List of Electronic Supplementary Information

Photo- and Electro-chromic Organometallics with Dithienylethene (DTE) Linker, L_2CpM-DTE-$MCpL_2$: Dually Stimuli-responsive Molecular Switch

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Experimental section for X-ray crystallography. 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.[1] 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.[2] Neutral scattering factors were obtained from the standard source.[3]

The structures were solved by a combination of the direct methods (SHELXS-86)[4] and Fourier synthesis (DIRDIF94).[5] Least-squares refinements were carried out using SHELXL-97 [4] (refined on F^2). The computation was done with wingx or YADOKARI software pakages.[6] 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. Because all fluorine atoms of the cyclopentene rings were found to be disordered, they were refined with fixing the C-F distances (~1.35 Å). The crystallographic data were deposited at the Cambridge Crystallographic Data Centre: CCDC 818896 (**1^{Fe}O**), 818897 (**1^{Fe}C**), 818899 (**1*^{Fe}O**), 8188978 (**3'^{Fe}O**), 820900 (DTE{RuCp(CO)}$_2$(μ-dppe)).

1^{Fe}O: The molecule sat on a crystallographic inversion center. The disordered F atoms (F1-4) were refined taking into account of two components with the occupancy factors of 0.5. Although a highly disordered CH_2Cl_2 molecule was found during the refinement, it could not be refined satisfactorily; then the structure was refined with the SQUEEZE routine (PLATON) with removing the solvate molecule. All hydrogen atoms except for the CH_2Cl_2 hydrogen atoms were refined isotropically.

1^{Fe}C: Hydrogen atoms attached to the methyl groups were refined with riding models.

1*^{Fe}O: Hydrogen atoms attached to the methyl groups were refined with riding models, and the other hydrogen atoms were refined isotropically.

3'^{Fe}O: The molecule sat on a crystallographic inversion center. The methyl groups in the η^5-C_5H_4Me ligands were disordered. The methyl group in the minor component (C76A) was attached to C73, and the occupancies were determined to be C76 : C76A= 0.51 : 0.49.

DTE{RuCp(CO)}(μ-dppe): A part of the cyclopentene ring was disordered and refined taking into account two components (C4-F5-C6 : C4A-F5A-F6A= 0.705 : 0.295). It was evident that two CH_2Cl_2 molecules were included in the crystal. One of them was refined isotropically with fixing one of the C-Cl distance (1.78 Å), and the other highly disordered one was not included in the refinement.

References

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Table S1. Crystallographic data for DTE complexes.

complex (sample No.) solvate	**1^{Fe}O** (1021 / CCDC 818896) -	**1^{Fe}C** (1098 / CCDC 818897) -	**1*^{Fe}O** (1091 / CCDC 818899) CH_2Cl_2	**3'^{Fe}O** (1027 / CCDC 818898) -
formula	$C_{29}H_{18}F_6Fe_2O_4S_2$	$C_{29}H_{18}F_6Fe_2O_4S_2$	$C_{40}H_{40}Cl_2F_6Fe_2O_4S_2$	$C_{79}H_{70}F_6Fe_2P_4S_2$
formula weight	720.25	720.25	945.44	1433.12
crystal system	orthorhombic	triclinic	triclinic	monoclinic
space group	*Pbcn*	*P-1*	*P-1*	*C2/c*
temp. / K	213(2)	213(2)	213(2)	213(2)
a / Å	20.688(8)	10.8074(18)	9.1297(12)	21.566(9)
b / Å	13.538(6)	11.2063(19)	13.572(3)	8.579(3)
c / Å	11.393(6)	12.978(2)	18.309(4)	38.084(17)
α / deg	90	97.203(8)	101.002(5)	90
β / deg	90	98.033(9)	103.323(11)	102.993(18)
γ / deg	90	114.204(6)	98.326(12)	90
V/ Å^3	3191(2)	1390.2(4)	2124.2(7)	6866(5)
Z	4	2	2	4
d_{calcd} / g·cm^{-3}	1.499	1.721	1.478	1.386
μ / mm^{-1}	1.107	1.270	0.972	0.637
R_{int}	0.033	0.050	0.077	0.090
no of all data collected	23728	11277	17161	25083
no of parameters	232	388	533	452
R1 for data with I > 2σ(I)	0.0556 (for 3233 data)	0.0600 (for 4346 data)	0.0577 (for 6061 data)	0.0483 (for 4206 data)
wR2	0.1965 (for 3645 all data)	0.1801 (for all 5762 data)	0.1688 (for 8830 all data)	0.1473 (for 7123 all data)

Table S1. Crystallographic data for DTE complexes. (cont'd.)

complex	DTE{RuCp(CO)}$_2$(μ-dppe)
(sample No.)	(1051 / CCDC 820900)
solvate	CH_2Cl_2
formula	$C_{54}H_{44}Cl_2F_6O_2P_2Ru_2S_2$
formula weight	1238.04
crystal system	triclinic
space group	*P-1*
temp. / K	213(2)
a / Å	11.8045(19)
b / Å	14.196(3)
c / Å	16.925(2)
α / deg	97.361(7)
β / deg	105.434(8)
γ / deg	93.453(5)
V/ Å^3	2698.1(7)
Z	2
d_{calcd} / g·cm^{-3}	1.524
μ / mm^{-1}	0.898
R_{int}	0.091
no of all data collected	21298
no of parameters	652
R1 for data with I > 2σ(I)	0.0800 (for 5492 data)
wR2	0.2244 (for 11168 all data)

Table S2. Interatomic distances (Å) and bond angles (deg) for **1^{Fe}O**.

ATOM	ATOM	DISTANCE
Fe1	C31	1.759(3)
Fe1	C32	1.772(3)
Fe1	C14	1.993(3)
Fe1	C24	2.092(3)
Fe1	C22	2.099(3)
Fe1	C23	2.100(3)
Fe1	C25	2.115(4)
Fe1	C21	2.121(3)
S2	C11	1.729(3)
S2	C14	1.744(3)
O31	C31	1.139(4)
C25	C21	1.414(5)
C25	C24	1.420(6)
C12	C11	1.373(4)
C12	C13	1.441(4)
C12	C1	1.463(4)
C23	C22	1.406(5)
C23	C24	1.435(6)
C1	C1	1.365(5)
C1	C2	1.506(4)
O32	C32	1.138(4)
C13	C14	1.377(4)
C22	C21	1.412(5)
C11	C15	1.501(4)
C2	F1A	1.346(2)
C2	F2	1.353(2)
C2	F2A	1.358(2)
C2	F1	1.360(2)
C2	C3	1.530(4)
C3	F4	1.347(2)
C3	F3	1.356(2)

Table S2. Interatomic distances (Å) and bond angles (deg) for **1^{Fe}O**. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C31	Fe1	C32	92.21(16)	C22	C23	Fe1	70.40(17)
C31	Fe1	C14	88.30(12)	C24	C23	Fe1	69.66(18)
C32	Fe1	C14	90.22(12)	C1	C1	C12	130.11(14)
C31	Fe1	C24	102.80(16)	C1	C1	C2	111.17(14)
C32	Fe1	C24	159.54(15)	C12	C1	C2	118.7(2)
C14	Fe1	C24	103.88(14)	C14	C13	C12	115.0(2)
C31	Fe1	C22	118.12(14)	O32	C32	Fe1	178.1(3)
C32	Fe1	C22	94.50(14)	C23	C22	C21	109.1(3)
C14	Fe1	C22	152.87(13)	C23	C22	Fe1	70.48(18)
C24	Fe1	C22	66.25(14)	C21	C22	Fe1	71.29(17)
C31	Fe1	C23	92.19(15)	C13	C14	S2	107.58(19)
C32	Fe1	C23	126.83(15)	C13	C14	Fe1	131.9(2)
C14	Fe1	C23	142.86(14)	S2	C14	Fe1	120.44(14)
C24	Fe1	C23	40.03(16)	C22	C21	C25	107.6(3)
C22	Fe1	C23	39.12(14)	C22	C21	Fe1	69.62(18)
C31	Fe1	C25	140.29(15)	C25	C21	Fe1	70.3(2)
C32	Fe1	C25	127.49(16)	C25	C24	C23	107.4(3)
C14	Fe1	C25	90.53(13)	C25	C24	Fe1	71.16(19)
C24	Fe1	C25	39.46(17)	C23	C24	Fe1	70.31(19)
C22	Fe1	C25	65.54(14)	C12	C11	C15	129.7(3)
C23	Fe1	C25	66.17(16)	C12	C11	S2	109.2(2)
C31	Fe1	C21	156.62(14)	C15	C11	S2	121.0(2)
C32	Fe1	C21	94.74(15)	O31	C31	Fe1	178.5(3)
C14	Fe1	C21	113.93(13)	F1A	C2	F2A	114.1(5)
C24	Fe1	C21	66.13(14)	F2	C2	F1	102.2(4)
C22	Fe1	C21	39.09(14)	F1A	C2	C1	119.1(4)
C23	Fe1	C21	65.89(15)	F2	C2	C1	115.5(4)
C25	Fe1	C21	39.00(13)	F2A	C2	C1	105.9(4)
C11	S2	C14	95.08(13)	F1	C2	C1	106.3(3)
C21	C25	C24	108.4(3)	F1A	C2	C3	113.1(4)
C21	C25	Fe1	70.7(2)	F2	C2	C3	122.3(3)
C24	C25	Fe1	69.4(2)	F2A	C2	C3	97.1(4)
C11	C12	C13	113.2(2)	F1	C2	C3	103.9(3)
C11	C12	C1	123.3(2)	C1	C2	C3	105.0(2)
C13	C12	C1	123.4(2)	F4	C3	F3	102.3(6)
C22	C23	C24	107.4(3)	F4	C3	C2	126.1(3)

Table S2. Interatomic distances (Å) and bond angles (deg) for **1^{Fe}O**. (cont'd.)

ATOM	ATOM	ATOM	ANGLE
F4	C3	C2	113.8(3)
C2	C3	C2	107.1(3)

Table S3. Interatomic distances (Å) and bond angles (deg) for **1^{Fe}C**.

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
C1	C112	1.358(5)	C211	C215	1.574(6)
C1	C2	1.454(5)	C211	S2	1.842(4)
C1	C5	1.492(5)	C212	C213	1.432(5)
C2	C212	1.349(5)	C213	C214	1.365(5)
C2	C3	1.484(5)	C214	S2	1.755(4)
C3	F1	1.3500(19)	C214	Fe2	1.983(4)
C3	F2	1.3530(19)	C221	C225	1.408(8)
C3	C4	1.531(5)	C221	C222	1.416(8)
C4	F4	1.3437(19)	C221	Fe2	2.090(4)
C4	F3	1.352(2)	C222	C223	1.393(8)
C4	C5	1.528(5)	C222	Fe2	2.083(4)
C5	F5	1.3488(19)	C223	C224	1.403(7)
C5	F6	1.3535(19)	C223	Fe2	2.097(4)
C111	C211	1.522(6)	C224	C225	1.356(7)
C111	C112	1.537(5)	C224	Fe2	2.122(5)
C111	C115	1.549(6)	C225	Fe2	2.117(4)
C111	S1	1.852(4)	C231	O231	1.142(6)
C112	C113	1.429(5)	C231	Fe2	1.765(5)
C113	C114	1.369(5)	C232	O232	1.153(6)
C114	S1	1.766(4)	C232	Fe2	1.759(5)
C114	Fe1	1.974(4)			
C121	C122	1.393(7)			
C121	C125	1.392(7)			
C121	Fe1	2.096(4)			
C122	C123	1.391(8)			
C122	Fe1	2.108(5)			
C123	C124	1.442(10)			
C123	Fe1	2.111(5)			
C124	C125	1.394(9)			
C124	Fe1	2.109(5)			
C125	Fe1	2.121(5)			
C131	O131	1.145(5)			
C131	Fe1	1.765(5)			
C132	O132	1.153(5)			
C132	Fe1	1.754(4)			
C211	C212	1.539(5)			

Table S3. Interatomic distances (Å) and bond angles (deg) for **1^{Fe}C**. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C112	C1	C2	122.1(3)	S1	C114	Fe1	121.0(2)
C112	C1	C5	128.4(3)	C122	C121	C125	109.8(5)
C2	C1	C5	109.5(3)	C122	C121	Fe1	71.1(3)
C212	C2	C1	121.3(3)	C125	C121	Fe1	71.7(3)
C212	C2	C3	129.8(3)	C123	C122	C121	107.6(5)
C1	C2	C3	108.8(3)	C123	C122	Fe1	70.9(3)
F1	C3	F2	104.9(3)	C121	C122	Fe1	70.2(3)
F1	C3	C2	115.4(3)	C122	C123	C124	107.6(5)
F2	C3	C2	113.4(3)	C122	C123	Fe1	70.6(3)
F1	C3	C4	110.8(3)	C124	C123	Fe1	70.0(3)
F2	C3	C4	108.8(3)	C125	C124	C123	107.3(5)
C2	C3	C4	103.5(3)	C125	C124	Fe1	71.2(3)
F4	C4	F3	105.0(3)	C123	C124	Fe1	70.1(3)
F4	C4	C5	114.2(3)	C121	C125	C124	107.7(5)
F3	C4	C5	108.7(3)	C121	C125	Fe1	69.8(3)
F4	C4	C3	114.5(3)	C124	C125	Fe1	70.3(3)
F3	C4	C3	108.5(3)	O131	C131	Fe1	178.3(4)
C5	C4	C3	105.8(2)	O132	C132	Fe1	179.4(4)
F5	C5	F6	103.6(3)	C111	C211	C212	109.6(3)
F5	C5	C1	114.7(3)	C111	C211	C215	111.1(3)
F6	C5	C1	113.9(3)	C212	C211	C215	108.2(4)
F5	C5	C4	110.7(3)	C111	C211	S2	115.6(3)
F6	C5	C4	109.9(3)	C212	C211	S2	103.6(3)
C1	C5	C4	104.2(3)	C215	C211	S2	108.3(3)
C211	C111	C112	108.7(3)	C2	C212	C213	132.0(4)
C211	C111	C115	110.5(4)	C2	C212	C211	116.7(3)
C112	C111	C115	110.1(4)	C213	C212	C211	111.0(3)
C211	C111	S1	114.5(3)	C214	C213	C212	116.6(3)
C112	C111	S1	102.8(3)	C213	C214	S2	111.2(3)
C115	C111	S1	109.9(3)	C213	C214	Fe2	128.9(3)
C1	C112	C113	131.1(4)	S2	C214	Fe2	119.9(2)
C1	C112	C111	116.4(3)	C225	C221	C222	107.1(4)
C113	C112	C111	112.4(3)	C225	C221	Fe2	71.5(3)
C114	C113	C112	116.3(3)	C222	C221	Fe2	69.9(3)
C113	C114	S1	110.8(3)	C223	C222	C221	107.6(5)
C113	C114	Fe1	128.2(3)	C223	C222	Fe2	71.1(3)

Table S3. Interatomic distances (Å) and bond angles (deg) for **1^{Fe}C**. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C221	C222	Fe2	70.4(3)	C131	Fe1	C125	92.4(2)
C222	C223	C224	107.5(5)	C114	Fe1	C125	130.5(2)
C222	C223	Fe2	70.0(3)	C121	Fe1	C125	38.54(18)
C224	C223	Fe2	71.5(3)	C122	Fe1	C125	65.2(2)
C225	C224	C223	109.4(5)	C124	Fe1	C125	38.5(3)
C225	C224	Fe2	71.2(3)	C123	Fe1	C125	65.3(2)
C223	C224	Fe2	69.6(3)	C232	Fe2	C231	96.9(2)
C224	C225	C221	108.5(4)	C232	Fe2	C214	86.73(19)
C224	C225	Fe2	71.5(3)	C231	Fe2	C214	90.32(18)
C221	C225	Fe2	69.4(3)	C232	Fe2	C222	91.1(2)
O231	C231	Fe2	177.7(4)	C231	Fe2	C222	122.5(2)
O232	C232	Fe2	176.9(5)	C214	Fe2	C222	147.1(2)
C114	S1	C111	94.06(18)	C232	Fe2	C221	98.9(2)
C214	S2	C211	93.56(18)	C231	Fe2	C221	156.1(2)
C132	Fe1	C131	92.1(2)	C214	Fe2	C221	108.3(2)
C132	Fe1	C114	89.13(17)	C222	Fe2	C221	39.7(2)
C131	Fe1	C114	87.10(17)	C232	Fe2	C223	119.7(2)
C132	Fe1	C121	153.5(2)	C231	Fe2	C223	91.0(2)
C131	Fe1	C121	113.7(2)	C214	Fe2	C223	153.1(2)
C114	Fe1	C121	97.75(17)	C222	Fe2	C223	38.9(2)
C132	Fe1	C122	115.4(2)	C221	Fe2	C223	65.6(2)
C131	Fe1	C122	152.3(2)	C232	Fe2	C225	135.5(2)
C114	Fe1	C122	95.38(17)	C231	Fe2	C225	127.5(2)
C121	Fe1	C122	38.7(2)	C214	Fe2	C225	93.76(17)
C132	Fe1	C124	103.1(2)	C222	Fe2	C225	65.5(2)
C131	Fe1	C124	107.3(3)	C221	Fe2	C225	39.1(2)
C114	Fe1	C124	160.4(2)	C223	Fe2	C225	64.58(18)
C121	Fe1	C124	64.7(2)	C232	Fe2	C224	155.9(2)
C122	Fe1	C124	65.7(2)	C231	Fe2	C224	94.7(2)
C132	Fe1	C123	90.8(2)	C214	Fe2	C224	114.3(2)
C131	Fe1	C123	146.6(3)	C222	Fe2	C224	64.8(2)
C114	Fe1	C123	126.2(3)	C221	Fe2	C224	64.4(2)
C121	Fe1	C123	64.5(2)	C223	Fe2	C224	38.8(2)
C122	Fe1	C123	38.5(2)	C225	Fe2	C224	37.3(2)
C124	Fe1	C123	40.0(3)				
C132	Fe1	C125	140.3(2)				

Table S4. Interatomic distances (Å) and bond angles (deg) for **1*^{Fe}O**.

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
Fe1	C132	1.758(5)	C2	C3	1.482(5)
Fe1	C131	1.760(5)	C3	C4	1.473(6)
Fe1	C114	1.986(4)	C4	C5	1.484(6)
Fe1	C122	2.097(4)	C111	C112	1.365(5)
Fe1	C121	2.101(4)	C111	C115	1.487(5)
Fe1	C123	2.104(4)	C112	C113	1.446(5)
Fe1	C124	2.118(4)	C113	C114	1.369(5)
Fe1	C120	2.135(4)	C120	C121	1.418(6)
Fe2	C231	1.750(4)	C120	C124	1.420(5)
Fe2	C232	1.763(5)	C120	C125	1.496(5)
Fe2	C214	1.980(4)	C121	C122	1.444(6)
Fe2	C220	2.106(4)	C121	C126	1.495(6)
Fe2	C221	2.106(4)	C122	C123	1.413(6)
Fe2	C222	2.106(4)	C122	C127	1.508(6)
Fe2	C224	2.111(4)	C123	C124	1.426(5)
Fe2	C223	2.143(4)	C123	C128	1.506(6)
Cl1	C300	1.682(10)	C124	C129	1.508(6)
Cl2	C300	1.679(10)	C211	C212	1.378(5)
S1	C111	1.734(4)	C211	C215	1.496(6)
S1	C114	1.737(4)	C212	C213	1.442(5)
S2	C211	1.724(4)	C213	C214	1.374(5)
S2	C214	1.732(4)	C220	C221	1.405(6)
F1	C3	1.345(2)	C220	C224	1.447(5)
F2	C3	1.347(2)	C220	C225	1.502(6)
F3	C4	1.345(2)	C221	C222	1.439(6)
F4	C4	1.342(2)	C221	C226	1.499(5)
F5	C5	1.3429(19)	C222	C223	1.414(5)
F6	C5	1.353(2)	C222	C227	1.496(6)
O131	C131	1.139(5)	C223	C224	1.417(6)
O132	C132	1.155(5)	C223	C228	1.508(5)
O231	C231	1.161(5)	C224	C229	1.497(6)
O232	C232	1.143(5)			
C1	C2	1.365(5)			
C1	C112	1.461(5)			
C1	C5	1.495(5)			
C2	C212	1.465(5)			

Table S4. Interatomic distances (Å) and bond angles (deg) for **1*^{Fe}O**. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C132	Fe1	C131	96.7(2)	C214	Fe2	C221	144.88(16)
C132	Fe1	C114	93.48(19)	C220	Fe2	C221	38.96(17)
C131	Fe1	C114	88.15(18)	C231	Fe2	C222	161.03(19)
C132	Fe1	C122	124.69(19)	C232	Fe2	C222	97.91(18)
C131	Fe1	C122	91.7(2)	C214	Fe2	C222	104.96(16)
C114	Fe1	C122	141.52(17)	C220	Fe2	C222	66.28(17)
C132	Fe1	C121	158.64(18)	C221	Fe2	C222	39.95(16)
C131	Fe1	C121	98.6(2)	C231	Fe2	C224	98.12(18)
C114	Fe1	C121	101.81(16)	C232	Fe2	C224	158.00(17)
C122	Fe1	C121	40.24(16)	C214	Fe2	C224	105.50(15)
C132	Fe1	C123	92.62(18)	C220	Fe2	C224	40.14(15)
C131	Fe1	C123	120.54(19)	C221	Fe2	C224	66.43(16)
C114	Fe1	C123	149.68(15)	C222	Fe2	C224	66.25(16)
C122	Fe1	C123	39.29(16)	C231	Fe2	C223	132.42(18)
C121	Fe1	C123	66.74(16)	C232	Fe2	C223	133.70(18)
C132	Fe1	C124	94.59(18)	C214	Fe2	C223	86.62(15)
C131	Fe1	C124	157.6(2)	C220	Fe2	C223	65.65(16)
C114	Fe1	C124	110.36(15)	C221	Fe2	C223	65.59(15)
C122	Fe1	C124	66.07(16)	C222	Fe2	C223	38.86(15)
C121	Fe1	C124	66.22(16)	C224	Fe2	C223	38.92(16)
C123	Fe1	C124	39.49(15)	C111	S1	C114	94.79(19)
C132	Fe1	C120	128.46(18)	C211	S2	C214	95.22(18)
C131	Fe1	C120	134.76(19)	C2	C1	C112	131.4(3)
C114	Fe1	C120	87.45(15)	C2	C1	C5 10	9.4(3)
C122	Fe1	C120	65.94(15)	C112	C1	C5 11	9.2(3)
C121	Fe1	C120	39.11(15)	C1	C2	C212	130.3(3)
C123	Fe1	C120	65.78(15)	C1	C2	C3 11	0.0(3)
C124	Fe1	C120	39.00(15)	C212	C2	C3 11	9.5(3)
C231	Fe2	C232	93.83(19)	F1	C3	F2 10	5.1(4)
C231	Fe2	C214	89.16(17)	F1	C3	C4 10	9.5(3)
C232	Fe2	C214	93.04(18)	F2	C3	C4 10	9.5(3)
C231	Fe2	C220	94.90(18)	F1	C3	C2 11	3.6(3)
C232	Fe2	C220	120.61(18)	F2	C3	C2 11	3.1(3)
C214	Fe2	C220	145.63(16)	C4	C3	C2 10	6.1(3)
C231	Fe2	C221	125.22(18)	F4	C4	F3 10	1.1(5)
C232	Fe2	C221	91.59(18)	F4	C4	C3 11	3.8(4)

Table S4. Interatomic distances (Å) and bond angles (deg) for **1*^{Fe}O**. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
F3	C4	C3	110.9(4)	C121	C122	Fe1	70.0(2)
F4	C4	C5	112.7(4)	C127	C122	Fe1	129.0(3)
F3	C4	C5	111.3(4)	C122	C123	C124	108.1(3)
C3	C4	C5	107.2(3)	C122	C123	C128	125.9(4)
F5	C5	F6	101.5(4)	C124	C123	C128	125.9(4)
F5	C5	C4	113.7(4)	C122	C123	Fe1	70.1(2)
F6	C5	C4	109.3(3)	C124	C123	Fe1	70.8(2)
F5	C5	C1	114.7(3)	C128	C123	Fe1	127.9(3)
F6	C5	C1	113.0(3)	C120	C124	C123	108.0(3)
C4	C5	C1	104.8(3)	C120	C124	C129	126.1(4)
C112	C111	C115	129.7(4)	C123	C124	C129	125.8(4)
C112	C111	S1	109.4(3)	C120	C124	Fe1	71.2(2)
C115	C111	S1	120.9(3)	C123	C124	Fe1	69.8(2)
C111	C112	C113	112.9(3)	C129	C124	Fe1	127.6(3)
C111	C112	C1	124.2(4)	O131	C131	Fe1	178.7(5)
C113	C112	C1	122.7(3)	O132	C132	Fe1	177.7(4)
C114	C113	C112	114.9(4)	C212	C211	C215	130.5(3)
C113	C114	S1	108.0(3)	C212	C211	S2	109.5(3)
C113	C114	Fe1	130.6(3)	C215	C211	S2	119.9(3)
S1	C114	Fe1	121.4(2)	C211	C212	C213	112.2(3)
C121	C120	C124	108.6(3)	C211	C212	C2	124.4(3)
C121	C120	C125	125.8(4)	C213	C212	C2	123.3(3)
C124	C120	C125	125.4(4)	C214	C213	C212	115.4(4)
C121	C120	Fe1	69.2(2)	C213	C214	S2	107.6(3)
C124	C120	Fe1	69.8(2)	C213	C214	Fe2	132.1(3)
C125	C120	Fe1	129.9(3)	S2	C214	Fe2	120.23(19)
C120	C121	C122	107.2(3)	C221	C220	C224	108.2(4)
C120	C121	C126	126.6(4)	C221	C220	C225	126.4(4)
C122	C121	C126	126.1(4)	C224	C220	C225	125.4(4)
C120	C121	Fe1	71.7(2)	C221	C220	Fe2	70.5(2)
C122	C121	Fe1	69.7(2)	C224	C220	Fe2	70.1(2)
C126	C121	Fe1	127.4(3)	C225	C220	Fe2	128.3(3)
C123	C122	C121	108.1(3)	C220	C221	C222	108.2(3)
C123	C122	C127	127.0(4)	C220	C221	C226	126.7(4)
C121	C122	C127	124.7(4)	C222	C221	C226	125.0(4)
C123	C122	Fe1	70.6(2)	C220	C221	Fe2	70.5(2)

Table S4. Interatomic distances (Å) and bond angles (deg) for **1*^{Fe}O**. (cont'd.)

ATOM	ATOM	ATOM	ANGLE
C222	C221	Fe2	70.0(2)
C226	C221	Fe2	129.0(3)
C223	C222	C221	107.6(4)
C223	C222	C227	126.7(4)
C221	C222	C227	125.5(4)
C223	C222	Fe2	72.0(2)
C221	C222	Fe2	70.0(2)
C227	C222	Fe2	127.7(3)
C222	C223	C224	108.9(3)
C222	C223	C228	125.4(4)
C224	C223	C228	125.6(4)
C222	C223	Fe2	69.2(2)
C224	C223	Fe2	69.3(2)
C228	C223	Fe2	129.4(3)
C223	C224	C220	107.1(4)
C223	C224	C229	126.4(4)
C220	C224	C229	126.2(4)
C223	C224	Fe2	71.8(2)
C220	C224	Fe2	69.8(2)
C229	C224	Fe2	128.8(3)
O231	C231	Fe2	177.3(4)
O232	C232	Fe2	177.3(4)
Cl2	C300	Cl1	119.1(5)

Table S5. Interatomic distances (Å) and bond angles (deg) for **3'^{Fe}O**.

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
Fe1	C14	2.014(3)	C35	C36	1.402(7)
Fe1	C75	2.092(4)	C41	C42	1.380(6)
Fe1	C74	2.108(3)	C41	C46	1.390(6)
Fe1	C72	2.111(4)	C42	C43	1.379(6)
Fe1	C71	2.127(4)	C43	C44	1.365(7)
Fe1	C73	2.126(4)	C44	C45	1.368(7)
Fe1	P1	2.1703(12)	C45	C46	1.389(6)
Fe1	P2	2.1723(13)	C51	C52	1.387(6)
S1	C11	1.728(4)	C51	C56	1.393(6)
S1	C14	1.749(4)	C52	C53	1.377(7)
P1	C31	1.845(4)	C53	C54	1.386(8)
P1	C41	1.850(4)	C54	C55	1.363(8)
P1	C21	1.863(5)	C55	C56	1.381(6)
P2	C51	1.833(4)	C61	C62	1.382(6)
P2	C22	1.844(4)	C61	C66	1.389(6)
P2	C61	1.863(4)	C62	C63	1.391(7)
F1	C2	1.351(2)	C63	C64	1.369(8)
F1A	C2	1.352(2)	C64	C65	1.379(8)
F2	C2	1.351(2)	C65	C66	1.394(6)
F2A	C2	1.350(2)	C71	C72	1.414(6)
F3	C3	1.349(2)	C71	C75	1.430(5)
F4	C3	1.350(2)	C71	C76	1.453(10)
C1	C1	1.361(7)	C72	C73	1.416(6)
C1	C12	1.458(5)	C73	C74	1.428(6)
C1	C2	1.497(5)	C73	C76A	1.459(11)
C2	C3	1.532(4)	C74	C75	1.411(6)
C11	C12	1.378(5)			
C11	C15	1.496(5)			
C12	C13	1.441(5)			
C13	C14	1.371(5)			
C21	C22	1.521(6)			
C31	C32	1.385(6)			
C31	C36	1.405(6)			
C32	C33	1.401(6)			
C33	C34	1.378(8)			
C34	C35	1.364(9)			

Table S5. Interatomic distances (Å) and bond angles (deg) for **3'^{Fe}O**. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C14	Fe1	C75	135.39(16)	C51	P2	C61	100.32(19)
C14	Fe1	C74	156.24(16)	C22	P2	C61	101.43(19)
C75	Fe1	C74	39.25(16)	C51	P2	Fe1	118.86(14)
C14	Fe1	C72	91.12(15)	C22	P2	Fe1	109.17(13)
C75	Fe1	C72	65.11(16)	C61	P2	Fe1	120.50(14)
C74	Fe1	C72	65.48(16)	C1	C1	C12	129.7(2) 2
C14	Fe1	C71	98.29(15)	C1	C1	C2	111.12(19)
C75	Fe1	C71	39.62(15)	C12	C1	C2	119.1(3)
C74	Fe1	C71	66.54(16)	F1	C2	F2	108.5(12)
C72	Fe1	C71	38.97(17)	F2A	C2	F1A	104.8(10)
C14	Fe1	C73	118.67(16)	F1	C2	C1	114.3(9)
C75	Fe1	C73	65.79(17)	F2A	C2	C1	115.2(9)
C74	Fe1	C73	39.41(16)	F2	C2	C1	109.0(10)
C72	Fe1	C73	39.06(16)	F1A	C2	C1	109.5(8)
C71	Fe1	C73	66.32(17)	F1	C2	C3	115.1(9)
C14	Fe1	P1	92.72(11)	F2A	C2	C3	116.3(9)
C75	Fe1	P1	131.88(12)	F2	C2	C3	103.8(9)
C74	Fe1	P1	98.13(12)	F1A	C2	C3	104.9(7)
C72	Fe1	P1	126.88(13)	C1	C2	C3	105.5(3)
C71	Fe1	P1	161.80(12)	F3	C3	F4	107.7(7)
C73	Fe1	P1	95.68(13)	F3	C3	C2	118.0(9)
C14	Fe1	P2	83.88(11)	F3	C3	C2	113.8(12)
C75	Fe1	P2	95.77(13)	F4	C3	C2	106.5(11)
C74	Fe1	P2	117.67(12)	F3	C3	C2	113.8(12)
C72	Fe1	P2	146.32(13)	F3	C3	C2	118.0(9)
C71	Fe1	P2	108.77(13)	F4	C3	C2	106.5(11)
C73	Fe1	P2	157.08(12)	F4	C3	C2	103.6(8)
P1	Fe1	P2	86.70(5)	C2	C3	C2	106.1(4)
C11	S1	C14	95.60(18)	C12	C11	C15	129.7(3)
C31	P1	C41	98.88(18)	C12	C11	S1	109.2(3)
C31	P1	C21	104.4(2)	C15	C11	S1	121.0(3)
C41	P1	C21	102.42(19)	C11	C12	C13	112.2(3)
C31	P1	Fe1	120.28(15)	C11	C12	C1	123.2(3)
C41	P1	Fe1	117.16(13)	C13	C12	C1	124.5(3)
C21	P1	Fe1	111.38(14)	C14	C13	C12	116.6(3)
C51	P2	C22	104.16(18)	C13	C14	S1	106.4(2)

Table S5. Interatomic distances (Å) and bond angles (deg) for **3'^{Fe}O**. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C13	C14	Fe1	136.5(3)	C72	C71	C75	105.4(4)
S1	C14	Fe1	117.04(19)	C72	C71	C76	129.4(5)
C22	C21	P1	111.3(3)	C75	C71	C76	123.3(5)
C21	C22	P2	110.7(3)	C72	C71	Fe1	69.9(2)
C32	C31	C36	118.9(4)	C75	C71	Fe1	68.9(2)
C32	C31	P1	119.7(3)	C76	C71	Fe1	137.1(4)
C36	C31	P1	121.3(4)	C71	C72	C73	110.6(4)
C31	C32	C33	120.7(4)	C71	C72	Fe1	71.1(2)
C34	C33	C32	119.7(5)	C73	C72	Fe1	71.0(2)
C35	C34	C33	120.3(5)	C72	C73	C74	106.7(4)
C34	C35	C36	120.9(5)	C72	C73	C76A	125.2(5)
C31	C36	C35	119.3(5)	C74	C73	C76A	126.4(5)
C42	C41	C46	117.4(4)	C72	C73	Fe1	69.9(2)
C42	C41	P1	121.5(3)	C74	C73	Fe1	69.6(2)
C46	C41	P1	120.9(3)	C76A	C73	Fe1	136.9(5)
C43	C42	C41	121.4(4)	C75	C74	C73	107.6(3)
C44	C43	C42	120.7(5)	C75	C74	Fe1	69.8(2)
C43	C44	C45	119.2(4)	C73	C74	Fe1	71.0(2)
C44	C45	C46	120.5(4)	C74	C75	C71	109.7(4)
C41	C46	C45	120.8(4)	C74	C75	Fe1	71.0(2)
C52	C51	C56	117.1(4)	C71	C75	Fe1	71.5(2)
C52	C51	P2	119.2(3)				
C56	C51	P2	123.6(3)				
C53	C52	C51	121.7(5)				
C52	C53	C54	120.0(5)				
C55	C54	C53	119.2(5)				
C54	C55	C56	120.8(5)				
C55	C56	C51	121.2(5)				
C62	C61	C66	118.2(4)				
C62	C61	P2	120.7(3)				
C66	C61	P2	121.0(3)				
C61	C62	C63	121.2(5)				
C64	C63	C62	120.2(5)				
C63	C64	C65	119.6(5)				
C64	C65	C66	120.4(5)				
C61	C66	C65	120.4(5)				

Table S6. Interatomic distances (Å) and bond angles (deg) for DTE{RuCp(CO)$_2$}(μ-dppe).

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
Ru1	C131	1.825(10)	F6	C5	1.345(5)
Ru1	C114	2.064(10)	F6A	C5	1.355(5)
Ru1	C122	2.252(11)	O131	C131	1.174(11)
Ru1	C124	2.254(10)	O231	C231	1.184(11)
Ru1	C123	2.260(11)	C1	C2	1.336(12)
Ru1	C121	2.267(9)	C1	C112	1.464(12)
Ru1	C125	2.267(10)	C1	C5	1.510(12)
Ru1	P1	2.283(2)	C2	C212	1.451(12)
Ru2	C231	1.824(11)	C2	C3	1.487(12)
Ru2	C214	2.057(10)	C3	C4A	1.50(4)
Ru2	C224	2.240(8)	C3	C4	1.542(18)
Ru2	C225	2.254(9)	C4	C5	1.488(18)
Ru2	C222	2.262(10)	C4A	C5	1.53(5)
Ru2	C223	2.267(9)	C111	C112	1.389(12)
Ru2	C221	2.269(10)	C111	C115	1.488(14)
Ru2	P2	2.284(2)	C112	C113	1.435(12)
Cl1	C401	1.776(5)	C113	C114	1.386(12)
Cl2	C401	1.74(3)	C121	C122	1.399(15)
S1	C111	1.698(11)	C121	C125	1.413(15)
S1	C114	1.734(10)	C122	C123	1.397(16)
S2	C211	1.730(10)	C123	C124	1.433(16)
S2	C214	1.762(9)	C124	C125	1.413(16)
P1	C331	1.820(9)	C211	C212	1.376(12)
P1	C321	1.830(9)	C211	C215	1.498(13)
P1	C311	1.841(9)	C212	C213	1.435(13)
P2	C341	1.810(10)	C213	C214	1.379(12)
P2	C351	1.820(9)	C221	C222	1.400(14)
P2	C312	1.836(9)	C221	C225	1.431(14)
F1	C3	1.355(11)	C222	C223	1.415(15)
F2	C3	1.350(11)	C223	C224	1.435(14)
F3	C4	1.351(5)	C224	C225	1.414(15)
F3A	C4A	1.350(5)	C311	C312	1.522(12)
F4	C4	1.354(5)	C321	C326	1.391(13)
F4A	C4A	1.351(5)	C321	C322	1.404(12)
F5	C5	1.360(5)	C322	C323	1.368(13)
F5A	C5	1.349(5)	C323	C324	1.377(15)

Table S6. Interatomic distances (Å) and bond angles (deg) for DTE{RuCp(CO)$_2$}(μ-dppe). (cont'd.)

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
C324	C325	1.403(15)			
C325	C326	1.403(14)			
C331	C332	1.379(11)			
C331	C336	1.404(12)			
C332	C333	1.347(13)			
C333	C334	1.388(15)			
C334	C335	1.379(13)			
C335	C336	1.377(13)			
C341	C342	1.382(12)			
C341	C346	1.415(13)			
C342	C343	1.365(15)			
C343	C344	1.402(18)			
C344	C345	1.335(18)			
C345	C346	1.384(16)			
C351	C356	1.385(13)			
C351	C352	1.406(12)			
C352	C353	1.378(13)			
C353	C354	1.385(16)			
C354	C355	1.361(15)			
C355	C356	1.409(13)			

Table S6. Interatomic distances (Å) and bond angles (deg) for DTE{RuCp(CO)$_2$}(μ-dppe). (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C131	Ru1	C114	90.9(4)	C224	Ru2	C222	61.7(4)
C131	Ru1	C122	99.8(4)	C225	Ru2	C222	61.4(4)
C114	Ru1	C122	146.8(4)	C231	Ru2	C223	122.5(4)
C131	Ru1	C124	161.0(4)	C214	Ru2	C223	148.5(4)
C114	Ru1	C124	105.2(4)	C224	Ru2	C223	37.1(4)
C122	Ru1	C124	61.2(4)	C225	Ru2	C223	61.2(4)
C131	Ru1	C123	126.7(5)	C222	Ru2	C223	36.4(4)
C114	Ru1	C123	142.1(4)	C231	Ru2	C221	140.5(4)
C122	Ru1	C123	36.1(4)	C214	Ru2	C221	89.8(4)
C124	Ru1	C123	37.0(4)	C224	Ru2	C221	61.1(4)
C131	Ru1	C121	104.1(4)	C225	Ru2	C221	36.9(4)
C114	Ru1	C121	110.9(4)	C222	Ru2	C221	36.0(4)
C122	Ru1	C121	36.1(4)	C223	Ru2	C221	60.2(4)
C124	Ru1	C121	61.1(4)	C231	Ru2	P2	91.1(3)
C123	Ru1	C121	60.3(4)	C214	Ru2	P2	92.5(2)
C131	Ru1	C125	136.2(5)	C224	Ru2	P2	129.7(3)
C114	Ru1	C125	90.3(4)	C225	Ru2	P2	158.6(3)
C122	Ru1	C125	60.3(4)	C222	Ru2	P2	98.3(3)
C124	Ru1	C125	36.4(4)	C223	Ru2	P2	98.7(3)
C123	Ru1	C125	60.5(4)	C221	Ru2	P2	128.4(3)
C121	Ru1	C125	36.3(4)	C111	S1	C114	96.2(5)
C131	Ru1	P1	88.7(3)	C211	S2	C214	95.5(4)
C114	Ru1	P1	85.7(2)	C331	P1	C321	102.2(4)
C122	Ru1	P1	125.5(3)	C331	P1	C311	105.7(4)
C124	Ru1	P1	102.2(3)	C321	P1	C311	104.4(4)
C123	Ru1	P1	98.2(3)	C331	P1	Ru1	116.3(3)
C121	Ru1	P1	158.5(3)	C321	P1	Ru1	115.9(3)
C125	Ru1	P1	135.0(3)	C311	P1	Ru1	111.1(3)
C231	Ru2	C214	86.3(4)	C341	P2	C351	102.1(4)
C231	Ru2	C224	97.1(4)	C341	P2	C312	101.3(4)
C214	Ru2	C224	137.4(4)	C351	P2	C312	102.2(4)
C231	Ru2	C225	105.8(4)	C341	P2	Ru2	116.8(3)
C214	Ru2	C225	101.5(4)	C351	P2	Ru2	113.0(3)
C224	Ru2	C225	36.7(4)	C312	P2	Ru2	119.1(3)
C231	Ru2	C222	158.0(4)	C2	C1	C112	128.4(9)
C214	Ru2	C222	113.0(4)	C2	C1	C5	108.4(8)

Table S6. Interatomic distances (Å) and bond angles (deg) for DTE{RuCp(CO)$_2$}(μ-dppe). (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C112	C1	C5	123.2(8)	C112	C111	C115	130.0(10)
C1	C2	C212	128.8(9)	C112	C111	S1	109.5(8)
C1	C2	C3	111.2(8)	C115	C111	S1	120.1(8)
C212	C2	C3	120.0(8)	C111	C112	C113	112.2(8)
F2	C3	F1	103.8(8)	C111	C112	C1	125.7(9)
F2	C3	C2	113.8(8)	C113	C112	C1	122.1(8)
F1	C3	C2	113.7(8)	C114	C113	C112	115.4(8)
F2	C3	C4A	93.0(16)	C113	C114	S1	106.7(7)
F1	C3	C4A	123.2(12)	C113	C114	Ru1	130.8(7)
C2	C3	C4A	107.5(17)	S1	C114	Ru1	122.5(5)
F2	C3	C4	116.1(8)	C122	C121	C125	107.8(10)
F1	C3	C4	104.2(8)	C122	C121	Ru1	71.4(6)
C2	C3	C4	105.1(8)	C125	C121	Ru1	71.9(6)
F3	C4	F4	105.9(9)	C123	C122	C121	108.7(10)
F3	C4	C5	114.5(12)	C123	C122	Ru1	72.3(6)
F4	C4	C5	109.4(10)	C121	C122	Ru1	72.5(6)
F3	C4	C3	113.5(11)	C122	C123	C124	108.3(10)
F4	C4	C3	111.6(11)	C122	C123	Ru1	71.7(6)
C5	C4	C3	102.0(8)	C124	C123	Ru1	71.3(6)
F3A	C4A	F4A	111(2)	C125	C124	C123	106.4(10)
F3A	C4A	C3	117(3)	C125	C124	Ru1	72.3(6)
F4A	C4A	C3	116(3)	C123	C124	Ru1	71.7(6)
F3A	C4A	C5	95(3)	C124	C125	C121	108.7(11)
F4A	C4A	C5	114(4)	C124	C125	Ru1	71.3(6)
C3	C4A	C5	101.9(18)	C121	C125	Ru1	71.8(6)
F6	C5	F5	100.4(11)	O131	C131	Ru1	179.0(10)
F6	C5	C4	115.2(10)	C212	C211	C215	128.2(9)
F5A	C5	C4	132.5(17)	C212	C211	S2	109.3(7)
F6A	C5	C4	78.5(13)	C215	C211	S2	122.5(7)
F5	C5	C4	107.9(8)	C211	C212	C213	112.5(8)
F6	C5	C1	114.2(9)	C211	C212	C2	122.0(9)
F5A	C5	C1	120.9(17)	C213	C212	C2	125.3(8)
F6A	C5	C1	99.7(13)	C214	C213	C212	116.9(9)
F5	C5	C1	112.5(9)	C213	C214	S2	105.8(7)
C4	C5	C1	106.5(8)	C213	C214	Ru2	131.3(7)
C1	C5	C4A	107.8(15)	S2	C214	Ru2	122.7(5)

Table S6. Interatomic distances (Å) and bond angles (deg) for DTE{RuCp(CO)$_2$}(μ-dppe). (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
C222	C221	C225	109.0(10)	C346	C341	P2	119.4(7) .
C222	C221	Ru2	71.7(6)	C343	C342	C341	121.9(10)
C225	C221	Ru2	71.0(6)	C342	C343	C344	119.0(11)
C221	C222	C223	107.8(9)	C345	C344	C343	120.0(12)
C221	C222	Ru2	72.2(6)	C344	C345	C346	122.2(12)
C223	C222	Ru2	72.0(5)	C345	C346	C341	118.6(10)
C222	C223	C224	108.1(9)	C356	C351	C352	119.4(8)
C222	C223	Ru2	71.6(6)	C356	C351	P2	118.8(7) .
C224	C223	Ru2	70.4(5)	C352	C351	P2	121.5(7) .
C225	C224	C223	107.7(9)	C353	C352	C351	119.8(9)
C225	C224	Ru2	72.2(5)	C352	C353	C354	121.1(9)
C223	C224	Ru2	72.5(5)	C355	C354	C353	119.1(9)
C224	C225	C221	107.3(9)	C354	C355	C356	121.5(10)
C224	C225	Ru2	71.1(5)	C351	C356	C355	119.1(9)
C221	C225	Ru2	72.1(5)	Cl2	C401	Cl1	100.2(15) .
O231	C231	Ru2	178.0(9)				
C312	C311	P1	120.2(6)				
C311	C312	P2	112.5(6)				
C326	C321	C322	117.4(8)				
C326	C321	P1	120.5(7)				
C322	C321	P1	122.1(7)				
C323	C322	C321	121.7(9)				
C322	C323	C324	120.9(9)				
C323	C324	C325	119.1(9)				
C324	C325	C326	119.7(10)				
C321	C326	C325	121.0(9)				
C332	C331	C336	117.4(9)				
C332	C331	P1	120.6(7)				
C336	C331	P1	121.4(7)				
C333	C332	C331	122.9(10)				
C332	C333	C334	119.9(9)				
C335	C334	C333	118.9(10)				
C336	C335	C334	120.8(9)				
C335	C336	C331	120.0(8)				
C342	C341	C346	118.2(9)				
C342	C341	P2	122.2(7)				

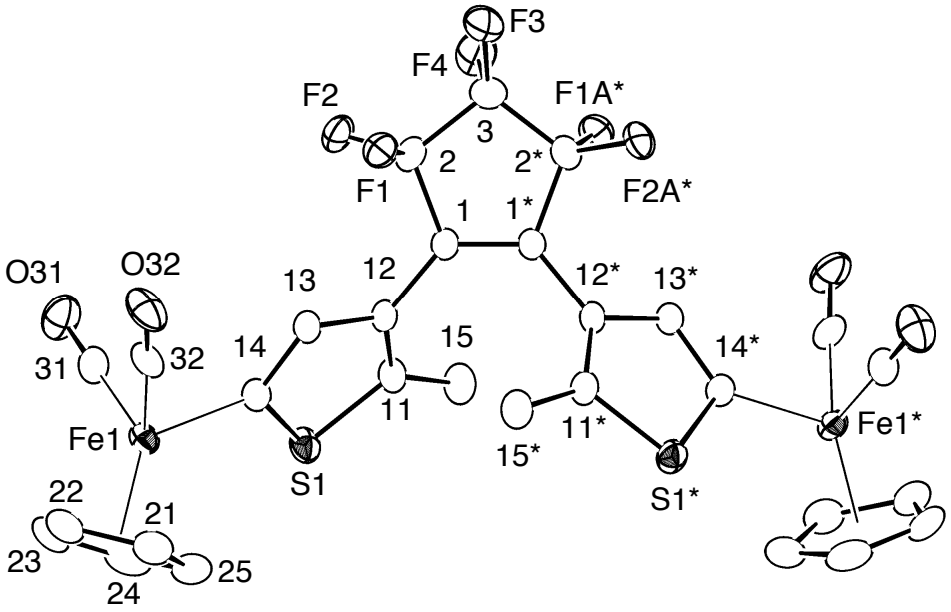

Figure S1. Molecular structure of **1^{Fe}O** drawn with thermal ellipsoids at the 30 % probability level. Labels without atom names are for carbon atoms.

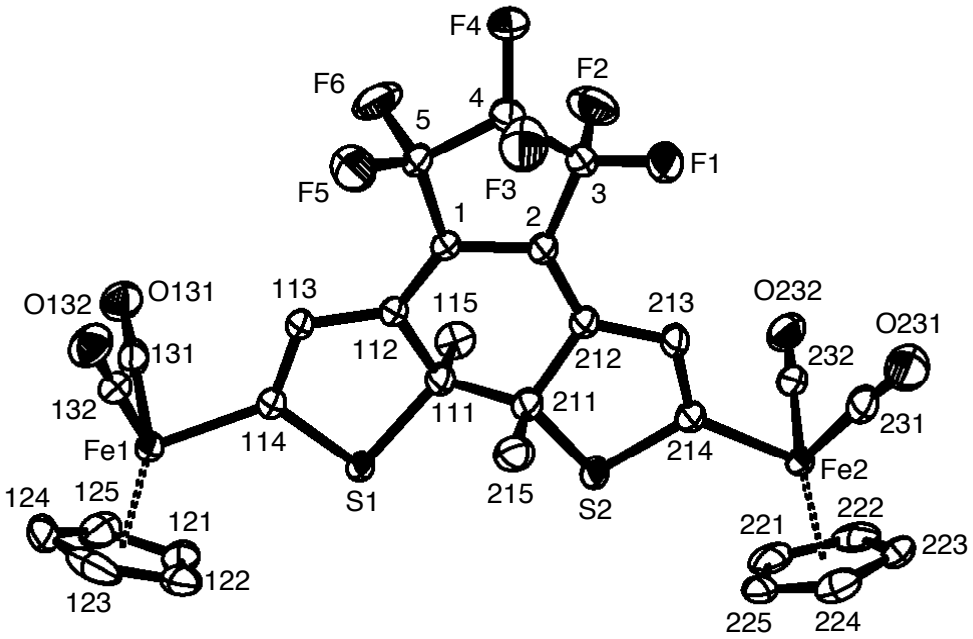

Figure S2. Molecular structure of **1^{Fe}C** drawn with thermal ellipsoids at the 30 % probability level. Labels without atom names are for carbon atoms.

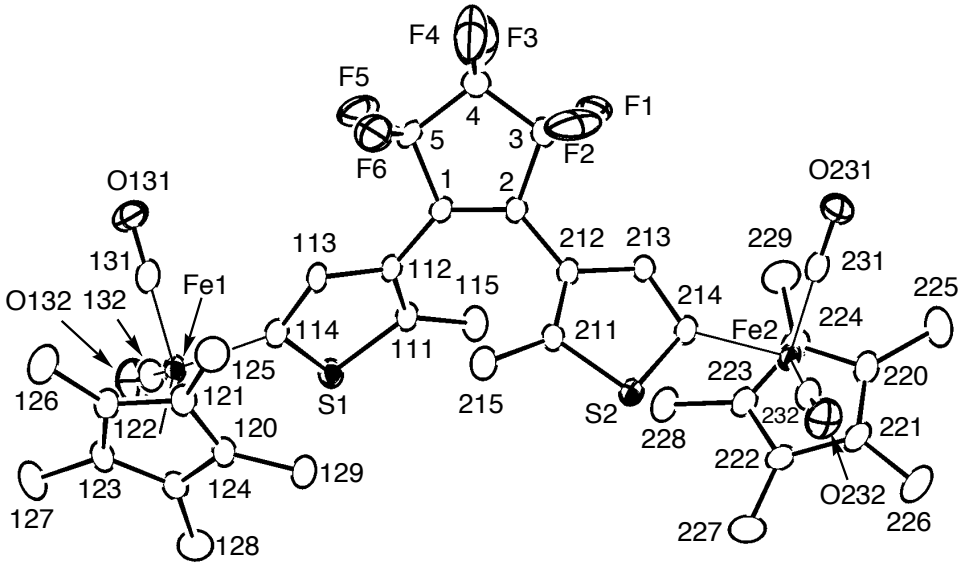

Figure S3. Molecular structure of **1*^{Fe}O** drawn with thermal ellipsoids at the 30 % probability level. Labels without atom names are for carbon atoms.

Figure S4. Molecular structure of **3'^{Fe}O** drawn with thermal ellipsoids at the 30 % probability level. Labels without atom names are for carbon atoms.

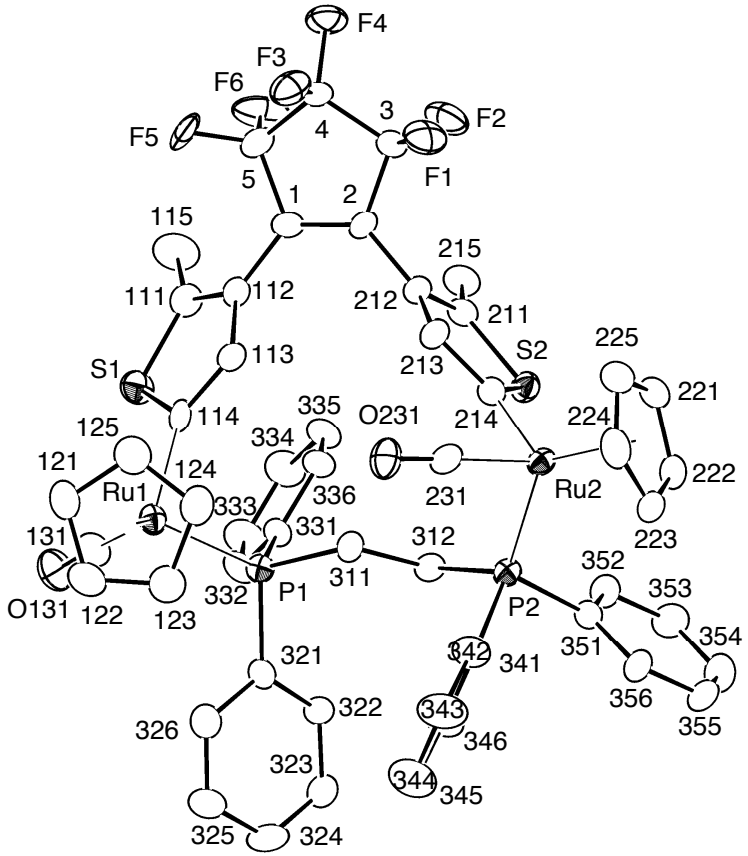

Figure S5. Molecular structure of DTE{RuCp(CO)}$_2$(μ-dppe) drawn with thermal ellipsoids at the 30 % probability level. Labels without atom names are for carbon atoms.

Table S7. Cartesian coordinates for $\mathbf{1}^{\mathbf{Fe}}\mathbf{O}$ obtained by TDDFT analysis.

# Atom	x	y	z
C	-0.16168300	0.66228600	1.82839100
C	0.16168300	-0.66228600	1.82839100
C	-0.21003900	1.21642300	3.23227100
C	0.21003900	-1.21642300	3.23227100
C	0.00000000	0.00000000	4.18967100
C	-0.49029200	1.54335900	0.70009300
C	0.49029200	-1.54335900	0.70009300
C	-1.36879800	1.20649400	-0.31334400
C	1.36879800	-1.20649400	-0.31334400
C	0.02065900	2.89165900	0.57083200
C	-0.02065900	-2.89165900	0.57083200
C	-0.41655800	3.57910400	-0.53219100
C	0.41655800	-3.57910400	-0.53219100
S	-1.52818200	2.54765300	-1.41725300
S	1.52818200	-2.54765300	-1.41725300
C	-2.16174300	-0.05008700	-0.52205300
C	2.16174300	0.05008700	-0.52205300
F	-1.39056500	1.84577100	3.50524100
F	1.39056500	-1.84577100	3.50524100
F	0.77795600	2.14966900	3.44801600
F	-0.77795600	-2.14966900	3.44801600
H	0.71604400	3.30756400	1.29134600
H	-0.71604400	-3.30756400	1.29134600
H	-3.10114800	0.15847900	-1.04595100
H	3.10114800	-0.15847900	-1.04595100
H	-1.60197500	-0.79067700	-1.10772200
H	1.60197500	0.79067700	-1.10772200
H	-2.40724600	-0.51703200	0.43773500
H	2.40724600	0.51703200	0.43773500
F	-1.08034800	-0.17982400	4.98710300
F	1.08034800	0.17982400	4.98710300
Fe	0.06590900	5.36275900	-1.24310500
Fe	-0.06590900	-5.36275900	-1.24310500
C	-1.64270100	5.82433200	-1.23937900
C	1.64270100	-5.82433200	-1.23937900
O	-2.74889900	6.14143600	-1.24808000
O	2.74889900	-6.14143600	-1.24808000
C	0.37332000	5.09612900	-3.36068200
C	-0.37332000	-5.09612900	-3.36068200

Table S7. Cartesian coordinates for **1^{Fe}O** obtained by TDDFT analysis. (cont'd.)

# Atom	x	y	z
C	1.37051400	4.35883200	-2.66479800
C	-1.37051400	-4.35883200	-2.66479800
C	2.13120800	5.26097400	-1.87570800
C	-2.13120800	-5.26097400	-1.87570800
C	1.62304400	6.58625900	-2.11418200
C	-1.62304400	-6.58625900	-2.11418200
C	0.54659100	6.48452200	-3.02690000
C	-0.54659100	-6.48452200	-3.02690000
H	-0.36375800	4.68920800	-4.03999800
H	0.36375800	-4.68920800	-4.03999800
H	1.48203500	3.28387300	-2.67731600
H	-1.48203500	-3.28387300	-2.67731600
H	2.95456200	5.00064900	-1.22393000
H	-2.95456200	-5.00064900	-1.22393000
H	1.98961600	7.49880000	-1.66184000
H	-1.98961600	-7.49880000	-1.66184000
H	-0.05597800	7.30604000	-3.39282000
H	0.05597800	-7.30604000	-3.39282000
C	-0.34295400	-5.92636800	0.41026800
O	-0.54416100	-6.30837000	1.47674300
C	0.34295400	5.92636800	0.41026800
O	0.54416100	6.30837000	1.47674300

Table S8. Cartesian coordinates for **1^{Ru}O** obtained by TDDFT analysis.

# Atom	x	y	z
C	0.39210000	0.55739000	1.97570900
C	-0.39210000	-0.55739000	1.97570900
C	0.77887900	0.95797000	3.37950100
C	-0.77887900	-0.95797000	3.37950100
C	0.00000000	0.00000000	4.33695400
C	0.83741200	1.38582100	0.84733700
C	-0.83741200	-1.38582100	0.84733700
C	0.00000000	1.83434400	-0.15751100
C	0.00000000	-1.83434400	-0.15751100
C	2.18912500	1.88678500	0.71502500
C	-2.18912500	-1.88678500	0.71502500
C	2.40597200	2.67741500	-0.38272500
C	-2.40597200	-2.67741500	-0.38272500
S	0.89663700	2.84816800	-1.25865100
S	-0.89663700	-2.84816800	-1.25865100
C	-1.46891800	1.60536300	-0.36110500
C	1.46891800	-1.60536300	-0.36110500
F	0.47783600	2.26120600	3.65247200
F	-0.47783600	-2.26120600	3.65247200
F	2.13156900	0.82599700	3.59323300
F	-2.13156900	-0.82599700	3.59323300
H	2.96607100	1.63536800	1.42781400
H	-2.96607100	-1.63536800	1.42781400
H	-1.93184300	2.45102600	-0.88165500
H	1.93184300	-2.45102600	-0.88165500
H	-1.66122800	0.69750100	-0.94726900
H	1.66122800	-0.69750100	-0.94726900
H	-1.97833300	1.48215400	0.60060000
H	1.97833300	-1.48215400	0.60060000
F	-0.84567400	0.69602800	5.13403100
F	0.84567400	-0.69602800	5.13403100
Ru	4.16255400	3.53091600	-1.13259000
Ru	-4.16255400	-3.53091600	-1.13259000
C	3.33462200	5.23263900	-1.11580000
C	-3.33462200	-5.23263900	-1.11580000
O	2.85559400	6.28192900	-1.13686700
O	-2.85559400	-6.28192900	-1.13686700
C	4.23415100	2.98388000	-3.39607400
C	-4.23415100	-2.98388000	-3.39607400

Table S8. Cartesian coordinates for **1^{Ru}O** obtained by TDDFT analysis. (cont'd.)

# Atom	x	y	z
C	4.30255500	1.76114800	-2.66855200
C	-4.30255500	-1.76114800	-2.66855200
C	5.49203200	1.76487700	-1.88895800
C	-5.49203200	-1.76487700	-1.88895800
C	6.19781300	2.99010300	-2.17315800
C	-6.19781300	-2.99010300	-2.17315800
C	5.42756200	3.73539500	-3.09805800
C	-5.42756200	-3.73539500	-3.09805800
H	3.45712300	3.26855100	-4.09297500
H	-3.45712300	-3.26855100	-4.09297500
H	3.54658600	0.98769100	-2.66337900
H	-3.54658600	-0.98769100	-2.66337900
H	5.83031000	0.96941500	-1.23816700
H	-5.83031000	-0.96941500	-1.23816700
H	7.15178600	3.28484600	-1.75529500
H	-7.15178600	-3.28484600	-1.75529500
H	5.68843500	4.70158800	-3.51045800
H	-5.68843500	-4.70158800	-3.51045800
C	-4.76449100	-3.75692000	0.64817800
O	-5.17127700	-3.88447300	1.71959000
C	4.76449100	3.75692000	0.64817800
O	5.17127700	3.88447300	1.71959000

Table S9. Cartesian coordinates for **2$^{\#Fe}$O** obtained by TDDFT analysis.

# Atom	x	y	z
C	0.06454500	-0.68014200	1.29219100
C	-0.06454500	0.68014200	1.29219100
C	0.02406500	1.22901300	2.69477400
C	0.00000000	0.00000000	3.64634500
C	-0.02406500	-1.22901300	2.69477400
C	0.29819300	-1.62268200	0.19778700
C	1.16556000	-1.41255300	-0.86120400
C	-0.26516000	-2.95430400	0.19370600
C	0.13479400	-3.77772200	-0.83007200
C	-0.29819300	1.62268200	0.19778700
C	-1.16556000	1.41255300	-0.86120400
C	0.26516000	2.95430400	0.19370600
C	-0.13479400	3.77772200	-0.83007200
S	1.24728700	-2.85863200	-1.83420200
S	-1.24728700	2.85863200	-1.83420200
C	-1.99870300	0.21259600	-1.19767800
C	1.99870300	-0.21259600	-1.19767800
F	-0.98909000	2.09230000	2.99722400
F	1.18969500	1.93059900	2.89318100
F	0.98909000	-2.09230000	2.99722400
F	-1.18969500	-1.93059900	2.89318100
H	-0.96978200	-3.26931000	0.95371900
H	0.96978200	3.26931000	0.95371900
H	-2.89967400	0.49911600	-1.75060300
H	-1.44306200	-0.51224200	-1.80694900
H	-2.30869500	-0.31008200	-0.28651700
H	2.89967400	-0.49911600	-1.75060300
H	1.44306200	0.51224200	-1.80694900
H	2.30869500	0.31008200	-0.28651700
F	1.09639700	-0.03084400	4.43790800
F	-1.09639700	0.03084400	4.43790800
Fe	0.39545200	5.63953700	-1.19746000
C	-0.91443500	5.95861800	-2.31155600
O	-1.74826800	6.22068700	-3.07324000
Fe	-0.39545200	-5.63953700	-1.19746000
C	0.91443500	-5.95861800	-2.31155600
O	1.74826800	-6.22068700	-3.07324000
P	-0.86667900	6.23000000	0.55407000
P	0.86667900	-6.23000000	0.55407000
C	-2.56759100	5.51862200	0.60773400

Table S9. Cartesian coordinates for **2$^{\#Fe}$O** obtained by TDDFT analysis. (cont'd.)

# Atom	x	y	z
C	-0.23054500	5.83870600	2.24532500
C	-1.21139300	8.04744700	0.68172200
C	1.21139300	-8.04744700	0.68172200
C	2.56759100	-5.51862200	0.60773400
C	0.23054500	-5.83870600	2.24532500
H	-0.89495300	6.25564300	3.01055900
H	0.77086400	6.25931000	2.37968300
H	-0.17689000	4.75530900	2.37712500
H	-1.70346200	8.38835500	-0.23482400
H	-0.27378600	8.60188700	0.78798700
H	-1.85589200	8.27520700	1.53826500
H	-3.10249400	5.76225500	-0.31496200
H	-2.49910000	4.43119300	0.68664900
H	-3.12692900	5.91299700	1.46302100
H	0.89495300	-6.25564300	3.01055900
H	0.17689000	-4.75530900	2.37712500
H	-0.77086400	-6.25931000	2.37968300
H	2.49910000	-4.43119300	0.68664900
H	3.10249400	-5.76225500	-0.31496200
H	3.12692900	-5.91299700	1.46302100
H	0.27378600	-8.60188700	0.78798700
H	1.85589200	-8.27520700	1.53826500
H	1.70346200	-8.38835500	-0.23482400
C	1.95448700	5.87220000	-2.67473000
C	-1.95448700	-5.87220000	-2.67473000
C	-2.37147400	-4.92280300	-1.71091800
C	2.37147400	4.92280300	-1.71091800
C	-2.42026400	-5.56408300	-0.43874000
C	2.42026400	5.56408300	-0.43874000
C	-2.05364900	-6.93146100	-0.63275700
C	2.05364900	6.93146100	-0.63275700
C	-1.75662200	-7.12805300	-2.00332000
C	1.75662200	7.12805300	-2.00332000
H	-1.44382100	-8.05570900	-2.46396600
H	-1.99853200	-7.68814000	0.13960600
H	-2.71021300	-5.10430100	0.49588700
H	-2.55639600	-3.87459500	-1.89619500
H	-1.80622300	-5.68469400	-3.72984300
H	1.80622300	5.68469400	-3.72984300
H	2.55639600	3.87459500	-1.89619500

Table S9. Cartesian coordinates for **2$^{\#Fe}$O** obtained by TDDFT analysis. (cont'd.)

# Atom	x	y	z
H	2.71021300	5.10430100	0.49588700
H	1.99853200	7.68814000	0.13960600
H	1.44382100	8.05570900	-2.46396600

Table S10. Cartesian coordinates for **2$^{\#Ru}$O** obtained by TDDFT analysis.

# Atom	x	y	z
C	0.08108800	-0.67833100	1.39798500
C	-0.08108800	0.67833100	1.39798500
C	-0.00510400	1.22939700	2.80064600
C	0.00000000	0.00000000	3.75209500
C	0.00510400	-1.22939700	2.80064600
C	0.33921300	-1.61480600	0.30388900
C	1.20364300	-1.38388100	-0.75257100
C	-0.18818400	-2.96131000	0.30349400
C	0.23775000	-3.76931500	-0.72144500
C	-0.33921300	1.61480600	0.30388900
C	-1.20364300	1.38388100	-0.75257100
C	0.18818400	2.96131000	0.30349400
C	-0.23775000	3.76931500	-0.72144500
S	1.32930000	-2.82746200	-1.72581900
S	-1.32930000	2.82746200	-1.72581900
C	-2.00700500	0.16319100	-1.08663200
C	2.00700500	-0.16319100	-1.08663200
F	-1.03763100	2.06866400	3.10327900
F	1.14428000	1.95776000	2.99768600
F	1.03763100	-2.06866400	3.10327900
F	-1.14428000	-1.95776000	2.99768600
H	-0.88360600	-3.29571300	1.06357300
H	0.88360600	3.29571300	1.06357300
H	-2.91830600	0.42665100	-1.63408400
H	-1.43586900	-0.54590600	-1.70003200
H	-2.29787600	-0.36825300	-0.17426300
H	2.91830600	-0.42665100	-1.63408400
H	1.43586900	0.54590600	-1.70003200
H	2.29787600	0.36825300	-0.17426300
F	1.09684100	-0.00490500	4.54355100
F	-1.09684100	0.00490500	4.54355100
Ru	0.32578800	5.73254400	-1.12317600
C	-1.11672400	6.02632300	-2.26851600
O	-1.97398000	6.26289700	-3.01857100
Ru	-0.32578800	-5.73254400	-1.12317600
C	1.11672400	-6.02632300	-2.26851600
O	1.97398000	-6.26289700	-3.01857100
P	-0.99825000	6.30100900	0.70678900
P	0.99825000	-6.30100900	0.70678900
C	-2.69150600	5.57298100	0.76077500

Table S10. Cartesian coordinates for **2$^{\#Ru}$O** obtained by TDDFT analysis.

# Atom	x	y	z
C	-0.33504800	5.87104600	2.37747100
C	-1.34507000	8.11132400	0.87525800
C	1.34507000	-8.11132400	0.87525800
C	2.69150600	-5.57298100	0.76077500
C	0.33504800	-5.87104600	2.37747100
H	-0.99769300	6.25329700	3.16243300
H	0.66049800	6.30519700	2.51106200
H	-0.26212800	4.78485300	2.47459900
H	-1.85438400	8.46829600	-0.02515900
H	-0.40444700	8.66147500	0.97435800
H	-1.97341900	8.31809100	1.74938500
H	-3.24217600	5.85005400	-0.14294900
H	-2.61206600	4.48377100	0.79460600
H	-3.23948500	5.92778700	1.64054000
H	0.99769300	-6.25329700	3.16243300
H	0.26212800	-4.78485300	2.47459900
H	-0.66049800	-6.30519700	2.51106200
H	2.61206600	-4.48377100	0.79460600
H	3.24217600	-5.85005400	-0.14294900
H	3.23948500	-5.92778700	1.64054000
H	0.40444700	-8.66147500	0.97435800
H	1.97341900	-8.31809100	1.74938500
H	1.85438400	-8.46829600	-0.02515900
C	2.12150800	5.85011000	-2.61621300
C	-2.12150800	-5.85011000	-2.61621300
C	-2.52052300	-5.02084700	-1.53538500
C	2.52052300	5.02084700	-1.53538500
C	-2.52652600	-5.80298100	-0.34379400
C	2.52652600	5.80298100	-0.34379400
C	-2.15986800	-7.14520000	-0.70548400
C	2.15986800	7.14520000	-0.70548400
C	-1.90783500	-7.17613500	-2.09853200
C	1.90783500	7.17613500	-2.09853200
H	-1.61930100	-8.04408600	-2.67673800
H	-2.10558600	-7.99140800	-0.03265300
H	-2.82598800	-5.46436600	0.63869400
H	-2.73061000	-3.96191600	-1.59615700
H	-2.02681700	-5.54690500	-3.65021700
H	2.02681700	5.54690500	-3.65021700
H	2.73061000	3.96191600	-1.59615700

Table S10. Cartesian coordinates for **2$^{\#Ru}$O** obtained by TDDFT analysis.

# Atom	x	y	z
H	2.82598800	5.46436600	0.63869400
H	2.10558600	7.99140800	-0.03265300
H	1.61930100	8.04408600	-2.67673800

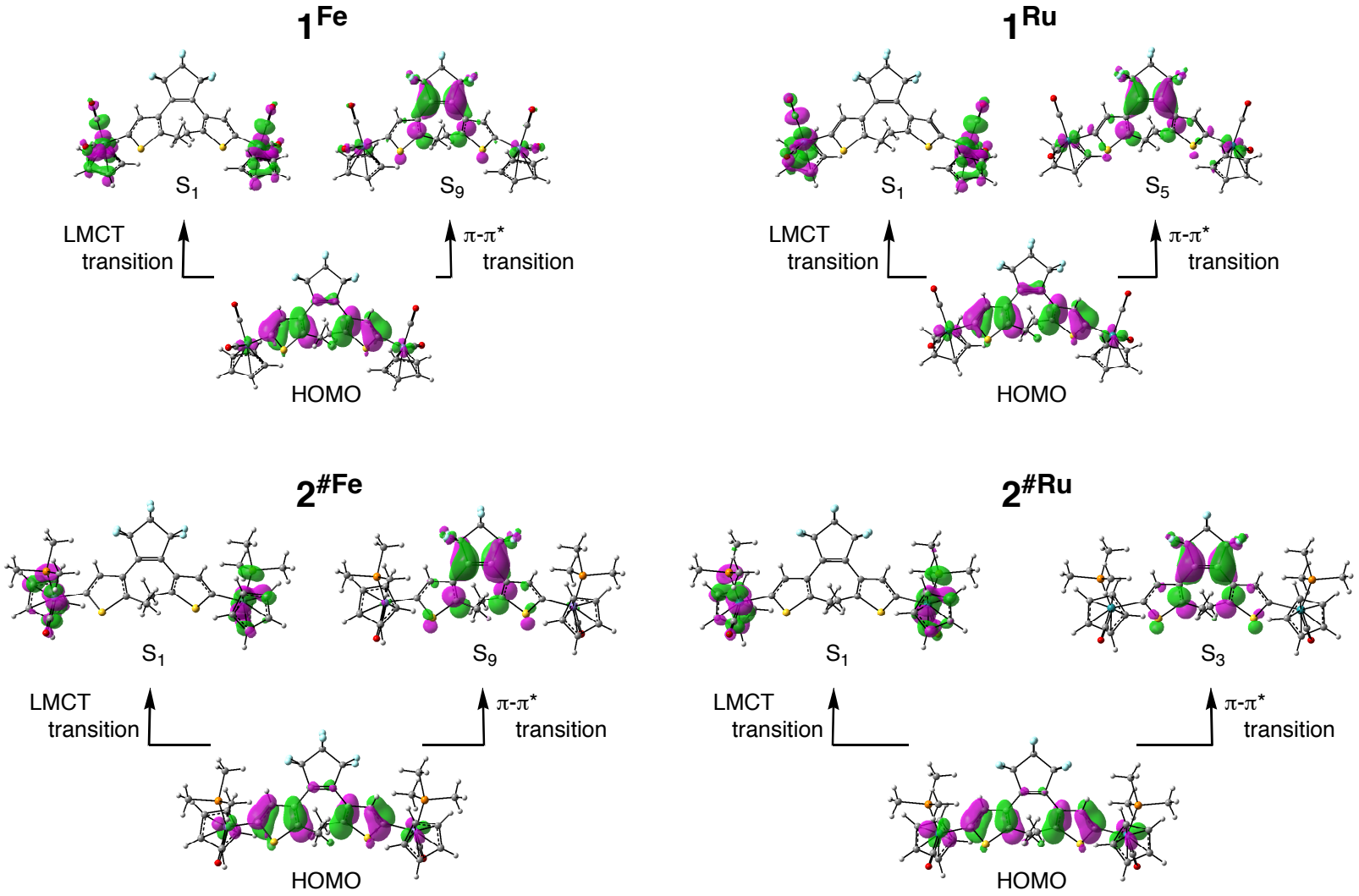

Figure S6. Ground states and the lowest metal- and ligand-based singlet excited states for $\mathbf{1^{Fe}O}$, $\mathbf{1^{Ru}O}$, $\mathbf{2^{\#Fe}O}$ and $\mathbf{2^{\#Ru}O}$.