Supplementary Material (ESI) for Chemical Communications

Supporting Materials

Structures of two haptotropic isomers generated by sliding of 1,3,5-triene ligands on a Pd–Pd–Pd Chain

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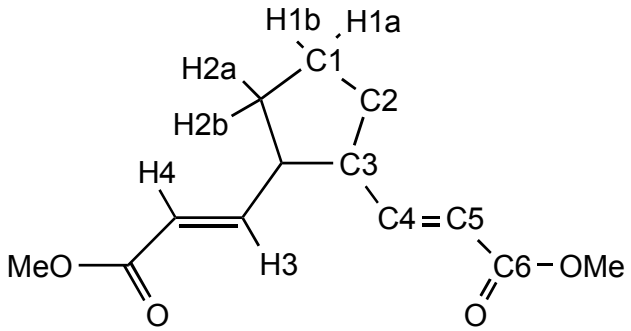
Experimental Details

General Consideration.

All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques. ^{1}H, ^{13}C nuclear magnetic resonance spectra were recorded on 270 MHz (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. Unless specified, all reagents were purchased from commercial suppliers and used without purification. $[Pd_2(CH_3CN)_6][BF_4]_2$, $Pd_2(dba)_3$, and DMVC were prepared according to the literature.[1-3]

Synthesis of $[Pd_3(\mu_3\text{-DMVC})_2(CH_3CN)_2][BF_4]_2$ (1)

To a solution of DMVC (= 1,2-di-(*E*)-carbomethoxyvinylcyclopentene) (236 mg, 1.00 mmol) in acetone (40 mL) was added $[Pd_2(CH_3CN)_6][BF_4]_2$ (127 mg, 0.200 mmol) and $Pd_2(dba)_3$ (104 mg, 0.100 mmol). The reaction mixture was stirred for 1.5 h at room temperature. The resultant reaction mixture was filtered, and benzene was added to the filtrate to give an orange precipitate. The precipitate was washed with benzene, *n*-hexane, and pentane to give an analytically pure orange powder of **1** (151 mg, 72% yield). ^{1}H NMR (400 MHz, CD_3NO_2, 25 ˚C) δ 6.09 (d, J = 11.6 Hz, 4H, H4), 4.23 (d, J = 11.6 Hz, 4H, H3), 3.80 (s, 12H, OCH_3), 2.84 (s, 6H, CH_3CN), 2.68 (m, 4H, H2a), 1.54 (m, 2H, H1a), 1.41 (dd, J = 7.8 Hz, J = 16.6 Hz, 4H, H2b), –0.17 (m, 2H, H1b). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, CD_3NO_2, 25 ˚C) δ 169.9 (s, C6), 130.0 (s, CH_3CN), 115.7 (s, C3), 86.6 (s, C4), 73.4 (s, C5), 54.7 (s, OCH$_3$), 36.8 (s, C2), 22.9 (s, C1), 4.4 (s, CH$_3$CN). Anal. Calcd. for $C_{30}H_{38}B_2F_8O_8N_2Pd_3$: C, 34.40; H, 3.66; N, 2.67. Found C, 34.52; H, 3.64; N, 2.73.



Crystal structure determination

The teXsan program package[4] was used for refinement of the crystal data.

Crystal data for ***s*-1**:

A. Crystal Data

Empirical Formula	$C_{30}H_{38}O_8F_8B_2N_2Pd_3$
Formula Weight	1047.45
Crystal Color, Habit	orange, prism
Crystal Dimensions	0.25 X 0.10 X 0.10 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	10587 (4.4 - 55.0°)
Indexing Images	2 oscillations at 2.5 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 10.3565(1) Å b = 12.3481(3) Å c = 14.3451(3) Å β = 95.920(2)° V = 1824.71(6) Å^3
Space Group	$P2_1/n$ (#14)
Z value	2
D_{calc}	1.906 g/cm^3
F_{000}	1032.00
μ(MoKα)	15.55 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated

Temperature	20.0 °C
Voltage, Current	50 kV, 40 mA
Collimator Size	0.8 mm
Detector Aperture	270.0 mm x 256.0 mm
Data Images	44 exposures at 0.7 minutes per degree
Oscillation Range (ϕ=0.0°,χ=45.0°)	ω 130.0 - 190.0° with 5.0° step
Oscillation Range (ϕ=180.0°,χ=45.0°)	ω 0.0 - 160.0° with 5.0° step
Camera Radius	127.40 mm
Pixel Size	0.125 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 16626 Unique: 4167 (R_{int} = 0.072)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.6531 - 0.8560)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares (SHELXL-97)
Function Minimized	$\Sigma w(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = [\sigma^2(Fo^2) + (0.1000P)^2 + 0.0000P]^{-1}$ where $P = (Fo^2 + 2Fc^2)/3$
No. of Reflections (All, 2θ<54.96°)	2480
No. Variables	241
Reflection/Parameter Ratio	10.29
Residuals: R; Rw	0.051 ; 0.143
Goodness of Fit Indicator	0.76
Max Shift/Error in Final Cycle	-0.06

Crystal data for ***u*-1**:

A. Crystal Data

Empirical Formula	$C_{30}H_{38}O_8Pd_3B_2F_8N_2$
Formula Weight	1047.45
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.10 X 0.10 X 0.10 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	3645 (4.7 - 54.9°)
Indexing Images	2 oscillations at 5.0 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 10.0065(1) $\AA$ b = 11.0597(8) $\AA$ c = 8.7843(8) $\AA$ α = 96.218(6)° β = 94.476(5)° γ = 68.120(6)° V = 896.1(1) $\AA^3$
Space Group	P1 (#2)
Z value	1
D_{calc}	1.941 g/cm^3
F_{000}	516.00
μ(MoKα)	15.83 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate

Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Temperature	23.0 °C
Voltage, Current	50 kV, 40 mA
Collimator Size	0.3 mm
Detector Aperture	270.0 mm x 256.0 mm
Data Images	44 exposures at 2.0 minutes per degree
Oscillation Range (ϕ=0.0°,χ=45.0°)	ω 130.0 - 190.0° with 5.0° step
Oscillation Range (ϕ=180.0°,χ=45.0°)	ω 0.0 - 160.0° with 5.0° step
Camera Radius	127.40 mm
Pixel Size	0.125 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 7764 Unique: 3985 (R_{int} = 0.096)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.2500 - 0.8536)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF94 PATTY)
Refinement	Full-matrix least-squares (SHELXL-97)
Function Minimized	$\Sigma w(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = [\sigma^2(Fo^2) + (0.1000P)^2 + 0.0000P]^{-1}$ where $P = (Fo^2 + 2Fc^2)/3$
No. of Reflections (All, 2θ<54.96°)	2078
No. Variables	277
Reflection/Parameter Ratio	7.50
Residuals: R; Rw	0.081 ; 0.221
Goodness of Fit Indicator	1.05
Max Shift/Error in Final Cycle	-0.16

References

1. T. Murahashi, T. Nagai, T. Okuno, T. Matsutani, H. Kurosawa, *Chem. Commun.* **2000**, 1689.
2. H. Ukai, H. Kawazura, Y. Ishii, *J. Organomet. Chem.* **1974**, *65*, 253.
3. K. Voigt, P. von Zezschwitz, K. Rosauer, A. Lansky, A. Adams, O. Reiser, A. de Meijere, *Eur. J. Org. Chem.* **1998**, 1521.
4. Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1999.