List of Supplementary Information

Highly Selective Photo-Catalytic Dimerization of α-Methylstyrene by Novel Palladium Complex with Photosensitizing Ruthenium(II) Polypyridyl Moiety

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General. All manipulations were carried out under an argon atmosphere with use of standard Schlenk techniques. Acetone, acetonitrile, and nitromethane were treated with appropriate drying agents, distilled, and stored under argon. α-Methylstyrene was washed three times with aq. 10% NaOH and six times with water, dried with $CaCl_2$ and distilled under vacuum. ^1H and ^{13}C NMR spectra were recorded on Brucker AC-200 and JEOL EX-400 spectrometers. Solvents for NMR measurements were dried over molecular sieves, degassed, stored under Ar. IR spectra (KBr pellets) were obtained on a JASCO FT/IR 5300 spectrometer. ESI-MS spectra were recorded on a ThermoQuest Finnigan LCQ Duo mass spectrometer. $[(bpy)_2Ru(bpm)](PF_6)_2$ were prepared according to the published method.[1] Other chemicals were purchased and used as received.

Preparation of $[(bpy)_2Ru(bpm)Pd(Me)Cl](PF_6)_2$.

$[(bpy)_2Ru(bpm)](PF_6)_2$ (300 mg, 0.35 mmol) and (1,5-cod)PdMeCl (110 mg, 0.42 mmol) was dissolved in 15 mL of CH_3NO_2 and stirred at ambient temperature for 3 h. The solvent was removed under reduced pressure and the resulting solid was washed with ether and then dissolved in 1 mL of CH_3NO_2 and precipitated with ether. Reddish-brown crystal was obtained from CH_3NO_2 / diethyl ether (346 mg, 0.34 mmol, 97.3 %).

◆Spectral Data for $[(bpy)_2Ru(bpm)Pd(Me)Cl](PF_6)_2$.

^1H NMR (200 MHz, CD_3COCD_3, RT, δ/ppm): 1.06 (s, 3 H, PdCH_3), 7.62 (dd, J = 7.2, 6.1 Hz, 4 H, bpy), 8.0-8.1 (m, 4 H, bpy, bpm), 8.2 – 8.3 (m, 4 H, bpy), 8.52 (m, 2 H, bpy), 8.72 (dd, J = 5.7, 1.6 Hz, 1 H, bpm), 8.76 (dd, J = 5.7, 1.6 Hz, 1 H, bpm), 8.84, (d, J = 7.8 Hz, 4 H, bpy), 9.14 (dd, J = 5.5,

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(1) Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1990**, *29*, 4750-4758.

1.6, 1.0 Hz, bpm), 9.17 (dd, *J* = 5.1, 1.8 Hz, 1 H, bpm)

^{13}C NMR (100 MHz, CD_3NO_2, RT, δ/ppm): -0.49 (q, J_{CH} = 135.1 Hz, Pd*C*H_3), 126.3 (d, J_{CH} = 167.7 Hz, bpy), 128.0 (d, J_{CH} = 144.9 Hz, bpm), 128.2 (d, J_{CH} = 142.0 Hz, bpm), 129.6 Hz, (d, J_{CH} = 171.4 Hz, bpy), 126.7 (d, J_{CH} = 171.4 Hz, bpy), 140.6 (d, J_{CH} = 169.8 Hz, bpy), 140.7 (d, J_{CH} = 169.8 Hz, bpy), 153.6 (d, J_{CH} = 183.9 Hz, bpy), 153.7 (d, J_{CH} = 183.9 Hz, bpy), 154.6 (d, J_{CH} = 176.4 Hz, bpy), 154.6 (d, J_{CH} = 176.4 Hz, bpy), 156.5 (d, J_{CH} = 181.8 Hz, bpm), 156.7 (d, J_{CH} = 196.3 Hz, bpm), 158.6 (s, bpy), 158.6 (s, bpy), 158.9 (s, bpy), 158.9 (s, bpy), 161.9 (d, J_{CH} = 192.6 Hz, bpm), 162.4 (d, J_{CH} = 191.7 Hz, bpm), 165.4 (s, bpm), 167.5 (s, bpm).

ESI-MS : m/z = 872.7 $\{M\cdot PF_6\}^+$, 1162 $\{M\cdot (PF_6)_3\}^-$

Anal. Calcd for $C_{29}H_{25}ClF_{12}N_8P_2PdRu$: C, 34.20; H, 2.47; N, 11.00. Found: C, 34.13; H, 2.74; N, 10.89.

Preparation of [(bpy)$_2$Ru(bpm)Pd(Me)(Me$_2$CO)](PF$_6$)$_2$(BF$_4$) (1).

$[(bpy)_2Ru(bpm)Pd(CH_3)Cl](PF_6)_2$ (325 mg, 0.32 mmol) and $AgBF_4$ (140 mg, 0.72 mmol) was dissolved in 7 mL of $(CH_3)_2CO$ and stirred at room temperature for 1 h. The solution was filtered and then concentrated. Brown solid was obtained after precipitation with 20 mL of diethyl ether. The solid was washed with diethyl ether and than dichloromethane and dried in vacuo. Reddish-brown crystal was obtained by diffusion of diethyl ether into $(CH_3)_2CO$ solution (329 mg, 0.29 mmol, 91.3 %).

◆Spectral Data for **1**

^{1}H NMR (200 MHz, CD_3NO_2, RT, δ/ppm):

δ 1.30 (s, 3H, Pd-*Me*), 2.23 (brs, 6H, Me_2CO), 7.44-7.58 (m, 4H, bpy), 7.80-7.85 (m, 4H, bpy), 8.07-8.24 (m, 6H, bpm (2H), bpy (4H), 8.46 (d, *J* = 5.5 Hz, 2H, bpm), 8.59 (d, *J* = 8.2 Hz, 4H, bpy), 8.74 (m, 1H, bpm), 8.94 (m, 1H, bpm).

^{13}C NMR (100 MHz, CD_3NO_2, RT, δ/ppm):

δ 5.2 (q, J_{CH} = 137.0 Hz, Pd-*Me*), 32.0 (q, J_{CH} = 127.0 Hz, *Me*$_2$CO), 125.8 (dd, J_{CH} = 167.5, 7.5 Hz, bpy), 127.8 (d, J_{CH} = 177.7 Hz, bpm), 128.1 (d, J_{CH} = 177.7 Hz, bpm), 129.2 (dd, J_{CH} = 170.8, 7.3 Hz, bpy) 129.4 (dd, J_{CH} = 170.8, 7.3 Hz, bpy), 140.2 (dd, J_{CH} = 164.2, 6.6 Hz, bpy), 140.4 (dd, J_{CH} = 164.2, 6.6 Hz, bpy), 153.1 (d, J_{CH} = 183.1 Hz, bpy), 154.0 (d, J_{CH} = 183.1 Hz, bpy), 156.4 (d, J_{CH} = 197.0 Hz, bpm), 157.5 (d, J_{CH} = 197.0 Hz, bpm), 158.1 (s, bpy), 158.3 (s, bpy), 162.3 (d, J_{CH} = 194.0 Hz, bpm), 162.6 (d, J_{CH} = 194.0 Hz, bpm), 164.4 (s, bpm), 167.1 (s, bpm).

^{1}H and ^{13}C NMR measurement at -25 °C gave a broad signal for the Me signal of the coordinated acetone ligand. Any signals attributable to the quarternary carbon signal of the acetone ligand was observed in the ^{13}C NMR spectrum at this temperature.

IR (KBr /cm^{-1}): 3436, 3086, 1696, 1605, 1313, 1243, 1082, 1031, 841 (ν_{PF}), 764 (ν_{BF}), 558.

ESI-MS : m/z = 1098 $\{M'\cdot(PF_6)(BF_4)_3\}^-$, 1156 $\{M'\cdot(PF_6)_2(BF_4)_2\}^-$, 1215 $\{M'\cdot(PF_6)_3(BF_4)\}^-$, 1273 $\{M'\cdot(PF_6)_4\}^-$. M' = $\{(bpy)_2Ru(bpm)Pd(CH_3)\}$.

Anal. Calcd for $C_{32}H_{31}BF_{16}N_8OP_2PdRu$: C, 34.08; H, 2.77; N, 9.94. Found: C, 34.52; H, 3.18; N, 9.48.

Preparation of [(bpy)$_2$Ru(bpm)Pd(Me)(MeCN)](PF$_6$)$_2$(BF$_4$) (2).

$[(bpy)_2Ru(bpm)Pd(CH_3)Cl](PF_6)_2$ (430 mg, 0.42 mmol) and $AgBF_4$ (106 mg, 0.54 mmol) was dissolved in 10 mL of CH_3CN and stirred at room temperature for 1 h. The solution was filtered and concentrated. Brown solid was obtained after precipitation with diethyl ether and dried. Reddish-brown crystal was obtained by diffusion of diethyl ether into CH_3CN solution (421 mg, 0.38 mmol, 90.5 %).

◆

Spectral Data for **2**

^{1}H NMR (200 MHz, CD_3NO_2, RT, δ/ppm):

δ 1.45 (s, 3H, Pd*Me*), 2.60 (s, 3H, NC*Me*), 7.52 (m, 4H, bpy), 7.86 (d, *J* = 7.0 Hz, 2H, bpy), 7.89 (dd, *J* = 5.9, 5.9 Hz, 2H, bpm), 8.0 – 8.3 (m, 6H, bpy), 8.50 (dd, *J* = 5.7, 1.6 Hz, 2H, bpm), 8.62 (d, *J* = 8.4 Hz, 4H, bpy), 9.02 (bs, 2H, bpm).

^{13}C NMR (100 MHz, CD_3NO_2, -10 °C, δ/ppm):

δ 3.60 (q, J_{CH} = 141.6 Hz, NCMe), 4.67 (q, J_{CH} = 137.5 Hz, PdMe), 125.7 (d, J_{CH} = 168.1 Hz, bpy), 127.5 (d, J_{CH} = 180.6 Hz, bpm), 128.1 (d, J_{CH} = 180.6 Hz, bpm), 129.1 (d, J_{CH} = 171.4 Hz, bpy), 129.2 (d, J_{CH} = 171.4 Hz, bpy), 140.1 (d, J_{CH} = 169.9 Hz, bpy), 140.2 (d, J_{CH} = 169.0 Hz, bpy), 153.1 (d, J_{CH} = 187.2 Hz, bpy), 154.0 (d, J_{CH} = 184.7 Hz, bpy), 156.6 (d, J_{CH} = 190.5 Hz, bpm), 156.7 (d, J_{CH} = 190.5 Hz, bpm), 158.0 (s, bpy), 158.2 (s, bpy), 162.7 (d, J_{CH} = 189.7 Hz, bpm), 164.4 (s, bpm), 167.3 (s, bpm),

IR (KBr /cm^{-1}): 3647, 3450, 3091, 1605, 1469, 1447, 1410, 1069, 830 (ν_{PF}), 764 (ν_{BF}), 558.

ESI-MS (CH_3CN) : m/z = 1098 $\{M'\cdot(PF_6)(BF_4)_3\}^-$, 1156 $\{M'\cdot(PF_6)_2(BF_4)_2\}^-$, 1215 $\{M'\cdot(PF_6)_3(BF_4)\}^-$. M' = $\{(bpy)_2Ru(bpm)Pd(CH_3)\}$.

Preparation of [(bpy)$_2$Ru(bpm)Pd(CMeEtPh)(L)](BF$_4$) (A) (L = Me$_2$CO).

Complex $[(bpy)_2Ru(bpm)Pd(Me)(Me_2CO)](PF_6)_2(BF_4)$ (**1**) (16.9 mg, 0.0150 mmol) was placed in the 5 mm NMR tube and 0.4 mL of acetone-*d*$_6$, 5.0 μL of α-methylstyrene (0.0384 mmol, 2.6 equiv) was added. The solution was immediately transferred to the Schlenk tube and concentrated under vacuum. After addition of diethylether, intermediate **A** was obtained as red-brown precipitate (11.0 mg, 0.00883 mmol, 58.9 %).

◆ Spectral Data for **A**

^{1}H NMR (200 MHz, CD_3NO_2, RT, δ/ppm):

δ 1.20 (t, *J* = 7.4 Hz, 3H, PdCCH$_2$C*H*$_3$), 1.27 (t, *J* = 7.4 Hz, 3H, PdCCH$_2$C*H*$_3$), 1.57 (s, 3H, PdC*Me*), 1.62 (s, 3H, PdC*Me*), 1.8-2.0 (m, 2H, PdCC*H*$_2$CH$_3$), 7.5-9.2 (m, 27H, *Ph*).

ESI-MS: m/z = 1101: $[\{(bpy)_2Ru(bpm)Pd(CMeEtPh)\}(PF_6)_2]^+$, 1043: $[\{(bpy)_2Ru(bpm)Pd(CMeEtPh)\}(BF_4)(PF_6)]^+$, 985: $[\{(bpy)_2Ru(bpm)Pd(CMeEtPh)\}(BF_4)_2]^+$.

Preparation of $[(bpy)_2Ru(bpm)Pd(CMe_2Ph)(L)](BF_4)$ (C) (L = solvent).

Complex $[(bpy)_2Ru(bpm)Pd(Me)(Me_2CO)](PF_6)_2(BF_4)$ (**1**) (80.0 mg, 0.067 mmol) and 0.5 mL of α-methylstyrene (3.4 mmol, 50 equiv) was stirred in CH_3NO_2 for 1h. Solvent was removed under reduced pressure and the residual solid was washed with diethylether, pentane, and CH_2Cl_2. Yellowish brown crystal was obtained after crystallization from CH_3NO_2/diethylether (68 mg, 0.058 mmol, 86 %).

◆ Spectroscopic data for **C**

^{1}H NMR (200 MHz, CD_3NO_2, RT, δ/ppm): δ 1.50 (s, 3H, PdC*Me*), 1.56 (s, 3H, PdC*Me*), 6.9-9.2 (m, 27H, aromatic).

^{13}C NMR (100 MHz, CD_3NO_2, RT, δ/ppm): δ 24.2 (q, J_{CH} = 127.6 Hz, PdC*Me*), 75.1 (s, Pd*C*Me), 106.4 (d, J_{CH} = 160.7Hz, *Ph*), 117.9 (s, *Ph*), 125.3 (d, J_{CH} = 167.0 Hz, bpy), 127.4 (d, J_{CH} = 178.1 Hz, bpm), 128.7 (d, J_{CH} = 170.8 Hz, bpy), 128.8 (d, J_{CH} = 170.8 Hz, bpy), 133.8 (d, J_{CH} = 165.6 Hz, *Ph*), 134.9 (d, J_{CH} = 165.6 Hz, *Ph*), 139.6 (d, J_{CH} = 168.9 Hz, bpy), 139.8 (d, J_{CH} = 168.9 Hz, bpy), 153.1 (d, J_{CH} = 187.2 Hz, bpy), 154.0 (d, J_{CH} = 184.7 Hz, bpy), 156.6 (d, J_{CH} = 190.5 Hz, bpm), 156.7 (d, J_{CH} = 190.5 Hz, bpm), 158.0 (s, bpy), 158.2 (s, bpy), 162.7 (d, J_{CH} = 189.7 Hz, bpm), 164.4 (s, bpm), 167.3 (s, bpm).

ESI-MS: m/z = 969.9: $[\{(bpy)_2Ru(bpm)Pd(CMe_2Ph)\}(BF_4)_2]^+$, 1027.8: $[\{(bpy)_2Ru(bpm)Pd(CMe_2Ph)\}(BF_4)(PF_6)]^+$, 1088.6: $[\{(bpy)_2Ru(bpm)Pd(CMe_2Ph)\}(PF_6)_2]^+$.

Experimental procedures for X-ray crystallography

Crystallographic data are summarized in Table S1. Single crystal of **2** was obtained by recrystallization from CH_3CN-Et_2O and mounted on glass fibers. **2** crystallized with 1 PF_6 and 2 BF_4 counter anions.

Data Collection

A red prismatic crystal of $C_{37}H_{37}B_2F_{14}N_{12}PPdRu$ having approximate dimensions of 0.10 x 0.10 x 0.05 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite monochromated Mo-Kα radiation.

Indexing was performed from 3 oscillations that were exposed for 360 seconds. The crystal-to-detector distance was 110.00 mm.

The data were collected at a temperature of $-60 \pm 1^{o}C$ to a maximum 2θ value of 55.0^{o}. A total of 36 oscillation images were collected. A sweep of data was done using ω oscillations from 0.0 to 180.0^{o} in 5.0^{o} steps. The exposure rate was 799.8 [sec./^{o}]. The crystal-to-detector distance was 110.00 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 16989 reflections that were collected, 9578 were unique (R_{int} = 0.1092); equivalent reflections were merged.

The linear absorption coefficient, μ, for Mo-Kα radiation is 8.8 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.66 to 1.38. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by a combination of the direct methods (SHELXS-86)[1] and Fourier synthesis (DIRDIF99).[2] Least-squares refinements were carried out using SHELXL-97 [1] (refined on F^2). All the non-hydrogen atoms except for the disordered BF_4 atoms are refined anisotropically. All the hydrogen atoms were fixed at the calculated positions.

References

(1) (a) Sheldrick, G.M, SHELXS-86: *Program for crystal structure determination,* University of Göttingen: Göttingen, Germany, 1986. (b) Sheldrick, G.M, SHELXL-97: *Program for crystal structure refinement,* University of Göttingen: Göttingen, Germany, 1997.

(2) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

Table S1. Crystallographic Data for **2**

	2
formula	$C_{37}H_{37}N_{12}RuPdPF_{14}B2$
formula weight	1175.85
crystal system	triclinic
space group	*P*-1 (#2)
a/Å	12.147(11)
b/Å	12.263(11)
c/Å	16.624(16)
α/deg	88.05(4)
β/deg	71.97(4)
γ/deg	89.15(4)
V/Å^3	2353(4)
Z	2
d_{calc}/g·cm^{-3}	1.691
temp	-60
radiation	MoKα (λ = 0.71069 Å)
μ/cm^{-1}	8.75
diffractometer	Rigaku RAXIS IV
max 2θ/deg	55.0
reflections collected	16991
independent reflections	9578 [R(int) = 0.1092]
no. of parameters refined	593
R1 ($I > 2\sigma$)	0.0764 for 3409 data
wR_2 ($I > 2\sigma$)	0.1798 for 3409 data
goodness of fit	0.840

Table 3. Bond lengths for **2**.

Pd(1)-N(9)	1.996(10)
Pd(1)-C(29)	2.016(12)
Pd(1)-N(6)	2.049(9)
Pd(1)-N(8)	2.185(9)
Ru(1)-N(4)	2.064(9)
Ru(1)-N(5)	2.069(8)
Ru(1)-N(7)	2.073(9)
Ru(1)-N(2)	2.075(9)
Ru(1)-N(3)	2.077(9)
Ru(1)-N(1)	2.092(9)
P(1)-F(6)	1.507(11)
P(1)-F(5)	1.514(10)
P(1)-F(4)	1.518(10)
P(1)-F(2)	1.553(10)
P(1)-F(3)	1.571(11)
P(1)-F(1)	1.585(10)
B(1)-F(13B)	1.27(3)
B(1)-F(13)	1.35(2)
B(1)-F(11)	1.355(17)
B(1)-F(14B)	1.38(3)
B(1)-F(12)	1.387(19)
B(1)-F(14)	1.53(2)
B(1)-F(12A)	1.58(3)
B(2)-F(24A)	1.05(6)
B(2)-F(24)	1.263(18)
B(2)-F(22)	1.27(2)
B(2)-F(22A)	1.36(3)
B(2)-F(23A)	1.36(3)
B(2)-F(21)	1.415(17)
B(2)-F(23)	1.527(19)
B(2)-F(21A)	1.62(2)
N(1)-C(1)	1.333(14)
N(1)-C(5)	1.398(13)
N(2)-C(6)	1.347(13)
N(2)-C(10)	1.351(14)
N(3)-C(11)	1.342(13)
N(3)-C(15)	1.376(13)
N(4)-C(20)	1.338(13)
N(4)-C(16)	1.386(13)
N(5)-C(25)	1.345(12)
N(5)-C(26)	1.356(13)
N(6)-C(25)	1.354(12)
N(6)-C(28)	1.375(14)
N(7)-C(24)	1.339(12)
N(7)-C(21)	1.366(13)
N(8)-C(24)	1.335(12)
N(8)-C(23)	1.337(13)
N(9)-C(30)	1.106(14)
N(10)-C(32)	1.083(19)
N(12)-C(36)	1.085(18)
C(1)-C(2)	1.373(16)
C(2)-C(3)	1.35(2)
C(3)-C(4)	1.372(19)
C(4)-C(5)	1.344(16)
C(5)-C(6)	1.480(15)
C(6)-C(7)	1.384(15)
C(7)-C(8)	1.347(19)
C(8)-C(9)	1.351(19)
C(9)-C(10)	1.384(16)
C(11)-C(12)	1.394(16)
C(12)-C(13)	1.357(17)
C(13)-C(14)	1.366(16)

C(14)-C(15)	1.406(14)	C(24)-C(25)	1.482(13)
C(15)-C(16)	1.471(15)	C(26)-C(27)	1.344(15)
C(16)-C(17)	1.382(15)	C(27)-C(28)	1.374(15)
C(17)-C(18)	1.394(17)	C(30)-C(31)	1.499(19)
C(18)-C(19)	1.371(16)	C(32)-C(33)	1.44(2)
C(19)-C(20)	1.372(16)	N(13)-C(34)	1.10(2)
C(21)-C(22)	1.356(14)	C(34)-C(35)	1.39(2)
C(22)-C(23)	1.374(15)	C(36)-C(37)	1.48(2)
C(17)-C(18)	1.401(17)		
C(18)-C(19)	1.393(17)		
C(19)-C(20)	1.367(17)		
C(21)-C(22)	1.382(15)		
C(22)-C(23)	1.370(16)		
C(24)-C(25)	1.482(14)		
C(26)-C(27)	1.359(16)		
C(27)-C(28)	1.390(16)		
C(30)-C(31)	1.471(19)		
C(32)-C(33)	1.43(3)		
C(34)-C(35)	1.43(3)		
C(36)-C(37)	1.48(2)		

Table 3. Bond angles [deg] for **2**.

N(9)-Pd(1)-C(29)	88.6(4)
N(9)-Pd(1)-N(6)	176.8(4)
C(29)-Pd(1)-N(6)	94.5(4)
N(9)-Pd(1)-N(8)	97.1(4)
C(29)-Pd(1)-N(8)	174.1(4)
N(6)-Pd(1)-N(8)	79.8(3)
N(4)-Ru(1)-N(5)	90.2(3)
N(4)-Ru(1)-N(7)	94.5(3)
N(5)-Ru(1)-N(7)	79.1(3)
N(4)-Ru(1)-N(2)	95.5(4)
N(5)-Ru(1)-N(2)	172.6(3)
N(7)-Ru(1)-N(2)	95.6(3)
N(4)-Ru(1)-N(3)	79.4(4)
N(5)-Ru(1)-N(3)	99.1(3)
N(7)-Ru(1)-N(3)	173.7(3)
N(2)-Ru(1)-N(3)	86.7(3)
N(4)-Ru(1)-N(1)	171.5(3)
N(5)-Ru(1)-N(1)	96.5(3)
N(7)-Ru(1)-N(1)	91.9(3)
N(2)-Ru(1)-N(1)	78.3(4)
N(3)-Ru(1)-N(1)	94.3(3)
F(6)-P(1)-F(5)	95.2(8)
F(6)-P(1)-F(4)	174.1(9)
F(5)-P(1)-F(4)	89.7(7)
F(6)-P(1)-F(2)	93.5(8)
F(5)-P(1)-F(2)	99.4(8)
F(4)-P(1)-F(2)	88.8(7)
F(6)-P(1)-F(3)	85.4(7)
F(5)-P(1)-F(3)	175.7(7)
F(4)-P(1)-F(3)	89.5(7)
F(2)-P(1)-F(3)	84.8(7)
F(6)-P(1)-F(1)	89.5(7)
F(5)-P(1)-F(1)	85.8(7)
F(4)-P(1)-F(1)	87.7(6)
F(2)-P(1)-F(1)	173.8(8)
F(3)-P(1)-F(1)	90.0(6)
F(13B)-B(1)-F(13)	44.4(14)
F(13B)-B(1)-F(11)	121.6(19)
F(13)-B(1)-F(11)	115.6(13)
F(13B)-B(1)-F(14B)	119(2)
F(13)-B(1)-F(14B)	134.6(19)
F(11)-B(1)-F(14B)	107.8(15)
F(13B)-B(1)-F(12)	118.8(19)
F(13)-B(1)-F(12)	109.5(16)
F(11)-B(1)-F(12)	119.5(13)
F(14B)-B(1)-F(12)	31.7(11)
F(13B)-B(1)-F(14)	55.9(16)
F(13)-B(1)-F(14)	100.2(13)
F(11)-B(1)-F(14)	105.0(13)
F(14B)-B(1)-F(14)	80.0(15)
F(12)-B(1)-F(14)	104.3(13)
F(13B)-B(1)-F(12A)	105(2)
F(13)-B(1)-F(12A)	62.6(15)
F(11)-B(1)-F(12A)	99.1(16)
F(14B)-B(1)-F(12A)	99(2)
F(12)-B(1)-F(12A)	68.4(15)
F(14)-B(1)-F(12A)	155.0(17)
F(24A)-B(2)-F(24)	113(4)
F(24A)-B(2)-F(22)	104(4)
F(24)-B(2)-F(22)	140.7(19)
F(24A)-B(2)-F(22A)	108(4)
F(24)-B(2)-F(22A)	82.6(16)

F(22)-B(2)-F(22A)	73.5(15)	C(20)-N(4)-Ru(1)	128.3(8)
F(24A)-B(2)-F(23A)	165(4)	C(16)-N(4)-Ru(1)	115.8(7)
F(24)-B(2)-F(23A)	72.5(17)	C(25)-N(5)-C(26)	115.3(9)
F(22)-B(2)-F(23A)	75.0(17)	C(25)-N(5)-Ru(1)	114.4(7)
F(22A)-B(2)-F(23A)	85.6(19)	C(26)-N(5)-Ru(1)	130.3(7)
F(24A)-B(2)-F(21)	78(4)	C(25)-N(6)-C(28)	114.6(9)
F(24)-B(2)-F(21)	110.3(13)	C(25)-N(6)-Pd(1)	114.9(7)
F(22)-B(2)-F(21)	89.5(14)	C(28)-N(6)-Pd(1)	130.5(7)
F(22A)-B(2)-F(21)	162.9(16)	C(24)-N(7)-C(21)	115.7(9)
F(23A)-B(2)-F(21)	87.6(17)	C(24)-N(7)-Ru(1)	115.1(7)
F(24A)-B(2)-F(23)	22(4)	C(21)-N(7)-Ru(1)	129.2(7)
F(24)-B(2)-F(23)	107.8(13)	C(24)-N(8)-C(23)	115.6(9)
F(22)-B(2)-F(23)	101.3(14)	C(24)-N(8)-Pd(1)	110.5(7)
F(22A)-B(2)-F(23)	86.2(14)	C(23)-N(8)-Pd(1)	133.7(8)
F(23A)-B(2)-F(23)	171.7(18)	C(30)-N(9)-Pd(1)	175.8(10)
F(21)-B(2)-F(23)	99.8(11)	N(1)-C(1)-C(2)	123.9(12)
F(24A)-B(2)-F(21A)	84(4)	C(3)-C(2)-C(1)	118.8(13)
F(24)-B(2)-F(21A)	33.9(10)	C(2)-C(3)-C(4)	118.8(13)
F(22)-B(2)-F(21A)	171.3(16)	C(5)-C(4)-C(3)	121.4(13)
F(22A)-B(2)-F(21A)	108.1(16)	C(4)-C(5)-N(1)	120.5(11)
F(23A)-B(2)-F(21A)	96.5(18)	C(4)-C(5)-C(6)	125.9(11)
F(21)-B(2)-F(21A)	88.3(11)	N(1)-C(5)-C(6)	113.5(10)
F(23)-B(2)-F(21A)	87.3(10)	N(2)-C(6)-C(7)	119.6(11)
C(1)-N(1)-C(5)	116.5(10)	N(2)-C(6)-C(5)	116.1(9)
C(1)-N(1)-Ru(1)	128.0(8)	C(7)-C(6)-C(5)	124.2(11)
C(5)-N(1)-Ru(1)	115.4(8)	C(8)-C(7)-C(6)	120.3(12)
C(6)-N(2)-C(10)	119.0(10)	C(7)-C(8)-C(9)	121.1(12)
C(6)-N(2)-Ru(1)	116.5(8)	C(8)-C(9)-C(10)	117.5(12)
C(10)-N(2)-Ru(1)	124.4(8)	N(2)-C(10)-C(9)	122.3(12)
C(11)-N(3)-C(15)	119.4(10)	N(3)-C(11)-C(12)	122.3(11)
C(11)-N(3)-Ru(1)	126.7(8)	C(13)-C(12)-C(11)	118.7(12)
C(15)-N(3)-Ru(1)	113.3(7)	C(12)-C(13)-C(14)	119.9(12)
C(20)-N(4)-C(16)	115.8(10)	C(13)-C(14)-C(15)	120.7(12)

N(3)-C(15)-C(14)	118.7(10)
N(3)-C(15)-C(16)	117.0(10)
C(14)-C(15)-C(16)	124.3(11)
C(17)-C(16)-N(4)	121.5(11)
C(17)-C(16)-C(15)	125.3(11)
N(4)-C(16)-C(15)	113.2(10)
C(16)-C(17)-C(18)	120.7(11)
C(19)-C(18)-C(17)	117.3(11)
C(18)-C(19)-C(20)	119.8(11)
N(4)-C(20)-C(19)	124.8(11)
C(22)-C(21)-N(7)	120.6(9)
C(21)-C(22)-C(23)	119.2(11)
N(8)-C(23)-C(22)	121.8(11)
N(8)-C(24)-N(7)	127.0(10)
N(8)-C(24)-C(25)	117.9(8)
N(7)-C(24)-C(25)	115.0(9)
N(5)-C(25)-N(6)	127.1(10)
N(5)-C(25)-C(24)	116.1(8)
N(6)-C(25)-C(24)	116.6(9)
C(27)-C(26)-N(5)	122.4(10)
C(26)-C(27)-C(28)	119.3(11)
C(27)-C(28)-N(6)	121.2(10)
N(9)-C(30)-C(31)	178.7(16)
N(10)-C(32)-C(33)	178(2)
N(13)-C(34)-C(35)	178(2)
N(12)-C(36)-C(37)	176.5(17)

Treatment of the disordered anions

Since charge of the complex **2** is 3+ there are three counter anions ((i), (ii), and (iii)) present per single cation in the crystal lattice. From their geometries, anions (i) and (ii) were determined as a PF_6 and a BF_4 (disordered), respectively. Focusing on the third anion (iii), following refinements as (1)-(3) were considered.

(1) PF_6: in total, 2 PF_6 and 1 BF_4

(2) disordered BF_4: in total, 1 PF_6 and 2 BF_4

(3) PF_6/BF_4 anion disordered on the same site

The treatment of the anion (iii) as PF_6 (refinement (1)) led to the markedly large anisotropic displacement parameters for both P and F atoms. This situation did not change whether the other PF_6 (i) and BF_4 anions (ii) were treated as disordered or not. So we treated the anion (iii) as a disordered BF_4 (refinement (2)), in which thermal parameters for the ill defined PF_6 became drastically small. We have also considered the anion as a PF_6/BF_4 disordered on the same site (refinement (3)), however, this refinement resulted in the repulsion of the P and B atoms as well as the distortion of the whole structure. Thus we adopted (2) to refine the anion (iii) as BF_4 although the anion composition is different from that in the solution.