Supplementary Materials

Reductive Coupling of Metal Triangles in Sandwich Complexes

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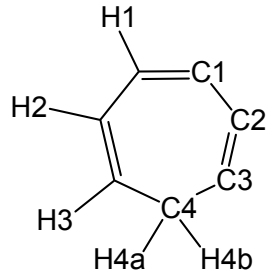
Experimental Section

General Consideration. All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectra were recorded on 270 (JEOL GSX-270) and 400 MHz (JEOL GSX-400) instruments. The chemical shifts were referenced to the residual resonances of deuterated solvents. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. X-ray crystal data were collected by Rigaku RAXIS-RAPID Imaging Plate diffractometer. Cyclic voltammograms were obtained by ALS 600A electrochemical analyzer. Unless specified, all reagents were purchased from commercial suppliers and used without purification. Dichloromethane, acetonitrile, THF, Et_2O, CD_2Cl_2, and CD_3CN were purified according to the standard procedures. $[Pd_2(CH_3CN)_6][BF_4]_2$,[11] $Pd_2(dba)_3$,[‡] and *tert*-Butylcycloheptatriene[§] were prepared according to the literature.

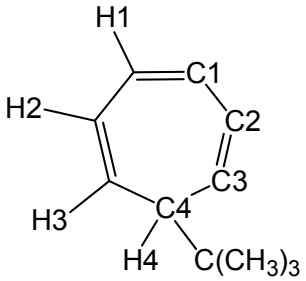
[‡] Ukai, H.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253.

[§] (a) Nozoe, T.; Takahashi, K.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3277. (b) Moriconi, E. J.; Hummel, C. F. *J. Org. Chem.* **1976**, *41*, 3583.

Synthesis of $[Pd_3(\mu_3\text{–}C_7H_8)_2(CH_3CN)_3][BF_4]_2$ (2-H): To a solution of cycloheptatriene (163 μL, 1.58 mmol) and $Pd_2(dba)_3$ (164 mg, 0.158 mmol) in CH_2Cl_2 (200 mL) was added $[Pd_2(CH_3CN)_6][BF_4]_2$ (200 mg, 0.316 mmol), and the mixture was stirred for 1 h at room temperature. The solution was filtered, and *n*-hexane was added to the filtrate. Crystallization at –20 °C gave an orange-red powder of **2-H** (230 mg, 91% yield). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 5.04 (m, 4H, H1), 4.89 (m, 4H, H3), 3.90 (m, 4H, H2), 3.23 (d, J = 19.6 Hz, 2H, H4a), 2.58 (m, 2H, H4b), 2.35 (s, 9H, CH_3CN). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ 124.3 (s, $CH_3\mathit{C}N$), 90.6 (s, C2), 82.4 (s, C3), 75.1 (s, C1), 33.6 (s, C4), 3.70 (s, $\mathit{C}H_3CN$). Anal. Calcd. for $C_{20}H_{25}B_2F_8N_3Pd_3$: C, 29.35; H, 3.33; N, 5.13. Found: C, 29.62; H, 3.09; N, 4.67.



Synthesis of $[Pd_3(\mu_3\text{–}C_7H_7(t\text{-Bu}))_2(CH_3CN)_3][BF_4]_2$ (2-^{t}Bu): To a solution of *tert*-butylcycloheptatriene (250 mg, 1.69 mmol) in CH_2Cl_2 (15 mL) was added $[Pd_2(CH_3CN)_6][BF_4]_2$ (215 mg, 0.34 mmol) and $Pd_2(dba)_3$ (176 mg, 0.17 mmol), and the mixture was stirred for 1 h at room temperature. The solution was filtered, and addition of Et_2O to the filtrate gave an orange-red precipitate. The precipitate was washed with Et_2O, and dried in vacuo to yield the analytically pure orange-red powder of **2-^{t}Bu** (251 mg, 81% yield). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 5.17 (t, J = 4.2 Hz, 4H, H1), 5.11 (dd, J = 5.0 Hz, J = 9.8 Hz, 4H, H3), 4.13 (m, 4H, H2), 2.42 (s, CH_3CN), 2.37 (t, J = 5.0 Hz, 2H, H4), 1.27 (s, 18H, –C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ 124.2 (s, CH_3CN), 91.2 (s, C2), 85.2 (s, C3), 75.9 (s, C1), 53.7 (s, C4), 41.8 (s, –C(CH_3)$_3$), 26.9 (s, –C(CH_3)$_3$), 3.46 (s, CH_3CN). Anal. Calcd. for $C_{28}H_{41}B_2F_8N_3Pd_3$: C, 36.85; H, 4.53; N, 4.60. Found: C, 36.78; H, 4.47; N, 4.77. A single crystal suitable to X-ray structure analysis was obtained by recrystallization from CH_3CN/Et_2O.



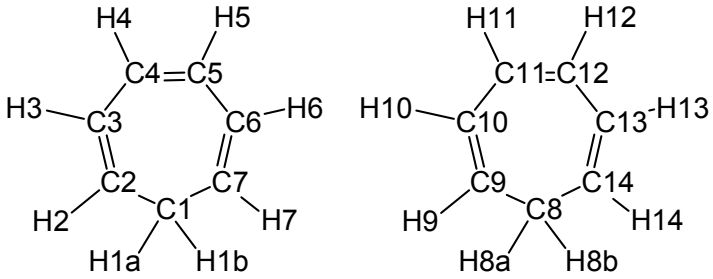
Synthesis of $[Pd_6(\mu_3\text{–}C_7H_7)_4(CH_3CN)_4][BF_4]_2$ (3a): To a solution of $[Pd_3(\mu_3\text{-}C_7H_7)_2(CH_3CN)_3][BF_4]_2$ (**1a**) (1.00 g, 1.25 mmol) in CH_3CN (20 mL) was added

$Li_2(C_8H_8)$ (3 mL, 0.282 M in THF) at –20 °C. Then the mixture was stirred for 1 h at room temperature. The reaction mixture was filtered and addition of Et_2O to the filtrate gave a deep-green precipitate. The precipitate was washed with Et_2O, and the volatiles were removed in vacuo to yield a deep-green powder of **3a** (642 mg, 76% yield). ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ 4.05 (s, 28H). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_3CN, 25 °C): δ 68.7 (s). A single crystal suitable to X-ray structure analysis was obtained by recrystallization from CH_3CN/Et_2O.

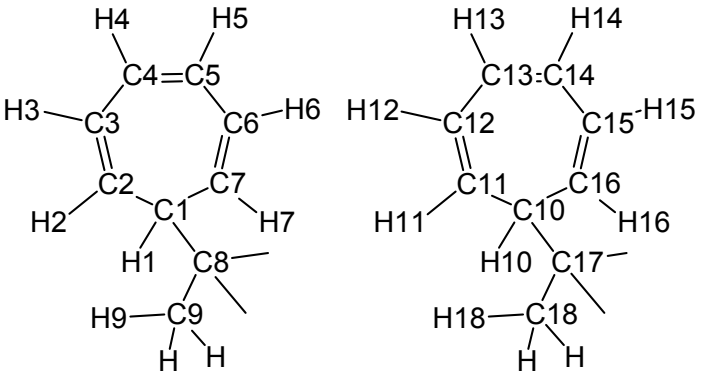
Synthesis of $[Pd_6(\mu_3\text{–}C_7H_7)_4(PPh_3)_4][BF_4]_2$ (3b): To a solution of $[Pd_6(\mu_3\text{–}C_7H_7)_4(CH_3CN)_4][BF_4]_2$ (**3a**) (100 mg, 0.746 mmol) in CH_3CN (5 mL) was added PPh_3 (78.2 mg, 298 mg), and the mixture was stirred for 15 min at room temperature. The reaction mixture was filtered and filtrate was concentrated in vacuo. Addition of toluene to the solution gave a deep-green precipitate. The precipitate was washed with toluene and n-hexane, and dried in vacuo to give a deep-green powder of **3b** (125 mg, 75% yield). ^{1}H NMR (270 MHz, CD_3CN, 25 °C): δ 7.53-7.24 (m, 60H, PPh_3), 3.73 (s, 28H). $^{31}P\{^1H\}$ NMR (109.5 MHz, CD_3CN, 25 °C): δ 17.4 (s).

Synthesis of $[Pd_6(\mu_3\text{–}C_7H_8)_4(CH_3CN)_4][BF_4]_2$ (4-H): To a solution of $[Pd_3(\mu_3\text{-}C_7H_8)_2(CH_3CN)_3][BF_4]_2$ (**2-H**) (200 mg, 0.25 mmol) in CH_3CN (10 mL) was added $Li_2(C_8H_8)$ (3 mL, 0.05 M in THF) at –20 °C. Then the mixture was stirred for 1 h at room temperature. The reaction mixture was filtered, and addition of Et_2O to the filtrate gave a black precipitate. The precipitate was washed with Et_2O and n-pentane, and the volatiles were removed in vacuo to yield a black powder of **4-H** (158 mg, 94% yield). ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ 5.40 (m, 2H, H14), 5.30 (t, J = 7.4 Hz, 2H, H11), 5.17 (t, J = 7.4 Hz, 2H, H4), 4.47 (t, J = 7.8 Hz, 2H, H12), 4.43 (m, 2H, H7), 4.19 (t, J = 7.6 Hz, 2H, H5), 4.14 (m, 2H, H9), 4.09 (m, 2H, H2), 3.84 (t, J = 8.4 Hz, 2H, H10), 3.73 (t, J = 8.4 Hz, 2H, H3), 3.26 (t, J = 8.2 Hz, 2H, H13), 3.10 (d, J = 18.4 Hz, 2H, H8a), 2.79 (d, J = 18.8 Hz, 2H, H1a),

2.64 (t, J = 8.2 Hz, 2H, H6), 2.16 (tt, J = 5.4 Hz, J = 18.4 Hz, 2H, H8b), 1.52 (tt, J = 5.1 Hz, J = 19.2 Hz, 2H, H1b). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, CD_3CN, 25 °C): δ 88.4 (s, C13), 86.8 (s, C10), 86.7 (s, C6), 86.6 (s, C3), 75.6 (s, C5), 74.9 (s, C9), 74.2 (s, C2), 72.9 (s, C12), 71.3 (s, C11), 70.3 (s, C4), 56.3 (s, C7), 54.3 (s, C14), 32.6 (s, C8), 32.1 (s, C1). A single crystal suitable to X-ray structure analysis was obtained by recrystallization from CH_3CN/Et_2O.

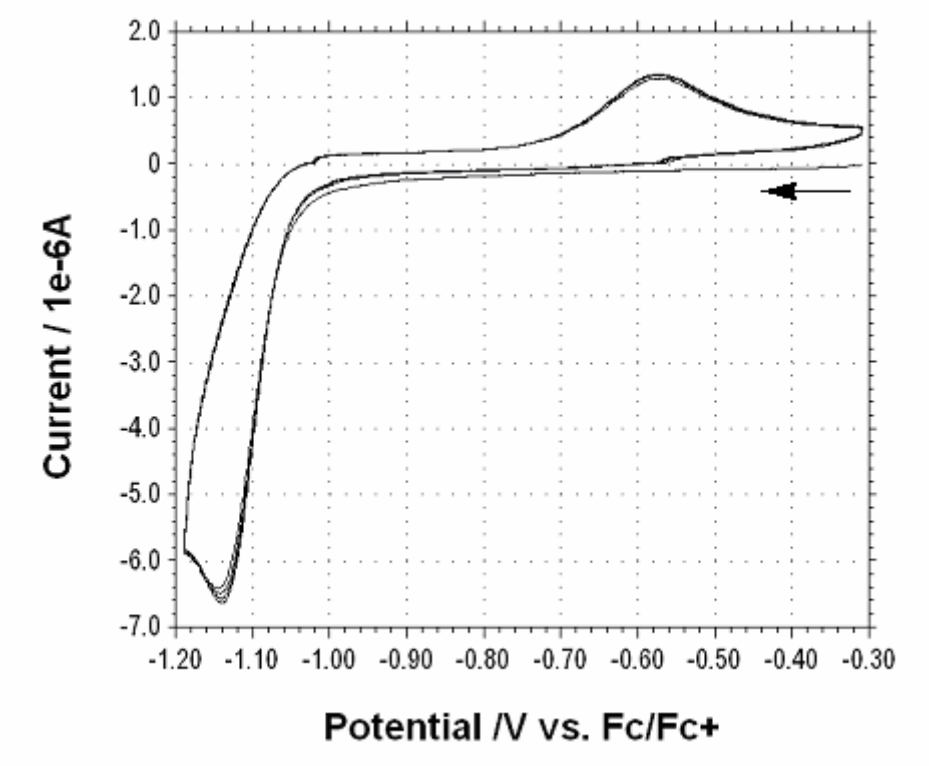


Synthesis of $[Pd_6(\mu_3\text{-}C_7H_7(t\text{-}Bu))_4(CH_3CN)_4][BF_4]_2$ (4-^{t}Bu): To a solution of $[Pd_3(\mu_3\text{-}C_7H_7(t\text{-}Bu))_2(CH_3CN)_3][BF_4]_2$ (**2-^{t}Bu**) (300 mg, 0.33 mmol) in CH_3CN (15 mL) was added $Li_2(C_8H_8)$ (3 mL, 0.066 M in THF) at –20 °C. Then the mixture was stirred for 1 h at room temperature. The reaction mixture was filtered, and addition of Et_2O to the filtrate gave a black precipitate. The precipitate was washed with Et_2O and *n*-pentane and dried in vacuo to afford a black powder of **4-^{t}Bu** (224.2 mg, 87% yield). ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ 5.80 (m, 2H, H16), 5.20 (t, J = 7.6 Hz, 2H, H13), 5.14 (t, J = 7.6 Hz, 2H, H4), 4.73 (m, 2H, H7), 4.44 (t, J = 7.8 Hz, 4H, H11, H14), 4.30 (m, 2H, H2), 4.21 (t, J = 7.8 Hz, 2H, H5), 4.03 (m, 2H, H12), 3.95 (m, 2H, H3), 3.43 (t, J = 7.2 Hz, 2H, H15), 2.90 (t, J = 8.2 Hz, 2H, H6), 1.91 (t, J = 6.2 Hz, 2H, H10), 1.32 (s, 18H, H18), 1.27 (t, J = 5.6 Hz, 2H, H1), 1.02 (s, 18H, H9). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, CD_3CN, 25 °C): δ 89.8 (s, C15), 89.5 (s, C6), 88.6 (s, C3), 88.2 (s, C12), 78.7 (s, C2), 76.7 (s, C11), 74.2 (s, C14), 72.9 (s, C5), 72.4 (s, C4), 72.2 (s, C13), 59.6 (s, C7), 56.5 (s, C16), 53.0 (s, C1), 52.7 (s, C10), 42.3 (s, C17), 41.7 (s, C8), 28.0 (s, C18), 27.1 (s, C9).



Cyclic voltammogram of 1a

1 mM in CH_3CN/0.1 M [*n*-Bu_4N][BF_4], scan rate = 0.1 V s^{-1}, T = 298 K.



X-ray Crystallographic Data for $[Pd_3(\mu_3\text{-}C_7H_7)_2(CH_3CN)_3][BF_4]_2$ (1a)

A. Crystal Data

Empirical Formula	$C_{20}H_{23}Pd_3B_2F_8N_3$
Formula Weight	798.23
Crystal Color, Habit	deep, prism
Crystal Dimensions	0.35 X 0.25 X 0.20 mm
Crystal System	monoclinic
Lattice Type	Primitive
Indexing Images	3 oscillations @ 180.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 12.7984(6) Å b = 10.5976(4) Å c = 18.0009(7) Å β = 97.7840(14) ° V = 2418.99(18) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4

D_{calc}	2.192 g/cm^3
F_{000}	1536.00
μ(MoKα)	22.850 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Detector Aperture	280 mm x 256 mm
Data Images	120 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	0.0 - 180.0^o
Exposure Rate	60.0 sec./^{o}
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 180.0^o
Exposure Rate	60.0 sec./^{o}
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	61.0^o

No. of Reflections Measured	Total: 48043 Unique: 7375 (R_{int} = 0.042)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	1
$2\theta_{max}$ cutoff	61.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	39116
No. Variables	384
Reflection/Parameter Ratio	101.86
Residuals: R (I>3.00σ(I))	0.0374
Residuals: Rw (I>3.00σ(I))	0.0436
Goodness of Fit Indicator	4.031
Max Shift/Error in Final Cycle	2.766
Maximum peak in Final Diff. Map	4.57 e$^-$/Å^3

Minimum peak in Final Diff. Map	-5.10 $e^-/Å^3$

X-ray Crystallographic Data for $[Pd_3(\mu_3\text{–}C_7H_7(t\text{-Bu}))_2(CH_3CN)_3][BF_4]_2$ (2-^{t}Bu)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{28}H_{41}N_3B_2F_8Pd_3$
Formula Weight	912.46
Crystal Color, Habit	red, block
Crystal Dimensions	0.60 X 0.50 X 0.25 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	44661 (6.1 - 61.0°)
Indexing Images	3 oscillations at 4.0 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 7.2569(3) Å b = 21.5621(8) Å c = 22.2397(7) Å β = 95.791(1)° V = 3462.2(2) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.750 g/cm^3
F_{000}	1800.00
μ(MoKα)	16.08 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated

Temperature	-150.0 °C
Voltage, Current	50 kV, 40 mA
Collimator Size	0.8 mm
Detector Aperture	280.0 mm x 256.0 mm
Data Images	180 exposures at 1.3 minutes per degree
Oscillation Range (ϕ=0.0°,χ=45.0°)	ω 0.0 - 180.0° with 2.0° step
Oscillation Range (ϕ=210.0°,χ=45.0°)	ω 0.0 - 180.0° with 2.0° step
Camera Radius	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	61.0°
No. of Reflections Measured	Total: 70500 Unique: 10558 (R_{int} = 0.047)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF94 PATTY)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$
p-factor	0.0500
Anomalous Dispersion	All non-hydrogen atoms
No. of Observations (I>3.00σ(I), 2θ<61.02°)	6280
No. Variables	397
Reflection/Parameter Ratio	15.82
Residuals: R; Rw	0.051 ; 0.058
Residuals: R1	0.051
No. of Reflections to calc R1	6280

Goodness of Fit Indicator	0.73
Max Shift/Error in Final Cycle	0.313
Maximum peak in Final Diff. Map	0.76 $e^-/\mathring{A}^3$
Minimum peak in Final Diff. Map	-0.58 $e^-/\mathring{A}^3$

X-ray Crystallographic Data for $[Pd_6(\mu_3-C_7H_7)_4(CH_3CN)_4][BF_4]_2 \bullet CH_3CN$ ($3a \bullet CH_3CN$)

A. Crystal Data

Empirical Formula	$C_{38}H_{43}Pd_6N_5B_2F_8$
Formula Weight	1381.80
Crystal Color, Habit	black, block
Crystal Dimensions	0.80 X 0.80 X 0.60 mm
Crystal System	triclinic
Lattice Type	Primitive
Indexing Images	3 oscillations @ 360.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 11.4203(4) Å b = 13.8401(6) Å c = 14.3530(6) Å α = 83.7870(12) ^{o} β = 77.0220(13) ^{o} γ = 71.2870(14) ^{o} V = 2092.18(14) Å^3
Space Group	P-1 (#2)

Z value	2
D_{calc}	2.193 g/cm^3
F_{000}	1328.00
μ(MoKα)	25.971 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Detector Aperture	280 mm x 256 mm
Data Images	74 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	130.0 - 190.0^o
Exposure Rate	60.0 sec./^{o}
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 162.0^o
Exposure Rate	60.0 sec./^{o}
Detector Position	127.40 mm
Pixel Size	0.100 mm

$2\theta_{max}$	54.9^{o}
No. of Reflections Measured	Total: 20643 Unique: 9494 (R_{int} = 0.068)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	1
$2\theta_{max}$ cutoff	54.9^{o}
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>2.00σ(I))	17981
No. Variables	575
Reflection/Parameter Ratio	31.27
Residuals: R (I>2.00σ(I))	0.0720
Residuals: Rw (I>2.00σ(I))	0.0941
Goodness of Fit Indicator	10.799

Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	6.35 $e^-/Å^3$
Minimum peak in Final Diff. Map	-3.05 $e^-/Å^3$

X-ray Crystallographic Data for $[Pd_6(\mu_3\text{–}C_7H_8)_4(CH_3CN)_4][BF_4]_2 \bullet CH_3CN$ (4-H•CH_3CN)

A. Crystal Data

Empirical Formula	$C_{38}H_{47}B_2F_8N_5Pd_6$
Formula Weight	1385.83
Crystal Color, Habit	deep, block
Crystal Dimensions	0.30 X 0.10 X 0.10 mm
Crystal System	monoclinic
Lattice Type	C-centered
No. of Reflections Used for Unit Cell Determination (2θ range)	2942 (6.0 - 54.8°)
Indexing Images	3 oscillations at 4.5 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 22.759(6) Å b = 18.556(5) Å c = 11.696(3) Å β = 116.826(4)° V = 4407(2) Å^3
Space Group	C2/c (#15)
Z value	4
D_{calc}	2.088 g/cm^3
F_{000}	2672.00
μ(MoKα)	24.66 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated

Temperature	-150.0 °C
Voltage, Current	50 kV, 40 mA
Collimator Size	0.8 mm
Detector Aperture	280.0 mm x 256.0 mm
Data Images	55 exposures at 1.7 minutes per degree
Oscillation Range (ϕ=0.0°,χ=45.0°)	ω 130.0 - 190.0° with 4.0° step
Oscillation Range (ϕ=180.0°,χ=45.0°)	ω 0.0 - 160.0° with 4.0° step
Camera Radius	127.40 mm
Pixel Size	0.200 mm
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 19228 Unique: 5016 (R_{int} = 0.054)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF94 PATTY)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$
p-factor	0.0500
Anomalous Dispersion	All non-hydrogen atoms
No. of Observations (I>3.00σ(I), 2θ<54.92°)	3651
No. Variables	320
Reflection/Parameter Ratio	11.41
Residuals: R; Rw	0.067 ; 0.095
Residuals: R1	0.067
No. of Reflections to calc R1	3651

Goodness of Fit Indicator	2.24
Max Shift/Error in Final Cycle	2.171
Maximum peak in Final Diff. Map	2.14 $e^-/\mathring{A}^3$
Minimum peak in Final Diff. Map	-1.75 $e^-/\mathring{A}^3$