SUPPORTING INFORMATION

Stereochemical Effects on Platinum Acetylide Two-Photon Chromophores

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Synthesis Procedures

1,5-Cyclooctadiene platinum(II) dichloride. This complex was synthesized by literature methods.[1] K_2PtCl_4 (500 mg, 1.205 mmol) was dissolved in 20 mL deionized water, argon-purged, and heated to 55°C with stirring. To this solution was slowly added a solution of 1,5-cyclooctadiene (500 μL, 4.077 mmol) in ethanol (234 mL) over 10 minutes. Stirring and heating was continued until the pale pinkish color of the solution faded, 40 minutes. The reaction was removed from heat, allowed to cool to room temperature, and cooled in an ice bath. The resulting mixture was vacuum-filtered and washed with four 5 mL aliquots of both cold deionized water and diethyl ether. The resulting slight tan powder was air-dried. Yield 328 mg (73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.29 (4H, m), 2.72 (4H, m), 5.63 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 100.06, 30.26.

***cis*-Diphenylphosphineethaneplatinum(II) dichloride**. This complex was synthesized by literature methods.[2] In a 100 mL round bottom flask was dissolved 1,5-cyclooctadieneplatinum(II) dichloride (300 mg, 0.802 mmol) in 28 mL deuterated chloroform. To the clear, colorless solution was added diphenylphosphinoethane (320 mg, 0.803 mmol), resulting in immediate precipitation. The reaction was stirred for 1 hour at room temperature. The solvent was removed in vacuo; the product was collected as a white solid. Yield 512 mg (96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (m, 8H), 7.51 (m, 12 H), 2.32-2.38 (dt, 4H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 42.25 with ^{195}Pt satellites J_{PtP} = 3615 Hz.

***cis*-Diphenylphosphinoethane-bis((4-phenylethynyl)phenyl)ethynyl) platinum(II)** (*cis*-PE2). This complex was synthesized by modification of similar literature methods.[3-4] *Cis*-diphenylphosphineethane platinum(II) dichloride (125.5 mg, 0.189 mmol) and (4-phenylethynyl)phenyl ethynylene (114.5 mg, 0.566 mmol) were added to an argon-purged 50 mL

round bottom flask, followed by 2.2 mL diisoproplyamine and 14 mL dichloromethane. The resulting cloudy white solution was further purged with argon for 30 minutes, followed by the addition of CuI (1.1 mg, 0.006 mmol). The resulting pale yellow and clear solution was stirred under argon for 27 hours. The solvent was removed in vacuo to yield a yellow-white crystalline solid. The solid was dried on a vacuum line for 24 hours and then purified by flash chromatography (2:3 DCM/hexanes gradient shifted to DCM with 5% MeOH by volume). Pale yellow-white crystals were collected and dried. Yield 154.5 mg (82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (m, 8H), 7.45 (m, 18H), 7.31 (m, 8H), 7.12 (d, 4H), 2.46 (dt, 4H). ^{31}P (121 MHz, $CDCl_3$) δ 42.35 with ^{195}Pt satellites J_{PtP} = 2280 Hz. EA calculated C 66.80, H 4.44. Found C 65.88, H 3.96.

***cis*-Diphenylphosphinoethane-bis(2-(9,9-diethyl-9*H*-fluoren-7-yl)benzo [*d*]thiazole)platinum(II)** (*cis*-BTF). This complex was synthesized by modification of similar literature methods.[3-4] To a 50 mL round bottom flask was added *cis*-diphenylphosphineethaneplatinum(II) dichloride (50 mg, 0.075 mmol), 2-(9,9-diethyl-9H-fluoren-7-yl)benzo[d]thiazole (84 mg, 0.221 mmol), 5.6 mL dichloromethane, and 0.84 mL diisopropylamine. The resulting yellow solution was argon-purged for 30 minutes prior to the addition of 99.999% CuI (0.5 mg, 0.0026 mmol). The reaction stirred at room temperature under argon for 24 hours. The solvent was then removed in vacuo to give a crude yellow powder, which was purified by flash chromatography with a 1:1 DCM/hexanes eluent. The resulting yellow powder was further purified by recrystallization by dissolving in minimum DCM and precipitating with hexanes. The resulting off-white crystals were collected via vacuum filtration and washed with cold hexanes. Yield 90 mg (88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (m, 8H), 7.92 (m, 8H), 7.83 (d, 2H), 7.61 (m, 2H), 7.38 (m, 18H), 7.30 (d, 2H), 2.46-2.52 (dt, 4H), 2.06 (two sets of

diastereotopic quart., 8H), 0.31 (t, 12H). ^{31}P (121 MHz, $CDCl_3$) δ 41.00 with ^{195}Pt satellites J_{PtP} = 2276 Hz. EA calculated C 66.37, H 4.78, N 2.07. Found C 66.98, H 4.82, N 1.81. MP 177.8 - 182.8 °C.

***cis*-Diphenylphosphinoethane-bis(9,9-diethyl-7-ethynyl-N,N-diphenyl-9H-fluoren-2-amine)platinum(II)** (*cis*-DPAF). This complex was synthesized by modification of similar literature methods.[3-4] To a 50 mL round bottom flask was added 11.2 mL chloroform and 1.8 mL diisopropylamine. The solution was argon-purged for 20 minutes, then *cis*-diphenylphosphineethane platinum(II) dichloride (100 mg, 0.151 mmol) and 9,9-diethyl-7-ethynyl-N,N-diphenyl-9H-fluoren-2-amine (189 mg, 0.357 mmol) were added, resulting in a cloudy pale yellow solution. The resulting solution was argon-purged for 30 minutes prior to the addition of 99.999% CuI (0.5 mg, 0.0026 mmol). The reaction was stirred at room temperature under argon for 24 hours. The solvent was then removed in vacuo to give a crude yellow crystalline solid, which was purified by flash chromatography with a 2:3 DCM/hexanes eluent. The resulting white powder was further purified by recrystallization by dissolving in minimum DCM and precipitating with hexanes. The resulting white crystals were collected via vacuum filtration and washed with cold hexanes. Yield 168 mg (78.5%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (m, 8H), 7.46 (m, 14H), 7.38 (m, 2H), 7.25 (m, 8H), 7.12 (d, 12H), 7.06 (d, 2H) 6.98 (t, 6H), 2.45-2.53 (dt, 4H), 1.81 (two sets of diastereotopic quart., 8H), 0.30 (t, 12H). ^{31}P (121 MHz, $CDCl_3$) δ 42.08 with ^{195}Pt satellites J_{PtP} = 2278 Hz. EA calculated C 74.51, H 5.40, N 1.97. Found C 74.58, H 5.65, N 1.79. MP 238.7 - 241.7 °C.

Table S-1. Fluorescence lifetimes in THF solution

	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	χ^2
trans-DPAF	9.6 (99.8%)	1945 (0.2%)	-	0.92
cis-DPAF	4.8 (99.7%)	682 (0.2%)	2354 (0.1%)	0.89
trans-BTF	11.2 (99.9%)	616 (0.1%)	-	1.07
cis-BTF	36 (76%)	410 (20.6%)	760 (3.4%)	1.15

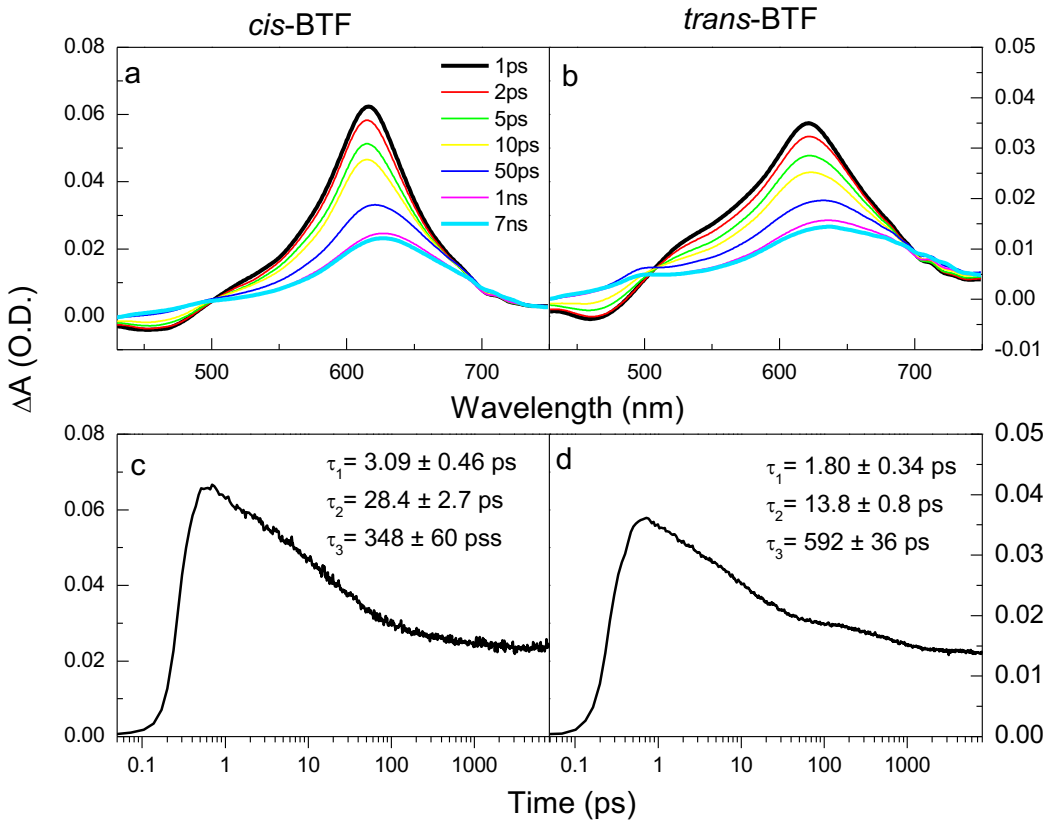

Figure S-1. Femtosecond transient absorption spectra and decays of *cis*-BTF (a) and *trans*-BTF (b) in THF after a 380 nm excitation pulse. Kinetics traces for *cis*-BTF (c) and *trans*-BTF (d) at 620 nm. The lifetimes shown in the insets were obtained by global analysis of the time resolved transient absorption spectral data.

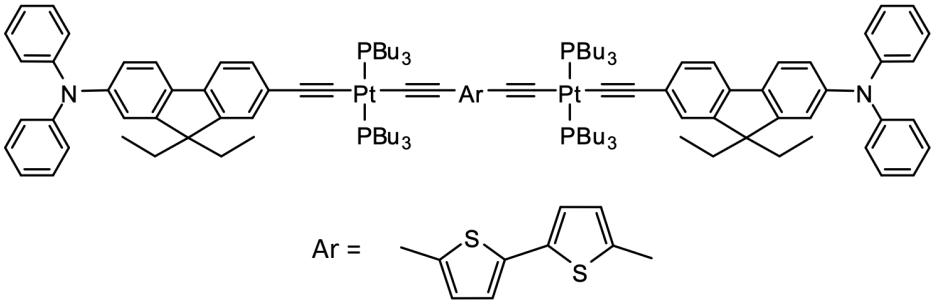

Figure S-2. Structure of platinum complex **T2** which was used as a benchmark in nanosecond z-scan experiments.

X-Ray Structure Data:

***cis*-PE2**. The asymmetric unit consists of two half Pt complexes (each located on 2-fold rotational axis of symmetry), and two half THF solvent molecules. The latter were disordered and could not be modeled properly, thus program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.[5] In the final cycle of refinement, 10398 reflections (of which 9524 are observed with I > 2□(I)) were used to refine 552 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 2.97%, 6.72% and 1.135, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

Crystal Data and Structure Refinement for *cis*-PE2

Identification code	abby2	
Empirical formula	C58 H42 P2 Pt	
Formula weight	995.95	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2	
Unit cell dimensions	a = 15.8357(11) Å	α= 90°.
	b = 8.9008(7) Å	β= 113.033(3)°.
	c = 18.9781(14) Å	λ = 90°.
Volume	2461.7(3) $Å^3$	

Z	2
Density (calculated)	1.344 Mg/m^3
Absorption coefficient	2.950 mm^{-1}
F(000)	996
Crystal size	0.42 x 0.14 x 0.05 mm^3
Theta range for data collection	2.14 to 27.50°.
Index ranges	$-20 \leq h \leq 20$, $-11 \leq k \leq 11$, $-24 \leq l \leq 24$
Reflections collected	23463
Independent reflections	10398 [R(int) = 0.0364]
Completeness to theta = 27.50°	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.8569 and 0.3726
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10398 / 1 / 552
Goodness-of-fit on F^2	1.135
Final R indices [I>2sigma(I)]	R1 = 0.0297, wR2 = 0.0672 [9524]
R indices (all data)	R1 = 0.0341, wR2 = 0.0687
Absolute structure parameter	0.146(6)
Largest diff. peak and hole	1.588 and -1.447 e.$Å^{-3}$

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(\square F_o^2)\square^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Crystal Structure Bond Lengths and Angles *cis*-PE2

Table B-1. Bond lengths (Å) for *cis*-PE2

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Pt1-C1A#1	2.015(8)	C20A-C21A	1.385(8)	C8B-H8B	0.9500
Pt1-C1A	2.015(8)	C18A-C19A	1.400(8)	C9B-C10B	1.184(8)
Pt1-P1#1	2.269(2)	C20A-H20A	0.9500	C10B-C11B	1.449(8)
Pt1-P1	2.269(2)	C21A-C22A	1.403(6)	C11B-C12B	1.364(8)
P1-C23A	1.807(5)	C21A-H21A	0.9500	C11B-C16B	1.422(10)
P1-C17A	1.824(5)	C22A-H22A	0.9500	C12B-C13B	1.411(8)
P1-C29A	1.850(5)	C23A-C28A	1.399(7)	C12B-H12B	0.9500
C1A-C2A	1.196(9)	C23A-C24A	1.400(7)	C13B-C14B	1.382(9)
C2A-C3A	1.434(7)	C24A-C25A	1.394(7)	C13B-H13B	0.9500
C3A-C8A	1.396(7)	C24A-H24A	0.9500	C14B-C15B	1.367(9)
C3A-C4A	1.418(7)	C25A-C26A	1.381(7)	C14B-H14B	0.9500
C4A-C5A	1.363(10)	C25A-H25A	0.9500	C15B-C16B	1.402(8)
C4A-H4A	0.9500	C26A-C27A	1.379(8)	C15B-H15B	0.9500
C5A-C6A	1.394(9)	C26A-H26A	0.9500	C16B-H16B	0.9500
C5A-H5A	0.9500	C27A-C28A	1.382(8)	C17B-C22B	1.387(7)
C6A-C7A	1.406(6)	C27A-H27A	0.9500	C17B-C18B	1.403(7)
C6A-C9A	1.426(7)	C28A-H28A	0.9500	C18B-C19B	1.382(7)
C7A-C8A	1.374(7)	C29A-C29A#1	1.561(9)	C18B-H18B	0.9500
C7A-H7A	0.9500	C29A-H29A	0.9900	C19B-C20B	1.381(8)
C8A-H8A	0.9500	C29A-H29B	0.9900	C19B-H19B	0.9500
C9A-C10A	1.200(7)	Pt2-C1B#2	2.011(8)	C20B-C21B	1.395(7)
C10A-C11A	1.436(8)	Pt2-C1B	2.011(8)	C20B-H20B	0.9500
C11A-C16A	1.394(9)	Pt2-P2#2	2.271(2)	C21B-C22B	1.398(6)
C11A-C12A	1.411(8)	Pt2-P2	2.271(2)	C21B-H21B	0.9500
C12A-C13A	1.358(8)	P2-C17B	1.810(5)	C22B-H22B	0.9500
C12A-H12A	0.9500	P2-C23B	1.821(5)	C23B-C24B	1.381(7)
C13A-C14A	1.395(9)	P2-C29B	1.846(5)	C23B-C28B	1.398(7)
C13A-H13A	0.9500	C1B-C2B	1.195(9)	C24B-C25B	1.414(6)
C14A-C15A	1.353(9)	C2B-C3B	1.435(7)	C24B-H24B	0.9500
C14A-H14A	0.9500	C3B-C4B	1.396(8)	C25B-C26B	1.388(7)
C15A-C16A	1.412(8)	C3B-C8B	1.419(6)	C25B-H25B	0.9500
C15A-H15A	0.9500	C4B-C5B	1.388(9)	C26B-C27B	1.400(8)
C16A-H16A	0.9500	C4B-H4B	0.9500	C26B-H26B	0.9500
C17A-C22A	1.380(8)	C5B-C6B	1.410(8)	C27B-C28B	1.378(7)
C17A-C18A	1.386(7)	C5B-H5B	0.9500	C27B-H27B	0.9500
C18A-C19A	1.400(8)	C6B-C7B	1.408(6)	C28B-H28B	0.9500
C18A-H18A	0.9500	C6B-C9B	1.434(7)	C29B-C29B#2	1.532(8)
C19A-C20A	1.38(1)	C7B-C8B	1.362(7)	C29B-H29A	0.9900
C19A-H19A	0.9500	C7B-H7B	0.9500	C29B-H29D	0.9900

Table B-2. Bond angles (degrees) for *cis*-PE2

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
C1A#1-Pt1-C1A	93.9(4)	C17A-C22A-C21A	119.8(5)	C12B-C11B-C10B	121.1(6)
C1A#1-Pt1-P1#1	175.8(3)	C17A-C22A-H22A	120.1	C16B-C11B-C10B	118.8(6)
C1A-Pt1-P1#1	89.9(2)	C21A-C22A-H22A	120.1	C11B-C12B-C13B	120.5(6)
C1A#1-Pt1-P1	89.9(2)	C28A-C23A-C24A	118.0(5)	C11B-C12B-H12B	119.7
C1A-Pt1-P1	175.8(3)	C28A-C23A-P1	120.3(4)	C13B-C12B-H12B	119.7
P1#1-Pt1-P1	86.36(11)	C24A-C23A-P1	121.3(4)	C14B-C13B-C12B	119.6(6)
C23A-P1-C17A	106.0(2)	C25A-C24A-C23A	120.6(4)	C14B-C13B-H13B	120.2
C23A-P1-C29A	106.5(2)	C25A-C24A-H24A	119.7	C12B-C13B-H13B	120.2
C17A-P1-C29A	105.0(3)	C23A-C24A-H24A	119.7	C15B-C14B-C13B	120.2(6)
C23A-P1-Pt1	115.5(2)	C26A-C25A-C24A	119.9(5)	C15B-C14B-H14B	119.9
C17A-P1-Pt1	115.3(2)	C26A-C25A-H25A	120.1	C13B-C14B-H14B	119.9
C29A-P1-Pt1	107.70(16)	C24A-C25A-H25A	120.1	C14B-C15B-C16B	121.4(6)
C2A-C1A-Pt1	171.7(6)	C27A-C26A-C25A	120.4(5)	C14B-C15B-H15B	119.3
C1A-C2A-C3A	174.2(6)	C27A-C26A-H26A	119.8	C16B-C15B-H15B	119.3
C8A-C3A-C4A	117.6(5)	C25A-C26A-H26A	119.8	C15B-C16B-C11B	118.2(6)
C8A-C3A-C2A	121.0(4)	C26A-C27A-C28A	119.9(5)	C15B-C16B-H16B	120.9
C4A-C3A-C2A	121.4(5)	C26A-C27A-H27A	120.1	C11B-C16B-H16B	120.9
C5A-C4A-C3A	120.4(6)	C28A-C27A-H27A	120.1	C22B-C17B-C18B	119.7(5)
C5A-C4A-H4A	119.8	C27A-C28A-C23A	121.2(5)	C22B-C17B-P2	120.6(4)
C3A-C4A-H4A	119.8	C27A-C28A-H28A	119.4	C18B-C17B-P2	119.7(4)
C4A-C5A-C6A	122.1(6)	C23A-C28A-H28A	119.4	C19B-C18B-C17B	119.5(5)
C4A-C5A-H5A	118.9	C29A#1-C29A-P1	108.2(2)	C19B-C18B-H18B	120.3
C6A-C5A-H5A	118.9	C29A#1-C29A-H29A	110.1	C22B-C17B-C18B	119.7(5)

C5A-C6A-C7A	117.5(5)	P1-C29A-H29A	110.1	C17B-C18B-H18B	120.3
C5A-C6A-C9A	122.0(5)	C29A#1-C29A-H29B	110.1	C20B-C19B-C18B	120.6(5)
C7A-C6A-C9A	120.4(5)	P1-C29A-H29B	110.1	C20B-C19B-H19B	119.7
C8A-C7A-C6A	120.9(5)	H29A-C29A-H29B	108.4	C18B-C19B-H19B	119.7
C8A-C7A-H7A	119.6	C1B#2-Pt2-C1B	94.0(5)	C19B-C20B-C21B	120.8(5)
C6A-C7A-H7A	119.6	C1B#2-Pt2-P2#2	175.8(3)	C19B-C20B-H20B	119.6
C7A-C8A-C3A	121.4(4)	C1B-Pt2-P2#2	90.1(2)	C21B-C20B-H20B	119.6
C7A-C8A-H8A	119.3	C1B#2-Pt2-P2	90.1(2)	C20B-C21B-C22B	118.5(5)
C3A-C8A-H8A	119.3	C1B-Pt2-P2	175.8(3)	C20B-C21B-H21B	120.7
C10A-C9A-C6A	178.4(7)	P2#2-Pt2-P2	85.77(11)	C22B-C21B-H21B	120.7
C9A-C10A-C11A	176.9(5)	C17B-P2-C23B	106.9(2)	C17B-C22B-C21B	120.9(5)
C16A-C11A-C12A	118.6(6)	C17B-P2-C29B	104.7(2)	C17B-C22B-H22B	119.5
C12A-C13A-C14A	120.0(6)	C23B-P2-C29B	107.3(2)	C21B-C22B-H22B	119.5
C12A-C13A-H13A	120.0	C17B-P2-Pt2	114.30(18)	C24B-C23B-C28B	119.9(4)
C14A-C13A-H13A	120.0	C23B-P2-Pt2	115.6(2)	C24B-C23B-P2	119.9(3)
C15A-C14A-C13A	120.2(6)	C29B-P2-Pt2	107.32(17)	C28B-C23B-P2	119.7(4)
C15A-C14A-H14A	119.9	C2B-C1B-Pt2	172.4(6)	C23B-C24B-C25B	120.0(4)
C13A-C14A-H14A	119.9	C1B-C2B-C3B	176.4(6)	C23B-C24B-H24B	120.0
C14A-C15A-C16A	121.1(6)	C4B-C3B-C8B	117.3(5)	C25B-C24B-H24B	120.0
C14A-C15A-H15A	119.5	C4B-C3B-C2B	121.2(5)	C26B-C25B-C24B	119.3(5)
C16A-C15A-H15A	119.5	C8B-C3B-C2B	121.5(4)	C26B-C25B-H25B	120.4
C11A-C16A-C15A	118.9(6)	C5B-C4B-C3B	122.3(6)	C24B-C25B-H25B	120.4
C11A-C16A-H16A	120.5	C5B-C4B-H4B	118.9	C25B-C26B-C27B	120.4(4)
C15A-C16A-H16A	120.5	C3B-C4B-H4B	118.9	C25B-C26B-H26B	119.8
C22A-C17A-C18A	120.7(4)	C4B-C5B-C6B	119.5(5)	C27B-C26B-H26B	119.8
C22A-C17A-P1	120.7(4)	C4B-C5B-H5B	120.3	C28B-C27B-C26B	119.7(5)

C18A-C17A-P1	118.6(4)	C6B-C5B-H5B	120.3	C28B-C27B-H27B	120.1
C17A-C18A-C19A	118.8(6)	C7B-C6B-C5B	118.5(4)	C26B-C27B-H27B	120.1
C17A-C18A-H18A	120.6	C7B-C6B-C9B	121.6(4)	C27B-C28B-C23B	120.6(5)
C19A-C18A-H18A	120.6	C5B-C6B-C9B	119.7(5)	C27B-C28B-H28B	119.7
C20A-C19A-C18A	121.2(7)	C8B-C7B-C6B	121.2(4)	C28B-C27B-C26B	119.7(5)
C20A-C19A-H19A	119.4	C8B-C7B-H7B	119.4	C23B-C28B-H28B	119.7
C18A-C19A-H19A	119.4	C6B-C7B-H7B	119.4	C29B#2-C29B-P2	107.8(2)
C19A-C20A-C21A	119.5(5)	C7B-C8B-C3B	121.3(4)	C29B#2-C29B-H29A	110.1
C19A-C20A-H20A	120.3	C7B-C8B-H8B	119.4	P2-C29B-H29A	110.1
C21A-C20A-H20A	120.3	C3B-C8B-H8B	119.4	C29B#2-C29B-H29D	110.1
C20A-C21A-C22A	120.0(5)	C10B-C9B-C6B	177.2(6)	P2-C29B-H29D	110.1
C20A-C21A-H21A	120.0	C9B-C10B-C11B	175.8(8)	H29A-C29B-H29D	108.5
C22A-C21A-H21A	120.0	C12B-C11B-C16B	120.1(6)		

***cis*-BTF**. The asymmetric unit consists of the Pt complex and two dichloromethane solvent molecules. There are two disordered regions in the complex. Methyl group C26 is refined in two parts (with C26') with their site occupation factors dependently refined. The second disordered region involves atoms S1/N1 and C17-C22. The two parts were also refined with their site occupation factors fixed at 0.8/0.2 for the major and minor parts, respectively. In the final cycle of refinement, 15721 reflections (of which 12308 are observed with I > 2□(I)) were used to refine 820 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 2.43%, 4.98% and 0.968, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

Crystal Data and Structure Refinement for *cis*-BTF

Identification code	abby3	
Empirical formula	C80 H68 Cl4 N2 P2 Pt S2	
Formula weight	1520.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.8880(12) Å	α= 90°.
	b = 17.4517(14) Å	β= 97.971(2)°.
	c = 30.725(2) Å	λ = 90°.
Volume	6843.9(10) $Å^3$	
Z	4	

Density (calculated)	1.476 Mg/m^3
Absorption coefficient	2.361 mm^{-1}
F(000)	3080
Crystal size	0.27 x 0.05 x 0.05 mm^3
Theta range for data collection	1.34 to 27.50°.
Index ranges	$-16 \leq h \leq 16$, $-22 \leq k \leq 22$, $-39 \leq l \leq 38$
Reflections collected	96259
Independent reflections	15721 [R(int) = 0.0515]
Completeness to theta = 27.50°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.8891 and 0.5681
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15721 / 16 / 811
Goodness-of-fit on F^2	0.968
Final R indices [I>2sigma(I)]	R1 = 0.0243, wR2 = 0.0498 [12308]
R indices (all data)	R1 = 0.0385, wR2 = 0.0584
Largest diff. peak and hole	0.905 and -0.580 e.$Å^{-3}$

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(\square F_o^2)\square^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Crystal Structure Bond Lengths and Angles *cis*-BTF

Table B-3. Bond lengths (Å) for *cis*-BTF

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Pt1-C27	2.010(3)	C18'-H18B	0.9500	C49-H49A	0.9900
Pt1-C1	2.013(3)	C19'-C20'	1.392(15)	C49-H49B	0.9900
Pt1-P1	2.2649(7)	C19'-H19B	0.9500	C50-H50A	0.9800
Pt1-P2	2.2709(7)	C20'-C21'	1.360(15)	C50-H50B	0.9800
S2-C43	1.727(3)	C20'-H20B	0.9500	C50-H50C	0.9800
S2-C42	1.761(3)	C21'-C22'	1.400(16)	C51-C52	1.529(4)
P1-C73	1.814(3)	C21'-H21B	0.9500	C51-H51A	0.9900
P1-C67	1.818(3)	C22'-N1'	1.382(6)	C51-H51B	0.9900
P1-C53	1.849(3)	C27-C28	1.201(4)	C52-H52A	0.9800
P2-C55	1.809(3)	C28-C29	1.438(4)	C52-H52B	0.9800
P2-C61	1.814(3)	C29-C34	1.408(4)	C52-H52C	0.9800
P2-C54	1.845(3)	C29-C30	1.413(4)	C55-C56	1.394(4)
Cl1-C79	1.769(3)	C34-C33	1.381(4)	C55-C60	1.395(4)
Cl2-C79	1.762(3)	C34-H34A	0.9500	C56-C57	1.388(4)
Cl3-C80	1.764(4)	C33-C32	1.405(4)	C56-H56A	0.9500
Cl4-C80	1.757(4)	C33-C35	1.530(3)	C57-C58	1.383(4)
N2-C42	1.303(3)	C32-C31	1.392(3)	C57-H57A	0.9500
N2-C48	1.393(3)	C32-C41	1.461(3)	C58-C59	1.384(4)
C1-C2	1.203(3)	C31-C30	1.379(4)	C58-H58A	0.9500
C2-C3	1.439(4)	C31-H31A	0.9500	C59-C60	1.378(4)
C3-C8	1.407(4)	C30-H30A	0.9500	C59-H59A	0.9500
C3-C4	1.409(4)	C35-C36	1.527(3)	C60-H60A	0.9500

C4-C5	1.391(4)	C35-C49	1.538(4)	C61-C66	1.385(4)
C4-H4A	0.9500	C35-C51	1.550(4)	C61-C62	1.400(4)
C5-C6	1.393(4)	C36-C37	1.385(3)	C62-C63	1.390(4)
C5-H5A	0.9500	C36-C41	1.408(3)	C62-H62A	0.9500
C6-C7	1.407(4)	C41-C40	1.387(3)	C63-C64	1.373(5)
C6-C15	1.471(4)	C37-C38	1.402(4)	C63-H63A	0.9500
C7-C8	1.377(4)	C37-H37A	0.9500	C64-C65	1.372(5)
C7-C9	1.529(4)	C38-C39	1.403(4)	C64-H64A	0.9500
C8-H8A	0.9500	C38-C42	1.468(4)	C65-C66	1.410(4)
C9-C10	1.527(4)	C39-C40	1.384(4)	C65-H65A	0.9500
C9-C23	1.536(4)	C39-H39A	0.9500	C66-H66A	0.9500
C9-C25	1.541(4)	C40-H40A	0.9500	C67-C72	1.394(3)
C10-C11	1.381(4)	C48-C47	1.397(4)	C67-C68	1.396(4)
C10-C15	1.411(4)	C48-C43	1.402(4)	C68-C69	1.386(4)
C15-C14	1.383(4)	C43-C44	1.404(4)	C68-H68A	0.9500
C14-C13	1.387(4)	C44-C45	1.385(4)	C69-C70	1.385(4)
C14-H14A	0.9500	C44-H44A	0.9500	C69-H69A	0.9500
C13-C12	1.403(4)	C45-C46	1.388(5)	C70-C71	1.382(4)
C13-H13A	0.9500	C45-H45A	0.9500	C70-H70A	0.9500
C12-C11	1.403(4)	C46-C47	1.383(4)	C71-C72	1.388(4)
C12-C16	1.471(4)	C46-H46A	0.9500	C71-H71A	0.9500
C11-H11A	0.9500	C47-H47A	0.9500	C72-H72A	0.9500
C16-N1	1.270(4)	C23-C24	1.516(4)	C73-C78	1.386(4)
C16-N1'	1.306(6)	C23-H23A	0.9900	C73-C74	1.393(4)
C16-S1'	1.753(5)	C23-H23B	0.9900	C78-C77	1.391(4)

C16-S1	1.761(3)	C24-H24A	0.9800	C78-H78A	0.9500
S1-C17	1.755(4)	C24-H24B	0.9800	C77-C76	1.380(4)
C17-C22	1.409(5)	C24-H24C	0.9800	C77-H77A	0.9500
C17-C18	1.409(5)	C25-C26	1.383(5)	C76-C75	1.382(4)
C18-C19	1.387(5)	C25-C26'	1.398(10)	C76-H76A	0.9500
C18-H18A	0.9500	C25-H25A	0.9900	C75-C74	1.393(4)
C19-C20	1.396(5)	C25-H25B	0.9900	C75-H75A	0.9500
C19-H19A	0.9500	C25-H25C	0.9900	C74-H74A	0.9500
C20-C21	1.381(4)	C25-H25D	0.9900	C53-C54	1.535(4)
C20-H20A	0.9500	C26-H25C	0.8406	C53-H53A	0.9900
C21-C22	1.398(5)	C26-H26A	0.9800	C53-H53B	0.9900
C21-H21A	0.9500	C26-H26B	0.9800	C54-H54A	0.9900
C22-N1	1.372(4)	C26-H26C	0.9800	C54-H54B	0.9900
S1'-C17'	1.742(6)	C26'-H26D	0.9800	C79-H79A	0.9900
C17'-C22'	1.399(15)	C26'-H26E	0.9800	C79-H79B	0.9900
C17'-C18'	1.399(16)	C26'-H26F	0.9800	C80-H80A	0.9900
C18'-C19'	1.361(15)	C49-C50	1.526(4)	C80-H80B	0.9900

Table B-4. Bond angles (degrees) for *cis*-BTF

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
C27-Pt1-C1	91.38(10)	C34-C29-C30	119.4(2)	C35-C49-H49B	108.4
C27-Pt1-P1	177.53(7)	C34-C29-C28	119.4(2)	H49A-C49-H49B	107.5
C1-Pt1-P1	90.82(7)	C30-C29-C28	121.2(2)	C49-C50-H50A	109.5
C27-Pt1-P2	91.42(7)	C33-C34-C29	119.9(2)	C49-C50-H50B	109.5

C1-Pt1-P2	176.18(7)	C33-C34-H34A	120.1	H50A-C50-H50B	109.5
P1-Pt1-P2	86.33(2)	C29-C34-H34A	120.1	C49-C50-H50C	109.5
C43-S2-C42	89.01(14)	C34-C33-C32	119.8(2)	H50A-C50-H50C	109.5
C73-P1-C67	105.23(12)	C34-C33-C35	129.0(2)	H50B-C50-H50C	109.5
C73-P1-C53	104.99(12)	C32-C33-C35	111.2(2)	C52-C51-C35	116.1(2)
C67-P1-C53	106.64(12)	C31-C32-C33	120.8(2)	C52-C51-H51A	108.3
C73-P1-Pt1	119.57(9)	C31-C32-C41	130.8(2)	C35-C51-H51A	108.3
C67-P1-Pt1	112.31(9)	C33-C32-C41	108.3(2)	C52-C51-H51B	108.3
C53-P1-Pt1	107.23(9)	C30-C31-C32	119.4(2)	C35-C51-H51B	108.3
C55-P2-C61	104.46(13)	C30-C31-H31A	120.3	H51A-C51-H51B	107.4
C55-P2-C54	104.15(12)	C32-C31-H31A	120.3	C51-C52-H52A	109.5
C61-P2-C54	108.25(13)	C31-C30-C29	120.6(2)	C51-C52-H52B	109.5
C55-P2-Pt1	116.63(9)	C31-C30-H30A	119.7	H52A-C52-H52B	109.5
C61-P2-Pt1	113.76(8)	C29-C30-H30A	119.7	C51-C52-H52C	109.5
C54-P2-Pt1	108.91(9)	C36-C35-C33	100.8(2)	H52A-C52-H52C	109.5
C42-N2-C48	110.2(2)	C36-C35-C49	112.3(2)	H52B-C52-H52C	109.5
C2-C1-Pt1	170.8(2)	C33-C35-C49	112.6(2)	C56-C55-C60	119.7(2)
C1-C2-C3	170.0(3)	C36-C35-C51	108.2(2)	C56-C55-P2	119.4(2)

C8-C3-C4	119.0(2)	C33-C35-C51	112.4(2)	C60-C55-P2	120.8(2)
C8-C3-C2	117.8(2)	C49-C35-C51	110.1(2)	C57-C56-C55	119.5(3)
C4-C3-C2	123.2(2)	C37-C36-C41	120.2(2)	C57-C56-H56A	120.3
C5-C4-C3	121.1(3)	C37-C36-C35	128.9(2)	C55-C56-H56A	120.3
C5-C4-H4A	119.5	C41-C36-C35	110.9(2)	C58-C57-C56	120.4(3)
C3-C4-H4A	119.5	C40-C41-C36	120.8(2)	C58-C57-H57A	119.8
C4-C5-C6	119.0(2)	C40-C41-C32	130.5(2)	C56-C57-H57A	119.8
C4-C5-H5A	120.5	C36-C41-C32	108.7(2)	C57-C58-C59	120.2(3)
C6-C5-H5A	120.5	C36-C37-C38	119.4(2)	C57-C58-H58A	119.9
C5-C6-C7	120.4(2)	C36-C37-H37A	120.3	C59-C58-H58A	119.9
C5-C6-C15	131.6(2)	C38-C37-H37A	120.3	C60-C59-C58	120.0(3)
C7-C6-C15	107.9(2)	C37-C38-C39	119.5(2)	C60-C59-H59A	120.0
C8-C7-C6	120.4(3)	C37-C38-C42	120.4(2)	C58-C59-H59A	120.0
C8-C7-C9	128.5(2)	C39-C38-C42	120.0(2)	C59-C60-C55	120.3(3)
C6-C7-C9	111.1(2)	C40-C39-C38	121.4(3)	C59-C60-H60A	119.9
C7-C8-C3	120.0(2)	C40-C39-H39A	119.3	C55-C60-H60A	119.9
C7-C8-H8A	120.0	C38-C39-H39A	119.3	C66-C61-C62	119.2(3)
C3-C8-H8A	120.0	C39-C40-C41	118.8(2)	C66-C61-P2	122.4(2)
C10-C9-C7	100.7(2)	C39-C40-H40A	120.6	C62-C61-P2	118.1(2)
C10-C9-C23	114.1(2)	C41-C40-H40A	120.6	C63-C62-C61	120.5(3)
C7-C9-C23	113.4(2)	N2-C42-C38	124.5(2)	C63-C62-H62A	119.8
C10-C9-C25	110.5(2)	N2-C42-S2	115.8(2)	C61-C62-H62A	119.8
C7-C9-C25	110.4(2)	C38-C42-S2	119.8(2)	C64-C63-C62	119.9(4)
C23-C9-C25	107.6(3)	N2-C48-C47	125.0(3)	C64-C63-H63A	120.1

C11-C10-C15	120.2(2)	N2-C48-C43	115.4(3)	C62-C63-H63A	120.1
C11-C10-C9	129.2(2)	C47-C48-C43	119.5(3)	C65-C64-C63	120.7(3)
C15-C10-C9	110.6(2)	C48-C43-C44	121.7(3)	C65-C64-H64A	119.6
C14-C15-C10	120.6(2)	C48-C43-S2	109.6(2)	C63-C64-H64A	119.6
C14-C15-C6	130.6(3)	C44-C43-S2	128.7(2)	C64-C65-C66	120.0(3)
C10-C15-C6	108.6(2)	C45-C44-C43	117.3(3)	C64-C65-H65A	120.0
C15-C14-C13	119.1(3)	C45-C44-H44A	121.4	C66-C65-H65A	120.0
C15-C14-H14A	120.4	C43-C44-H44A	121.4	C61-C66-C65	119.7(3)
C13-C14-H14A	120.4	C44-C45-C46	121.4(3)	C61-C66-H66A	120.1
C14-C13-C12	120.9(2)	C44-C45-H45A	119.3	C65-C66-H66A	120.1
C14-C13-H13A	119.5	C46-C45-H45A	119.3	C72-C67-C68	119.4(3)
C12-C13-H13A	119.5	C47-C46-C45	121.3(3)	C72-C67-P1	122.3(2)
C13-C12-C11	119.6(2)	C47-C46-H46A	119.4	C68-C67-P1	118.3(2)
C13-C12-C16	119.9(2)	C45-C46-H46A	119.4	C69-C68-C67	120.1(3)
C11-C12-C16	120.4(2)	C46-C47-C48	118.8(3)	C69-C68-H68A	119.9
C10-C11-C12	119.4(3)	C46-C47-H47A	120.6	C67-C68-H68A	119.9
C10-C11-H11A	120.3	C48-C47-H47A	120.6	C70-C69-C68	120.2(3)
C12-C11-H11A	120.3	C24-C23-C9	115.3(2)	C70-C69-H69A	119.9

N1-C16-N1'	110.7(6)	C24-C23-H23A	108.5	C68-C69-H69A	119.9
N1-C16-C12	123.6(2)	C9-C23-H23A	108.5	C71-C70-C69	119.9(3)
N1'-C16-C12	125.7(6)	C24-C23-H23B	108.5	C71-C70-H70A	120.0
N1-C16-S1'	7.1(3)	C9-C23-H23B	108.5	C69-C70-H70A	120.0
N1'-C16-S1'	117.2(6)	H23A-C23-H23B	107.5	C70-C71-C72	120.5(3)
C12-C16-S1'	117.1(3)	C23-C24-H24A	109.5	C70-C71-H71A	119.8
N1-C16-S1	115.2(2)	C23-C24-H24B	109.5	C72-C71-H71A	119.8
N1'-C16-S1	4.7(6)	H24A-C24-H24B	109.5	C71-C72-C67	119.9(3)
C12-C16-S1	121.24(19)	C23-C24-H24C	109.5	C71-C72-H72A	120.0
S1'-C16-S1	121.7(3)	H24A-C24-H24C	109.5	C67-C72-H72A	120.0
C17-S1-C16	88.63(16)	H24B-C24-H24C	109.5	C78-C73-C74	119.2(2)
C22-C17-C18	122.5(3)	C26-C25-C26'	70.0(5)	C78-C73-P1	118.9(2)
C22-C17-S1	108.6(3)	C26-C25-C9	118.7(3)	C74-C73-P1	121.9(2)
C18-C17-S1	128.9(3)	C26'-C25-C9	130.4(5)	C73-C78-C77	120.4(3)
C19-C18-C17	116.8(3)	C26-C25-H25A	107.7	C73-C78-H78A	119.8
C19-C18-H18A	121.6	C26'-C25-H25A	115.7	C77-C78-H78A	119.8
C17-C18-H18A	121.6	C9-C25-H25A	107.7	C76-C77-C78	120.3(3)
C18-C19-C20	121.2(3)	C26-C25-H25B	107.7	C76-C77-H77A	119.9

C18-C19-H19A	119.4	C26'-C25-H25B	37.8	C78-C77-H77A	119.9
C20-C19-H19A	119.4	C9-C25-H25B	107.7	C77-C76-C75	119.8(3)
C21-C20-C19	121.7(3)	H25A-C25-H25B	107.1	C77-C76-H76A	120.1
C21-C20-H20A	119.2	C26-C25-H25C	37.0	C75-C76-H76A	120.1
C19-C20-H20A	119.2	C26'-C25-H25C	104.7	C76-C75-C74	120.1(3)
C20-C21-C22	118.9(3)	C9-C25-H25C	104.6	C76-C75-H75A	119.9
C20-C21-H21A	120.6	H25A-C25-H25C	81.3	C74-C75-H75A	119.9
C22-C21-H21A	120.6	H25B-C25-H25C	142	C73-C74-C75	120.2(3)
N1-C22-C21	126.5(4)	C26-C25-H25D	126.7	C73-C74-H74A	119.9
N1-C22-C17	114.6(4)	C26'-C25-H25D	104.7	C75-C74-H74A	119.9
C21-C22-C17	118.9(3)	C9-C25-H25D	104.7	C54-C53-P1	109.70(18)
C16-N1-C22	112.9(3)	H25A-C25-H25D	24.8	C54-C53-H53A	109.7
C17'-S1'-C16	88.5(7)	H25B-C25-H25D	85.1	P1-C53-H53A	109.7
C22'-C17'-C18'	135.9(11)	H25C-C25-H25D	105.7	C54-C53-H53B	109.7
C22'-C17'-S1'	108.3(12)	C25-C26-H25C	45.2	P1-C53-H53B	109.7

C18'-C17'-S1'	115.0(12)	C25-C26-H26A	109.5	H53A-C53-H53B	108.2
C19'-C18'-C17'	111.7(13)	H25C-C26-H26A	113.9	C53-C54-P2	111.94(18)
C19'-C18'-H18B	124.2	C25-C26-H26B	109.5	C53-C54-H54A	109.2
C17'-C18'-H18B	124.2	H25C-C26-H26B	65.8	P2-C54-H54A	109.2
C18'-C19'-C20'	117.8(14)	H26A-C26-H26B	109.5	C53-C54-H54B	109.2
C18'-C19'-H19B	121.1	C25-C26-H26C	109.5	P2-C54-H54B	109.2
C20'-C19'-H19B	121.1	H25C-C26-H26C	135.3	H54A-C54-H54B	107.9
C21'-C20'-C19'	125.7(15)	H26A-C26-H26C	109.5	Cl2-C79-Cl1	111.11(16)
C21'-C20'-H20B	117.2	H26B-C26-H26C	109.5	Cl2-C79-H79A	109.4
C19'-C20'-H20B	117.2	C25-C26'-H26D	109.5	Cl1-C79-H79A	109.4
C20'-C21'-C22'	122.5(14)	C25-C26'-H26E	109.5	Cl2-C79-H79B	109.4
C20'-C21'-H21B	118.8	H26D-C26'-H26E	109.5	Cl1-C79-H79B	109.4
C22'-C21'-H21B	118.8	C25-C26'-H26F	109.5	H79A-C79-H79B	108
N1'-C22'-C17'	117.5(15)	H26D-C26'-H26F	109.5	Cl4-C80-Cl3	112.7(2)
N1'-C22'-C21'	136.2(15)	H26E-C26'-H26F	109.5	Cl4-C80-H80A	109.1
C17'-C22'-C21'	106.2(11)	C50-C49-C35	115.4(2)	Cl3-C80-H80A	109.1
C16-N1'-C22'	108.3(11)	C50-C49-H49A	108.4	Cl4-C80-H80B	109.1
C28-C27-Pt1	178.1(2)	C35-C49-H49A	108.4	Cl3-C80-H80B	109.1

C27-C28-C29	176.9(3)	C50-C49-H49B	108.4	H80A-C80-H80B	107.8

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