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Remarkable Switching Behavior of Bimodally Stimuli-responsive Photochromic Dithienylethenes with Redox-active Organometallic Attachments

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Experimental part.

General Methods. All manipulations were carried out under an inert atmosphere by using standard Schlenk tube techniques. THF, ether, pentane, hexane, toluene (Na-K alloy) and MeCN, CH_2Cl_2 (P_2O_5) were treated with appropriate drying agents, distilled, and stored under N_2 atmosphere. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC-200 spectrometer (^1H, 200 MHz; ^{31}P, 81 MHz) and a JEOL EX-400 (^{13}C: 100 MHz). Chemical shifts (downfield from TMS (^1H and ^{13}C) and H_3PO_4 (^{31}P)) and coupling constants are reported in ppm and in Hz, respectively. Solvents for NMR measurements containing 0.5% TMS were dried over molecular sieves, degassed, distilled under reduced pressure, and stored under N_2. IR and UV-vis spectra were obtained on a JASCO FT/IR 4200 spectrometer and a JASCO V-670 spectrometer, respectively. UV and visible light irradiations were performed with an Ushio high pressure mercury lamp (UM-452; $\lambda < 360$ nm with a U-360 cutoff filter) and a Soma Kogaku Xe lamp (150W; $\lambda > 420$ nm with an L42 cut-off filter), respectively. Electrochemical measurements were made with a BAS 100B/W analyzer (observed in CH_2Cl_2; [complex]= ~1 x 10^{-3} M; [NBu_4PF_6]= 0.1 M; Pt electrode; reported with respect to the $[FeCp_2]/[FeCp_2]^+$ couple (+0.65 V vs. Ag/Ag^+ (in CH_2Cl_2)).[1] Simulation of the electrochemical data was performed with Origin 6.1. Elemental analyses were performed at the Center for Advanced Materials Analysis, Technical Department, Tokyo Institute of Technology. 1,2-di(5-bromo-2-methylthien-3-yl)perfluorocyclopentene,[2] I-FeCp(CO)$_2$ [23] and Cl-RuCp(CO)$_2$ [4] were prepared according to the published procedures. Other chemicals were purchased and used as received.

Preparation of $\mathbf{1^{Fe}}$: To a THF solution (2 mL) of 1,2-di(5-bromo-2-methylthien-3-yl)perfluorocyclopentene (309 mg, 0.587 mmol) cooled at –78°C was added *n*-BuLi (1.58 M, 0.9 mL, 1.42 mmol), and the resulting mixture was stirred for 5 min at the same temperature. Then I-FeCp(CO)$_2$ (612 mg, 2.01 mmol) dissolved in THF (5 mL) cooled at -78°C was added and the mixture was stirred for 1 h and gradually warmed to room temperature. A small amount of MeOH was added to destroy the excess lithium reagent and then the volatiles were removed under reduced pressure. The residue was extracted with ether, passed through an alumina plug, and subjected to alumina column chromatography. Elution with hexane-CH_2Cl_2 (80 : 20) gave the mononuclear complex and subsequent elution with hexane-CH_2Cl_2 (65 : 35) afforded $\mathbf{1^{Fe}}$ as yellow crystals (215 mg, 0.299 mmol, 51 % yield). $\mathbf{1^{Fe}}$: analysis: found (calcd. for $C_{29}H_{18}O_4F_6S_2Fe_2$): C, 48.44 (48.36), H, 2.78 (2.52), S, 8.73 (8.90); δ_H (C_6D_6) 2.04 (6H, s, Me attached to the thienyl (Th) ring), 4.03 (10H, s, Cp), 7.02 (2H, s, H attached to Th); IR (KBr) 2028, 1971 cm^{-1} (ν(CO)); UV-vis: λ_{max} / nm (ε / $M^{-1}cm^{-1}$) (in toluene) = ~355 (sh) (4.0 x 10^3); CV / mV: -78 ($E_{1/2}^1$), 117 ($E_{1/2}^2$), 540, 558 (2 irreversible E_a) [4] ($E_{1/2}^1$ and $E_{1/2}^2$ are for the closed isomer $\mathbf{1^{Fe}C}$ resulting from the oxidation-induced cyclization); ΔE / mV (K_C) [5] = 18 (2.0) ($\mathbf{1^{Fe}}$), 216 (4.5 x 10^3) ($\mathbf{1^{Fe}C}$).

Preparation of $\mathbf{1^{Ru}}$: prepared in a manner analogous to the preparation of $\mathbf{1^{Fe}}$. $\mathbf{1^{Ru}}$ (55 % yield; colorless crystals): analysis: found (calcd. for

$C_{29}H_{18}O_4F_6S_2Ru_2$) C, 42.89 (42.96); H, (2.22); S: 7.86 (7.91); δ_H (C_6D_6) 2.05 (6H, s, Me attached to Th), 4.46 (10H, s, Cp), 7.00 (2H, s, H attached to Th); IR (KBr) 2035, 1974 cm^{-1} (ν(CO)); UV-vis: λ_{max} / nm (ε / $M^{-1}cm^{-1}$) (in toluene) = ~334 (sh) (5.0 x 10^3); CV / mV: -53 ($E_{1/2}{}^1$), 163 ($E_{1/2}{}^2$), 626, 673 (2 irreversible E_a) [5] ($E_{1/2}{}^1$ and $E_{1/2}{}^2$ are for the closed isomer **1RuC** resulting from the oxidation-induced cyclization); ΔE / mV (K_C) [4] = 47 (6.2) (**1Ru**), 228 (7.2 x 10^3) (**1RuC**).

Preparation of 2Fe: **1Fe** (295 mg, 0.410 mmol) and PPh_3 (430 mg, 1.64 mmol) were dissolved in a mixture of toluene (47.5 mL) and MeCN (2.5 mL) and irradiated by a UV lamp for 9 h. The progress of the reaction was followed by TLC. After consumption of **1Fe** was confirmed, the volatiles were removed under reduced pressure and the residue was subjected to silica gel column chromatography, which afforded **2Fe** as red brown crystals (268 mg, 0.225 mmol, 55 % yield; a mixture of two diastereomers). **2Fe**: δ_H (C_6D_6) 1.87 (6H, s, Me attached to Th), 4.24 (10H, s, Cp), 6.77 (2H, s, H attached to Th); 7 – 8 (15H, m, Ph); (CD_3CN) 2.14 (6H, s, Me attached to Th), 4.52, 4.53 (10H, s, Cp), 6.31, 6.33 (2H, s, H attached to Th); 7.2 – 7.8 (15H, m, Ph); δ_P (CD_3CN) 71.61, 71.69; (C_6D_6) 6754, 67,62; IR (KBr) 1931 cm^{-1} (ν(CO)); UV-vis: λ_{max} / nm (ε / $M^{-1}cm^{-1}$) (in toluene) = ~395 (sh) 2.8 x 10^3), 498 (6.2 x 10^2); CV / mV: -464 ($E_{1/2}{}^1$), -231($E_{1/2}{}^2$), -12, 13 (2 irreversible E_a) [5] ($E_{1/2}{}^1$ and $E_{1/2}{}^2$ are for the closed isomer **2FeC** resulting from the oxidation-induced cyclization); ΔE / mV (K_C) [4] = 25 (2.7) (**2Fe**), 248 (1.6 x 10^4) (**2FeC**).

Preparation of 2Ru: prepared in a manner analogous to the preparation of **2Fe** (irradiated for 40 h). **2Ru** (21 % yield; colorless crystals; a mixture of two diastereomers): δ_H (C_6D_6) 1.84, 1.86 (6H, s, Me attached to Th), 4.65 (10H, s, Cp), 6.66, 6.68 (2H, s, H attached to Th); 7.0 – 7.4 (15H, m, Ph); δ_P (C_6D_6) 55.9, 56.2; IR (KBr) 1942 cm^{-1} (ν(CO)); UV-vis: λ_{max} / nm (ε / $M^{-1}cm^{-1}$) (in toluene) = ~370 (sh) (3.0 x 10^3); CV / mV: -428 ($E_{1/2}{}^1$), -169 ($E_{1/2}{}^2$), 166, 199 (irreversible E_a) [5] ($E_{1/2}{}^1$ and $E_{1/2}{}^2$ are for the closed isomer **2RuC** resulting from the oxidation-induced cyclization); ΔE / mV (K_C) [4] = 33 (3.6) (**2Ru**), 256 (2.2 x 10^4) (**2RuC**).

Preparation of 3'Fe: 1'Fe (171 mg, 0.229 mmol; prepared from I-FeCp'$(CO)_2$ in a manner analogous to the preparation of **1Fe**) and PPh_3 (318 mg, 0.800 mmol) were dissolved in a mixture of toluene (47.5 mL) and MeCN (2.5 mL) and irradiated by a UV lamp for 16 h. The progress of the reaction was followed by TLC. After consumption of **1Fe** was confirmed, the volatiles were removed under reduced pressure and the residue was crystallized from CH_2Cl_2-hexane to give **3'Fe** as red brown crystals (202 mg, 0.141 mmol, 61 % yield). **3'Fe**: analysis: found (calcd. for $C_{79}H_{70}F_6S_2P_4Fe_2$) C, 66.14 (66.21); H, 4.99 (4.92); S, 4.30 (4.47); δ_H (C_6D_6) δ_H 1.78, 1.89 (6H x 2, s x 2, Me attached to Th and Me in Cp'), 2.04, 2.67 (2H x 2, br x 2, dppe), 3.74, 4.43 (4H x 2, s x 2, η^5-C_5H_4), 5.84 (2H, s, H attached to Th); 7.0 – 7.5 (40H, m, Ph); δ_P (C_6D_6) 103; UV-vis: λ_{max} / nm (ε / $M^{-1}cm^{-1}$) (observed in THF because of low solubility in toluene) = 318 (2.42 x 10^4); CV /mV: -600 ($E_{1/2}{}^1$), -480 ($E_{1/2}{}^2$), 631 ($E_c{}^3$: irreversible), 745 ($E_a{}^3$: irreversible), 799 ($E_c{}^4$: irreversible), 853 ($E_a{}^4$: irreversible), ΔE / mV (K_C) [5] = 114 (85).

Photochromic properties. Photochromic properties of the DTE complexes were studied by ^{1}H NMR and UV-vis spectrum.

NMR: Under N_2 atmosphere the DTE complexes were dissolved in an appropriate deuterated solvent, sealed and irradiated by an Ushio high pressure mercury lamp (UM-452; $\lambda < 360$ nm with a U-360 cutoff filter). The progress of the cyclization was monitored by appearance of the signals for the closed isomers. After reaching an equilibrium, the resultant NMR sample was irradiated by a Soma Kogaku Xe lamp (150W; $\lambda > 420$ nm with an L42 cut-off filter) and the ring closing process was monitored on the basis of the disappearance of the signals for the closed isomers. Selected ^{1}H NMR data for the closed isomers: $\mathbf{1^{Fe}C}$: δ_H (C_6D_6) 2.23 (6H, s, Me attached to Th), 3.95 (10H, s, Cp), 6.62 (2H, s, H attached to Th); $\mathbf{1^{Ru}C}$: δ_H (C_6D_6) 2.29 (6H, s, Me attached to Th), 4.39 (10H, s, Cp), 6.56 (2H, s, H attached to Th); $\mathbf{2^{Ru}C}$: δ_H (C_6D_6) 1.65, 1.85, 2.27 (6H, s, Me attached to Th), 4.61, 4.62 (10H, s, Cp), 6.20, 6.22, 6.38, 6.41 (2H, s, H attached to Th); The photochemical ring closure for the other complexes $\mathbf{2^{Fe}}$ and $\mathbf{3'^{Fe}}$ couldn't be detected by ^{1}H NMR, although $\mathbf{2^{Fe}}$ underwent the cyclization to a small extent as detected by the coloration and UV-vis spectroscopy.

UV-vis: Under N_2 atmosphere the DTE complexes were dissolved in an appropriate solvent, sealed and irradiated by the high pressure mercury lamp. The progress of the cyclization was monitored by appearance of the visible absorption band(s) for the closed isomers. After reaching an equilibrium, the resultant UV-vis sample was irradiated by the Xe lamp and the ring closing process was monitored on the basis of the disappearance of the visible absorption band for the closed isomers. λ_{max} / nm (in toluene) for the closed isomers were as follows: $\mathbf{1^{Fe}}$: 580; $\mathbf{1^{Ru}}$: 580, 350; $\mathbf{2^{Fe}}$: ~350 (sh), 590; $\mathbf{2^{Ru}}$: 336, ~360 (sh), 578. For the electrochemical data for $\mathbf{1^{Fe}}$, $\mathbf{1^{Ru}}$, $\mathbf{2^{Fe}}$, and $\mathbf{2^{Ru}}$, see the parts for the corresponding open isomers (see above).

Oxidative cyclization of DTE complexes: The oxidative cyclization was in situ confirmed by CV (see Fig. 1). For complexes $\mathbf{2^{Fe}}$ and $\mathbf{3'^{Fe}}$, which could be oxidized by $[FeCp_2]PF_6$, the corresponding closed dicationic species were isolated as described below. The other DTE complexes $\mathbf{1^{Fe}}$, $\mathbf{1^{Ru}}$ and $\mathbf{2^{Ru}}$ couldn't be oxidized by $[FeCp_2]PF_6$ and attempted oxidation with $[N(p\text{-}Br\text{-}C_6H_4)_3]SbF_6$ afforded an intractable mixture of products.

$[\mathbf{2^{Fe}C'^{2+}}](\mathbf{PF_6})_2$: Under N_2 atmosphere the neutral complex $\mathbf{2^{Fe}}$ (155 mg, 0.131 mmol) was treated with $[FeCp_2]PF_6$ (89.0 mg, 0.269 mmol) in CH_2Cl_2. After the mixture was stirred for 10 min, the volatiles were removed under reduced pressure and the resultant residue was washed with ether 5 times. Recrystallization of the obtained residue from acetone-pentane gave $[\mathbf{2^{Fe}C'}^{2+}](PF_6)_2$ as dark green crystals (130 mg, 0.0879 mmol, 67 % yield). $[\mathbf{2^{Fe}C'}^{2+}](PF_6)_2$: δ_H (acetone-d_6) ~1.2 (6H, br, Me attached to Th), 5.54 (10H, brs, Cp), 7.3 – 8.0 (Ph + H attached to Th); δ_P (acetone-d_6) 59.9; λ_{max} / nm (ε / $M^{-1}cm^{-1}$) (in CH_3CN)= 424 (1.5 x 10^4), 576 (9.7 x 10^3); CV / mV: -464 ($E_{1/2}{}^1$), -231 ($E_{1/2}{}^2$); ΔE / mV (K_C) [4] = 248 (1.6 x 10^4).

[3'^{Fe}C'$^{2+}$](PF$_6$)$_2$: prepared in a manner analogous to the preparation of [**2**^{Fe}**C**'$^{2+}$](PF$_6$)$_2$. [**3'**^{Fe}**C'**$^{2+}$](PF$_6$)$_2$ (dark green crystals; 73 % yield): δ_H (acetone-d_6) 0.17 (6H, s, Me attached to Th), 1.90 (6H, brs, C_5H_4*Me*), 3.68 (8H, br, PCH_2), 4.51 (4H, brs, C_5*H*$_4$Me), 5.18 (4H, brd, J= 10 Hz, C_5*H*$_4$Me), 6.97 (2H, brs, H attached to Th), 7.55 – 7.28 (20H, m, Ph); δ_P (acetone-d_6) 108.6; δ_C (acetone-d_6) 281.7 (t, J= 25.6 Hz, Fe=C); λ_{max} / nm (ε / M^{-1}cm^{-1}) (in CH_3CN)= 424 (1.3 x 10^4), 673 (1.1 x 10^4); CV / mV: -948 ($E_{1/2}^1$), -662 ($E_{1/2}^2$), 669 ($E_{1/2}^3$), 834 ($E_{1/2}^4$); ΔE / mV (K_C) [4] = 288 (7.5 x 10^4).

X-ray crystallography. Single crystals of **1**^{Ru} (CH_2Cl_2-hexane), **1**^{Ru}**C** (CH_2Cl_2-pentane), **2**^{Fe} (MeCN) and **2**^{Fe}**C**$^{2+}$(PF$_6$)$_2$ (acetone-pentane) were obtained by recrystallization from the solvent systems shown in the parentheses. Diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with Mo Kα radiation (λ= 0.71069 Å) at –60°C. Indexing was performed from 3 oscillation images, which were exposed for 3 min. The crystal-to-detector distance was 110 mm ($2\theta_{max}$= 55°). In the reduction of data, Lorentz and polarization corrections and empirical absorption corrections were made.[6] The crystallographic data are summarized in Table S1.

The structural analysis was performed on an IRIS O2 computer using teXsan structure solving program system obtained from the Rigaku Corp., Tokyo, Japan.[7] Neutral scattering factors were obtained from the standard source.[8]

The structures were solved by a combination of the direct methods (SHELXS-86)[9] and Fourier synthesis (DIRDIF94).[10] Least-squares refinements were carried out using SHELXL-97 [9] (refined on F^2) linked to teXsan. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically, methyl hydrogen atoms were refined using riding models, and other hydrogen atoms were fixed at the calculated positions. The crystallographic results were deposited at the Cambridge Crystallographic Data Centre: CCDC 689366 (**1**^{Ru}), CCDC 689367 (**1**^{Ru}**C**), CCDC 689368 (**2**^{Fe}) and CCDC 689369 ([**2**^{Fe}**C'**$^{2+}$](PF$_6$)$_2$).

1^{Ru}: The molecule sat on a C_2-axis. The disordered perfluorocyclopentene ring part was refined by taking into account of two components (C(2)F(1-2) : C(2A)F(1A-2A)= 0.5 : 0.5); the disordered C and F atoms were refined isotropically and anisotropically, respectively. All hydrogen atoms located at the calculated positions were not refined. The disordered CH_2Cl_2 solvate molecule was refined isotopically with fixing the C-Cl distance.

1^{Ru}**C**: The data completeness was low presumably because of the needle shape of the crystal. Disorder was suggested for the slightly large B_{eq} values for a couple of the Cp ring carbon atoms, as pointed out by the reviewer, but was not analyzed in detail, because this phenomenon is frequently associated with the CpM complexes and the values were in the acceptable range compared with related compounds.

2^{Fe}: The molecule sat on a C_2-axis. Hydrogen atoms were fixed at the calculated positions. The disordered perfluorocyclopentene ring part was refined taking into account two components (C(2)F(1-2) : C(2A)F(1A-2A)= 0.5 : 0.5). A highly disordered MeCN solvate molecule was found but not included in the refinement.

2^{Fe}C$^{2+}(PF_6)_2$: The disordered perfluorocyclopentene ring part was refined with isotropic thermal parameters by taking into account two components (C(2-4)F(1-6) : C(2A-4A)F(1A-6A)= 0.51 : 0.49). The acetone solvate molecule disordered with respect to the pseudo-C_3 axis passing through the central carbon atom was refined isotropically with fixing the C-C and C=O distances, and hydrogen atoms attached to it were not included in the refinement. A large void pointed out by the referee may be filled with acetone solvate molecules, which could not be refined successfully.

References

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(5) ΔE values for calculation of the K_C values were determined on the basis of the DPV data for the anodic peaks. The unresolved waves were analyzed by simulation with the Origin 6.1 software. When K_C values less than 4 (the theoretically minimum value for a statistical distribution) were obtained, K_C values were described as "~4" in Scheme 2.

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Table S1. Crystallographic data for DTE complexes.

complex	$\mathbf{1^{Ru}}$	$\mathbf{1^{Ru}C}$	$\mathbf{2^{Fe}}$	$[\mathbf{2^{Fe}C'}^{2+}](PF_6)_2$
solvate	CH_2Cl_2	-		acetone
formula	$C_{30}H_{20}Cl_2F_6O_4S_2Ru_2$	$C_{29}H_{18}F_6O_4S_2Ru_2$	$C_{63}H_{48}F_6Fe_2O_2P_2S_2$	$C_{66}H_{48}F_{18}Fe_2O_3P_4S_2$
formula weight	895.6	810.7	1188.8	1530.78
crystal system	orthorhombic	triclinic	monoclinic	triclinic
space group	*Pbcn*	*P-1*	*P2/c*	*P-1*
a / Å	20.883(2)	11.026(6)	8.607(6)	13.983(3)
b / Å	13.9416(7)	11.113(5)	16.521(9)	15.898(3)
c / Å	11.3024(9)	13.278(7)	20.230(10)	17.997(3)
α / deg	90	97.04(2)	90	92.44(1)
β / deg	90	98.67(2)	100.12(2)	110.64(1)
γ / deg	90	114.02(2)	90	100.416(7)
V/ Å^3	3290.7(4)	1438(1)	2832(2)	3657(1)
Z	4	2	2	2
d_{calcd} / g·cm^{-3}	1.804	1.872	1.394	1.390
μ / mm^{-1}	1.276	1.269	0.705	0.628
no of diffractions collected	25860	7214	22615	29754
no of variable	229	390	388	916
R1 for data	0.0623	0.0534	0.0724	0.0902
with I > 2σ(I)	(for 2910 data)	(for 4732 data)	(for 3973 data)	(for 7097 data)
wR2	0.2260	0.1678	0.2142	0.2652
	(for all 3770 data)	(for all 5194 data)	(for all 6387 data)	(for all 15210 data)

Table S2. Interatomic distances (Å) and bond angles (deg) for $\mathbf{1}^{\mathbf{Ru}}$.

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
Ru(1)	C(14)	2.103(5)	O(31)	C(31)	1.117(7)
Ru(1)	C(21)	2.277(6)	O(32)	C(32)	1.124(7)
Ru(1)	C(22)	2.254(6)	C(1)	C(1)[1)]	1.349(9)
Ru(1)	C(23)	2.246(7)	C(1)	C(2)	1.49(1)
Ru(1)	C(24)	2.234(6)	C(1)	C(2A)	1.50(1)
Ru(1)	C(25)	2.268(7)	C(1)	C(12)	1.450(7)
Ru(1)	C(31)	1.875(6)	C(2)	C(3)	1.58(1)
Ru(1)	C(32)	1.886(6)	C(2A)	C(3)	1.45(2)
Cl(1)	C(41)	1.69(4)	C(11)	C(12)	1.385(7)
Cl(1)	C(41)[1)]	1.71(3)	C(11)	C(15)	1.500(8)
S(1)	C(11)	1.718(5)	C(12)	C(13)	1.454(7)
S(1)	C(14)	1.734(5)	C(13)	C(14)	1.348(7)
F(1)	C(2)	1.33(2)	C(21)	C(22)	1.406(9)
F(1A)	C(2A)	1.34(2)	C(21)	C(25)	1.410(9)
F(2)	C(2)	1.39(1)	C(22)	C(23)	1.41(1)
F(2A)	C(2A)	1.30(2)	C(23)	C(24)	1.41(1)
F(3)	C(3)	1.31(1)	C(24)	C(25)	1.41(1)
F(4)	C(3)	1.43(1)	C(11)	C(11)[1)]	3.59(1)

1) -X+1, Y, -Z+3/2;

Table S2. Interatomic distances (Å) and bond angles (deg) for $\mathbf{1}^{\mathbf{Ru}}$. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C(14)	Ru(1)	C(21)	114.4(2)	F(1)	C(2)	C(3)	108.2(9)
C(14)	Ru(1)	C(22)	150.4(2)	F(2)	C(2)	C(1)	112.2(9)
C(14)	Ru(1)	C(23)	142.3(2)	F(2)	C(2)	C(3)	114.2(9)
C(14)	Ru(1)	C(24)	106.2(2)	C(1)	C(2)	C(3)	102.1(8)
C(14)	Ru(1)	C(25)	92.9(2)	F(1A)	C(2A)	F(2A)	107(1)
C(14)	Ru(1)	C(31)	87.3(2)	F(1A)	C(2A)	C(1)	112(1)
C(14)	Ru(1)	C(32)	88.7(2)	F(1A)	C(2A)	C(3)	109(1)
C(21)	Ru(1)	C(22)	36.2(2)	F(2A)	C(2A)	C(1)	113(1)
C(21)	Ru(1)	C(23)	60.5(2)	F(2A)	C(2A)	C(3)	106(1)
C(21)	Ru(1)	C(24)	60.8(2)	C(1)	C(2A)	C(3)	108(1)
C(21)	Ru(1)	C(25)	36.2(2)	F(3)	C(3)	F(4)	100.9(7)
C(21)	Ru(1)	C(31)	156.4(2)	F(3)	C(3)	C(2)	112.7(6)
C(21)	Ru(1)	C(32)	98.8(2)	F(3)	C(3)	C(2)	130.7(6)
C(22)	Ru(1)	C(23)	36.4(2)	F(3)	C(3)	C(2A)	121.5(7)
C(22)	Ru(1)	C(24)	61.0(2)	F(3)	C(3)	C(2A)	122.3(7)
C(22)	Ru(1)	C(25)	60.4(2)	F(3)	C(3)	F(4)	45.7(6)
C(22)	Ru(1)	C(31)	121.1(2)	F(3)	C(3)	F(4)	100.9(7)
C(22)	Ru(1)	C(32)	98.3(2)	F(3)	C(3)	C(2)	130.7(6)
C(23)	Ru(1)	C(24)	36.7(3)	F(3)	C(3)	C(2)	112.7(6)
C(23)	Ru(1)	C(25)	60.7(3)	F(3)	C(3)	C(2A)	122.3(7)
C(23)	Ru(1)	C(31)	96.8(2)	F(3)	C(3)	C(2A)	121.5(7)
C(23)	Ru(1)	C(32)	128.5(3)	F(4)	C(3)	F(4)	146(1)
C(24)	Ru(1)	C(25)	36.5(3)	F(4)	C(3)	C(2)	102.9(6)
C(24)	Ru(1)	C(31)	105.8(3)	F(4)	C(3)	C(2)	97.0(6)
C(24)	Ru(1)	C(32)	158.2(3)	F(4)	C(3)	C(2A)	112.3(7)
C(25)	Ru(1)	C(31)	140.4(2)	F(4)	C(3)	C(2)	97.0(6)
C(25)	Ru(1)	C(32)	129.3(3)	F(4)	C(3)	C(2)	102.9(6)
C(31)	Ru(1)	C(32)	90.3(2)	F(4)	C(3)	C(2A)	112.3(7)
C(41)	Cl(1)	C(41)	62(2)	C(2)	C(3)	C(2)	107.3(9)
C(11)	S(1)	C(14)	94.6(2)	C(2)	C(3)	C(2A)	104.4(8)
C(1)	C(1)	C(2)	112.4(5)	S(1)	C(11)	C(12)	110.0(4)
C(1)	C(1)	C(12)	130.0(3)	S(1)	C(11)	C(15)	120.8(4)
C(2)	C(1)	C(12)	117.5(6)	C(12)	C(11)	C(15)	129.2(5)
C(2A)	C(1)	C(12)	120.7(7)	C(1)	C(12)	C(11)	124.4(4)
F(1)	C(2)	F(2)	104(1)	C(1)	C(12)	C(13)	124.3(4)
F(1)	C(2)	C(1)	116(1)	C(11)	C(12)	C(13)	111.2(4)

Table S2. Interatomic distances (Å) and bond angles (deg) for $\mathbf{1^{Ru}}$. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C(12)	C(13)	C(14)	115.4(4)				
Ru(1)	C(14)	S(1)	119.0(3)				
Ru(1)	C(14)	C(13)	132.3(4)				
S(1)	C(14)	C(13)	108.7(4)				
Ru(1)	C(21)	C(22)	71.0(4)				
Ru(1)	C(21)	C(25)	71.6(4)				
C(22)	C(21)	C(25)	107.9(6)				
Ru(1)	C(22)	C(21)	72.8(3)				
Ru(1)	C(22)	C(23)	71.5(4)				
C(21)	C(22)	C(23)	108.3(6)				
Ru(1)	C(23)	C(22)	72.1(4)				
Ru(1)	C(23)	C(24)	71.2(4)				
C(22)	C(23)	C(24)	108.0(6)				
Ru(1)	C(24)	C(23)	72.1(4)				
Ru(1)	C(24)	C(25)	73.0(4)				
C(23)	C(24)	C(25)	107.8(6)				
Ru(1)	C(25)	C(21)	72.3(4)				
Ru(1)	C(25)	C(24)	70.4(4)				
C(21)	C(25)	C(24)	108.0(7)				
Ru(1)	C(31)	O(31)	176.7(5)				
Ru(1)	C(32)	O(32)	177.5(5)				
Cl(1)	C(41)	Cl(1)	103(2)				

Table S3. Interatomic distances (Å) and bond angles (deg) for $\mathbf{1^{Ru}C}$.

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
Ru(1)	C(114)	2.089(4)	C(4)	C(5)	1.554(8)
Ru(1)	C(121)	2.254(8)	C(111)	C(112)	1.536(6)
Ru(1)	C(122)	2.244(7)	C(111)	C(115)	1.546(7)
Ru(1)	C(123)	2.262(6)	C(111)	C(211)	1.543(7)
Ru(1)	C(124)	2.267(8)	C(112)	C(113)	1.435(5)
Ru(1)	C(125)	2.234(6)	C(113)	C(114)	1.350(6)
Ru(1)	C(131)	1.897(6)	C(121)	C(122)	1.358(9)
Ru(1)	C(132)	1.863(5)	C(121)	C(125)	1.44(2)
Ru(2)	C(214)	2.093(4)	C(122)	C(123)	1.39(1)
Ru(2)	C(221)	2.265(6)	C(123)	C(124)	1.41(1)
Ru(2)	C(222)	2.25(1)	C(124)	C(125)	1.38(1)
Ru(2)	C(223)	2.237(5)	C(211)	C(212)	1.520(6)
Ru(2)	C(224)	2.244(6)	C(211)	C(215)	1.561(7)
Ru(2)	C(225)	2.265(8)	C(212)	C(213)	1.445(5)
Ru(2)	C(231)	1.868(7)	C(213)	C(214)	1.357(7)
Ru(2)	C(232)	1.890(6)	C(221)	C(222)	1.45(1)
S(1)	C(111)	1.856(4)	C(221)	C(225)	1.34(1)
S(1)	C(114)	1.763(4)	C(222)	C(223)	1.43(1)
S(2)	C(211)	1.856(4)	C(223)	C(224)	1.38(1)
S(2)	C(214)	1.764(5)	C(224)	C(225)	1.423(7)
F(1)	C(3)	1.325(7)			
F(2)	C(3)	1.381(7)			
F(3)	C(4)	1.378(9)			
F(4)	C(4)	1.298(8)			
F(5)	C(5)	1.355(5)			
F(6)	C(5)	1.362(8)			
O(131)	C(131)	1.122(8)			
O(132)	C(132)	1.157(6)			
O(231)	C(231)	1.14(1)			
O(232)	C(232)	1.133(9)			
C(1)	C(2)	1.454(6)			
C(1)	C(5)	1.482(7)			
C(1)	C(112)	1.366(6)			
C(2)	C(3)	1.492(7)			
C(2)	C(212)	1.366(6)			
C(3)	C(4)	1.536(7)			

Table S3. Interatomic distances (Å) and bond angles (deg) for $\mathbf{1^{Ru}C}$. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C(114)	Ru(1)	C(121)	126.4(3)	C(221)	Ru(2)	C(223)	60.8(2)
C(114)	Ru(1)	C(122)	97.6(2)	C(221)	Ru(2)	C(224)	59.9(2)
C(114)	Ru(1)	C(123)	98.1(2)	C(221)	Ru(2)	C(225)	34.4(3)
C(114)	Ru(1)	C(124)	129.2(2)	C(221)	Ru(2)	C(231)	131.1(3)
C(114)	Ru(1)	C(125)	156.8(2)	C(221)	Ru(2)	C(232)	135.3(3)
C(114)	Ru(1)	C(131)	87.1(2)	C(222)	Ru(2)	C(223)	37.2(3)
C(114)	Ru(1)	C(132)	86.9(2)	C(222)	Ru(2)	C(224)	61.2(3)
C(121)	Ru(1)	C(122)	35.2(3)	C(222)	Ru(2)	C(225)	60.5(3)
C(121)	Ru(1)	C(123)	60.0(2)	C(222)	Ru(2)	C(231)	155.4(3)
C(121)	Ru(1)	C(124)	60.6(3)	C(222)	Ru(2)	C(232)	100.6(3)
C(121)	Ru(1)	C(125)	37.4(4)	C(223)	Ru(2)	C(224)	35.7(3)
C(121)	Ru(1)	C(131)	146.2(3)	C(223)	Ru(2)	C(225)	60.1(2)
C(121)	Ru(1)	C(132)	95.7(2)	C(223)	Ru(2)	C(231)	121.8(2)
C(122)	Ru(1)	C(123)	36.0(2)	C(223)	Ru(2)	C(232)	95.9(2)
C(122)	Ru(1)	C(124)	60.1(3)	C(224)	Ru(2)	C(225)	36.8(2)
C(122)	Ru(1)	C(125)	60.2(3)	C(224)	Ru(2)	C(231)	94.2(3)
C(122)	Ru(1)	C(131)	153.2(2)	C(224)	Ru(2)	C(232)	123.0(2)
C(122)	Ru(1)	C(132)	117.1(2)	C(225)	Ru(2)	C(231)	99.9(3)
C(123)	Ru(1)	C(124)	36.3(2)	C(225)	Ru(2)	C(232)	156.1(2)
C(123)	Ru(1)	C(125)	60.3(2)	C(231)	Ru(2)	C(232)	93.5(3)
C(123)	Ru(1)	C(131)	117.2(2)	C(111)	S(1)	C(114)	93.5(2)
C(123)	Ru(1)	C(132)	153.0(2)	C(211)	S(2)	C(214)	93.0(2)
C(124)	Ru(1)	C(125)	35.7(3)	C(2)	C(1)	C(5)	109.8(4)
C(124)	Ru(1)	C(131)	96.6(3)	C(2)	C(1)	C(112)	121.4(4)
C(124)	Ru(1)	C(132)	143.5(2)	C(5)	C(1)	C(112)	128.8(4)
C(125)	Ru(1)	C(131)	109.6(4)	C(1)	C(2)	C(3)	109.2(4)
C(125)	Ru(1)	C(132)	108.6(3)	C(1)	C(2)	C(212)	121.5(4)
C(131)	Ru(1)	C(132)	89.4(2)	C(3)	C(2)	C(212)	129.2(4)
C(214)	Ru(2)	C(221)	96.1(2)	F(1)	C(3)	F(2)	104.6(4)
C(214)	Ru(2)	C(222)	112.3(3)	F(1)	C(3)	C(2)	116.5(5)
C(214)	Ru(2)	C(223)	149.5(2)	F(1)	C(3)	C(4)	111.9(5)
C(214)	Ru(2)	C(224)	149.5(2)	F(2)	C(3)	C(2)	111.9(5)
C(214)	Ru(2)	C(225)	112.9(2)	F(2)	C(3)	C(4)	107.2(5)
C(214)	Ru(2)	C(231)	88.2(2)	C(2)	C(3)	C(4)	104.6(3)
C(214)	Ru(2)	C(232)	87.1(2)	F(3)	C(4)	F(4)	106.1(6)
C(221)	Ru(2)	C(222)	37.4(3)	F(3)	C(4)	C(3)	106.3(5)

Table S3. Interatomic distances (Å) and bond angles (deg) for $\mathbf{1^{Ru}C}$. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
F(3)	C(4)	C(5)	106.7(4)	Ru(1)	C(125)	C(124)	73.4(4)
F(4)	C(4)	C(3)	116.2(4)	C(121)	C(125)	C(124)	107.9(7)
F(4)	C(4)	C(5)	115.7(5)	Ru(1)	C(131)	O(131)	179.1(4)
C(3)	C(4)	C(5)	105.1(5)	Ru(1)	C(132)	O(132)	179.7(5)
F(5)	C(5)	F(6)	104.2(4)	S(2)	C(211)	C(111)	114.2(3)
F(5)	C(5)	C(1)	115.2(4)	S(2)	C(211)	C(212)	103.9(2)
F(5)	C(5)	C(4)	110.5(5)	S(2)	C(211)	C(215)	107.8(3)
F(6)	C(5)	C(1)	113.3(5)	C(111)	C(211)	C(212)	109.8(4)
F(6)	C(5)	C(4)	108.3(5)	C(111)	C(211)	C(215)	112.0(3)
C(1)	C(5)	C(4)	105.2(4)	C(212)	C(211)	C(215)	108.7(4)
S(1)	C(111)	C(112)	102.8(2)	C(2)	C(212)	C(211)	116.8(3)
S(1)	C(111)	C(115)	108.9(4)	C(2)	C(212)	C(213)	131.3(4)
S(1)	C(111)	C(211)	115.1(3)	C(211)	C(212)	C(213)	111.8(4)
C(112)	C(111)	C(115)	108.5(4)	C(212)	C(213)	C(214)	116.0(4)
C(112)	C(111)	C(211)	108.4(4)	Ru(2)	C(214)	S(2)	118.5(2)
C(115)	C(111)	C(211)	112.5(3)	Ru(2)	C(214)	C(213)	129.7(3)
C(1)	C(112)	C(111)	117.0(3)	S(2)	C(214)	C(213)	111.7(3)
C(1)	C(112)	C(113)	130.5(4)	Ru(2)	C(221)	C(222)	70.6(5)
C(111)	C(112)	C(113)	112.4(4)	Ru(2)	C(221)	C(225)	72.8(4)
C(112)	C(113)	C(114)	115.9(4)	C(222)	C(221)	C(225)	109.3(6)
Ru(1)	C(114)	S(1)	119.5(2)	Ru(2)	C(222)	C(221)	72.0(4)
Ru(1)	C(114)	C(113)	128.5(3)	Ru(2)	C(222)	C(223)	71.0(5)
S(1)	C(114)	C(113)	112.0(3)	C(221)	C(222)	C(223)	104.8(8)
Ru(1)	C(121)	C(122)	72.0(4)	Ru(2)	C(223)	C(222)	71.8(4)
Ru(1)	C(121)	C(125)	70.6(5)	Ru(2)	C(223)	C(224)	72.4(3)
C(122)	C(121)	C(125)	106.8(7)	C(222)	C(223)	C(224)	109.2(5)
Ru(1)	C(122)	C(121)	72.8(5)	Ru(2)	C(224)	C(223)	71.8(4)
Ru(1)	C(122)	C(123)	72.7(4)	Ru(2)	C(224)	C(225)	72.4(4)
C(121)	C(122)	C(123)	110.2(7)	C(223)	C(224)	C(225)	107.5(5)
Ru(1)	C(123)	C(122)	71.3(4)	Ru(2)	C(225)	C(221)	72.8(4)
Ru(1)	C(123)	C(124)	72.0(4)	Ru(2)	C(225)	C(224)	70.8(4)
C(122)	C(123)	C(124)	107.2(5)	C(221)	C(225)	C(224)	109.3(6)
Ru(1)	C(124)	C(123)	71.6(4)	Ru(2)	C(231)	O(231)	177.2(6)
Ru(1)	C(124)	C(125)	70.9(5)	Ru(2)	C(232)	O(232)	174.8(5)
C(123)	C(124)	C(125)	107.9(9)				
Ru(1)	C(125)	C(121)	72.0(4)				

Table S4. Interatomic distances (Å) and bond angles (deg) for **2**^{Fe}.

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
Fe(1)	P(1)	2.207(2)	C(22)	C(23)	1.42(1)
Fe(1)	C(14)	1.974(4)	C(23)	C(24)	1.35(1)
Fe(1)	C(21)	2.160(7)	C(24)	C(25)	1.50(1)
Fe(1)	C(22)	2.137(6)	C(41)	C(42)	1.407(8)
Fe(1)	C(23)	2.107(6)	C(41)	C(46)	1.393(8)
Fe(1)	C(24)	2.099(8)	C(42)	C(43)	1.38(1)
Fe(1)	C(25)	2.121(9)	C(43)	C(44)	1.34(1)
Fe(1)	C(31)	1.739(6)	C(44)	C(45)	1.36(1)
S(1)	C(11)	1.722(5)	C(45)	C(46)	1.415(9)
S(1)	C(14)	1.740(5)	C(51)	C(52)	1.368(8)
P(1)	C(41)	1.841(6)	C(51)	C(56)	1.404(9)
P(1)	C(51)	1.837(5)	C(52)	C(53)	1.403(8)
P(1)	C(61)	1.837(5)	C(53)	C(54)	1.36(1)
F(1)	F(1A)	0.41(3)	C(54)	C(55)	1.39(1)
F(1)	C(2)	1.49(5)	C(55)	C(56)	1.364(8)
F(1A)	C(2A)	1.24(5)	C(61)	C(62)	1.395(7)
F(2)	C(2)	1.31(6)	C(61)	C(66)	1.385(7)
F(2A)	C(2A)	1.41(6)	C(62)	C(63)	1.381(8)
F(3)	C(3)	1.29(5)	C(63)	C(64)	1.383(8)
F(4)	C(3)	1.34(4)	C(64)	C(65)	1.385(8)
O(31)	C(31)	1.142(8)	C(65)	C(66)	1.367(7)
C(1)	C(1)$^{1)}$	1.358(8)			
C(1)	C(2)	1.58(3)			
C(1)	C(2A)	1.40(3)			
C(1)	C(12)	1.479(6)			
C(2)	C(3)	1.46(5)			
C(2)	C(3)$^{1)}$	1.38(5)			
C(2A)	C(3)	1.67(5)			
C(11)	C(12)	1.358(7)			
C(11)	C(15)	1.506(8)			
C(12)	C(13)	1.445(6)			
C(13)	C(14)	1.379(6)			
C(21)	C(22)	1.44(1)			
C(21)	C(25)	1.45(1)			

1) –X, -Y, -Z-1/2

Table S4. Interatomic distances (Å) and bond angles (deg) for **2**^{Fe}. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
P(1)	Fe(1)	C(14)	92.8(2)	C(1)	C(1)	C(2A)	115(1)
P(1)	Fe(1)	C(21)	108.4(2)	C(1)	C(1)	C(12)	128.4(2)
P(1)	Fe(1)	C(22)	93.2(2)	C(2)	C(1)	C(12)	125(1)
P(1)	Fe(1)	C(23)	111.7(3)	C(2A)	C(1)	C(12)	116(1)
P(1)	Fe(1)	C(24)	148.9(3)	F(1)	C(2)	F(2)	104(3)
P(1)	Fe(1)	C(25)	147.7(3)	F(1)	C(2)	C(1)	107(2)
P(1)	Fe(1)	C(31)	94.4(3)	F(1)	C(2)	C(3)	106(3)
C(14)	Fe(1)	C(21)	94.6(2)	F(1)	C(2)	C(3)	124(3)
C(14)	Fe(1)	C(22)	132.2(2)	F(2)	C(2)	C(1)	109(3)
C(14)	Fe(1)	C(23)	152.8(3)	F(2)	C(2)	C(3)	125(4)
C(14)	Fe(1)	C(24)	118.1(3)	F(2)	C(2)	C(3)	104(4)
C(14)	Fe(1)	C(25)	87.5(2)	C(1)	C(2)	C(3)	105(2)
C(14)	Fe(1)	C(31)	93.8(2)	C(1)	C(2)	C(3)	109(2)
C(21)	Fe(1)	C(22)	39.1(3)	F(1A)	C(2A)	F(2A)	107(3)
C(21)	Fe(1)	C(23)	67.2(3)	F(1A)	C(2A)	C(1)	119(3)
C(21)	Fe(1)	C(24)	68.6(3)	F(1A)	C(2A)	C(3)	112(3)
C(21)	Fe(1)	C(25)	39.6(3)	F(2A)	C(2A)	C(1)	116(3)
C(21)	Fe(1)	C(31)	155.2(3)	F(2A)	C(2A)	C(3)	114(3)
C(22)	Fe(1)	C(23)	39.0(3)	C(1)	C(2A)	C(3)	104(2)
C(22)	Fe(1)	C(24)	64.6(3)	C(1)	C(2A)	C(3)	104(2)
C(22)	Fe(1)	C(25)	64.1(3)	F(3)	C(3)	F(4)	106(2)
C(22)	Fe(1)	C(31)	132.8(3)	F(3)	C(3)	C(2)	116(4)
C(23)	Fe(1)	C(24)	37.5(4)	F(3)	C(3)	C(2)	110(4)
C(23)	Fe(1)	C(25)	65.5(3)	F(4)	C(3)	C(2)	112(4)
C(23)	Fe(1)	C(31)	95.8(3)	F(4)	C(3)	C(2)	123(4)
C(24)	Fe(1)	C(25)	41.5(3)	F(4)	C(3)	C(2)	129(4)
C(24)	Fe(1)	C(31)	86.9(3)	F(4)	C(3)	C(3)	102(3)
C(25)	Fe(1)	C(31)	117.8(4)	C(2)	C(3)	C(2)	107(3)
C(11)	S(1)	C(14)	95.4(2)	C(2)	C(3)	C(3)	71(8)
Fe(1)	P(1)	C(41)	110.0(2)	S(1)	C(11)	C(12)	109.4(3)
Fe(1)	P(1)	C(51)	118.2(2)	S(1)	C(11)	C(15)	120.9(4)
Fe(1)	P(1)	C(61)	117.4(2)	C(12)	C(11)	C(15)	129.7(4)
C(41)	P(1)	C(51)	101.5(2)	C(1)	C(12)	C(11)	123.5(4)
C(41)	P(1)	C(61)	105.5(2)	C(1)	C(12)	C(13)	123.2(4)
C(51)	P(1)	C(61)	102.4(2)	C(11)	C(12)	C(13)	113.3(4)
C(1)	C(1)	C(2)	107(1)	C(12)	C(13)	C(14)	114.7(4)

Table S4. Interatomic distances (Å) and bond angles (deg) for **2**^{Fe}. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
Fe(1)	C(14)	S(1)	120.2(2)	P(1)	C(61)	C(66)	120.6(4)
Fe(1)	C(14)	C(13)	132.3(4)	C(62)	C(61)	C(66)	117.6(4)
S(1)	C(14)	C(13)	107.2(3)	C(61)	C(62)	C(63)	120.3(5)
Fe(1)	C(21)	C(22)	69.6(4)	C(62)	C(63)	C(64)	121.1(5)
Fe(1)	C(21)	C(25)	68.8(4)	C(63)	C(64)	C(65)	118.7(5)
C(22)	C(21)	C(25)	103.0(6)	C(64)	C(65)	C(66)	120.0(5)
Fe(1)	C(22)	C(21)	71.3(4)	C(61)	C(66)	C(65)	122.3(5)
Fe(1)	C(22)	C(23)	69.3(4)				
C(21)	C(22)	C(23)	111.6(7)				
Fe(1)	C(23)	C(22)	71.6(4)				
Fe(1)	C(23)	C(24)	70.9(4)				
C(22)	C(23)	C(24)	109.5(7)				
Fe(1)	C(24)	C(23)	71.6(5)				
Fe(1)	C(24)	C(25)	70.0(4)				
C(23)	C(24)	C(25)	106.7(7)				
Fe(1)	C(25)	C(21)	71.7(4)				
Fe(1)	C(25)	C(24)	68.5(5)				
C(21)	C(25)	C(24)	109.1(7)				
Fe(1)	C(31)	O(31)	177.2(7)				
P(1)	C(41)	C(42)	116.7(5)				
P(1)	C(41)	C(46)	124.0(4)				
C(42)	C(41)	C(46)	119.0(5)				
C(41)	C(42)	C(43)	119.8(6)				
C(42)	C(43)	C(44)	121.4(7)				
C(43)	C(44)	C(45)	120.0(7)				
C(44)	C(45)	C(46)	121.4(7)				
C(41)	C(46)	C(45)	118.3(6)				
P(1)	C(51)	C(52)	120.6(4)				
P(1)	C(51)	C(56)	121.0(4)				
C(52)	C(51)	C(56)	118.3(5)				
C(51)	C(52)	C(53)	119.5(6)				
C(52)	C(53)	C(54)	121.6(6)				
C(53)	C(54)	C(55)	119.3(6)				
C(54)	C(55)	C(56)	119.4(6)				
C(51)	C(56)	C(55)	121.9(6)				
P(1)	C(61)	C(62)	121.7(4)				

Table S5. Interatomic distances (Å) and bond angles (deg) for **2**^{Fe}**C'**$^{2+}$$(PF_6)_2$.

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
Fe(1)	P(1)	2.240(2)	P(4)	F(15)	1.568(5)
Fe(1)	C(114)	1.872(6)	P(4)	F(15)	1.568(5)
Fe(1)	C(121)	2.12(1)	P(5)	F(16)	1.59(2)
Fe(1)	C(122)	2.116(9)	P(5)	F(17)	1.87(4)
Fe(1)	C(123)	2.126(8)	P(5)	F(18)	1.51(2)
Fe(1)	C(124)	2.110(8)	F(1)	F(1A)	0.87(2)
Fe(1)	C(125)	2.121(8)	F(1)	F(2A)	1.24(2)
Fe(1)	C(131)	1.732(7)	F(1)	C(3)	1.35(2)
Fe(2)	P(2)	2.250(2)	F(1A)	C(3A)	1.31(2)
Fe(2)	C(214)	1.858(6)	F(2)	C(3)	1.24(2)
Fe(2)	C(221)	2.125(8)	F(2A)	C(3A)	1.39(2)
Fe(2)	C(222)	2.125(8)	F(3)	C(4)	1.39(2)
Fe(2)	C(223)	2.134(8)	F(3A)	C(4A)	1.28(2)
Fe(2)	C(224)	2.143(9)	F(4)	C(4)	1.22(2)
Fe(2)	C(225)	2.129(8)	F(4A)	C(4A)	1.45(2)
Fe(2)	C(231)	1.731(9)	F(5)	C(5)	1.50(2)
S(1)	C(111)	1.827(7)	F(5A)	C(5)	1.31(2)
S(1)	C(114)	1.705(5)	F(6)	C(5)	1.26(1)
S(2)	C(211)	1.845(5)	F(6A)	C(5)	1.52(1)
S(2)	C(214)	1.712(7)	O(131)	C(131)	1.165(8)
P(1)	C(141)	1.839(8)	O(231)	C(231)	1.14(1)
P(1)	C(151)	1.827(7)	O(301)	C(302)	1.35(2)
P(1)	C(161)	1.802(6)	C(1)	C(2)	1.44(2)
P(2)	C(241)	1.832(8)	C(1)	C(2A)	1.29(2)
P(2)	C(251)	1.820(5)	C(1)	C(5)	1.465(9)
P(2)	C(261)	1.822(7)	C(1)	C(112)	1.438(9)
P(3)	F(7)	1.55(1)	C(2)	C(3)	1.55(2)
P(3)	F(8)	1.524(8)	C(2)	C(3A)	1.50(3)
P(3)	F(9)	1.52(1)	C(2)	C(212)	1.43(1)
P(3)	F(10)	1.525(7)	C(2A)	C(3)	1.67(2)
P(3)	F(11)	1.56(1)	C(2A)	C(3A)	1.50(2)
P(3)	F(12)	1.49(1)	C(2A)	C(212)	1.51(2)
P(4)	F(13)	1.584(5)	C(3)	C(4)	1.36(2)
P(4)	F(13)	1.584(5)	C(3A)	C(4A)	1.51(2)
P(4)	F(14)	1.575(5)	C(4)	C(5)	1.65(2)
P(4)	F(14)	1.575(5)	C(4A)	C(5)	1.43(2)

Table S5. Interatomic distances (Å) and bond angles (deg) for $\mathbf{2}^{\mathbf{Fe}}\mathbf{C}'^{2+}(PF_6)_2$.

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
C(111)	C(112)	1.511(7)	C(224)	C(225)	1.37(1)
C(111)	C(115)	1.54(1)	C(241)	C(242)	1.38(1)
C(111)	C(211)	1.52(1)	C(241)	C(246)	1.37(1)
C(112)	C(113)	1.349(9)	C(242)	C(243)	1.44(1)
C(113)	C(114)	1.443(9)	C(243)	C(244)	1.39(2)
C(121)	C(122)	1.393(9)	C(244)	C(245)	1.37(2)
C(121)	C(125)	1.40(1)	C(245)	C(246)	1.39(2)
C(122)	C(123)	1.43(1)	C(251)	C(252)	1.38(1)
C(123)	C(124)	1.383(9)	C(251)	C(256)	1.39(1)
C(124)	C(125)	1.39(1)	C(252)	C(253)	1.396(8)
C(141)	C(142)	1.39(1)	C(253)	C(254)	1.38(1)
C(141)	C(146)	1.38(1)	C(254)	C(255)	1.36(1)
C(142)	C(143)	1.37(1)	C(255)	C(256)	1.392(8)
C(143)	C(144)	1.36(1)	C(261)	C(262)	1.40(1)
C(144)	C(145)	1.37(2)	C(261)	C(266)	1.383(9)
C(145)	C(146)	1.38(2)	C(262)	C(263)	1.40(1)
C(151)	C(152)	1.39(1)	C(263)	C(264)	1.38(1)
C(151)	C(156)	1.383(9)	C(264)	C(265)	1.38(1)
C(152)	C(153)	1.39(1)	C(265)	C(266)	1.40(1)
C(153)	C(154)	1.38(1)	C(301)	C(302)	1.39(2)
C(154)	C(155)	1.41(1)	C(302)	C(303)	1.41(3)
C(155)	C(156)	1.37(1)			
C(161)	C(162)	1.38(1)			
C(161)	C(166)	1.36(1)			
C(162)	C(163)	1.39(1)			
C(163)	C(164)	1.30(2)			
C(164)	C(165)	1.39(2)			
C(165)	C(166)	1.41(1)			
C(211)	C(212)	1.491(9)			
C(211)	C(215)	1.55(1)			
C(212)	C(213)	1.332(8)			
C(213)	C(214)	1.474(9)			
C(221)	C(222)	1.46(1)			
C(221)	C(225)	1.43(1)			
C(222)	C(223)	1.41(2)			
C(223)	C(224)	1.38(1)			

Table S5. Interatomic distances (Å) and bond angles (deg) for $\mathbf{2}^{\mathbf{Fe}}\mathbf{C}'^{2+}(PF_6)_2$.

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
P(1)	Fe(1)	C(114)	94.0(2)	C(214)	Fe(2)	C(222)	155.1(3)
P(1)	Fe(1)	C(121)	152.1(2)	C(214)	Fe(2)	C(223)	137.6(4)
P(1)	Fe(1)	C(122)	143.3(2)	C(214)	Fe(2)	C(224)	101.7(3)
P(1)	Fe(1)	C(123)	104.6(2)	C(214)	Fe(2)	C(225)	91.6(3)
P(1)	Fe(1)	C(124)	90.9(2)	C(214)	Fe(2)	C(231)	95.4(3)
P(1)	Fe(1)	C(125)	113.5(2)	C(221)	Fe(2)	C(222)	40.0(4)
P(1)	Fe(1)	C(131)	90.4(3)	C(221)	Fe(2)	C(223)	66.0(4)
C(114)	Fe(1)	C(121)	93.1(3)	C(221)	Fe(2)	C(224)	65.5(4)
C(114)	Fe(1)	C(122)	122.7(3)	C(221)	Fe(2)	C(225)	39.3(4)
C(114)	Fe(1)	C(123)	158.3(3)	C(221)	Fe(2)	C(231)	92.0(4)
C(114)	Fe(1)	C(124)	132.5(2)	C(222)	Fe(2)	C(223)	38.8(4)
C(114)	Fe(1)	C(125)	98.1(3)	C(222)	Fe(2)	C(224)	64.5(4)
C(114)	Fe(1)	C(131)	91.7(3)	C(222)	Fe(2)	C(225)	64.7(3)
C(121)	Fe(1)	C(122)	38.4(3)	C(222)	Fe(2)	C(231)	93.3(4)
C(121)	Fe(1)	C(123)	65.3(3)	C(223)	Fe(2)	C(224)	37.8(4)
C(121)	Fe(1)	C(124)	64.8(3)	C(223)	Fe(2)	C(225)	63.3(4)
C(121)	Fe(1)	C(125)	38.7(3)	C(223)	Fe(2)	C(231)	127.0(4)
C(121)	Fe(1)	C(131)	116.4(3)	C(224)	Fe(2)	C(225)	37.5(4)
C(122)	Fe(1)	C(123)	39.5(3)	C(224)	Fe(2)	C(231)	156.1(3)
C(122)	Fe(1)	C(124)	64.6(3)	C(225)	Fe(2)	C(231)	126.4(4)
C(122)	Fe(1)	C(125)	64.3(3)	C(111)	S(1)	C(114)	97.2(3)
C(122)	Fe(1)	C(131)	89.6(3)	C(211)	S(2)	C(214)	96.8(3)
C(123)	Fe(1)	C(124)	38.1(3)	Fe(1)	P(1)	C(141)	113.0(3)
C(123)	Fe(1)	C(125)	64.5(3)	Fe(1)	P(1)	C(151)	112.1(3)
C(123)	Fe(1)	C(131)	99.2(3)	Fe(1)	P(1)	C(161)	116.4(3)
C(124)	Fe(1)	C(125)	38.5(3)	C(141)	P(1)	C(151)	104.5(3)
C(124)	Fe(1)	C(131)	135.6(3)	C(141)	P(1)	C(161)	102.4(4)
C(125)	Fe(1)	C(131)	153.3(4)	C(151)	P(1)	C(161)	107.4(3)
P(2)	Fe(2)	C(214)	92.3(2)	Fe(2)	P(2)	C(241)	115.4(2)
P(2)	Fe(2)	C(221)	151.1(3)	Fe(2)	P(2)	C(251)	113.0(2)
P(2)	Fe(2)	C(222)	111.0(3)	Fe(2)	P(2)	C(261)	114.6(3)
P(2)	Fe(2)	C(223)	90.3(3)	C(241)	P(2)	C(251)	105.1(3)
P(2)	Fe(2)	C(224)	106.2(3)	C(241)	P(2)	C(261)	103.5(3)
P(2)	Fe(2)	C(225)	143.3(3)	C(251)	P(2)	C(261)	104.0(3)
P(2)	Fe(2)	C(231)	89.5(3)	F(7)	P(3)	F(8)	89.6(5)
C(214)	Fe(2)	C(221)	116.3(3)	F(7)	P(3)	F(9)	176.9(5)

Table S5. Interatomic distances (Å) and bond angles (deg) for $\mathbf{2}^{\mathbf{Fe}}\mathbf{C}'^{2+}(PF_6)_2$.

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
F(7)	P(3)	F(10)	90.4(5)	F(16)	P(5)	F(18)	89(1)
F(7)	P(3)	F(11)	88.7(6)	F(17)	P(5)	F(17)	180
F(7)	P(3)	F(12)	91.1(7)	F(17)	P(5)	F(18)	76(1)
F(8)	P(3)	F(9)	92.9(5)	F(17)	P(5)	F(18)	104(1)
F(8)	P(3)	F(10)	173.0(5)	F(17)	P(5)	F(18)	104(1)
F(8)	P(3)	F(11)	87.9(5)	F(17)	P(5)	F(18)	76(1)
F(8)	P(3)	F(12)	94.8(5)	F(18)	P(5)	F(18)	180
F(9)	P(3)	F(10)	87.3(5)	C(2)	C(1)	C(5)	110.2(8)
F(9)	P(3)	F(11)	93.2(6)	C(2)	C(1)	C(112)	120.6(8)
F(9)	P(3)	F(12)	86.8(7)	C(2A)	C(1)	C(5)	111.5(9)
F(10)	P(3)	F(11)	85.1(5)	C(2A)	C(1)	C(112)	119.6(8)
F(10)	P(3)	F(12)	92.2(5)	C(5)	C(1)	C(112)	128.5(6)
F(11)	P(3)	F(12)	177.3(5)	C(1)	C(2)	C(3)	108(1)
F(13)	P(4)	F(13)	180.00	C(1)	C(2)	C(212)	118(1)
F(13)	P(4)	F(14)	89.5(3)	C(3)	C(2)	C(212)	133(1)
F(13)	P(4)	F(14)	90.5(3)	C(3A)	C(2)	C(212)	129(1)
F(13)	P(4)	F(15)	90.4(3)	C(1)	C(2A)	C(3A)	112(1)
F(13)	P(4)	F(15)	89.6(3)	C(1)	C(2A)	C(212)	123(1)
F(13)	P(4)	F(14)	90.5(3)	C(3A)	C(2A)	C(212)	123(1)
F(13)	P(4)	F(14)	89.5(3)	F(1)	C(3)	F(2)	108(1)
F(13)	P(4)	F(15)	89.6(3)	F(1)	C(3)	C(2)	110(1)
F(13)	P(4)	F(15)	90.4(3)	F(1)	C(3)	C(4)	122(2)
F(14)	P(4)	F(14)	180.00	F(2)	C(3)	C(2)	107(1)
F(14)	P(4)	F(15)	88.7(3)	F(2)	C(3)	C(4)	100(1)
F(14)	P(4)	F(15)	91.3(3)	C(2)	C(3)	C(4)	108(1)
F(14)	P(4)	F(15)	91.3(3)	F(1A)	C(3A)	F(2A)	99(1)
F(14)	P(4)	F(15)	88.7(3)	F(1A)	C(3A)	C(2A)	111(1)
F(15)	P(4)	F(15)	180.00	F(1A)	C(3A)	C(4A)	107(1)
F(16)	P(5)	F(16)	180.00	F(2A)	C(3A)	C(2A)	118(2)
F(16)	P(5)	F(17)	80(1)	F(2A)	C(3A)	C(4A)	120(1)
F(16)	P(5)	F(17)	100(1)	C(2)	C(3A)	C(2A)	15.1(9)
F(16)	P(5)	F(18)	89(1)	C(2A)	C(3A)	C(4A)	102(1)
F(16)	P(5)	F(18)	91(1)	F(3)	C(4)	F(4)	106(1)
F(16)	P(5)	F(17)	100(1)	F(3)	C(4)	C(3)	120(1)
F(16)	P(5)	F(17)	80(1)	F(3)	C(4)	C(5)	107(1)
F(16)	P(5)	F(18)	91(1)	F(3A)	C(4)	C(5)	86.5(9)

Table S5. Interatomic distances (Å) and bond angles (deg) for $\mathbf{2}^{\mathbf{Fe}}\mathbf{C}'^{2+}(PF_6)_2$. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
F(4)	C(4)	C(3)	107(1)	Fe(1)	C(122)	C(121)	71.1(5)
F(4)	C(4)	C(5)	108(1)	Fe(1)	C(122)	C(123)	70.7(5)
C(3)	C(4)	C(5)	108(1)	C(121)	C(122)	C(123)	108.5(6)
F(3A)	C(4A)	F(4A)	98(1)	Fe(1)	C(123)	C(122)	69.9(5)
F(3A)	C(4A)	C(3A)	104(1)	Fe(1)	C(123)	C(124)	70.3(5)
F(3A)	C(4A)	C(5)	117(1)	C(122)	C(123)	C(124)	106.6(6)
F(4A)	C(4A)	C(3A)	118(1)	Fe(1)	C(124)	C(123)	71.6(5)
F(4A)	C(4A)	C(5)	111(1)	Fe(1)	C(124)	C(125)	71.2(4)
C(3A)	C(4A)	C(5)	109(1)	C(123)	C(124)	C(125)	109.3(7)
F(5)	C(5)	F(6)	101.0(8)	Fe(1)	C(125)	C(121)	70.7(5)
F(5)	C(5)	C(1)	107.0(7)	Fe(1)	C(125)	C(124)	70.3(4)
F(5)	C(5)	C(4)	114.2(9)	C(121)	C(125)	C(124)	108.3(6)
F(5A)	C(5)	F(6A)	100.7(7)	Fe(1)	C(131)	O(131)	177.4(7)
F(5A)	C(5)	C(1)	118.4(8)	P(1)	C(141)	C(142)	119.0(5)
F(5A)	C(5)	C(4A)	115(1)	P(1)	C(141)	C(146)	122.0(7)
F(6)	C(5)	C(1)	119.0(8)	C(142)	C(141)	C(146)	119.0(8)
F(6)	C(5)	C(4)	112.9(8)	C(141)	C(142)	C(143)	121.8(7)
F(6A)	C(5)	C(4A)	109.5(8)	C(142)	C(143)	C(144)	118(1)
C(1)	C(5)	C(4)	103.1(7)	C(143)	C(144)	C(145)	121(1)
C(1)	C(5)	C(4A)	105.7(7)	C(144)	C(145)	C(146)	120(1)
S(1)	C(111)	C(112)	102.2(4)	C(141)	C(146)	C(145)	119.2(9)
S(1)	C(111)	C(115)	108.1(4)	P(1)	C(151)	C(152)	121.6(5)
S(1)	C(111)	C(211)	115.1(5)	P(1)	C(151)	C(156)	119.4(5)
C(112)	C(111)	C(115)	111.3(6)	C(152)	C(151)	C(156)	119.0(6)
C(112)	C(111)	C(211)	106.0(5)	C(151)	C(152)	C(153)	119.7(6)
C(115)	C(111)	C(211)	113.5(5)	C(152)	C(153)	C(154)	120.7(8)
C(1)	C(112)	C(111)	116.0(5)	C(153)	C(154)	C(155)	119.4(7)
C(1)	C(112)	C(113)	128.2(5)	C(154)	C(155)	C(156)	119.0(6)
C(111)	C(112)	C(113)	115.6(5)	C(151)	C(156)	C(155)	122.2(7)
C(112)	C(113)	C(114)	116.4(5)	P(1)	C(161)	C(162)	121.8(7)
Fe(1)	C(114)	S(1)	122.3(4)	P(1)	C(161)	C(166)	121.7(6)
Fe(1)	C(114)	C(113)	129.2(4)	C(162)	C(161)	C(166)	116.4(6)
S(1)	C(114)	C(113)	108.1(4)	C(161)	C(162)	C(163)	122.5(9)
Fe(1)	C(121)	C(122)	70.5(5)	C(162)	C(163)	C(164)	121.0(8)
Fe(1)	C(121)	C(125)	70.6(5)	C(163)	C(164)	C(165)	119.1(8)
C(122)	C(121)	C(125)	107.4(7)	C(164)	C(165)	C(166)	120(1)

Table S5. Interatomic distances (Å) and bond angles (deg) for $\mathbf{2^{Fe}C'}^{2+}(PF_6)_2$. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C(161)	C(166)	C(165)	120.5(9)	C(241)	C(242)	C(243)	121.3(8)
S(2)	C(211)	C(111)	113.8(4)	C(242)	C(243)	C(244)	117.4(9)
S(2)	C(211)	C(212)	102.1(4)	C(243)	C(244)	C(245)	121(1)
S(2)	C(211)	C(215)	107.6(5)	C(244)	C(245)	C(246)	121(1)
C(111)	C(211)	C(212)	108.3(6)	C(241)	C(246)	C(245)	120.1(8)
C(111)	C(211)	C(215)	112.7(5)	P(2)	C(251)	C(252)	119.1(5)
C(212)	C(211)	C(215)	111.9(5)	P(2)	C(251)	C(256)	122.4(5)
C(2)	C(212)	C(2A)	15.1(9)	C(252)	C(251)	C(256)	118.5(5)
C(2)	C(212)	C(211)	114.4(8)	C(251)	C(252)	C(253)	121.5(7)
C(2)	C(212)	C(213)	127.8(9)	C(252)	C(253)	C(254)	118.6(7)
C(2A)	C(212)	C(211)	113.2(8)	C(253)	C(254)	C(255)	120.9(6)
C(2A)	C(212)	C(213)	127.2(9)	C(254)	C(255)	C(256)	120.0(7)
C(211)	C(212)	C(213)	117.7(5)	C(251)	C(256)	C(255)	120.5(7)
C(212)	C(213)	C(214)	115.5(6)	P(2)	C(261)	C(262)	120.8(5)
Fe(2)	C(214)	S(2)	122.7(4)	P(2)	C(261)	C(266)	119.6(5)
Fe(2)	C(214)	C(213)	129.5(5)	C(262)	C(261)	C(266)	119.5(6)
S(2)	C(214)	C(213)	107.7(4)	C(261)	C(262)	C(263)	120.0(6)
Fe(2)	C(221)	C(222)	70.0(5)	C(262)	C(263)	C(264)	119.3(7)
Fe(2)	C(221)	C(225)	70.5(5)	C(263)	C(264)	C(265)	121.0(7)
C(222)	C(221)	C(225)	104.1(9)	C(264)	C(265)	C(266)	119.7(6)
Fe(2)	C(222)	C(221)	70.0(4)	C(261)	C(266)	C(265)	120.5(7)
Fe(2)	C(222)	C(223)	71.0(4)	O(301)	C(302)	C(301)	102(1)
C(221)	C(222)	C(223)	107.8(8)	O(301)	C(302)	C(303)	96(2)
Fe(2)	C(223)	C(222)	70.2(5)	C(301)	C(302)	C(303)	146(1)
Fe(2)	C(223)	C(224)	71.5(5)				
C(222)	C(223)	C(224)	108.8(9)				
Fe(2)	C(224)	C(223)	70.8(5)				
Fe(2)	C(224)	C(225)	70.7(5)				
C(223)	C(224)	C(225)	108.4(9)				
Fe(2)	C(225)	C(221)	70.2(4)				
Fe(2)	C(225)	C(224)	71.8(5)				
C(221)	C(225)	C(224)	110.8(8)				
Fe(2)	C(231)	O(231)	176.4(6)				
P(2)	C(241)	C(242)	120.2(6)				
P(2)	C(241)	C(246)	120.4(6)				
C(242)	C(241)	C(246)	119.4(8)				

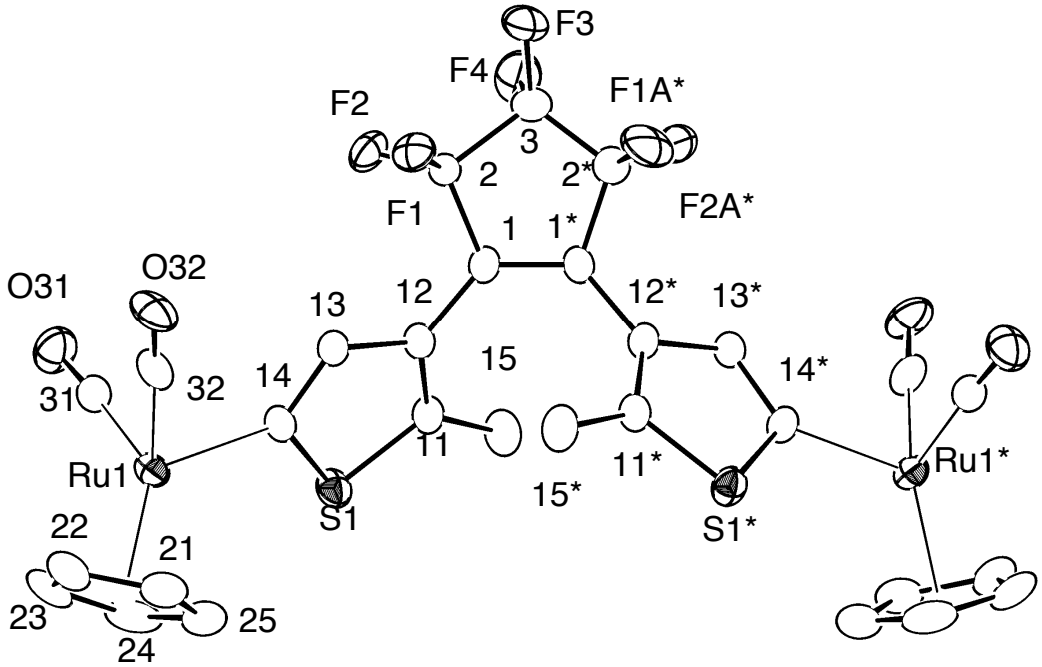

Figure S1. Molecular structure of $\mathbf{1^{Ru}}$ drawn with thermal ellipsoids at the 30 % probability level. Labels without atom names are for carbon atoms. The disordered atoms, hydrogen atoms and the CH_2Cl_2 solvate molecule are not included for clarity.

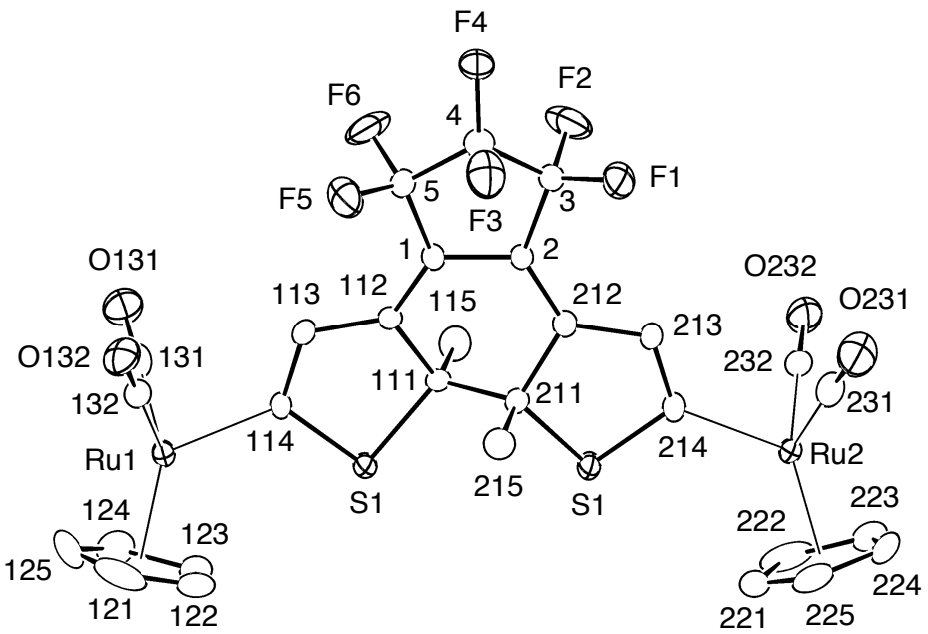

Figure S2. Molecular structure of $\mathbf{1^{Ru}C}$ drawn with thermal ellipsoids at the 30 % probability level. Labels without atom names are for carbon atoms. Hydrogen atoms are not included for clarity

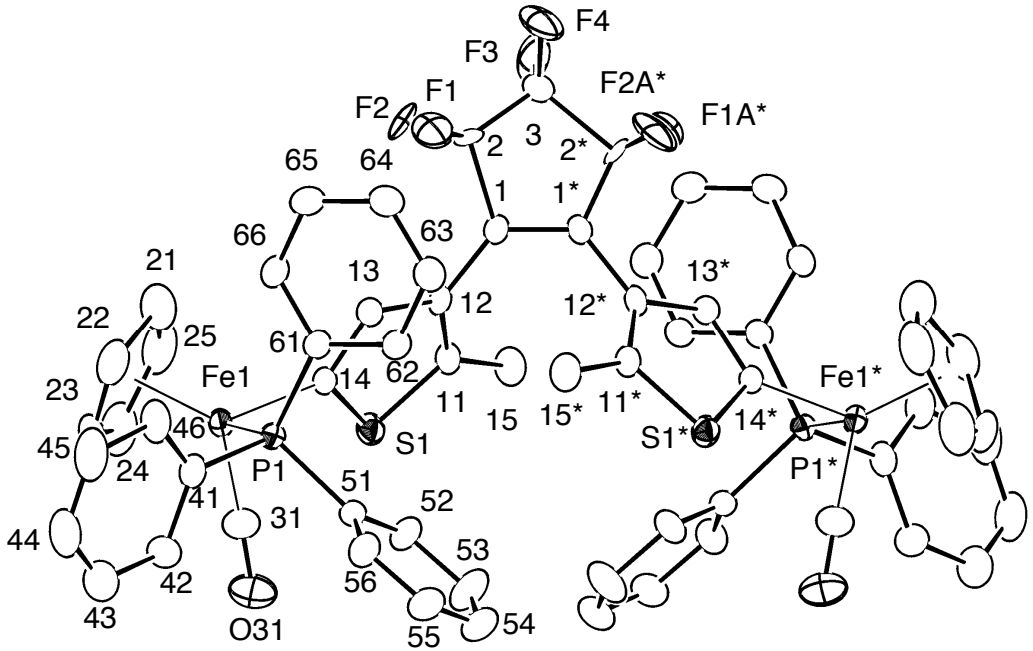

Figure S3. Molecular structure of $\mathbf{2^{Fe}}$ drawn with thermal ellipsoids at the 30 % probability level. Labels without atom names are for carbon atoms. The disordered atoms and hydrogen atoms are not included for clarity.

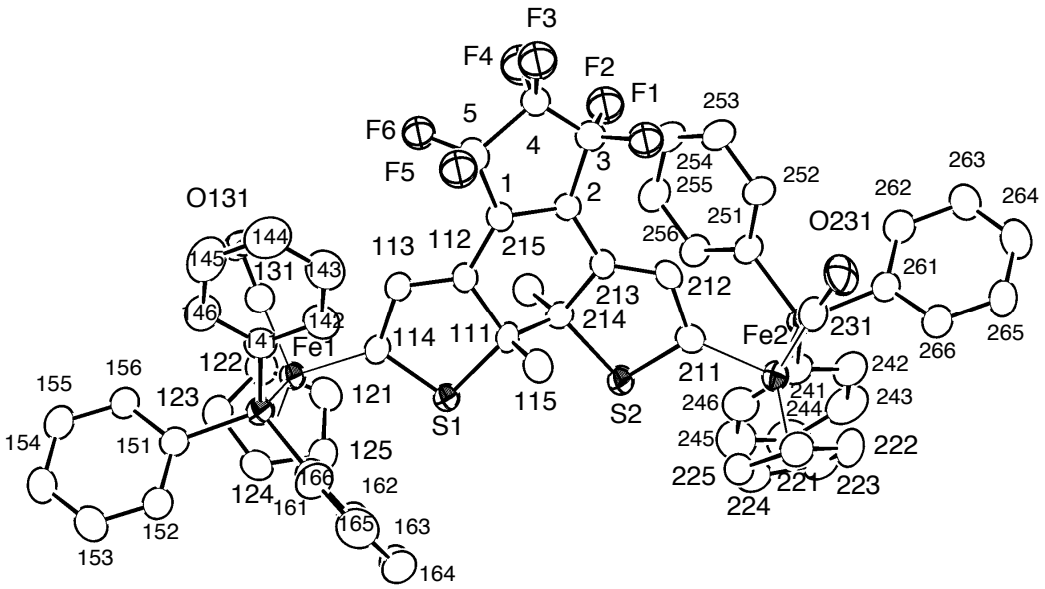

Figure S4. Molecular structure of the cationic part of $\mathbf{2^{FeC'}}^{2+}(PF_6)_2$ drawn with thermal ellipsoids at the 30 % probability level. Labels without atom names are for carbon atoms. The disordered atoms, hydrogen atoms and the acetone solvate molecule are not included for clarity.