	121.9(3)	C(7)	C(8)	C(9)	117.1(3)
C(7)	C(8)	C(11)	120.8(4)	C(9)	C(8)	C(11)	122.1(4)
C(8)	C(9)	C(10)	121.5(3)	C(5)	C(10)	C(9)	121.5(4)
P(1)	C(12)	C(13)	122.3(3)	P(1)	C(12)	C(17)	119.4(3)
C(13)	C(12)	C(17)	118.2(4)	C(12)	C(13)	C(14)	120.4(4)
C(13)	C(14)	C(15)	121.0(4)	C(14)	C(15)	C(16)	120.3(4)
C(15)	C(16)	C(17)	119.4(4)	C(12)	C(17)	C(16)	120.7(4)
P(1)	C(18)	C(19)	120.7(3)	P(1)	C(18)	C(23)	120.5(3)
C(19)	C(18)	C(23)	118.6(4)	C(18)	C(19)	C(20)	120.7(4)
C(19)	C(20)	C(21)	120.0(4)	C(20)	C(21)	C(22)	120.0(4)
C(21)	C(22)	C(23)	120.8(4)	C(18)	C(23)	C(22)	119.9(4)
P(1)	C(24)	C(25)	112.4(3)				

Table 17. Torsion Angles(°) of **9**.

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Pd(1)	P(1)	C(12)	C(13)	-104.8(3)	Pd(1)	P(1)	C(12)	C(17)	72.8(3)
Pd(1)	P(1)	C(18)	C(19)	-168.1(3)	Pd(1)	P(1)	C(18)	C(23)	16.8(3)
Pd(1)	P(1)	C(24)	C(25)	-72.9(3)	Pd(1)	N(1)	C(2)	C(1)	34(14)
Pd(1)	C(1)	C(2)	N(1)	-16(14)	Pd(1)	C(5)	C(6)	C(7)	177.8(3)
Pd(1)	C(5)	C(10)	C(9)	-176.0(3)	P(1)	Pd(1)	N(1)	C(2)	135.8(8)
P(1)	Pd(1)	C(1)	C(2)	139.8(9)	P(1)	Pd(1)	C(1)	C(3)	-99(1)
P(1)	Pd(1)	C(1)	C(4)	24(1)	P(1)	Pd(1)	C(5)	C(6)	-86.4(3)
P(1)	Pd(1)	C(5)	C(10)	92.8(3)	P(1)	C(12)	C(13)	C(14)	178.0(3)
P(1)	C(12)	C(17)	C(16)	-177.8(3)	P(1)	C(18)	C(19)	C(20)	-174.5(3)
P(1)	C(18)	C(23)	C(22)	175.6(3)	N(1)	Pd(1)	P(1)	C(12)	66.9(2)
N(1)	Pd(1)	P(1)	C(18)	-50.0(1)	N(1)	Pd(1)	P(1)	C(24)	-171.9(2)
N(1)	Pd(1)	C(1)	C(2)	-17.3(3)	N(1)	Pd(1)	C(1)	C(3)	-137.8(3)
N(1)	Pd(1)	C(1)	C(4)	97.7(2)	N(1)	C(2)	C(1)	C(3)	-143(14)
N(1)	C(2)	C(1)	C(4)	96(14)	C(1)	Pd(1)	P(1)	C(12)	170.6(10)
C(1)	Pd(1)	P(1)	C(18)	-72.5(10)	C(1)	Pd(1)	P(1)	C(24)	49(1)
C(1)	Pd(1)	N(1)	C(2)	-48.9(8)	C(1)	Pd(1)	C(5)	C(6)	98.9(3)
C(1)	Pd(1)	C(5)	C(10)	-82.0(3)	C(2)	N(1)	Pd(1)	C(5)	-46(1)
C(2)	C(1)	Pd(1)	C(5)	-153.7(3)	C(3)	C(1)	Pd(1)	C(5)	-33.3(3)
C(4)	C(1)	Pd(1)	C(5)	91.2(3)	C(5)	Pd(1)	P(1)	C(12)	104.1(2)
C(5)	Pd(1)	P(1)	C(18)	-138.9(2)	C(5)	Pd(1)	P(1)	C(24)	-17.1(2)
C(5)	C(6)	C(7)	C(8)	-1.3(6)	C(5)	C(10)	C(9)	C(8)	-2.3(6)
C(6)	C(5)	C(10)	C(9)	3.1(5)	C(6)	C(7)	C(8)	C(9)	2.2(5)
C(6)	C(7)	C(8)	C(11)	-176.3(3)	C(7)	C(6)	C(5)	C(10)	-1.4(5)
C(7)	C(8)	C(9)	C(10)	-0.5(6)	C(10)	C(9)	C(8)	C(11)	178.0(3)
C(12)	P(1)	C(18)	C(19)	-45.8(3)	C(12)	P(1)	C(18)	C(23)	139.1(3)
C(12)	P(1)	C(24)	C(25)	161.0(3)	C(12)	C(13)	C(14)	C(15)	-0.3(7)
C(12)	C(17)	C(16)	C(15)	-0.4(6)	C(13)	C(12)	P(1)	C(18)	132.4(3)
C(13)	C(12)	P(1)	C(24)	25.7(4)	C(13)	C(12)	C(17)	C(16)	-0.1(6)
C(13)	C(14)	C(15)	C(16)	-0.3(7)	C(14)	C(13)	C(12)	C(17)	0.5(6)
C(14)	C(15)	C(16)	C(17)	0.6(7)	C(17)	C(12)	P(1)	C(18)	-50.1(3)
C(17)	C(12)	P(1)	C(24)	-156.7(3)	C(18)	P(1)	C(24)	C(25)	54.0(3)
C(18)	C(19)	C(20)	C(21)	-1.0(6)	C(18)	C(23)	C(22)	C(21)	-1.2(7)
C(19)	C(18)	P(1)	C(24)	60.9(3)	C(19)	C(18)	C(23)	C(22)	0.4(6)
C(19)	C(20)	C(21)	C(22)	0.3(7)	C(20)	C(19)	C(18)	C(23)	0.7(6)

C(20) C(21) C(22) C(23) 0.8(7) C(23) C(18) P(1) C(24) -114.2(3)

Table 18. Non-bonded Contacts out to 3.60 Å of **9**.

atom	atom	distance	ADC	atom	atom	distance	ADC
C(3)	C(15)	3.512(6)	56404	C(3)	C(16)	3.550(6)	56404

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus $\pm$4 lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

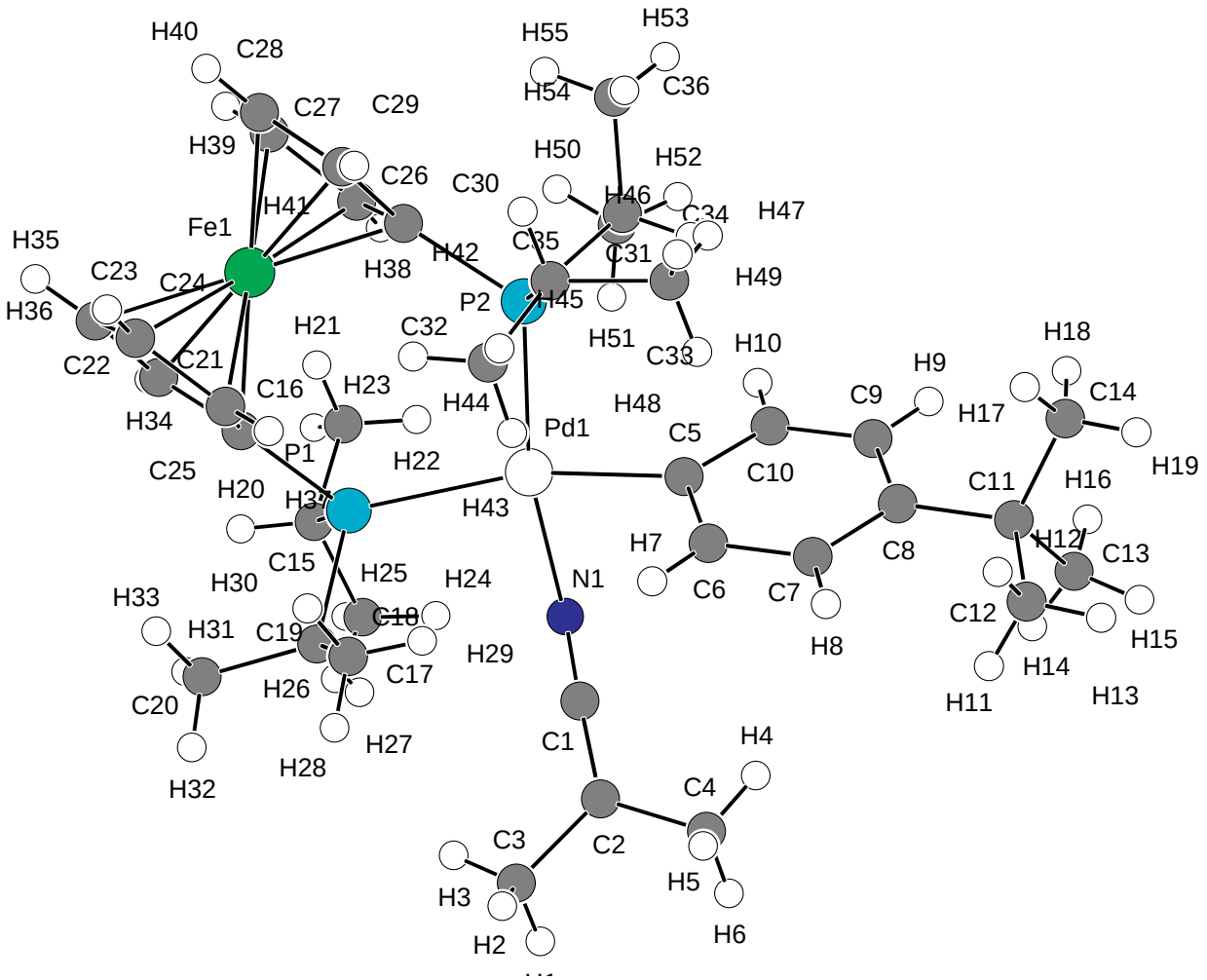
The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure are given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

(1)	X,	Y,	Z	(2)	-X,	Y,	1/2-Z
(3)	-X,	-Y,	-Z	(4)	X,	-Y,	1/2+Z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H23
H21
P1
C25
H20
H37
C15
H30
H33
H31
C19
C18
C20
H32
H26
C17
H27
H28
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C32
H44
Pd1
H43
N1
C1
C4
H4
C3
C2
H5
H3
H2
H6
H55
H53
H54
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H50
H52
C30
H46
C34
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C31
H49
H42
H38
P2
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H17
C14
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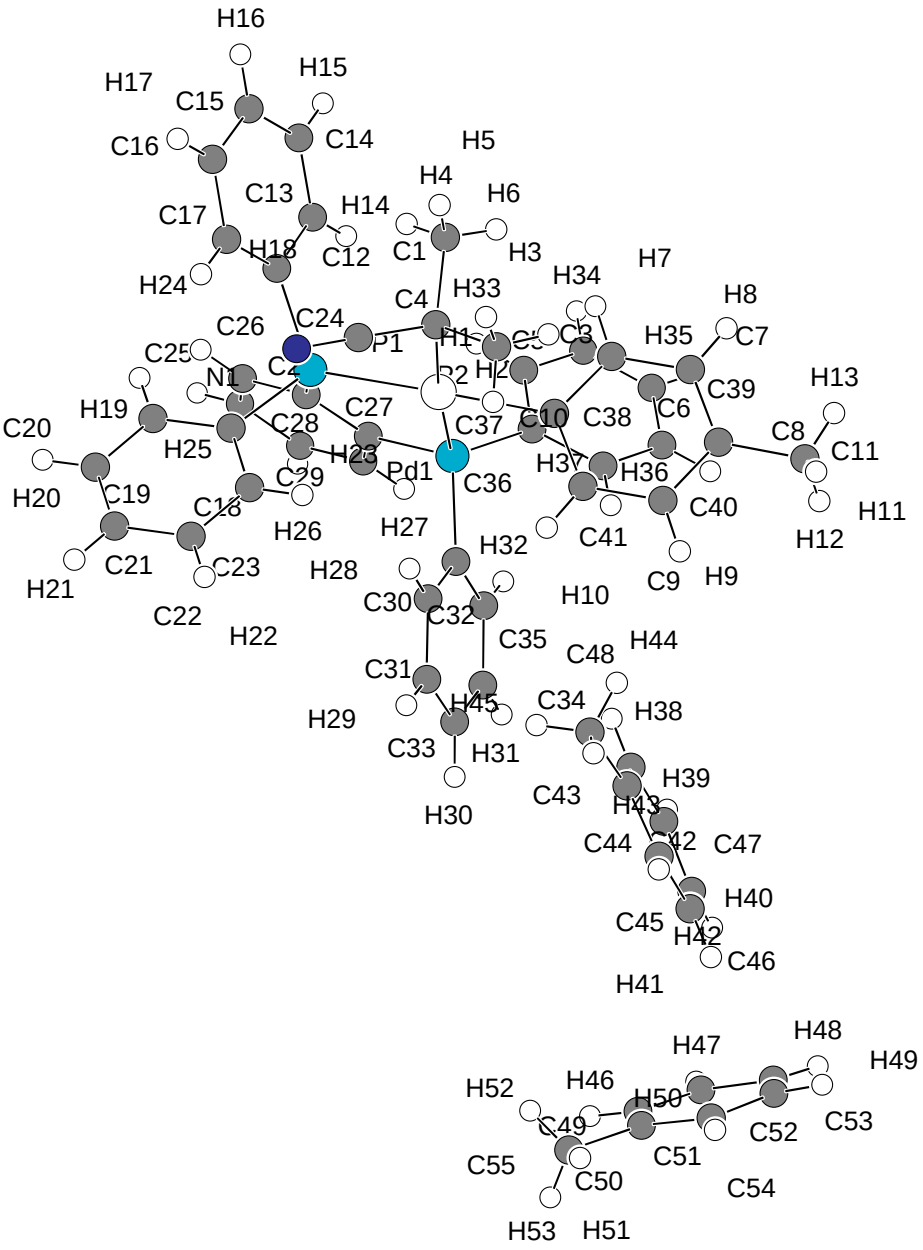
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H34
H33
H8
C4
C24
C26
P1
H1
C3
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C7
C25
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C38
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C20
C28
C8
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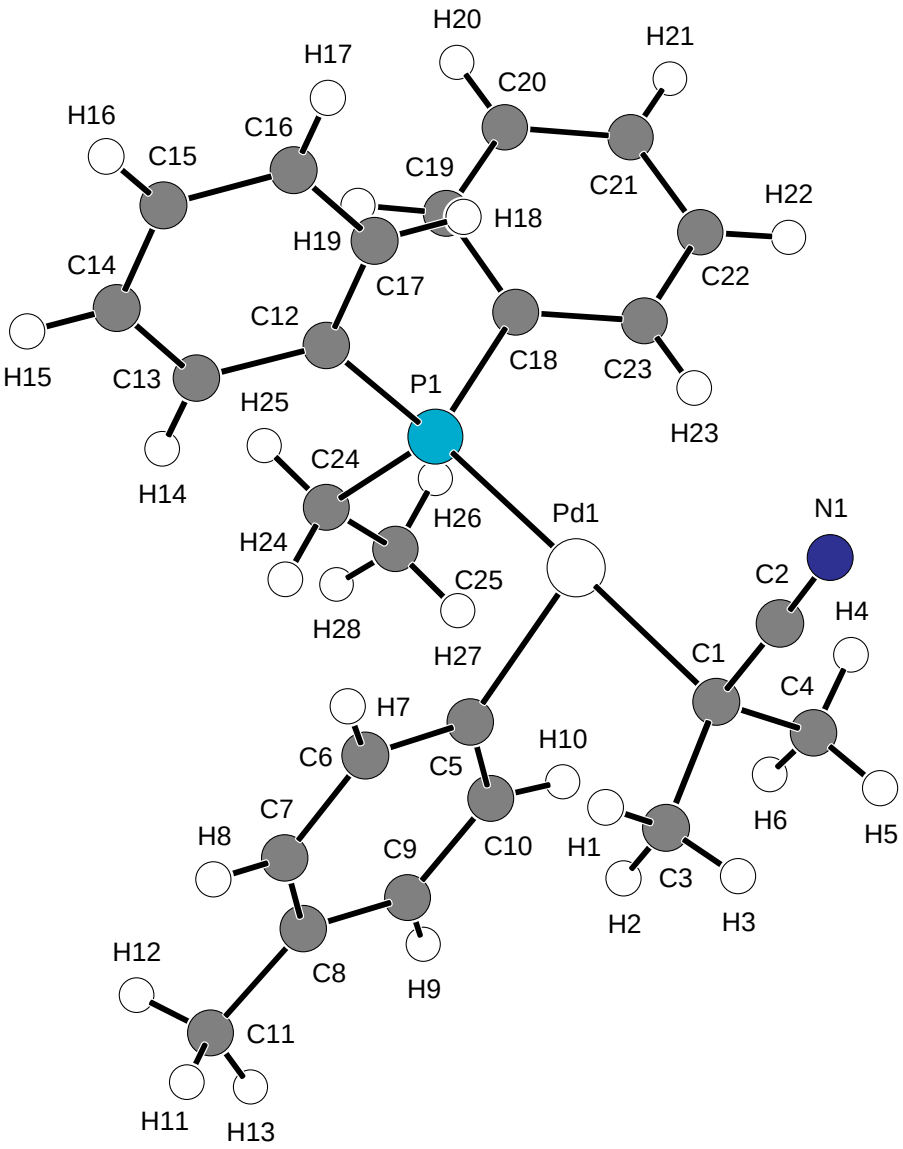
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C23
H15
C13
P1
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H23
C24
H14
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N1
H24
C2
H4
C25
H28
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