Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Chemistry Department, X-ray Lab
(Chernoff Hall, Room 107)

X-Ray Crystallographic Analysis Report for

Pd(dimethylbenzyl amine)(pyridine)(trifluoromethanesulfonate), or Pd(dmba)(py)(OTf)

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Sample ID: Pd(dmba)(py)(OTf)

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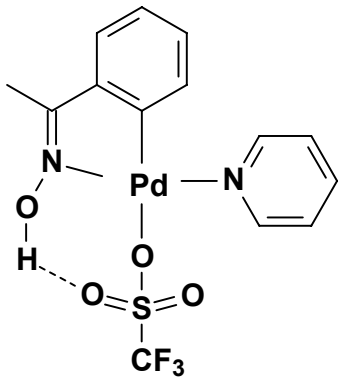
Date: December 22, 2004



A crystal of the compound (ligh-yellow, plate-shaped, size 0.40 x 0.40 x 0.15mm) was mounted on a glass fiber with grease and cooled to -93 °C in a stream of nitrogen gas controlled with Crysostream Controller 700. Data collection was performed on a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 2θ ranges of 4.50 ~ 56.48º. No significant decay was observed during the data collection.

Data were processed on a Pentium PC using the Bruker AXS Crystal Structure Analysis Package, Version 5.10.[1] Neutral atom scattering factors were taken from Cromer and Waber.[2] The raw intensity data were integrated using the program SAINT-Plus, which corrects for *L*p and decay. Absorption corrections were applied using program SADABS. The crystal is orthorhombic space group *P*bca, based on the systematic absences, *E* statistics and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-square refinements minimizing the function $\sum w (F_o^2 - F_c^2)^2$ were applied to the compound. All non-hydrogen atoms were refined anisotropically. The positions for all hydrogen atoms were located gradually in difference Fourier map and their contributions were included in the structure factor calculations.

Convergence to final R_1 = 0.0215 and wR_2 = 0.0542 by using 1976 independent reflections and 278 parameters were achieved,[3] with the largest residual peak and hole to be 0.620 and – 0.326 e/Å^3, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles and hydrogen bond information are given in Table 1 to 7. The molecular structure and the cell packing are shown in Figures 1 and 2.

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[1] Bruker AXS Crystal Structure Analysis Package, Version 5.10 (SMART NT (Version 5.053), SAINT-Plus (Version 6.01), SHELXTL (Version 5.1)); Bruker AXS Inc.: Madison, WI, 1999.

[2] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK, 1974; Vol. 4, Table 2.2 A.

[3] $R_1 = \sum | |Fo| - |Fc| | / \sum |Fo|$

$wR_2 = \{\sum [w (Fo^2 - Fc^2)^2] / \sum [w(Fo^2)^2]\}^{1/2}$

($w = 1 / [\sigma^2(Fo^2) + (0.0318P)^2 + 0.35P]$, where $P = [\text{Max}(Fo^2, 0) + 2Fc^2] / 3$)

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Table 1. Crystal data and structure refinement for Pd(dmba)(py)(OTf)

Identification code	Pd(dmba)(py)(OTf)	
Empirical formula	C14 H13 F3 N2 O4 Pd S	
Formula weight	468.72	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.1786(16) Å	α= 118.529(3)°.
	b = 10.4602(17) Å	β= 97.970(3)°.
	c = 10.6954(18) Å	γ = 104.498(3)°.
Volume	832.2(2) $Å^3$	
Z	2	
Density (calculated)	1.870 Mg/m^3	
Absorption coefficient	1.294 mm^{-1}	
F(000)	464	
Crystal size	0.40 x 0.40 x 0.15 mm^3	
Theta range for data collection	2.25 to 28.24°.	
Index ranges	-12<=h<=12, -13<=k<=13, -13<=l<=13	
Reflections collected	5074	
Independent reflections	3393 [R(int) = 0.0108]	
Completeness to theta = 28.24°	82.8 %	
Absorption correction	Empirical (Bruker SADABS)	
Max. and min. transmission	1.0000 and 0.7950	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3393 / 0 / 278	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0213, wR2 = 0.0543	
R indices (all data)	R1 = 0.0231, wR2 = 0.0551	
Largest diff. peak and hole	0.620 and -0.326 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Pd(dmba)(py)(OTf). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2438(1)	3320(1)	2236(1)	24(1)
S(1)	2941(1)	1485(1)	-1084(1)	28(1)
N(1)	3024(2)	1787(2)	2639(2)	28(1)
N(2)	1865(2)	4982(2)	2016(2)	27(1)
O(1)	3100(2)	377(2)	1594(2)	40(1)
O(2)	1880(2)	1970(2)	-210(2)	36(1)
O(3)	3867(2)	787(2)	-605(2)	38(1)
O(4)	3769(2)	2596(2)	-1398(2)	50(1)
C(1)	2830(2)	4432(3)	4412(2)	27(1)
C(2)	2797(3)	5897(3)	5365(3)	33(1)
C(3)	3122(3)	6505(3)	6898(3)	39(1)
C(4)	3447(3)	5653(3)	7484(3)	40(1)
C(5)	3482(3)	4184(3)	6551(3)	35(1)
C(6)	3197(2)	3581(3)	5031(3)	29(1)
C(7)	3331(2)	2103(3)	3989(3)	30(1)
C(8)	3818(4)	1087(4)	4439(3)	42(1)
C(9)	2790(2)	5775(3)	1549(2)	28(1)
C(10)	2452(3)	6889(3)	1349(3)	32(1)
C(11)	1099(3)	7187(3)	1603(3)	35(1)
C(12)	142(3)	6363(3)	2064(3)	36(1)
C(13)	562(3)	5287(3)	2274(3)	33(1)
C(14)	1553(3)	-132(3)	-2883(3)	39(1)
F(1)	704(2)	-1268(2)	-2762(2)	63(1)
F(2)	2322(2)	-731(2)	-3850(2)	53(1)
F(3)	583(2)	330(2)	-3457(2)	69(1)

Table 3. Bond lengths [Å] and angles [°] for Pd(dmba)(py)(OTf).

Pd(1)-C(1)	1.968(2)
Pd(1)-N(1)	2.0179(16)
Pd(1)-N(2)	2.0422(17)
Pd(1)-O(2)	2.1993(16)
S(1)-O(4)	1.4288(17)
S(1)-O(3)	1.4372(15)
S(1)-O(2)	1.4578(16)
S(1)-C(14)	1.822(3)
N(1)-C(7)	1.287(3)
N(1)-O(1)	1.389(2)
N(2)-C(13)	1.345(3)
N(2)-C(9)	1.348(3)
C(1)-C(2)	1.388(3)
C(1)-C(6)	1.412(3)
C(2)-C(3)	1.398(3)
C(3)-C(4)	1.375(4)
C(4)-C(5)	1.389(4)
C(5)-C(6)	1.390(3)
C(6)-C(7)	1.461(3)
C(7)-C(8)	1.493(3)
C(9)-C(10)	1.378(3)
C(10)-C(11)	1.386(3)
C(11)-C(12)	1.380(3)
C(12)-C(13)	1.378(3)
C(14)-F(1)	1.322(3)
C(14)-F(3)	1.323(3)
C(14)-F(2)	1.329(3)

C(1)-Pd(1)-N(1)	80.32(8)
C(1)-Pd(1)-N(2)	94.83(8)
N(1)-Pd(1)-N(2)	175.14(7)
C(1)-Pd(1)-O(2)	176.63(7)
N(1)-Pd(1)-O(2)	98.32(7)
N(2)-Pd(1)-O(2)	86.52(7)

O(4)-S(1)-O(3)	115.93(11)
O(4)-S(1)-O(2)	114.39(11)
O(3)-S(1)-O(2)	113.72(9)
O(4)-S(1)-C(14)	104.61(12)
O(3)-S(1)-C(14)	104.28(11)
O(2)-S(1)-C(14)	101.74(11)
C(7)-N(1)-O(1)	115.15(17)
C(7)-N(1)-Pd(1)	118.16(16)
O(1)-N(1)-Pd(1)	126.66(13)
C(13)-N(2)-C(9)	118.21(18)
C(13)-N(2)-Pd(1)	122.34(14)
C(9)-N(2)-Pd(1)	119.42(13)
S(1)-O(2)-Pd(1)	127.80(10)
C(2)-C(1)-C(6)	118.4(2)
C(2)-C(1)-Pd(1)	128.60(16)
C(6)-C(1)-Pd(1)	113.04(16)
C(1)-C(2)-C(3)	120.4(2)
C(4)-C(3)-C(2)	120.7(3)
C(3)-C(4)-C(5)	119.8(2)
C(4)-C(5)-C(6)	120.0(2)
C(5)-C(6)-C(1)	120.7(2)
C(5)-C(6)-C(7)	123.6(2)
C(1)-C(6)-C(7)	115.67(19)
N(1)-C(7)-C(6)	112.68(18)
N(1)-C(7)-C(8)	123.3(2)
C(6)-C(7)-C(8)	123.9(2)
N(2)-C(9)-C(10)	122.30(19)
C(9)-C(10)-C(11)	119.2(2)
C(12)-C(11)-C(10)	118.6(2)
C(13)-C(12)-C(11)	119.5(2)
N(2)-C(13)-C(12)	122.3(2)
F(1)-C(14)-F(3)	108.7(2)
F(1)-C(14)-F(2)	107.4(2)
F(3)-C(14)-F(2)	107.7(2)
F(1)-C(14)-S(1)	111.22(18)
F(3)-C(14)-S(1)	111.34(19)

F(2)-C(14)-S(1)	110.40(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Pd(dmba)(py)(OTf). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	28(1)	27(1)	25(1)	17(1)	11(1)	13(1)
S(1)	32(1)	30(1)	27(1)	17(1)	10(1)	13(1)
N(1)	35(1)	27(1)	31(1)	19(1)	13(1)	14(1)
N(2)	27(1)	28(1)	28(1)	17(1)	9(1)	13(1)
O(1)	65(1)	33(1)	38(1)	24(1)	24(1)	27(1)
O(2)	43(1)	45(1)	28(1)	19(1)	12(1)	27(1)
O(3)	40(1)	49(1)	36(1)	25(1)	15(1)	26(1)
O(4)	56(1)	48(1)	57(1)	38(1)	20(1)	11(1)
C(1)	23(1)	31(1)	27(1)	17(1)	8(1)	8(1)
C(2)	33(1)	34(1)	32(1)	16(1)	11(1)	13(1)
C(3)	37(1)	37(2)	32(1)	11(1)	12(1)	12(1)
C(4)	35(1)	51(2)	26(1)	18(1)	10(1)	11(1)
C(5)	30(1)	47(2)	32(1)	26(1)	10(1)	10(1)
C(6)	24(1)	33(1)	31(1)	20(1)	8(1)	6(1)
C(7)	28(1)	33(1)	34(1)	23(1)	8(1)	9(1)
C(8)	54(2)	40(2)	40(2)	29(2)	8(1)	17(1)
C(9)	28(1)	32(1)	28(1)	18(1)	10(1)	13(1)
C(10)	36(1)	32(1)	32(1)	19(1)	11(1)	13(1)
C(11)	38(1)	31(1)	37(1)	19(1)	7(1)	18(1)
C(12)	29(1)	37(2)	42(1)	19(1)	11(1)	18(1)
C(13)	30(1)	35(1)	38(1)	21(1)	14(1)	14(1)
C(14)	43(1)	40(2)	33(1)	16(1)	11(1)	21(1)
F(1)	51(1)	47(1)	63(1)	19(1)	13(1)	-2(1)
F(2)	72(1)	54(1)	35(1)	17(1)	24(1)	35(1)
F(3)	78(1)	76(1)	36(1)	14(1)	-4(1)	49(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Pd(dmba)(py)(OTf).

	x	y	z	U(eq)
H(01)	3310(30)	470(30)	1000(30)	36(8)
H(2)	2590(30)	6480(30)	5020(30)	35(7)
H(3)	3160(40)	7510(40)	7520(40)	56(9)
H(4)	3700(30)	6110(30)	8540(30)	42(7)
H(5)	3660(30)	3590(30)	6910(30)	39(7)
H(8C)	2960(40)	390(40)	4340(40)	58(9)
H(8B)	4380(40)	550(40)	3820(40)	66(10)
H(8A)	4530(40)	1670(40)	5410(40)	69(10)
H(9)	3690(30)	5540(30)	1340(30)	27(6)
H(10)	3110(30)	7410(30)	1010(30)	40(7)
H(11)	870(30)	7880(30)	1440(30)	30(6)
H(12)	-790(30)	6540(30)	2260(30)	38(7)
H(13)	-40(30)	4720(30)	2580(30)	36(7)

Table 6. Torsion angles [°] for Pd(dmba)(py)(OTf).

C(1)-Pd(1)-N(1)-C(7)	1.87(16)
N(2)-Pd(1)-N(1)-C(7)	-0.7(9)
O(2)-Pd(1)-N(1)-C(7)	-175.01(16)
C(1)-Pd(1)-N(1)-O(1)	-179.74(18)
N(2)-Pd(1)-N(1)-O(1)	177.7(7)
O(2)-Pd(1)-N(1)-O(1)	3.38(18)
C(1)-Pd(1)-N(2)-C(13)	-66.55(19)
N(1)-Pd(1)-N(2)-C(13)	-64.1(8)
O(2)-Pd(1)-N(2)-C(13)	110.35(19)
C(1)-Pd(1)-N(2)-C(9)	115.67(18)
N(1)-Pd(1)-N(2)-C(9)	118.2(8)
O(2)-Pd(1)-N(2)-C(9)	-67.43(17)
O(4)-S(1)-O(2)-Pd(1)	-88.64(14)
O(3)-S(1)-O(2)-Pd(1)	47.70(16)
C(14)-S(1)-O(2)-Pd(1)	159.21(12)
C(1)-Pd(1)-O(2)-S(1)	-128.7(11)
N(1)-Pd(1)-O(2)-S(1)	-62.80(13)
N(2)-Pd(1)-O(2)-S(1)	117.67(13)
N(1)-Pd(1)-C(1)-C(2)	176.4(2)
N(2)-Pd(1)-C(1)-C(2)	-3.8(2)
O(2)-Pd(1)-C(1)-C(2)	-117.2(11)
N(1)-Pd(1)-C(1)-C(6)	-3.12(14)
N(2)-Pd(1)-C(1)-C(6)	176.66(14)
O(2)-Pd(1)-C(1)-C(6)	63.3(12)
C(6)-C(1)-C(2)-C(3)	0.0(3)
Pd(1)-C(1)-C(2)-C(3)	-179.53(17)
C(1)-C(2)-C(3)-C(4)	-1.3(4)
C(2)-C(3)-C(4)-C(5)	1.2(4)
C(3)-C(4)-C(5)-C(6)	0.3(3)
C(4)-C(5)-C(6)-C(1)	-1.6(3)
C(4)-C(5)-C(6)-C(7)	175.1(2)
C(2)-C(1)-C(6)-C(5)	1.5(3)
Pd(1)-C(1)-C(6)-C(5)	-178.92(16)
C(2)-C(1)-C(6)-C(7)	-175.52(18)

Pd(1)-C(1)-C(6)-C(7)	4.1(2)
O(1)-N(1)-C(7)-C(6)	-178.71(17)
Pd(1)-N(1)-C(7)-C(6)	-0.1(2)
O(1)-N(1)-C(7)-C(8)	3.0(3)
Pd(1)-N(1)-C(7)-C(8)	-178.39(18)
C(5)-C(6)-C(7)-N(1)	-179.5(2)
C(1)-C(6)-C(7)-N(1)	-2.6(3)
C(5)-C(6)-C(7)-C(8)	-1.3(3)
C(1)-C(6)-C(7)-C(8)	175.6(2)
C(13)-N(2)-C(9)-C(10)	0.8(3)
Pd(1)-N(2)-C(9)-C(10)	178.68(18)
N(2)-C(9)-C(10)-C(11)	-1.4(4)
C(9)-C(10)-C(11)-C(12)	0.6(4)
C(10)-C(11)-C(12)-C(13)	0.7(4)
C(9)-N(2)-C(13)-C(12)	0.6(4)
Pd(1)-N(2)-C(13)-C(12)	-177.21(19)
C(11)-C(12)-C(13)-N(2)	-1.4(4)
O(4)-S(1)-C(14)-F(1)	179.46(17)
O(3)-S(1)-C(14)-F(1)	57.28(19)
O(2)-S(1)-C(14)-F(1)	-61.20(18)
O(4)-S(1)-C(14)-F(3)	-59.2(2)
O(3)-S(1)-C(14)-F(3)	178.62(18)
O(2)-S(1)-C(14)-F(3)	60.1(2)
O(4)-S(1)-C(14)-F(2)	60.4(2)
O(3)-S(1)-C(14)-F(2)	-61.83(19)
O(2)-S(1)-C(14)-F(2)	179.69(16)

Symmetry transformations used to generate equivalent atoms:

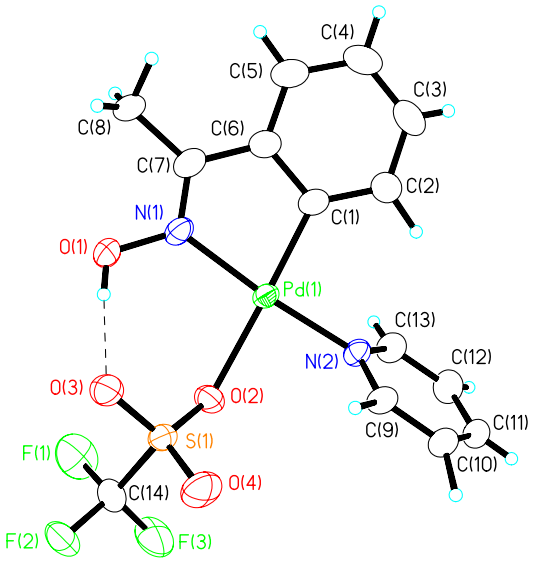
Table 7. Hydrogen bonds for Pd(dmba)(py)(OTf) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(01)...O(3)	0.73(3)	2.01(3)	2.736(2)	178(3)

Symmetry transformations used to generate equivalent atoms:

Figure 1. Molecular Structure of Pd(dmba)(py)(OTf) (Displacement ellipsoids for non-H atoms are shown at the 50% probability level and H atoms are represented by circles of arbitrary size.)

a)



b)

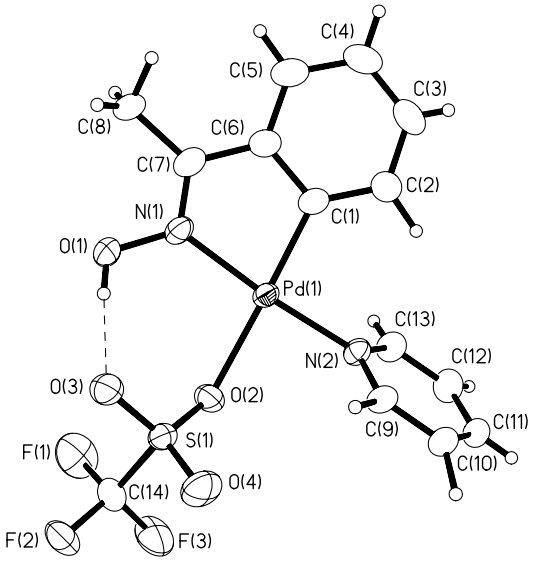
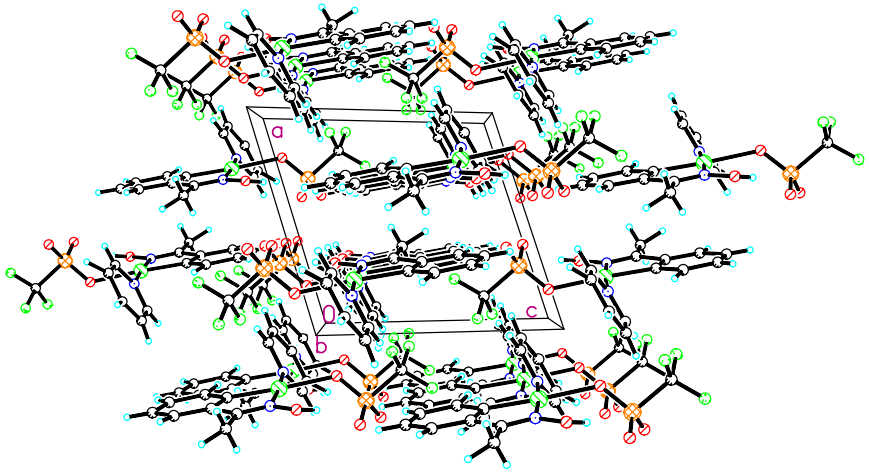


Figure 2. Unit Cell Packing of $_{Pd(dmba)(py)(OTf)}$

a)



b)