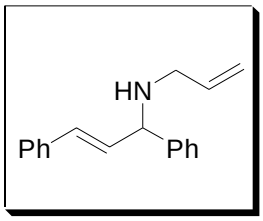
Supporting Information

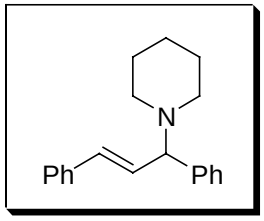
Palladium / BINAP(S) Catalyzed Asymmetric Allylic Amination

J.W. Faller* and Jeremy C. Wilt

Experimental methods: All synthetic manipulations were carried out using standard Schlenk techniques under inert atmosphere. Dichloromethane and thf were distilled over appropriate drying agents prior to use. Ethyl acetate was dried over $MgSO_4$ and degassed with a stream of N_2 before use. Allylic substrates were prepared by stirring the appropriate alcohol with ethyl chloroformate in thf in the presence of pyridine and a catalytic amount of 4-dimethylaminopyridine at room temperature. Allylpalladium chloride dimer and (η^3-1,3-diphenylallyl)palladium chloride dimer were prepared according to their literature procedures.[1] (*S*)-BINAP, (*S*)-TolBINAP, (*S*)-3,5-xylyl-BINAP, $NaBF_4$, and $NaSbF_6$ (Strem) were used without further purification. All spectra were recorded on either a Bruker 400 or 500 MHz spectrometer. Spectral characterization and optical rotation data of product amines **3a**[2], **3c**[3,4], **3e**[5], **4b**[2], **5b**=**6c**[6], **8b**[7], and **9b**[2] were consistent with their respective literature data. Enantiomeric excesses were determined by ^{1}H NMR chiral shift experiments using (-)-MTPA[8] (See general experimental procedure below). Optical rotations were measured on a Perkin-Elmer model 341 polarimeter at 589 nm and 25° C, using a 1 dm path length.

Product 3b: 

^{1}H NMR (400 MHz, C_6D_6): δ 7.50-7.20 (10 H, aryl region); 6.61 (d, 1H, *J* = 16.0 Hz); 6.33 (dd, 1H, *J* = 7.5, 16.0 Hz); 5.97 (m, 1H); 5.22 (d, 1H, *J* = 17 Hz); 5.15 (d, 1H, J = 10.0 Hz); 4.44 (d, 1H, *J* = 7.5 Hz); 3.28 (m, 2H accidentily isochronous). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.11, 137.20, 137.01, 132.78, 130.61, 128.89, 128.78, 127.72, 127.60, 127.56, 126.69, 116.28, 64.99, 50.28 (See ^{13}C NMR below).

Product 3d: 

^{1}H NMR (400 MHz, C_6D_6): δ 7.63-7.20 (10 H, aryl region); 6.60 (d, 1H, J = 16.0 Hz); 6.49 (dd, 1H, J = 8.6, 16.0 Hz); 3.92 (d, 1H, J = 8.6 Hz); 2.60 (br s, 2H); 2.49 (br s, 2H); 1.64 (br s, 4H); 1.45 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.69, 137.38, 132.57, 131.21, 128.80, 128.78, 128.36, 127.65, 127.29, 126.66, 75.04, 53.04, 26.52, 25.00 (See ^{13}C NMR below).

Preparation of (*S*)-TolBINAP(S):

To a flame-dried 3-neck flask equipped with a stir bar under positive pressure of N_2 was added (*S*)-TolBINAP (1 g, 1.47 mmol) and thf (10 mL). When the solution became homogeneous, sulfur (33 mg, 1.03 mmol) was added under positive pressure of N_2. The resulting cloudy solution was stirred at RT until it became clear (~ 4 h), and the solvent was removed under reduced pressure. The resulting crude solid was subjected to column

chromatography over silica gel (10% EtOAc : hexanes) to provide first unreacted (*S*)-TolBINAP (365 mg), followed by (*S*)-TolBINAP(S) (395 mg, 59% with respect to reacted (*S*)-TolBINAP), and finally (*S*)-TolBINAP$(S)_2$ (240 mg). The spectral characteristics of the mono-and disulfide of (*S*)-TolBINAP match those previously reported.[9]

Preparation of (*S*)-3,5-xylyl-BINAP(S):

To a flame-dried 3-neck flask equipped with a stir bar under positive pressure of N_2 was added (*S*)-3,5-xylyl-BINAP (0.5 g, 0.68 mmol) and thf (5 mL). When the solution became homogeneous, sulfur (15.3 mg, 0.47 mmol) was added under positive pressure of N_2. The resulting cloudy solution was stirred at RT until it became clear (~ 4 h), and the solvent was removed under reduced pressure. The resulting crude solid was subjected to column chromatography over silica gel (10% EtOAc : hexanes) to provide first unreacted (*S*)-3,5-xylyl-BINAP (207 mg), followed by (*S*)-3,5-xylyl-BINAP(S) (210 mg, 69% with respect to reacted (*S*)-3,5-xylyl-BINAP). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (dd, 1H, *J* = 8.9, 13.3 Hz); 8.00 (d, 1H, *J* = 8.6 Hz); 7.79 (d, 1H, *J* = 8.4 Hz); 7.57 (d, 1H, *J* = 8.2 Hz); 7.53 (d, 1H, *J* = 8.6 Hz); 7.38-7.08 (m, 9H); 6.92 (s, 1H); 6.91 (s, 1H); 6.89 (s, 1H); 6.77 (s, 1H); 6.75 (s, 1H); 6.69 (s, 1H); 6.43 (m, 3H); 6.20 (d, 1H, *J* = 8.4 Hz); 2.22 (s, 6H); 2.05 (s, 6H); 2.04 (s, 6H); 2.01 (s, 6H). ^{31}P NMR (162 MHz, $CDCl_3$); δ 47.36 (s, P=S); -13.99 (s, P). ^{13}C NMR δ 142.5-125.4 aryl region, 48 C); 21.76, 21.63, 21.58, 21.53 (xylyl carbons). Anal. Calcd. for $C_{52}H_{48}P_2S$: C, 81.43; H, 6.31. Found: C, 80.90 H, 6.73.

Preparation of [(η^3-allyl)Pd(*S*-TolBINAP(S))]SbF_6 (10): To a flame-dried 3-neck flask was added allylpalladium chloride dimer (12.8 mg, 0.035 mmol), (*S*)-TolBINAP(S) (50 mg, 0.07 mmol), and $NaSbF_6$ (25 mg, 0.09 mmol). The solids were placed under inert atmosphere, and

CH_2Cl_2 (5 mL) was added. The resulting light yellow solution was stirred at RT for 12 h, then was filtered through a pad of Celite, concentrated, and the residue washed with Et_2O to leave the desired product (64 mg, 84%) as a yellow powder. Complex **10** exists as a 1:1 diastereomeric ratio in $CDCl_3$ solution. **Diastereomer #1:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.2-5.9 (aryl region, 28 H); 5.5 (dddd, 1H, *J* = 6.8, 7.0, 12.2, 13.5Hz); 4.36 (dd, 1H, *J* = 7.0, 13.5 Hz); 4.16 (d, 1H, *J* = 6.8 Hz); 3.32 (dd, 1H, *J* = 10.5, 13.5 Hz); 2.29 (d, 1H, *J* = 12.2 Hz); 2.56-2.04 (p-tolyl region, 4s, 12H). **Diastereomer #2:** δ 8.2-5.9 (aryl region, 28 H); 5.19(dddd, 1H, *J* = 6.8, 7.0, 12.2, 13.5Hz); 4.76 (dd, 1H, *J* = 7.0, 13.5 Hz); 3.62 (d, 1H, *J* = 6.8 Hz); 3.20 (dd, 1H, *J* = 10.5, 13.5 Hz); 2.62 (d, 1H, *J* = 12.2 Hz); 2.56-2.04 (p-tolyl region, 4s, 12H). ^{31}P NMR (both diastereomers, 162 MHz, $CDCl_3$); δ 43.08 (P=S, d, *J* = 4 Hz); 42.43 (P=S, d, *J* = 4 Hz); 26.18 (P, d, *J* = 4 Hz); 23.67 (P, d, *J* = 4 Hz). ^{13}C NMR (both diastereomers, 125 MHz, $CDCl_3$, allylic carbons only): δ 119.7 (central, d, J_{PC} = 6 Hz); 117.7 (central, d, J_{PC} = 6 Hz); 79.8 (trans to P, d, *J* = 30 Hz); 75.8 (trans to P, d, *J* = 30 Hz); 67.2 (trans to S, s); 63.5 (trans to S, s). Anal. Calcd. for $C_{51}H_{45}F_6P_2PdSSb$: C, 55.99; H, 4.15. Found: C, 55.94; H, 4.29.

Preparation of [(η^3-allyl)Pd(*S*-3,5-xylyl-BINAP(S))]SbF_6 (11): To a flame-dried 3-neck flask was added allylpalladium chloride dimer (12 mg, 0.033 mmol), (*S*)-3,5-xylyl-BINAP(S) (50.3 mg, 0.066 mmol), and $NaSbF_6$ (25 mg, 0.09 mmol). The solids were placed under inert atmosphere, and CH_2Cl_2 (5 mL) was added. The resulting light yellow solution was stirred at RT for 12 h, then was filtered through a pad of Celite, concentrated, and the residue washed with Et_2O to leave the desired product (60 mg, 80%) as a yellow powder. Complex **11** exists as a 1.4:1 diastereomeric ratio in $CDCl_3$ solution. ^{1}H NMR (**Major diastereomer**, 400 MHz, $CDCl_3$): δ 8.3-5.9 (aryl region, 48 H); 5.17 (dddd, 1H, *J* = 6.8, 7.0, 12.2, 13.5 Hz); 4.75

(dd, 1H, *J* = 6.8, 13.5 Hz); 3.6 (d, 1H, *J* = 7.0 Hz); 3.18 (dd, 1H, *J* = 10.5, 13.5 Hz); 2.56 (d, 1H, *J* = 12.2 Hz). **Minor diastereomer**: δ 5.4 (dddd, 1H, *J* = 6.8, 7.0, 12.2, 13.5 Hz); 4.43 (dd, 1H, *J* = 6.8, 13.5 Hz); 4.09 (d, 1H, *J* = 7.0 Hz); 3.33 (dd, 1H, *J* = 10.5, 13.5 Hz); 2.36 (d, 1H, *J* = 12.2 Hz). ^{31}P NMR (both diastereomers, 162 MHz, $CDCl_3$); δ 43.83 (d, coincident P=S, *J* = 4 Hz); 25.94 (d, P_{minor}, *J* = 4 Hz); 24.21 (d, P_{major}, *J* = 4 Hz); ^{13}C NMR (both diastereomers, 125 MHz, $CDCl_3$, allylic carbons only): δ 119.2 (central, d, J_{PC} = 6 Hz); 116.8 (central, d, J_{PC} = 6 Hz); 80.1 (trans to P, d, *J* = 30 Hz); 75.6 (trans to P, d, *J* = 30 Hz); 67.4 (trans to S, s); 63.6 (trans to S, s). Anal. Calcd. for $C_{55}H_{53}F_6P_2PdSSb$: C, 57.43; H, 4.64. Found: C, 57.34; H, 4.63.

Preparation of (*S*)-BINAP(S)PdCl$_2$ (12): Dichlorobis(benzonitrile)palladium (14.6 mg, 0.0382 mmol) and (*S*)-BINAP(S) (25 mg, 0.0382 mmol) were placed under inert atmosphere and CH_2Cl_2 (5 mL) was added. The clear, orange solution was stirred at RT for 1 h, then excess hexanes was added to precipitate a bright yellow powder. The powder was filtered, washed with hexanes, and dried to leave the desired product (30 mg, 95%). Crystals suitable for X-ray crystallography were obtained from CH_2Cl_2 / pentane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (m, 2H); 8.11 (m, 2H); 7.93 (dd, 1H, *J* = 8.6, 11.6 Hz); 7.84 (m, 2H); 7.73 (d, 1H, *J* = 8.2 Hz); 7.69-7.48 (m, 8H); 7.40 (m, 3H); 7.26-7.10 (m, 4H); 6.93 (m, 2H); 6.84 (m, 2H); 6.63 (m, 3H); 6.27 (d, 1H, *J* = 8.6 Hz); 6.14 (d, 1H, *J* = 8.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$); δ 39.77 (s, P=S); 29.68 (s, P). Anal. Calcd. for $C_{44}H_{32}Cl_2P_2PdS.CH_2Cl_2$: C, 58.94; H, 3.74. Found: C, 58.51; H, 3.73.

Preparation of [(η^3-1,3-diphenylallyl)Pd(*S*-BINAP(S))]BF$_4$ (13): To a flame-dried 3-neck flask was added (η^3-1,3-diphenylallyl)palladium chloride dimer (25.6 mg, 0.0382 mmol), (*S*)-BINAP(S) (50 mg, 0.0764 mmol), and $NaBF_4$ (20 mg, 0.18 mmol). -The flask was placed

under inert atmosphere, and CH_2Cl_2 (5 mL) was added. The resulting orange-yellow solution was stirred at RT for 12 h, then filtered through a pad of Celite and concentrated to leave the crude product (69 mg, 87%). X-ray quality crystals were grown from CH_2Cl_2 / hexanes as orange needles. Complex **13** appears as a 6:1 ratio of diastereomers in $CDCl_3$ solution. ^{1}H NMR (**Major diastereomer**, 400 MHz, $CDCl_3$): δ 8.62-6.3 (41 H, aryl regions); 5.99 (dd, 1H, central allylic proton, J = 11.4, 12.8 Hz); 5.79 (d, 1H, J = 8.6 Hz); 5.25 (dd, 1H, allylic proton trans to P, J_{HH} = 12.8 Hz, J_{PH} = 10.4 Hz); 4.97 (d, 1H, allylic proton trans to S, J = 11.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.1 (s, P=S); 28.3 (s, P); ^{13}C NMR (allyl resonances only): δ 109.9 (d, central allylic C, J_{PC} = 6.5 Hz); 101.2 (d, trans to P, J_{PC} = 25 Hz); 80.12 (trans to S). **Minor diastereomer**: δ 8.62-6.3 (41 H, aryl regions); 5.97 (dd, 1H, central allylic proton, J = 11.4, 12.8 Hz); 5.84 (d, 1H, J = 8.6 Hz); 5.15 (dd, 1H, allylic proton trans to P, J_{HH} = 12.8 Hz, J_{PH} = 10.4 Hz); 4.38 (d, 1H, allylic proton trans to S, J = 11.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 44.1 (s, P=S); 24.1 (s, P). Anal. Calcd. for $C_{59}H_{45}BF_4P_2PdS{\cdot}CH_2Cl_2$: C, 63.99; H, 4.21. Found: C, 64.09; H, 4.15.

General Procedure for Allylic Aminations with $BnNH_2$ and Enantiomeric Excess Determination: To a flame-dried round-bottom flask was added [(η^3-allyl)Pd(*S*-BINAP(S))]SbF_6 (3 mg, 2.89 μmol), and an allylic carbonate (57.7 μmol). The contents were placed under inert atmosphere, and EtOAc (2 mL) was added via syringe. The resulting pale yellow solution was then cooled to the desired temperature, and benzylamine (20 μL, 175 μmol) was added. After the indicated amount of time, the reaction was quenched by the addition of excess pentane (10 mL), filtered though a pad of Celite, and concentrated. Column chromatography over silica gel (25-50% Et_2O : hexanes) provided the desired allylic amine.

Enantiomeric excesses were determined by the careful addition of (-)-MTPA to the purified amine in C_6D_6, followed by the integration of the appropriate resonances (α to nitrogen) from the produced diastereomeric salts. Optimal chemical shift inequivalence was usually obtained with 1-3 molar equivalents of (-)-MTPA with respect to the amine. The shift differences observed with (-)-MTPA were inconclusive for the cycloalkenyl amines and HPLC on a chiral column [Chiracel OD-H, flow rate 0.5 mL/min, 99.5: 0.5 hexanes: *i*-PrOH. (*R*)-enantiomer: t_R = 20.32 min, (*S*)-enantiomer: t_R = 21.50 min] was used for them.

(1) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301-6311.

(2) Evans, D. A.; Campos, K. R.; Tedrow, J. S.; Michael, F. E.; Gagne, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 7905-7920.

(3) Tollabi, M.; Framery, E.; Goux-Henry, C.; Sinou, D. *Tetrahedron: Asymmetry* **2003**, *14*, 3329-3333.

(4) Feuerstein, M.; Laurenti, D.; Doucet, H.; Santelli, M. *J. Mol. Catal. A-Chem.* **2002**, *182*, 471-480.

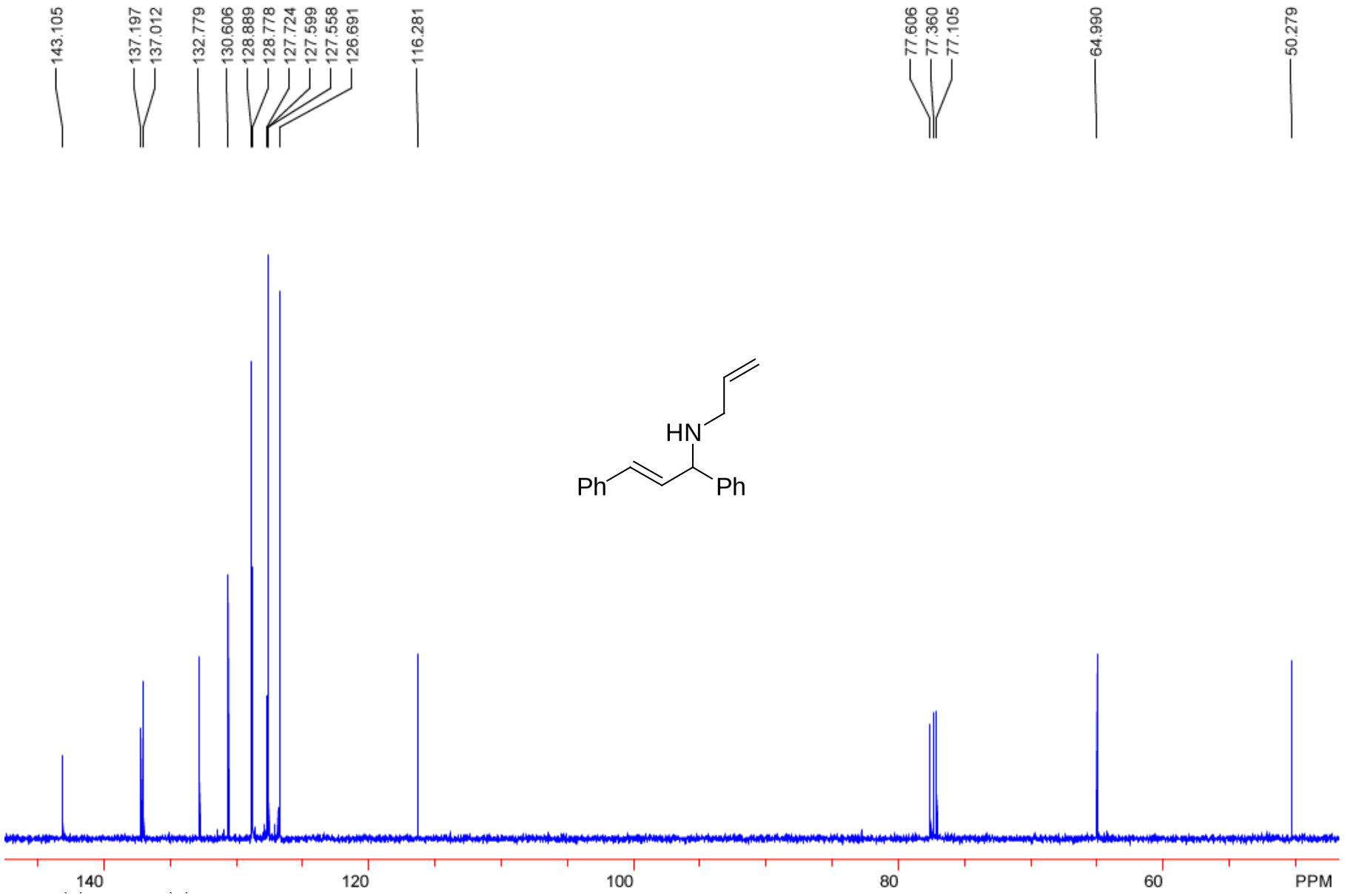
(5) Sudo, A.; Saigo, K. *J. Org. Chem.* **1997**, *62*, 5508-5513.

(6) You, S. L.; Zhu, X. Z.; Luo, Y. M.; Hou, X. L.; Dai, L. X. *J. Am. Chem. Soc.* **2001**, *123*, 7471-7472.

(7) Davies, S. G.; Fox, J. F.; Jones, S.; Price, A. J.; Sanz, M. A.; Sellers, T. G. R.; Smith, A. D.; Teixeira, F. C. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1757-1765.

(8) Benson, S. C.; Cai, P.; Colon, M.; Haiza, M. A.; Tokles, M.; Snyder, J. K. *J. Org. Chem.* **1988**, *53*, 5335-5341.

(9) Gladiali, S.; Medici, S.; Pirri, G.; Pulacchini, S.; Fabbri, D. *Can. J. Chem.* **2001**, *79*, 670-678.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126.691
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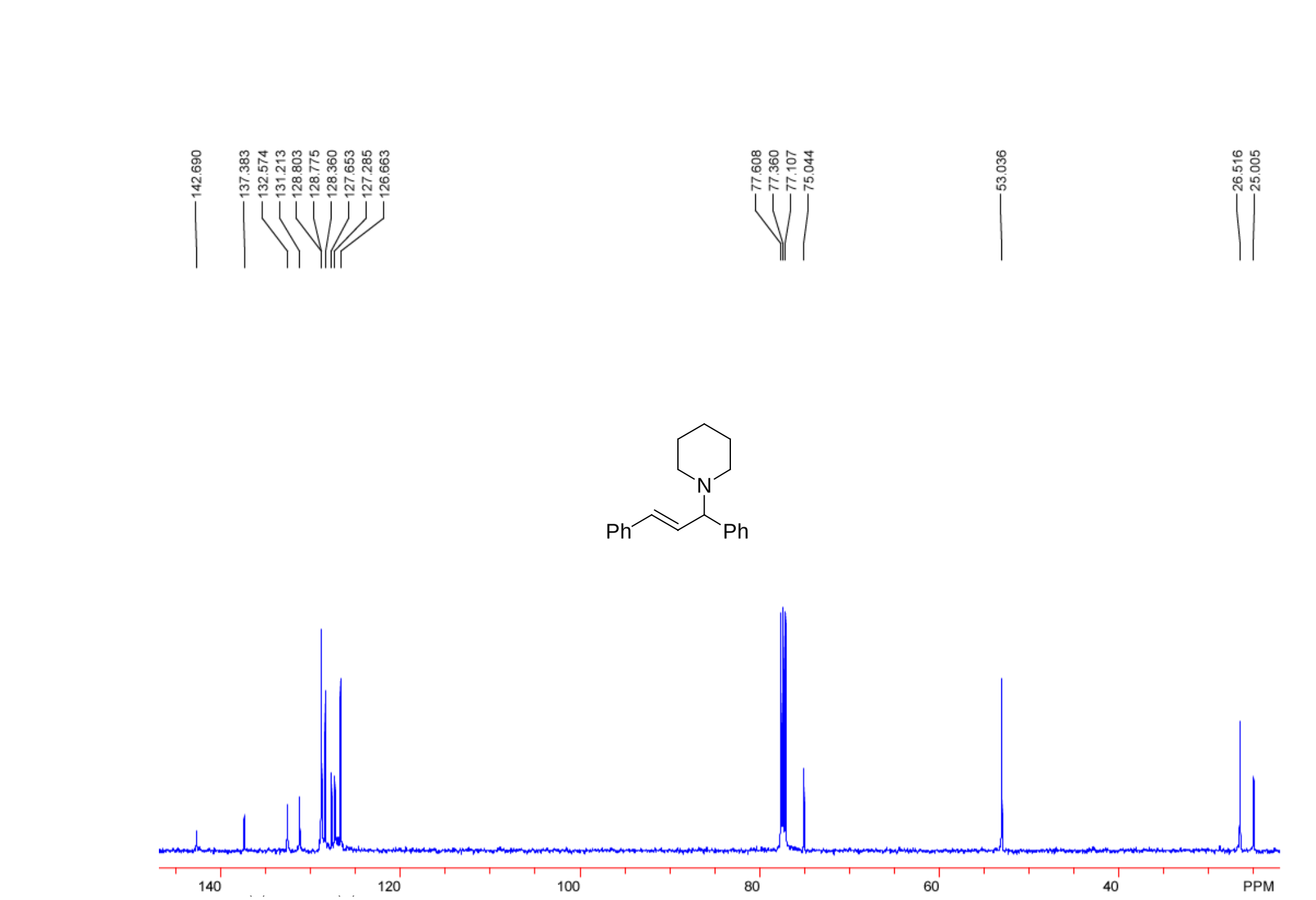
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126.663
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77.107
75.044
53.036
26.516
25.005
N
Ph
Ph
140
120
100
80
60
40
PPM

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{45}H_{34}Cl_4P_2PdS$
Formula Weight	916.98
Crystal Color, Habit	orange, needle
Crystal Dimensions	0.10 × 0.10 × 0.17 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 10.2671(2) Å b = 15.7860(4) Å c = 24.4303(4) Å V = 3959.58(14) Å^3
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.538 g/cm^3
F_{000}	1856.00
μ(MoKα)	9.05 cm^{-1}
T	-100^o C

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Data Images	168 exposures @ 117.0 seconds
ω oscillation Range	1.3^{o}
Detector Position	35.00 mm
$2\theta_{max}$	55.0^{o}
No. of Reflections Measured	Total: 8821 Unique: 5062 (R_{int} = 0.042)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	3925
No. Variables	496
Reflection/Parameter Ratio	7.91
Residuals: R; Rw	0.054 ; 0.054
Goodness of Fit Indicator	2.43
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	1.67 $e^-/Å^3$
Minimum peak in Final Diff. Map	-2.23 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
Pd(1)	0.76343(4)	0.45992(2)	0.506943(13)	1.844(8)	
Cl(1)	0.60074(13)	0.38291(10)	0.46182(5)	2.99(3)	
Cl(2)	0.7790(1)	0.55218(8)	0.43366(5)	3.00(3)	
Cl(3)	0.4850(3)	0.0482(2)	0.65094(11)	4.56(7)	3/4
Cl(4)	0.5800(4)	0.1051(3)	0.7557(2)	7.67(11)	3/4
Cl(5)	0.581(2)	0.1573(7)	0.7599(6)	9.6(4)	1/4
Cl(6)	0.5359(9)	0.0190(6)	0.6853(4)	6.5(3)	1/4
S(1)	0.78214(13)	0.35095(8)	0.56983(5)	2.21(3)	
P(1)	0.93145(13)	0.52621(8)	0.54824(5)	1.78(3)	
P(2)	0.67605(13)	0.38664(9)	0.63402(5)	1.92(3)	
C(1)	0.9646(5)	0.5108(3)	0.6211(2)	1.79(12)	
C(2)	0.8728(4)	0.5329(3)	0.6611(2)	1.39(10)	
C(3)	0.9094(4)	0.5359(3)	0.7181(2)	1.61(10)	
C(4)	0.8268(5)	0.5619(3)	0.7604(2)	2.26(12)	
C(5)	0.8616(5)	0.5590(3)	0.8140(2)	2.18(12)	
C(6)	0.9886(6)	0.5327(4)	0.8284(2)	3.3(2)	
C(7)	1.0730(5)	0.5091(4)	0.7889(2)	2.41(13)	
C(8)	1.0379(5)	0.5100(3)	0.7333(2)	1.89(12)	
C(9)	1.1264(5)	0.4848(3)	0.6916(2)	2.53(13)	
C(10)	1.0907(5)	0.4844(3)	0.6373(2)	2.06(12)	
C(11)	0.7410(5)	0.5594(3)	0.6454(2)	1.62(10)	
C(12)	0.6433(5)	0.5001(3)	0.6324(2)	2.08(12)	
C(13)	0.5230(5)	0.5239(4)	0.6125(2)	2.9(1)	
C(14)	0.4899(5)	0.6090(4)	0.6077(2)	3.0(1)	
C(15)	0.5792(5)	0.6729(4)	0.6249(2)	2.59(13)	
C(16)	0.5483(6)	0.7585(4)	0.6229(3)	3.3(2)	
C(17)	0.6348(7)	0.8180(4)	0.6412(2)	3.7(2)	
C(18)	0.7595(6)	0.7940(3)	0.6591(2)	3.00(13)	
C(19)	0.7947(5)	0.7116(3)	0.6603(2)	2.01(12)	
C(20)	0.7074(5)	0.6467(3)	0.6435(2)	1.68(11)	
C(21)	1.0709(5)	0.4835(3)	0.5118(2)	2.17(11)	
C(22)	1.1388(5)	0.5316(3)	0.4756(2)	2.23(11)	
C(23)	1.2378(7)	0.4954(4)	0.4444(2)	3.5(1)	
C(24)	1.2654(6)	0.4105(4)	0.4498(2)	3.1(1)	
C(25)	1.1964(6)	0.3621(4)	0.4856(2)	3.7(2)	
C(26)	1.0966(6)	0.3972(4)	0.5164(2)	3.1(1)	
C(27)	0.9502(5)	0.6420(3)	0.5456(2)	1.81(11)	
C(28)	1.0624(6)	0.6772(4)	0.5640(2)	2.48(13)	
C(29)	1.0803(5)	0.7640(4)	0.5617(2)	2.49(13)	
C(30)	0.9831(6)	0.8171(3)	0.5414(2)	2.69(13)	

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
C(31)	0.8677(6)	0.7808(3)	0.5235(2)	2.9(1)	
C(32)	0.8523(5)	0.6935(3)	0.5240(2)	2.39(13)	
C(33)	0.7558(5)	0.3522(3)	0.6960(2)	1.98(11)	
C(34)	0.8562(6)	0.2921(4)	0.6921(2)	2.7(1)	
C(35)	0.9121(7)	0.2591(4)	0.7396(2)	3.8(2)	
C(36)	0.8688(6)	0.2860(4)	0.7897(2)	3.7(2)	
C(37)	0.7729(6)	0.3480(4)	0.7949(2)	2.96(13)	
C(38)	0.7143(5)	0.3807(3)	0.7473(2)	2.21(12)	
C(39)	0.5199(5)	0.3348(3)	0.6346(2)	1.92(12)	
C(40)	0.4384(6)	0.3362(4)	0.6807(2)	3.9(2)	
C(41)	0.3192(5)	0.2953(4)	0.6797(3)	3.9(2)	
C(42)	0.2786(6)	0.2529(4)	0.6344(3)	3.8(2)	
C(43)	0.3581(6)	0.2469(5)	0.5884(3)	4.6(2)	
C(44)	0.4776(6)	0.2893(4)	0.5896(2)	3.6(2)	
C(45)	0.5832(7)	0.1198(5)	0.6859(3)	5.2(2)	
H(1)	0.7426	0.5825	0.7512	2.731	
H(2)	0.8010	0.5745	0.8417	2.614	
H(3)	1.0146	0.5317	0.8657	3.928	
H(4)	1.1581	0.4914	0.7989	2.895	
H(5)	1.2121	0.4677	0.7014	3.042	
H(6)	1.1515	0.4663	0.6103	2.462	
H(7)	0.4621	0.4817	0.6019	3.513	
H(8)	0.4078	0.6246	0.5928	3.654	
H(9)	0.4665	0.7760	0.6085	3.913	
H(10)	0.6103	0.8761	0.6420	4.451	
H(11)	0.8198	0.8362	0.6704	3.589	
H(12)	0.8794	0.6967	0.6727	2.411	
H(13)	1.1187	0.5900	0.4715	2.674	
H(14)	1.2863	0.5293	0.4196	4.206	
H(15)	1.3326	0.3856	0.4284	3.730	
H(16)	1.2169	0.3037	0.4896	4.416	
H(17)	1.0464	0.3628	0.5403	3.748	
H(18)	1.1293	0.6419	0.5784	2.978	
H(19)	1.1599	0.7878	0.5742	2.988	
H(20)	0.9957	0.8766	0.5398	3.230	
H(21)	0.7988	0.8157	0.5109	3.438	
H(22)	0.7752	0.6688	0.5097	2.856	
H(23)	0.8861	0.2739	0.6572	3.254	
H(24)	0.9797	0.2182	0.7373	4.529	
H(25)	0.9051	0.2616	0.8219	4.446	

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
H(26)	0.7476	0.3679	0.8300	3.566	
H(27)	0.6470	0.4218	0.7501	2.653	
H(28)	0.4652	0.3654	0.7128	4.659	
H(29)	0.2648	0.2968	0.7111	4.729	
H(30)	0.1950	0.2272	0.6341	4.567	
H(31)	0.3321	0.2150	0.5573	5.569	
H(32)	0.5320	0.2867	0.5582	4.317	
H(33)	0.6703	0.1133	0.6734	6.198	
H(34)	0.5538	0.1755	0.6780	6.198	

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

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Pd(1)	Cl(1)	2.342(2)	Pd(1)	Cl(2)	2.314(2)
Pd(1)	S(1)	2.314(2)	Pd(1)	P(1)	2.256(2)
Cl(3)	Cl(6)	1.09(2)	Cl(3)	C(45)	1.739(12)
Cl(4)	Cl(5)	0.83(2)	Cl(4)	Cl(6)	2.24(2)
Cl(4)	C(45)	1.721(12)	Cl(5)	C(45)	1.90(2)
Cl(6)	C(45)	1.66(2)	S(1)	P(2)	1.991(3)
P(1)	C(1)	1.828(8)	P(1)	C(21)	1.817(8)
P(1)	C(27)	1.839(8)	P(2)	C(12)	1.822(8)
P(2)	C(33)	1.806(7)	P(2)	C(39)	1.800(8)
C(1)	C(2)	1.402(10)	C(1)	C(10)	1.416(10)
C(2)	C(3)	1.444(9)	C(2)	C(11)	1.468(10)
C(3)	C(4)	1.397(10)	C(3)	C(8)	1.430(10)
C(4)	C(5)	1.360(10)	C(5)	C(6)	1.412(12)
C(6)	C(7)	1.350(12)	C(7)	C(8)	1.405(11)
C(8)	C(9)	1.422(10)	C(9)	C(10)	1.376(10)
C(11)	C(12)	1.409(10)	C(11)	C(20)	1.421(9)
C(12)	C(13)	1.380(11)	C(13)	C(14)	1.391(13)
C(14)	C(15)	1.426(12)	C(15)	C(16)	1.390(12)
C(15)	C(20)	1.452(10)	C(16)	C(17)	1.368(13)
C(17)	C(18)	1.406(13)	C(18)	C(19)	1.350(11)
C(19)	C(20)	1.423(10)	C(21)	C(22)	1.358(10)
C(21)	C(26)	1.391(11)	C(22)	C(23)	1.392(11)
C(23)	C(24)	1.377(11)	C(24)	C(25)	1.360(11)
C(25)	C(26)	1.388(11)	C(27)	C(28)	1.354(11)
C(27)	C(32)	1.396(10)	C(28)	C(29)	1.385(11)
C(29)	C(30)	1.394(11)	C(30)	C(31)	1.387(12)
C(31)	C(32)	1.386(11)	C(33)	C(34)	1.404(11)
C(33)	C(38)	1.398(10)	C(34)	C(35)	1.396(11)
C(35)	C(36)	1.368(12)	C(36)	C(37)	1.395(12)
C(37)	C(38)	1.406(10)	C(39)	C(40)	1.405(11)
C(39)	C(44)	1.383(11)	C(40)	C(41)	1.384(12)
C(41)	C(42)	1.359(12)	C(42)	C(43)	1.390(12)
C(43)	C(44)	1.398(13)			

Table 5. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
Cl(1)	Pd(1)	Cl(2)	90.68(8)	Cl(1)	Pd(1)	S(1)	89.19(8)
Cl(1)	Pd(1)	P(1)	175.48(8)	Cl(2)	Pd(1)	S(1)	167.40(8)
Cl(2)	Pd(1)	P(1)	90.06(8)	S(1)	Pd(1)	P(1)	89.11(7)
Cl(6)	Cl(3)	C(45)	67.6(9)	Cl(5)	Cl(4)	Cl(6)	134.4(21)
Cl(5)	Cl(4)	C(45)	89.4(20)	Cl(6)	Cl(4)	C(45)	47.5(6)
Cl(4)	Cl(5)	C(45)	64.8(16)	Cl(3)	Cl(6)	Cl(4)	115.6(11)
Cl(3)	Cl(6)	C(45)	75.1(11)	Cl(4)	Cl(6)	C(45)	49.7(6)
Pd(1)	S(1)	P(2)	105.49(11)	Pd(1)	P(1)	C(1)	121.1(3)
Pd(1)	P(1)	C(21)	102.2(3)	Pd(1)	P(1)	C(27)	121.7(3)
C(1)	P(1)	C(21)	106.3(4)	C(1)	P(1)	C(27)	98.4(4)
C(21)	P(1)	C(27)	105.6(4)	S(1)	P(2)	C(12)	111.2(3)
S(1)	P(2)	C(33)	109.1(3)	S(1)	P(2)	C(39)	111.4(3)
C(12)	P(2)	C(33)	113.4(4)	C(12)	P(2)	C(39)	106.4(4)
C(33)	P(2)	C(39)	105.1(4)	P(1)	C(1)	C(2)	121.4(6)
P(1)	C(1)	C(10)	118.8(6)	C(2)	C(1)	C(10)	119.5(7)
C(1)	C(2)	C(3)	120.4(6)	C(1)	C(2)	C(11)	120.6(6)
C(3)	C(2)	C(11)	118.8(6)	C(2)	C(3)	C(4)	124.4(7)
C(2)	C(3)	C(8)	118.7(6)	C(4)	C(3)	C(8)	117.0(7)
C(3)	C(4)	C(5)	122.8(7)	C(4)	C(5)	C(6)	119.5(8)
C(5)	C(6)	C(7)	119.7(8)	C(6)	C(7)	C(8)	121.7(8)
C(3)	C(8)	C(7)	119.3(7)	C(3)	C(8)	C(9)	119.0(7)
C(7)	C(8)	C(9)	121.8(7)	C(8)	C(9)	C(10)	121.4(7)
C(1)	C(10)	C(9)	120.8(7)	C(2)	C(11)	C(12)	121.7(7)
C(2)	C(11)	C(20)	120.6(7)	C(12)	C(11)	C(20)	117.7(7)
P(2)	C(12)	C(11)	121.2(6)	P(2)	C(12)	C(13)	116.2(7)
C(11)	C(12)	C(13)	122.4(8)	C(12)	C(13)	C(14)	120.8(9)
C(13)	C(14)	C(15)	120.0(8)	C(14)	C(15)	C(16)	122.1(8)
C(14)	C(15)	C(20)	118.2(7)	C(16)	C(15)	C(20)	119.7(8)
C(15)	C(16)	C(17)	120.6(9)	C(16)	C(17)	C(18)	120.5(8)
C(17)	C(18)	C(19)	120.7(8)	C(18)	C(19)	C(20)	121.2(8)
C(11)	C(20)	C(15)	120.5(7)	C(11)	C(20)	C(19)	122.3(7)
C(15)	C(20)	C(19)	117.2(7)	P(1)	C(21)	C(22)	121.1(6)
P(1)	C(21)	C(26)	118.2(6)	C(22)	C(21)	C(26)	120.2(8)
C(21)	C(22)	C(23)	120.1(8)	C(22)	C(23)	C(24)	119.9(9)
C(23)	C(24)	C(25)	120.0(9)	C(24)	C(25)	C(26)	120.6(8)
C(21)	C(26)	C(25)	119.1(8)	P(1)	C(27)	C(28)	119.0(6)
P(1)	C(27)	C(32)	121.1(6)	C(28)	C(27)	C(32)	119.9(8)
C(27)	C(28)	C(29)	120.4(8)	C(28)	C(29)	C(30)	120.9(8)
C(29)	C(30)	C(31)	118.4(8)	C(30)	C(31)	C(32)	120.3(8)
C(27)	C(32)	C(31)	120.0(8)	P(2)	C(33)	C(34)	118.6(6)

Table 5. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
P(2)	C(33)	C(38)	121.1(6)	C(34)	C(33)	C(38)	120.2(7)
C(33)	C(34)	C(35)	119.7(8)	C(34)	C(35)	C(36)	119.7(9)
C(35)	C(36)	C(37)	121.8(8)	C(36)	C(37)	C(38)	119.1(7)
C(33)	C(38)	C(37)	119.4(7)	P(2)	C(39)	C(40)	122.0(6)
P(2)	C(39)	C(44)	120.7(7)	C(40)	C(39)	C(44)	117.3(7)
C(39)	C(40)	C(41)	120.3(8)	C(40)	C(41)	C(42)	121.1(9)
C(41)	C(42)	C(43)	120.7(9)	C(42)	C(43)	C(44)	117.8(9)
C(39)	C(44)	C(43)	122.7(9)	Cl(3)	C(45)	Cl(4)	112.8(7)
Cl(3)	C(45)	Cl(5)	131.4(10)	Cl(3)	C(45)	Cl(6)	37.3(6)
Cl(4)	C(45)	Cl(5)	25.9(6)	Cl(4)	C(45)	Cl(6)	82.8(8)
Cl(5)	C(45)	Cl(6)	107.6(10)				

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{60}H_{47}BCl_2F_4P_2PdS$
Formula Weight	1126.15
Crystal Color, Habit	orange, needle
Crystal Dimensions	0.10 × 0.10 × 0.12 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 11.0986(2) Å b = 14.0338(2) Å c = 33.1907(6) Å V = 5169.64(15) Å^3
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.447 g/cm^3
F_{000}	2296.00
μ(MoKα)	6.19 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Data Images	267 exposures @ 81.0 seconds
ω oscillation Range	0.9^{o}
Detector Position	40.00 mm
$2\theta_{max}$	55.3^{o}
No. of Reflections Measured	Total: 11362 Unique: 6596 (R_{int} = 0.048)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	4619
No. Variables	640
Reflection/Parameter Ratio	7.22
Residuals: R; Rw	0.048 ; 0.042
Goodness of Fit Indicator	2.18
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	1.16 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.74 $e^-/Å^3$

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

atom	x	y	z	B_{eq}
Pd(1)	0.79343(3)	0.93056(2)	0.621026(10)	1.699(7)
Cl(1)	0.5990(2)	0.4739(2)	0.66423(6)	11.79(9)
Cl(2)	0.6612(2)	0.3463(2)	0.59748(7)	8.11(6)
S(1)	0.78771(11)	1.03957(8)	0.56582(3)	2.24(3)
P(1)	0.89868(11)	1.02871(9)	0.66549(4)	1.74(3)
P(2)	0.95544(11)	1.04023(8)	0.54433(4)	1.77(3)
F(1)	0.9440(4)	0.5156(3)	0.6390(2)	10.2(2)
F(2)	0.9947(4)	0.6524(3)	0.66257(12)	9.4(1)
F(3)	0.9114(3)	0.6488(3)	0.60288(10)	7.36(12)
F(4)	1.1007(3)	0.5921(2)	0.61287(10)	5.75(10)
C(1)	0.7476(4)	0.8050(3)	0.65790(13)	1.92(11)
C(2)	0.6576(4)	0.8228(3)	0.63041(12)	1.51(10)
C(3)	0.6808(4)	0.8240(3)	0.58872(13)	1.96(11)
C(4)	0.7252(4)	0.8100(3)	0.70190(13)	1.87(11)
C(5)	0.6451(4)	0.8737(3)	0.7182(2)	2.51(13)
C(6)	0.6228(5)	0.8745(4)	0.7592(2)	2.80(13)
C(7)	0.6788(4)	0.8115(4)	0.7844(1)	2.72(13)
C(8)	0.7606(4)	0.7483(4)	0.7690(1)	3.1(1)
C(9)	0.7831(5)	0.7467(3)	0.7276(1)	2.64(12)
C(10)	0.5912(4)	0.8531(3)	0.5571(1)	2.11(12)
C(11)	0.6128(4)	0.8299(3)	0.5176(1)	2.19(12)
C(12)	0.5332(5)	0.8541(4)	0.4883(1)	2.77(13)
C(13)	0.4280(5)	0.9032(4)	0.4977(1)	2.84(13)
C(14)	0.4069(4)	0.9271(4)	0.5377(2)	2.80(12)
C(15)	0.4881(5)	0.9017(4)	0.5671(1)	2.9(1)
C(16)	0.9912(4)	1.1287(3)	0.64658(12)	1.51(11)
C(17)	1.0937(4)	1.1118(3)	0.6222(1)	1.72(10)
C(18)	1.1730(4)	1.1880(3)	0.61292(13)	1.42(10)
C(19)	1.2828(5)	1.1730(3)	0.59121(13)	2.36(11)
C(20)	1.3560(5)	1.2455(4)	0.5827(2)	2.77(13)
C(21)	1.3259(5)	1.3404(4)	0.5938(2)	3.0(1)
C(22)	1.2243(5)	1.3573(3)	0.6142(2)	2.83(13)
C(23)	1.1453(4)	1.2819(3)	0.6252(1)	2.00(11)
C(24)	1.0387(5)	1.2973(3)	0.6478(1)	2.56(13)
C(25)	0.9661(5)	1.2230(3)	0.6590(1)	2.30(12)
C(26)	1.0594(4)	0.9732(3)	0.57613(13)	1.64(11)
C(27)	1.1204(4)	1.0126(3)	0.60879(13)	1.53(10)
C(28)	1.2040(4)	0.9566(3)	0.63104(11)	1.42(10)
C(29)	1.2736(4)	0.9938(3)	0.66320(13)	2.05(11)
C(30)	1.3480(4)	0.9366(4)	0.68484(13)	2.06(11)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
C(31)	1.3577(4)	0.8372(3)	0.67617(13)	2.22(12)
C(32)	1.2914(5)	0.7996(3)	0.64568(13)	2.10(11)
C(33)	1.2142(4)	0.8567(3)	0.62169(13)	1.70(9)
C(34)	1.1435(5)	0.8184(3)	0.5906(1)	2.20(12)
C(35)	1.0710(5)	0.8742(3)	0.5681(1)	1.92(12)
C(36)	0.7778(4)	1.0883(3)	0.6935(1)	2.21(11)
C(37)	0.6859(5)	1.1303(4)	0.6711(1)	3.2(1)
C(38)	0.5878(5)	1.1684(4)	0.6899(2)	4.0(2)
C(39)	0.5767(5)	1.1659(4)	0.7316(2)	4.1(2)
C(40)	0.6653(6)	1.1237(4)	0.7538(2)	3.5(2)
C(41)	0.7686(4)	1.0844(4)	0.7354(2)	2.89(13)
C(42)	0.9974(4)	0.9730(4)	0.70297(13)	1.89(11)
C(43)	1.0200(4)	0.8764(4)	0.7007(1)	2.14(12)
C(44)	1.0946(5)	0.8319(4)	0.7277(2)	2.85(13)
C(45)	1.1454(5)	0.8852(4)	0.7588(2)	3.5(2)
C(46)	1.1233(5)	0.9816(5)	0.7617(2)	3.5(2)
C(47)	1.0486(5)	1.0254(4)	0.7340(1)	2.44(12)
C(48)	0.9642(4)	0.9800(3)	0.49598(13)	1.92(11)
C(49)	1.0752(4)	0.9521(3)	0.4796(1)	2.46(12)
C(50)	1.0801(5)	0.9075(4)	0.4431(2)	3.1(1)
C(51)	0.9745(6)	0.8871(4)	0.4227(2)	3.6(2)
C(52)	0.8651(5)	0.9135(4)	0.4384(2)	3.3(1)
C(53)	0.8601(5)	0.9601(3)	0.4752(1)	2.49(12)
C(54)	1.0009(4)	1.1625(3)	0.53495(13)	1.81(11)
C(55)	0.9340(4)	1.2363(3)	0.5502(1)	2.30(12)
C(56)	0.9653(5)	1.3294(3)	0.5407(2)	2.93(13)
C(57)	1.0622(5)	1.3488(4)	0.5163(2)	3.3(1)
C(58)	1.1305(5)	1.2766(4)	0.5015(2)	3.2(1)
C(59)	1.1002(5)	1.1831(3)	0.5105(2)	2.80(13)
C(61)	0.6982(8)	0.4114(8)	0.6378(2)	15.7(4)
B(1)	0.9894(8)	0.6000(5)	0.6283(2)	4.6(2)
H(1)	0.7942	0.7508	0.6507	2.305
H(2)	0.5803	0.8414	0.6399	1.813
H(3)	0.7267	0.7702	0.5805	2.351
H(4)	0.6046	0.9176	0.7012	3.014
H(5)	0.5678	0.9196	0.7701	3.354
H(6)	0.6611	0.8115	0.8124	3.260
H(7)	0.8018	0.7057	0.7865	3.754
H(8)	0.8387	0.7018	0.7170	3.168
H(9)	0.6843	0.7964	0.5107	2.628

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
H(10)	0.5495	0.8373	0.4611	3.324
H(11)	0.3720	0.9200	0.4772	3.412
H(12)	0.3360	0.9611	0.5447	3.361
H(13)	0.4728	0.9179	0.5945	3.508
H(14)	1.3037	1.1104	0.5828	2.827
H(15)	1.4296	1.2335	0.5690	3.319
H(16)	1.3778	1.3916	0.5868	3.653
H(17)	1.2044	1.4208	0.6215	3.396
H(18)	1.0173	1.3603	0.6554	3.077
H(19)	0.8976	1.2351	0.6754	2.762
H(20)	1.2682	1.0595	0.6697	2.458
H(21)	1.3944	0.9631	0.7061	2.475
H(22)	1.4100	0.7979	0.6916	2.666
H(23)	1.2970	0.7332	0.6403	2.521
H(24)	1.1470	0.7519	0.5852	2.645
H(25)	1.0267	0.8468	0.5465	2.300
H(26)	0.6916	1.1325	0.6426	3.830
H(27)	0.5260	1.1971	0.6743	4.798
H(28)	0.5084	1.1931	0.7444	4.889
H(29)	0.6572	1.1206	0.7823	4.204
H(30)	0.8305	1.0560	0.7511	3.461
H(31)	0.9830	0.8400	0.6800	2.567
H(32)	1.1114	0.7658	0.7252	3.420
H(33)	1.1956	0.8550	0.7782	4.144
H(34)	1.1594	1.0179	0.7826	4.228
H(35)	1.0322	1.0916	0.7363	2.933
H(36)	1.1475	0.9643	0.4940	2.949
H(37)	1.1557	0.8906	0.4317	3.741
H(38)	0.9778	0.8546	0.3976	4.301
H(39)	0.7930	0.8999	0.4240	3.948
H(40)	0.7844	0.9783	0.4861	2.983
H(41)	0.8667	1.2238	0.5671	2.764
H(42)	0.9190	1.3805	0.5513	3.516
H(43)	1.0815	1.4130	0.5098	3.984
H(44)	1.1986	1.2900	0.4851	3.825
H(45)	1.1473	1.1325	0.4999	3.363
H(46)	0.7568	0.4559	0.6287	18.833
H(47)	0.7343	0.3684	0.6563	18.833

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

Table 2. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Pd(1)	S(1)	2.388(2)	Pd(1)	P(1)	2.332(2)
Pd(1)	C(1)	2.205(6)	Pd(1)	C(2)	2.158(6)
Pd(1)	C(3)	2.225(7)	Cl(1)	C(61)	1.660(10)
Cl(2)	C(61)	1.670(10)	S(1)	P(2)	1.994(3)
P(1)	C(16)	1.848(7)	P(1)	C(36)	1.834(7)
P(1)	C(42)	1.833(7)	P(2)	C(26)	1.825(7)
P(2)	C(48)	1.816(7)	P(2)	C(54)	1.815(7)
F(1)	B(1)	1.335(11)	F(2)	B(1)	1.356(11)
F(3)	B(1)	1.389(12)	F(4)	B(1)	1.342(12)
C(1)	C(2)	1.376(8)	C(1)	C(4)	1.483(8)
C(2)	C(3)	1.408(8)	C(3)	C(10)	1.502(9)
C(4)	C(5)	1.372(9)	C(4)	C(9)	1.390(9)
C(5)	C(6)	1.384(9)	C(6)	C(7)	1.366(9)
C(7)	C(8)	1.366(9)	C(8)	C(9)	1.397(9)
C(10)	C(11)	1.371(9)	C(10)	C(15)	1.373(9)
C(11)	C(12)	1.357(9)	C(12)	C(13)	1.392(10)
C(13)	C(14)	1.388(9)	C(14)	C(15)	1.378(9)
C(16)	C(17)	1.416(9)	C(16)	C(25)	1.414(9)
C(17)	C(18)	1.419(8)	C(17)	C(27)	1.492(8)
C(18)	C(19)	1.431(9)	C(18)	C(23)	1.413(9)
C(19)	C(20)	1.333(9)	C(20)	C(21)	1.422(10)
C(21)	C(22)	1.337(10)	C(22)	C(23)	1.421(9)
C(23)	C(24)	1.418(9)	C(24)	C(25)	1.369(9)
C(26)	C(27)	1.393(8)	C(26)	C(35)	1.421(9)
C(27)	C(28)	1.423(8)	C(28)	C(29)	1.418(8)
C(28)	C(33)	1.441(8)	C(29)	C(30)	1.357(9)
C(30)	C(31)	1.428(9)	C(31)	C(32)	1.358(9)
C(32)	C(33)	1.418(9)	C(33)	C(34)	1.404(9)
C(34)	C(35)	1.348(9)	C(36)	C(37)	1.393(9)
C(36)	C(41)	1.394(9)	C(37)	C(38)	1.364(10)
C(38)	C(39)	1.388(10)	C(39)	C(40)	1.365(10)
C(40)	C(41)	1.412(10)	C(42)	C(43)	1.380(9)
C(42)	C(47)	1.388(9)	C(43)	C(44)	1.370(9)
C(44)	C(45)	1.395(10)	C(45)	C(46)	1.377(10)
C(46)	C(47)	1.381(10)	C(48)	C(49)	1.402(9)
C(48)	C(53)	1.375(9)	C(49)	C(50)	1.365(9)
C(50)	C(51)	1.383(10)	C(51)	C(52)	1.373(10)
C(52)	C(53)	1.387(9)	C(54)	C(55)	1.371(9)
C(54)	C(59)	1.399(9)	C(55)	C(56)	1.388(9)
C(56)	C(57)	1.375(10)	C(57)	C(58)	1.358(10)
C(58)	C(59)	1.387(9)			

Table 4. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
S(1)	Pd(1)	P(1)	96.92(6)	S(1)	Pd(1)	C(1)	158.7(2)
S(1)	Pd(1)	C(2)	122.8(2)	S(1)	Pd(1)	C(3)	92.6(2)
P(1)	Pd(1)	C(1)	103.7(2)	P(1)	Pd(1)	C(2)	132.3(2)
P(1)	Pd(1)	C(3)	169.6(2)	C(1)	Pd(1)	C(2)	36.7(2)
C(1)	Pd(1)	C(3)	66.5(2)	C(2)	Pd(1)	C(3)	37.4(2)
Pd(1)	S(1)	P(2)	104.64(9)	Pd(1)	P(1)	C(16)	120.8(2)
Pd(1)	P(1)	C(36)	102.9(2)	Pd(1)	P(1)	C(42)	118.5(3)
C(16)	P(1)	C(36)	103.4(3)	C(16)	P(1)	C(42)	102.8(3)
C(36)	P(1)	C(42)	106.7(3)	S(1)	P(2)	C(26)	112.4(2)
S(1)	P(2)	C(48)	111.4(2)	S(1)	P(2)	C(54)	109.0(2)
C(26)	P(2)	C(48)	103.7(3)	C(26)	P(2)	C(54)	114.3(3)
C(48)	P(2)	C(54)	105.9(3)	Pd(1)	C(1)	C(2)	69.7(4)
Pd(1)	C(1)	C(4)	123.2(4)	C(2)	C(1)	C(4)	121.5(6)
Pd(1)	C(2)	C(1)	73.5(4)	Pd(1)	C(2)	C(3)	73.9(4)
C(1)	C(2)	C(3)	121.4(6)	Pd(1)	C(3)	C(2)	68.7(4)
Pd(1)	C(3)	C(10)	121.7(4)	C(2)	C(3)	C(10)	124.6(6)
C(1)	C(4)	C(5)	121.9(6)	C(1)	C(4)	C(9)	119.8(6)
C(5)	C(4)	C(9)	118.3(6)	C(4)	C(5)	C(6)	120.6(7)
C(5)	C(6)	C(7)	120.9(7)	C(6)	C(7)	C(8)	119.7(7)
C(7)	C(8)	C(9)	119.7(7)	C(4)	C(9)	C(8)	120.7(7)
C(3)	C(10)	C(11)	119.1(7)	C(3)	C(10)	C(15)	121.1(6)
C(11)	C(10)	C(15)	119.7(7)	C(10)	C(11)	C(12)	120.8(7)
C(11)	C(12)	C(13)	120.6(6)	C(12)	C(13)	C(14)	118.4(7)
C(13)	C(14)	C(15)	120.4(7)	C(10)	C(15)	C(14)	120.1(7)
P(1)	C(16)	C(17)	120.9(5)	P(1)	C(16)	C(25)	120.1(5)
C(17)	C(16)	C(25)	118.8(6)	C(16)	C(17)	C(18)	119.7(6)
C(16)	C(17)	C(27)	119.1(6)	C(18)	C(17)	C(27)	121.0(6)
C(17)	C(18)	C(19)	121.7(6)	C(17)	C(18)	C(23)	120.3(6)
C(19)	C(18)	C(23)	117.9(6)	C(18)	C(19)	C(20)	120.9(6)
C(19)	C(20)	C(21)	121.1(7)	C(20)	C(21)	C(22)	119.7(7)
C(21)	C(22)	C(23)	121.3(7)	C(18)	C(23)	C(22)	119.0(6)
C(18)	C(23)	C(24)	118.5(6)	C(22)	C(23)	C(24)	122.5(6)
C(23)	C(24)	C(25)	121.3(6)	C(16)	C(25)	C(24)	121.2(7)
P(2)	C(26)	C(27)	123.6(5)	P(2)	C(26)	C(35)	117.0(6)
C(27)	C(26)	C(35)	119.3(6)	C(17)	C(27)	C(26)	120.4(6)
C(17)	C(27)	C(28)	119.3(6)	C(26)	C(27)	C(28)	120.1(6)
C(27)	C(28)	C(29)	122.9(6)	C(27)	C(28)	C(33)	118.5(6)
C(29)	C(28)	C(33)	118.5(6)	C(28)	C(29)	C(30)	120.8(6)
C(29)	C(30)	C(31)	121.1(6)	C(30)	C(31)	C(32)	119.3(6)
C(31)	C(32)	C(33)	121.7(6)	C(28)	C(33)	C(32)	118.5(6)

Table 4. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(28)	C(33)	C(34)	119.1(6)	C(32)	C(33)	C(34)	122.3(6)
C(33)	C(34)	C(35)	121.2(6)	C(26)	C(35)	C(34)	121.3(7)
P(1)	C(36)	C(37)	117.3(5)	P(1)	C(36)	C(41)	122.7(6)
C(37)	C(36)	C(41)	119.7(7)	C(36)	C(37)	C(38)	120.4(7)
C(37)	C(38)	C(39)	121.1(8)	C(38)	C(39)	C(40)	119.1(7)
C(39)	C(40)	C(41)	121.3(7)	C(36)	C(41)	C(40)	118.4(7)
P(1)	C(42)	C(43)	119.4(6)	P(1)	C(42)	C(47)	121.5(6)
C(43)	C(42)	C(47)	119.1(7)	C(42)	C(43)	C(44)	121.5(7)
C(43)	C(44)	C(45)	118.9(7)	C(44)	C(45)	C(46)	120.4(8)
C(45)	C(46)	C(47)	119.9(8)	C(42)	C(47)	C(46)	120.2(7)
P(2)	C(48)	C(49)	121.4(5)	P(2)	C(48)	C(53)	119.5(5)
C(49)	C(48)	C(53)	119.1(6)	C(48)	C(49)	C(50)	120.5(7)
C(49)	C(50)	C(51)	119.7(7)	C(50)	C(51)	C(52)	120.5(6)
C(51)	C(52)	C(53)	119.8(7)	C(48)	C(53)	C(52)	120.3(7)
P(2)	C(54)	C(55)	120.0(5)	P(2)	C(54)	C(59)	120.9(5)
C(55)	C(54)	C(59)	119.0(6)	C(54)	C(55)	C(56)	119.5(7)
C(55)	C(56)	C(57)	121.0(7)	C(56)	C(57)	C(58)	120.1(7)
C(57)	C(58)	C(59)	119.5(7)	C(54)	C(59)	C(58)	120.8(7)
Cl(1)	C(61)	Cl(2)	123.4(8)	F(1)	B(1)	F(2)	105.9(9)
F(1)	B(1)	F(3)	111.3(10)	F(1)	B(1)	F(4)	112.1(8)
F(2)	B(1)	F(3)	105.6(8)	F(2)	B(1)	F(4)	108.9(10)
F(3)	B(1)	F(4)	112.5(9)				