Supporting Information

Reductive Elimination of C_6F_5-C_6F_5 in Reaction of

Bis(pentafluorophenyl)palladium(II) Complexes with Protic Acids

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Experimental

General and Materials. ^{1}H and ^{19}F NMR spectra were recorded on a JEOL EX-400 spectrometer. IR spectra were recorded on a JASCO IR 810 spectrophotometer. UV-Vis spectra were measured with a Shimadzu UV-2550 UV-visible spectrophotometer. [PdCl$_2$(cod)][1] was prepared according to literature method. Other reagents were purchased from Aldrich co. Ltd. and Tokyo Kasei Kogyo Co. Ltd.

Synthesis of [Pd(C$_6$F$_5$)$_2$(dppb)] (5). To a CH$_2$Cl$_2$ solution (10 mL) of **1** (100 mg, 0.182 mmol) added 1,4-bis(diphenylphosphino)butane (90 mg, 0.211mmol) and refluxed for 2 h. The solution was concentrated *ca.* 5mL, and hexane (20 mL) was added to the solution. The resultant colorless solid was collected by filtration and dried in vacuo. Yield: 146 mg (88%). Anal. Calcd for C$_{40}$H$_{28}$F$_{10}$P$_2$Pd: C, 55.41; H, 3.26; F, 21.91. Found: C, 55.14; H, 3.37; F, 21.98. ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C, TMS) δ 7.50 (m, 20H, Ph), 2.66 (4H, P-C*H$_2$*), 1.97 (4H, P-CH$_2$-C*H$_2$*). ^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$, 23 °C, CF$_3$COOD) δ -115.3 (*o*-F), -162.5 (*p*-F), -163.5 (*m*-F).

Acidolysis of complexes. General procedure for the acidolysis of the complexes are as follows.

Method A: To a solution of complex **1** (20 mg, 0.037 mmol) in a THF-*d$_8$*/CDCl$_3$ mixture (1/3 v/v, 0.75 mL) was added 0.25 mL of 13.4 M HNO$_3$, and the mixture was stirred vigorously in a capped vial tube at r.t.. After 12 h, the solution was transferred to a NMR tube, and the products were identified by ^{19}F{^{1}H} NMR spectroscopy.

Method B: To a solution of complex **1** (20 mg, 0.037 mmol) in THF (3 mL) was added 0.2 mL of conc. HCl, and the mixture was stirred vigorously in a capped vial tube at r.t.. After 48 h, the solvent was removed by evaporation. CDCl$_3$ (0.6 mL) was added to the residue

and the solution was transferred to a NMR tube. The products were identified by $^{19}F\{^{1}H\}$

NMR spectroscopy.

X-ray diffraction study

Crystals of **1**, **2**, **3**, and **5** suitable for crystallography were obtained by recrystallization

from THF-hexane mixtures. Crystals were mounted on a glass fiber. Data were collected

on a Saturn CCD area detector coupled with a Rigaku/MSC diffractometer with

graphite-monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å) and processed using Crystal

Clear. Space group was determined on the basis of systematic analysis of intensity

distribution, and the successful solution and refinement of the structure. The data were

collected at a temperature of 173 K to a maximum 2θ value of 55.0˚. A total of 720

oscillation images were collected. A first sweep of data was done using scans from

-110.0 to 70.0˚ in 0.50 step, at $\chi = 45.0$˚ and $\phi = 0.0$˚ and a second was done using scans

from -11.0 to 70.0˚ in 0.50 step, at $\chi = 45.0$˚ and $\phi = 90.0$˚. The crystal-to-detector

distance was 45.00 mm and the detector swing angle was 20.24 ˚. A numerical absorption

correction was applied. The data were collected for Lorentz and polarization factors. All

the structures were solved using a Crystal Structure package. The non-hydrogen atoms

were refined anisotropically by full-matrix least-squares refinement of F. Refinements

were performed anisotropically for all non-hydrogen atoms by the full-matrix

least-square method. Hydrogen atoms were placed at the calculated positions and were

included in the structure calculation without further refinement of the parameters. Details

of crystal parameters and structure refinement are given in Table S4.

1) D. Drew, J. R.Doyle, *Inorg. Synth*. **1972**, *13*, 52.
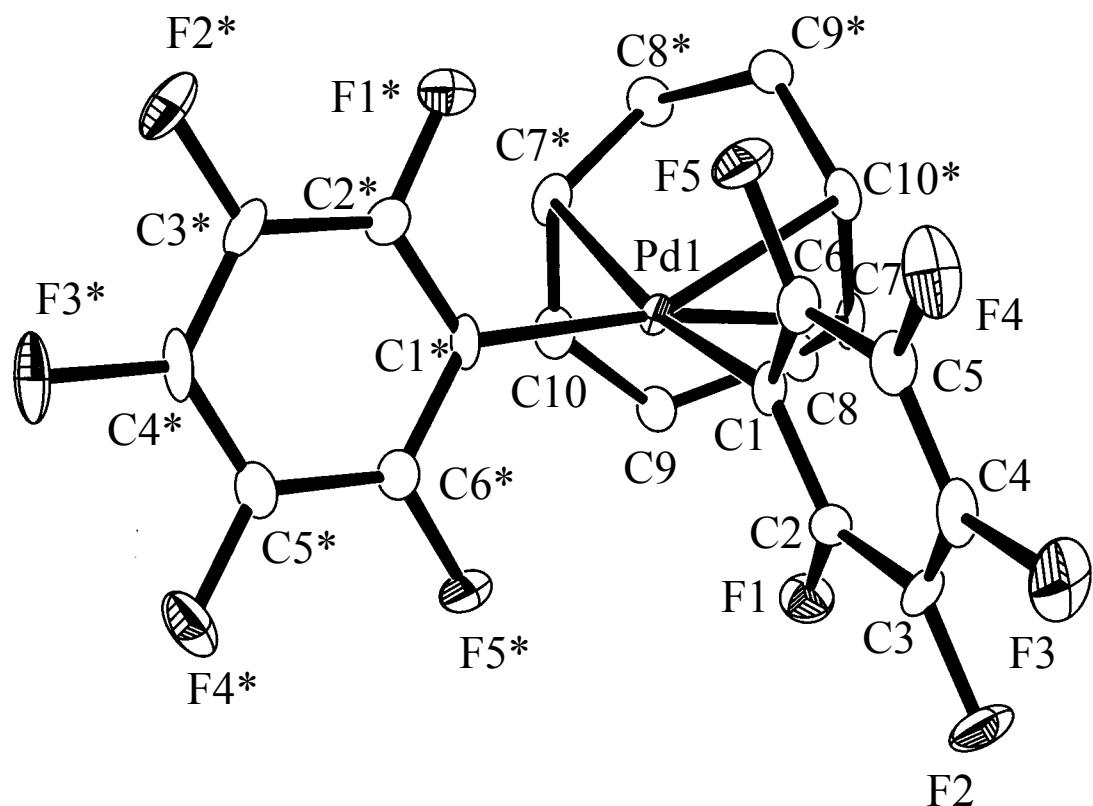
Figure S1.   ORTEP drawing of [Pd(C$_6$F$_5$)$_2$(cod)] (**1**) with 50% ellipsoidal level. Hydrogen atoms are omitted for clarity.
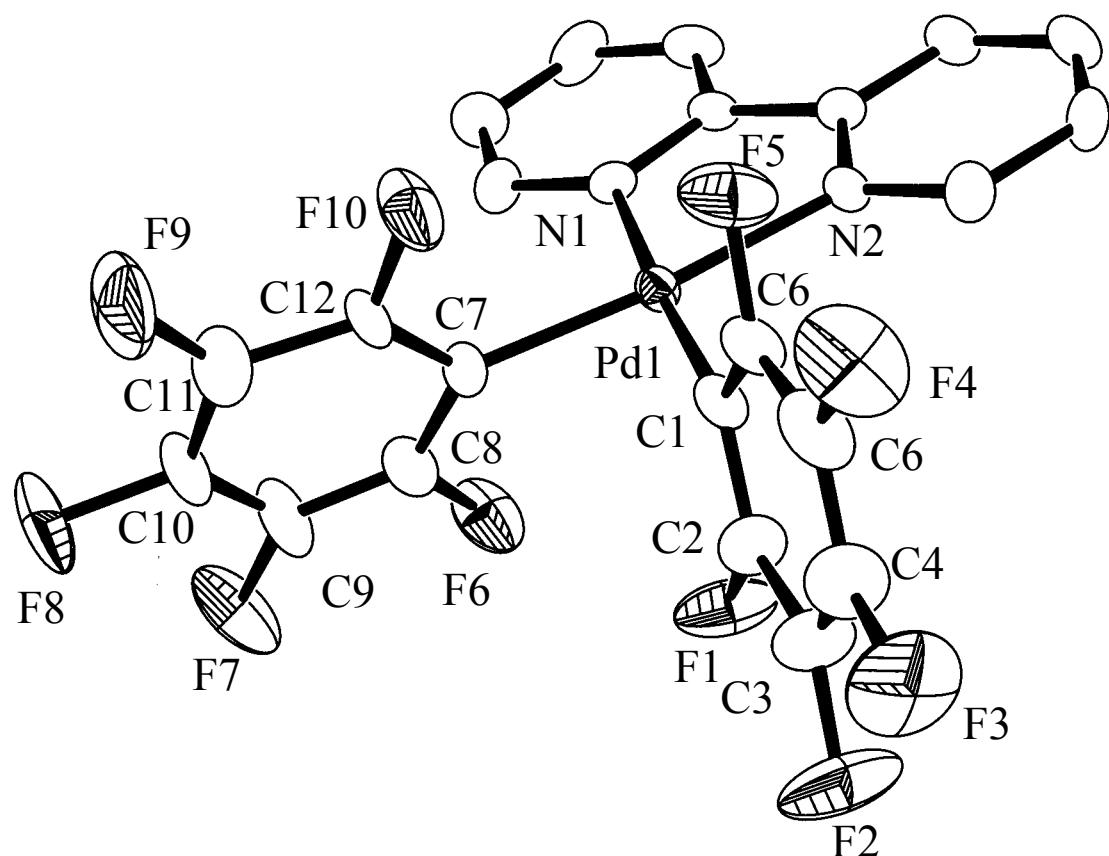
Figure S2. ORTEP drawing of [Pd(C$_6$F$_5$)$_2$(bpy)] (**2**) with 50% ellipsoidal level. Hydrogen atoms are omitted for clarity.
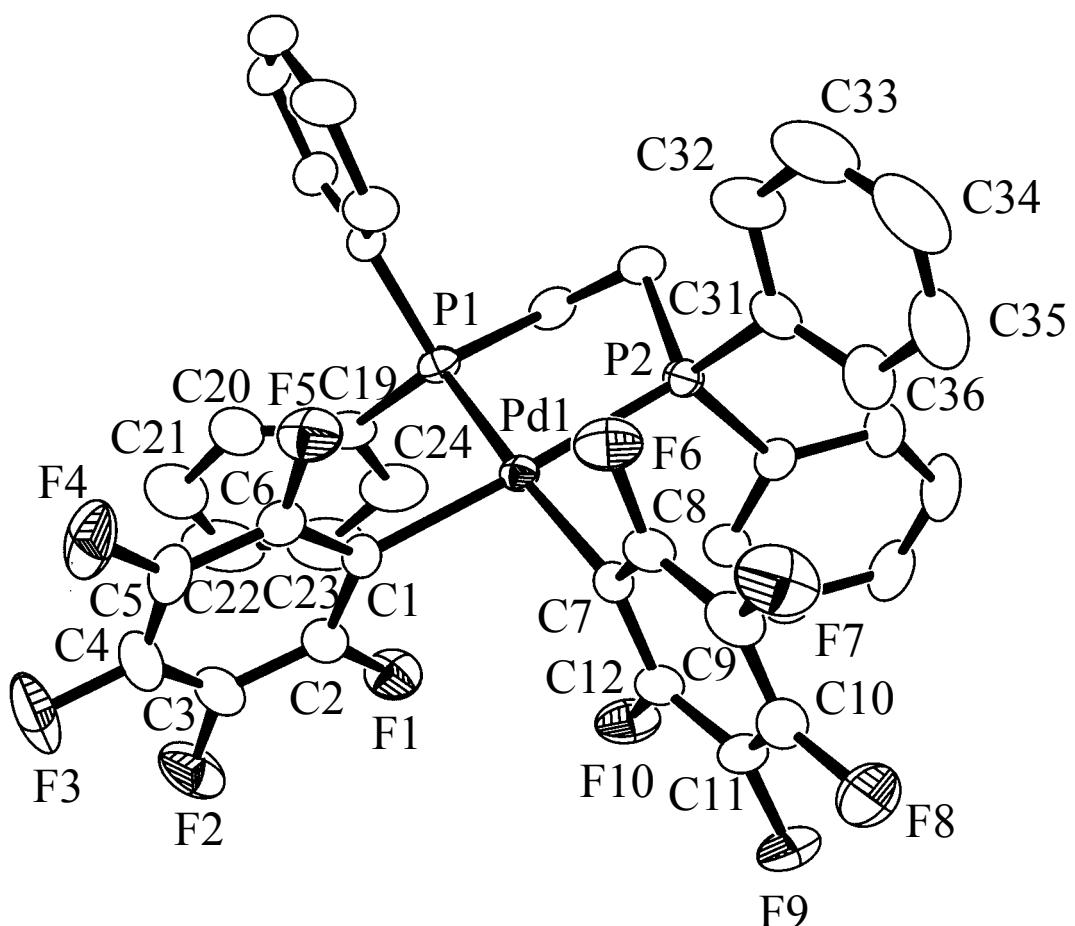
Figure S3. ORTEP drawing of $[Pd(C_6F_5)_2(dppe)]$ (**3**) with 50% ellipsoidal level. Hydrogen atoms are omitted for clarity.
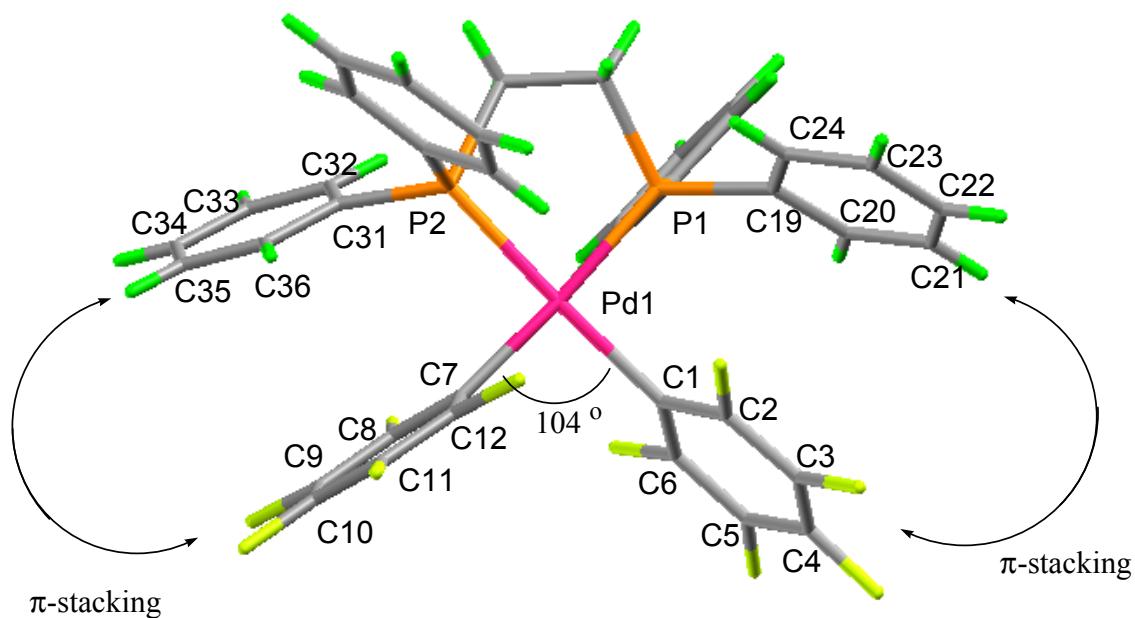
Figure S4. Side view of Complex **3**. Selected bond lengths and dihedral angles: C2-C20, 3.484(3) Å; C8-C36, 3.325(3) Å; C_6F_5(C1-C6)-C_6H_5(C19-C24), 18.5(1) °; C_6F_5(C7-C12)-C_6H_5(C31-C36), 13.1(1) °.
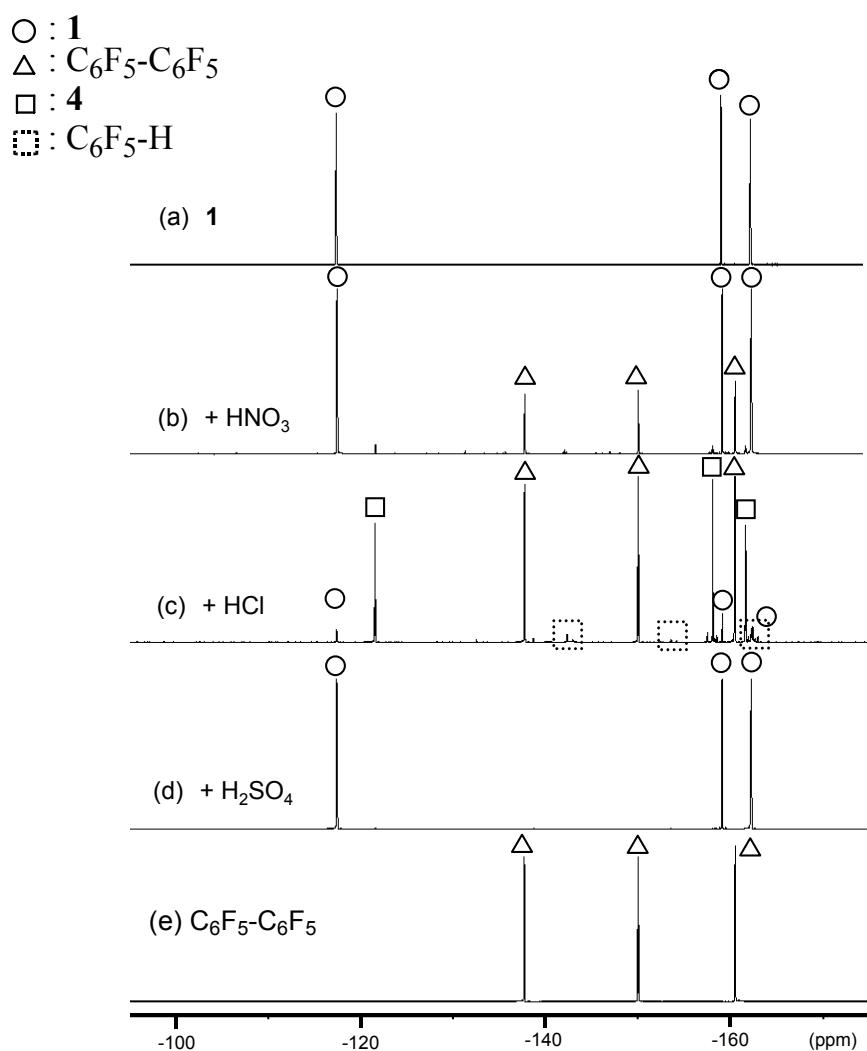
Figure S5. (a) $^{19}F\{^1H\}$ NMR spectrum of original **1**. (b)-(c) $^{19}F\{^1H\}$ NMR spectra after the reaction with protic acids: (b) with HNO_3 (13.4 M), (c) with HCl (12 M) and (d) with H_2SO_4 (2.0 M). Reaction conditions: in THF for 12 h at room temperature. (e) $^{19}F\{^1H\}$ NMR spectrum of C_6F_5-C_6F_5. Assignment of the peaks is shown by the ○, △, □, and ⬚ marks.
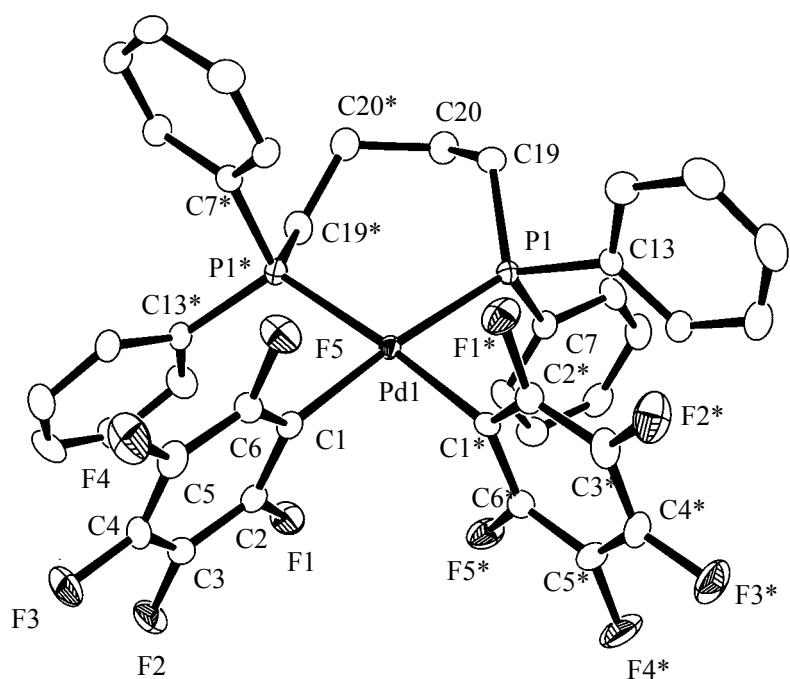
Figure S6. Molecular structure of **5** with 50% ellipsoidal level. Hydrogen atoms are omitted for clarity

Table S1. Selected bond lengths (Å), angles (deg), and a dihedral angle of 1.

Pd1-C1	2.022(5)	Pd1-C7	2.322(6)
Pd1-C10	2.270(5)	C8-C9	1.533(7)
C7-C10*	1.373(11)	C1···C1*	2.808(8)
C1-Pd1-C1*	88.2(4)	C7-Pd1-C7*	86.0(2)
Plane 1(C1-C6)-Plane 1* (C1-C6)	88.9		

Table S2. Selected bond lengths (Å), angles (deg), and a dihedral angle of 2.

Pd1-C1	2.010(5)	Pd1-C7	1.995(6)
Pd1-N1	2.081(5)	Pd1-N2	2.084(4)
C1···C7	2.741(8)		
C1-Pd1-C7	86.4(2)	N1-Pd1-N2	78.5(2)
N1-Pd1-C1	175.9(2)	N2-Pd1-C7	174.8(2)
N2-Pd1-C1	97.9(2)	N2-Pd1-C7	97.3(2)
Plane $1_{(C1-C6)}$-Plane $2_{(C7-C12)}$		91.0(3)	

Table S3. Selected bond lengths (Å), angles (deg), and a dihedral angle of 3.

Pd1-C1	2.078(2)	Pd1-C7	2.099(2)
Pd1-P1	2.2849(5)	Pd1-P2	2.2915(5)
C1⋯C7	3.028(3)		
C1-Pd1-C7	92.94(8)	P1-Pd1-P2	84.87(2)
P1-Pd1-C1	91.61(5)	P2-Pd1-C7	90.57(5)
P2-Pd1-C1	176.48(5)	P2-Pd1-C7	90.57(5)
Plane 1$_{(C1-C6)}$-Plane 2 $_{(C7-C12)}$	104.08(8)		
Plane 1$_{(C1-C6)}$-Plane 4 $_{(C19-C24)}$	18.6(1)		
Plane 2$_{(C7-C12)}$-Plane 6 $_{(C31-C36)}$	13.0(1)		

Table S4. Selected bond lengths (Å), angles (deg), and a dihedral angle of 5.

Pd1-C1	2.063(2)	Pd1-P1	2.3202(7)
C1···C1*	2.828(3)		
C1-Pd1-C1*	86.57(9)	P1-Pd1-P1*	96.70(3)
P1-Pd1-C1	88.57(9)	P1-Pd1-C1*	174.89(7)
Plane $1_{(C1-C6)}$-Plane $2_{(C7-C12)}$		86.59	

Table S5. Crystal data and details of the structure refinement of 1 , 2, 3, and 5.

	1	2	3	5
Formula	$C_{20}H_{12}F_{10}Pd$	$C_{22}H_8F_{10}N_2Pd$	$C_{38}H_{24}F_{10}P_2Pd$	$C_{40}H_{28}F_{10}P_2Pd$
Mol weight	547.70	596.70	838.94	866.99
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$C2$ (No. 5)
a (Å)	19.002(10)	13.450(4)	13.599(3)	16.622(6)
b (Å)	8.037(4)	7.1639(19)	16.667(4)	9.954(3)
c (Å)	13.386(7)	25.045(7)	15.613(3)	11.013(4)
β (°)	117.9746(17)	90.3929(13)	98.7837(11)	109.1665(14)
V (Å^3)	1805.4(16)	2413.2(11)	3497.2(13)	1721.1(10)
Z	4	4	4	2
μ (cm^{-1})	11.328	8.578	7.033	7.175
$F(000)$	1056.00	1160.00	1672.00	868.00
D_{calc} (g cm^{-3})	2.004	1.642	1.593	1.673
No. unique reflns	3481	4966	7352	3234
No. reflns used	3481	4966	7352	3234
No. variables	147	324	484	296
$R_1{}^a$	0.0461	0.0542	0.0316	0.0160
R	0.0586	0.0872	0.0399	0.0162
$R_w{}^b$	0.0969^c	0.0983^d	0.0408^e	0.0186^f

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[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $I > 2.0\sigma(I)$ data. [b] $R_w = \Sigma[w(F_o{}^2-F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$. [c] Weighting scheme $1/\sigma^2(F_o)$. [d] Weighting scheme $1/[0.0010F_o{}^2+3.0000\sigma(F_o{}^2)+0.50000]$. [e] Weighting scheme $1/[0.0005F_o{}^2+1.0000\sigma(F_o{}^2)]$. [f] Weighting scheme $1/[0.0005F_o{}^2+1.0000\sigma(F_o{}^2)]$.