Supplementary Materials

Metallocenoids of Platinum: Syntheses and Structures of Triangular Triplatinum Sandwich Complexes of Cycloheptatrienyl

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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 MHz (JEOL GSX-270) and 400 MHz (JEOL GSX-400, Brucker DPX-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. Dichloromethane, acetonitrile, Et_2O, *n*-hexane, CD_2Cl_2, and CD_3CN were purified according to the standard procedures. $Pt_2(dba)_3$[1,2] and $NaB(Ar^F)_4$[3] were prepared according to the literature.

Synthesis of $[Pt_3(\mu_3\text{–}C_7H_7)_2(CH_3CN)_3][BF_4]_2$ (1-CH$_3$CN): To a CH_2Cl_2 solution (250 mL) of $Pt_2(dba)_3$ (300 mg, 0.25 mmol) was added $[C_7H_7][BF_4]$ (58 mg, 0.33 mmol) and CH_3CN (131 μL). The reaction mixture was stirred for 11 h at room temperature. The recipitate was collected through filtration, and washed with CH_2Cl_2. Then extraction with CH_3CN followed by filtration, concentration, and precipitation by adding Et_2O gave a brown powder of **1-CH$_3$CN** (122 mg, 69% yield). ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ 4.20 (s, C_7H_7). ^{13}C{^{1}H} NMR (100.5 MHz, CD_3NO_2, 25 °C): δ 122.6 (s, CH_3CN), 59.7 (s, C_7H_7), 2.9 (s, CH_3CN). Anal. Calcd. for $C_{20}H_{23}B_2F_8N_3Pt_3$: C, 22.57; H, 2.18; N, 3.95. Found: C, 22.59; H, 2.22; N, 3.88. Crystalline samples of **1-CH$_3$CN** were obtained by recrystallization from CH_3CN/Et_2O.

Synthesis of $[Pt_3(\mu_3\text{–}C_7H_7)_2(CH_3CN)_3][B(Ar^F)_4]_2$ (1′-CH$_3$CN): To a CH_2Cl_2 solution of **1-CH$_3$CN** (310 mg, 0.292 mmol) was added $NaB(Ar^F)_4$ (505.7 mg, 0.571 mmol). After stirring for 3 h at room temperature, the mixture was filtered and the filtrate was concentrated. Addition of *n*-hexane gave a brown powder of **1′-CH$_3$CN** (686 mg, 90% yield). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.73 (s, 16H, $B(Ar^F)_4$), 7.57 (s, 8H, $B(Ar^F)_4$), 4.07 (s, 14H, C_7H_7), 2.43 (s, 9H, CH_3CN). Anal. Calcd. for $C_{84}H_{47}B_2F_{48}N_3Pt_3$: C, 38.55; H, 1.81; N, 1.61.

Found: C, 38.34; H, 1.84; N, 1.54.

Synthesis of $[Pt_3(\mu_3\text{–}C_7H_7)_2(C_2H_4)_3][B(Ar^F)_4]_2$ (1′-C_2H_4): The tris-acetonitrile sandwich complex **1′-CH_3CN** (504 mg, 0.19 mmol) was dissolved in CH_2Cl_2, and ethylene gas was bubbled until volatiles were removed. This was repeated four times. The resultants were dissolved in CH_2Cl_2, and filtered. Addition of *n*-hexane to the solution gave yellow powder of **1′-C_2H_4** (457 mg, 93% yield). ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 7.79 (s, 16H, $B(Ar^F)_4$), 7.68 (s, 8H, $B(Ar^F)_4$), 4.62 (s, 14H, C_7H_7), 4.45 (s, 12H, C_2H_4, ^{195}Pt satellite doublet, $J_{Pt\text{-}H}$ = 70 Hz). ^{13}C{^{1}H} NMR (100.5 MHz, acetone-d_6, 25 °C): δ 162.6 (q, $J_{C\text{-}B}$ = 50 Hz, $B(Ar^F)_4$), 135.5 (s, $B(Ar^F)_4$), 130.0 (m, $J_{C\text{-}F}$ = 29 Hz, $B(Ar^F)_4$), 125.4 (q, $J_{C\text{-}F}$ = 270 Hz, $B(Ar^F)_4$), 118.5 (m, $B(Ar^F)_4$), 70.4 (s, C_2H_4), 58.1 (s, C_7H_7, ^{195}Pt satellite doublet, $J_{Pt\text{-}H}$ = 13 Hz). Anal. Calcd. for $C_{84}H_{50}B_2F_{48}Pt_3$: C, 39.13; H, 1.95. Found: C, 38.46; H, 1.85.

Synthesis of $[Pt_3(C_7H_7)_2(PPh_3)_3][BF_4]_2$ (1-PPh_3): To a CH_3CN solution of **1-CH_3CN** (201 mg, 0.19 mmol) was added PPh_3 (303 mg, 1.16 mmol). The reaction mixture was stirred for 3 h, and then the mixture was filtered, and the filtrate was concentrated. Addition of Et_2O to the solution gave a brown powder. Recrystallization from CH_3CN/Et_2O gave reddish brown crystals (276 mg, 84% yield). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.62 (m, 9H, PPh_3), 7.57 (m, 18H, PPh_3), 7.31 (m, 18H, PPh_3), 3.40 (s, 14H, C_7H_7). ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ 134.3 (PPh_3), 132.6 (PPh_3), 129.8 (PPh_3), 128.1 (PPh_3), 52.3 (C_7H_7). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ 9.7 (m, $^1J_{Pt\text{–}P}$ = 4516 Hz, $^2J_{Pt\text{–}P}$ = 227 Hz, and $^3J_{P\text{–}P}$ = 76 Hz, PPh_3). Anal. Calcd. for $C_{68}H_{59}B_2F_8P_3Pt_3$: C, 47.27; H, 3.44. Found: C, 46.51; H, 3.31.

Synthesis of $[Pt_3(C_7H_7)_2(py)_3][BF_4]_2$ (1-py): To a CH_3CN solution of **1-CH_3CN** (152 mg, 0.142 mmol) was added pyridine (88.0 mg, 1.11 mmol). The reaction mixture was stirred for 5 h, and then the mixture was filtered, and the filtrate was concentrated. Addition of Et_2O to the solution gave a brown powder. Recrystallization from CH_3NO_2/Et_2O gave reddish brown crystals (107 mg, 64% yield). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 8.42 (m, 6H, *o*-py), 7.89 (m, 3H, *p*-py), 7.42 (m, 6H, *m*-py), 3.98 (s, 14H, C_7H_7). ^{13}C{^{1}H} NMR (100.5 MHz,

CD_2Cl_2, 25 °C): δ 156.9 (s, *o*-py), 139.8 (s, *p*-py), 127.6 (s, *m*-py), 57.1 (s, C_7H_7). Anal. Calcd. for $C_{29}H_{29}B_2F_8N_3Pt_3$: C, 29.56; H, 2.48; N, 3.57. Found: C, 29.27; H, 2.48; N, 3.62.

Synthesis of $[Pt(C_7H_7)(PPh_3)_2][BF_4]$ (2-PPh_3): To a solution of $Pt(C_2H_4)(PPh_3)_2$ (69.3 mg, 0.093 mmol) in CH_2Cl_2 was added $[C_7H_7][BF_4]$ (16.9 mg, 0.095 mmol), and the mixture was stirred for 3.5 h. The reaction mixture was filtered, and the filtrate was concentrated. Addition of Et_2O gave a yellow powder of crude **2-PPh_3**. Recrystallization from CH_2Cl_2/toluene/*n*-hexane gave yellow crystals of **2-PPh_3** (57.9 mg, 69% yield). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.45 (m, 6H, PPh_3), 7.33 (m, 12H, PPh_3), 7.24 (m, 12H, PPh_3), 4.80 (s, 7H, C_7H_7, ^{195}Pt satellite doublet, $J_{Pt\text{-}H}$ = 10 Hz). ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ 133.8 (m, PPh_3), 131.8 (s, PPh_3), 129.8 (m, PPh_3), 129.2 (m, PPh_3), 108.5 (s, C_7H_7). ^{31}P{^{1}H} NMR (109.3 MHz, CD_2Cl_2, 25 °C): δ 23.7 (s, ^{195}Pt satellite doublet, $J_{Pt\text{-}H}$ = 4216 Hz). Anal. Calcd. for $C_{43}H_{37}B_1F_4P_3Pt_1$: C, 57.54; H, 4.15. Found: C, 56.85; H, 4.00.

Synthesis of $[Pt_3(\mu_3\text{–}C_7H_7)_2(CH_3CN)_2Ph][BF_4]_2$ (3-CH_3CN-Ph): To a CH_3CN solution of the complex **1-CH_3CN** (120 mg, 0.113 mmol) was added a CH_3CN solution of $NaBPh_4$ (38.6 mg, 0.113 mmol), and the reaction mixture was stirred for 6 h at 60 °C. The reaction mixture was then cooled to ambient temperature, and filtered. The filtrate was concentrated and Et_2O was added. Resultant brown precipitate was collected and dried in vacuo. Recrystallization from CH_3CN/Et_2O gave brown crystals of **3-CH_3CN-Ph** (89.5 mg, 78% yield). ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ 7.05 (d, J = 7 Hz, 2H, *o*-Ph, ^{195}Pt satellite dd, $J_{Pt\text{-}H}$ = 39 Hz), 6.93 (t, J = 7 Hz, 2H, *m*-Ph), 6.86 (t, J = 7 Hz, 2H, *p*-Ph), 3.91 (s, 14H, C_7H_7). ^{13}C{^{1}H} NMR (100.5 MHz, CD_3CN, 25 °C): δ 142.5 (s, *o*-Ph), 129.2 (s, *m*-Ph), 124.6 (s, *p*-Ph), 54.4 (s, C_7H_7). The *ipso*-carbon signal of the phenyl ligand was not assigned. Anal. Calcd. for $C_{24}H_{25}B_1F_4N_2Pt_3$: C, 28.44; H, 2.49; N, 2.76. Found: C, 28.97; H, 2.52; N, 2.44.

Synthesis of $[Pt_3(\mu_3\text{–}C_7H_7)_2(C_2H_4)_2Ph][B(Ar^F)_4]_2$ (3′-C_2H_4-Ph): To a suspension of **1-Ph-CH_3CN** (69.7 mg, 0.069 mmol) in CH_2Cl_2 was added $NaB(Ar^F)_4$ (62.5 mg, 0.070 mmol), and then ethylene gas (1 atm) was bubbled until the solvent was removed. The resultant powder was resolved in CH_2Cl_2, and ethylene gas was bubbled again until the solvent was

removed. This ethylene flow evaporation was repeated 6 times. Then the CH_2Cl_2 solution was filtered, and the filtrate was concentrated. Addition of *n*-hexane gave orange powder. Recrystallization from CH_2Cl_2/*n*-hexane under ethylene atmosphere gave reddish orange crystals of **3′-C_2H_4-Ph** (87.6 mg, 72% yield). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.73 (s, 8H, B(Ar^F)$_4$), 7.57 (s, 4H, B(Ar^F)$_4$), 7.08 (d, J = 5 Hz, 2H, *o*-Ph, ^{195}Pt satellite double doublet, J_{PtH} = 50 Hz), 7.05 (t, J = 5 Hz, 2H, *m*-Ph), 6.97 (m, 1H, *p*-Ph), 3.88 (s, 14H, C_7H_7), 3.59 (s, 8H, C_2H_4, ^{195}Pt satellite doublet, J_{Pt-H} = 60 Hz). ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ 162.1 (q, J_{C-B} = 50 Hz, B(Ar^F)$_4$), 141.7 (s, *o*-Ph, ^{195}Pt satellite doublet, J_{PtC} = 28 Hz), 135.2 (s, B(Ar^F)$_4$), 129.9 (s, *m*-Ph), 129.2 (m, J_{C-F} = 29 Hz, B(Ar^F)$_4$), 125.1 (s, *p*-Ph), 125.0 (q, J_{C-F} = 270 Hz, B(Ar^F)$_4$), 117.9 (m, B(Ar^F)$_4$), 66.0 (s, C_2H_4, non simple ^{195}Pt satellite), 52.6 (s, C_7H_7). The ipso-carbon signal of the phenyl ligand was not assigned. Anal. Calcd. for $C_{56}H_{39}B_1F_{24}Pt_3$: C, 38.13; H, 2.23. Found: C, 37.86; H, 2.12.

Comment on [Pt(C_7H_7)(Ar^F)(C_2H_4)$_2$][BF_4] (3′-C_2H_4-Ar^F): The reaction of Pt_2(dba)$_3$ with [C_7H_7][B(Ar^F)$_4$] in the presence of ethylene at 25 °C in CD_2Cl_2 unexpectedly gave the cationic triplatinum sandwich complex [Pt_3(μ_3-C_7H_7)$_2$(Ar^F)(C_2H_4)$_2$][B(Ar^F)$_4$] (**3′-C_2H_4-Ar^F**) bearing a 3,5-di-trifluoromethylphenyl ligand, where only a trace amount of tris-ethylene complex **1′-C_2H_4** was formed. We confirmed that **1′-C_2H_4** was stable in CD_2Cl_2. Probably, mono- or dinuclear intermediates are electrophillic enough to accept an Ar^F group from the weakly nucleophilic [B(Ar^F)$_4$]$^-$.[18] ^{1}H NMR spectra of **3′-C_2H_4-Ar^F** in CD_2Cl_2 showed a singlet signal for the cycloheptatrienyl protons at δ = 3.89 ppm, and a singlet signal for the ethylene protons at δ = 3.69 ppm with a ^{195}Pt satellite doublet ($J_{Pt–H}$ = 63 Hz). The structure of **3′-C_2H_4-Ar^F** was determined by X-ray crystallographic analysis (Figure S1). The Pt_3 triangle is distorted to an isosceles triangle with the base Pt–Pt length (Pt2–Pt3 = 2.7554(4) Å) being shorter than the other two Pt–Pt lengths (Pt1–Pt2 2.8157(4) Å, Pt3–Pt1 2.8170(5) Å). The C–C lengths of the ethylene ligands (C15–C16 1.37(1) Å, C17–C18 1.38(1) Å) are comparable to those in **1′-C_2H_4**.

References

1. K. Moseley, P. M. Maitlis, *J. Chem. Soc., Dalton Trans.* 1974, 169.
2. H. Tanaka, H. Kawazura, *Bull. Chem. Soc. Jpn.* 1979, **52**, 2815.
3. N. A. Yakelis, R. G. Bergman, *Organometallics*, 2005, **24**, 3579.

X-ray Crystallographic Data for $[Pt_3(\mu_3\text{-}C_7H_7)_2(C_2H_4)_3][B(Ar^F)_4]_2$ (1′-C_2H_4).

A. Crystal Data

Empirical Formula	$C_{84}H_{50}Pt_3B_2F_{48}$
Formula Weight	2578.13
Crystal Color, Habit	yellow, platelet
Crystal Dimensions	0.20 X 0.10 X 0.10 mm
Crystal System	monoclinic
Lattice Type	C-centered
No. of Reflections Used for Unit Cell Determination (2θ range)	31893 (6.2 - 54.9°)
Indexing Images	3 oscillations at 3.5 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 19.6876(5) Å b = 18.0489(4) Å c = 24.2236(7) Å β = 104.8498(9)° V = 8320.1(4) Å^3
Space Group	C2/c (#15)
Z value	4
D_{calc}	2.058 g/cm^3
F_{000}	4920.00
μ(MoKα)	51.66 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=90.0°,χ=45.0°)	ω 130.0 - 190.0° with 4.0° step
Oscillation Range (ϕ=270.0°,χ=45.0°)	ω 0.0 - 160.0° with 4.0° step
Camera Radius	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	0.0°
No. of Reflections Measured	Total: 40753 Unique: 9496 (R_{int} = 0.119)
Corrections	Lorentz-polarization

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<0.00°)	8507
No. Variables	645
Reflection/Parameter Ratio	13.19
Residuals: R; Rw	0.052 ; 0.172
Goodness of Fit Indicator	1.20
Max Shift/Error in Final Cycle	0.02
Maximum peak in Final Diff. Map	7.13 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-5.11 $e^-/\AA^3$

X-ray Crystallographic Data for $[Pt(C_7H_7)(PPh_3)_2][BF_4]\bullet(C_6H_6)$ (2-PPh_3)

A. Crystal Data

Empirical Formula	$C_{49}H_{43}P_2BF_4Pt$
Formula Weight	975.72
Crystal Color, Habit	orange, block
Crystal Dimensions	0.40 X 0.20 X 0.20 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	15382 (6.0 - 55.0°)
Indexing Images	3 oscillations at 3.0 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 13.742(1) Å b = 20.974(2) Å c = 14.377(2) Å β = 99.419(3)° V = 4088.2(8) Å^3
Space Group	$P2_1/a$ (#14)
Z value	4
D_{calc}	1.585 g/cm^3
F_{000}	1944.00
μ(MoKα)	35.50 cm^{-1}

B. Intensity Measurements

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

Temperature	-100.0 °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	0.100 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 40033 Unique: 9335 (R_{int} = 0.089)
Corrections	Lorentz-polarization

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<54.97°)	6062
No. Variables	455
Reflection/Parameter Ratio	13.32
Residuals: R; Rw	0.077 ; 0.219
Goodness of Fit Indicator	1.29
Max Shift/Error in Final Cycle	11.03
Maximum peak in Final Diff. Map	2.43 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-1.73 $e^-/\AA^3$

X-ray Crystallographic Data for $[Pt_3(\mu_3\text{-}C_7H_7)_2(Ar^F)(C_2H_4)_2][B(Ar^F)_4]\bullet(C_2H_4Cl_2)$ ($3'\text{-}C_2H_4\text{-}Ar^F$).

A. Crystal Data

Empirical Formula	$C_{60}H_{41}Pt_3BF_{30}Cl_2$
Formula Weight	1998.92
Crystal Color, Habit	orange, block
Crystal Dimensions	0.15 X 0.10 X 0.10 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	21420 (6.0 - 54.9°)
Indexing Images	3 oscillations at 3.5 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 12.3189(5) Å b = 15.2911(6) Å c = 16.4704(5) Å α = 97.219(1)° β = 90.674(1)° γ = 105.503(1)° V = 2962.6(2) Å^3
Space Group	P1 (#2)
Z value	2
D_{calc}	2.241 g/cm^3
F_{000}	1888.00
μ(MoKα)	72.64 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate

Radiation	MoKα (λ = 0.71075 $\AA$) 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 2.5 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	0.100 mm
$2\theta_{max}$	0.0°
No. of Reflections Measured	Total: 29229 Unique: 13421 (R_{int} = 0.103)
Corrections	Lorentz-polarization

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<0.00°)	11375
No. Variables	892
Reflection/Parameter Ratio	12.75
Residuals: R; Rw	0.056 ; 0.157
Goodness of Fit Indicator	0.99
Max Shift/Error in Final Cycle	0.52

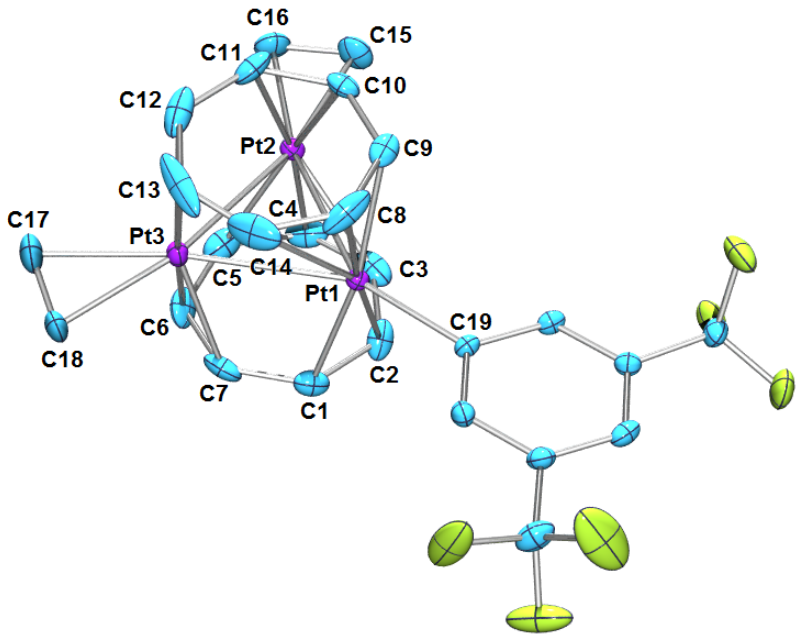

Figure S1. ORTEP drawing of $[Pt_3(\mu_3\text{-}C_7H_7)_2(Ar^F)(C_2H_4)_2][B(Ar^F)_4]$ (**3′-C_2H_4-Ar^F**) (30% probability ellipsoids. Counter anion and solvents are omitted for clarity). Pt1–Pt2 2.8157(4), Pt2–Pt3 2.7554(4), Pt3–Pt1 2.8170(5), Pt2–C15 2.220(8), Pt2–C16 2.219(8), Pt3–C17 2.24(1), Pt3–C18 2.236(9), Pt1–C19 2.080(6), C15–C16 1.37(1), C17–C18 1.38(1), Pt2–Pt1–Pt3 58.573(10), Pt1–Pt2–Pt3 60.74(1).

X-ray Crystallographic Data for $[Pt_3(\mu_3\text{-}C_7H_7)_2(Ph)(C_2H_4)_2][B(Ar^F)_4]$ (3′-C_2H_4-Ph).

A. Crystal Data

Empirical Formula	$C_{56}H_{39}Pt_3BF_{24}$
Formula Weight	1763.97
Crystal Color, Habit	reddish, block
Crystal Dimensions	0.25 X 0.20 X 0.15 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	28245 (6.0 - 54.9°)
Indexing Images	3 oscillations at 3.5 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 11.4558(4) Å b = 19.1713(7) Å c = 25.517(1) Å β = 103.809(1)° V = 5442.2(3) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	2.153 g/cm^3
F_{000}	3320.00
μ(MoKα)	77.83 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	44 exposures at 1.7 minutes per degree
Oscillation Range (ϕ=90.0°,χ=45.0°)	ω 130.0 - 190.0° with 5.0° step
Oscillation Range (ϕ=270.0°,χ=45.0°)	ω 0.0 - 160.0° with 5.0° step
Camera Radius	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 53410 Unique: 12424 (R_{int} = 0.070)
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>2.00σ(I), 2θ<54.95°)	5862
No. Variables	757
Reflection/Parameter Ratio	7.74
Residuals: R; Rw	0.045 ; 0.056
Residuals: R1	0.045
No. of Reflections to calc R1	5862
Goodness of Fit Indicator	1.08
Max Shift/Error in Final Cycle	3.115
Maximum peak in Final Diff. Map	1.45 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-1.24 $e^-/\AA^3$