Electronic Supplementary Information

Synthesis, Electronic Structure, and Redox Properties of the Diruthenium Sandwich Complexes $[Cp^*Ru(\mu\text{-}C_{10}H_8)RuCp^*]^x$ ($x = 0, 1+$; $C_{10}H_8$ = naphthalene)

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Contents:

1. Crystallographic details

Table S1. Crystal and structure refinement data of [**1**], [**1**]BAr^F_4, and [**3**]PF_6.

Compound	**1**	[**1**]BAr^F_4	[**3**]PF_6
Empirical formula	$C_{30}H_{38}Ru_2$	$C_{124}H_{100}B_2F_{48}Ru_4$	$C_{34}H_{47}OF_6PRu_2$
Formula weight	600.74	2927.93	818.82
Temperature/K	123.0(1)	123.1(2)	123.0(6)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	8.6703(3)	10.52733(11)	12.2572(3)
b/Å	11.0228(3)	23.1371(2)	12.5519(3)
c/Å	13.1457(4)	24.6760(3)	12.7014(4)
α/°	90	87.0962(9)	115.951(3)
β/°	91.186(3)	89.0569(9)	100.575(3)
γ/°	90	87.5307(9)	98.837(2)
Volume/Å^3	1256.08(7)	5996.46(12)	1665.66(9)
Z	2	2	2
ρ_{calc}g/cm^3	1.588	1.622	1.633
μ/mm^{-1}	9.828	5.110	8.316
F(000)	612.0	2924.0	832.0
Crystal size/mm^3	0.2 × 0.2 × 0.1	0.1815 × 0.1278 × 0.09	0.2198 × 0.1267 × 0.0755
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.474 to 153.056	7.174 to 133.508	7.608 to 133.61
Index ranges	$-10 \le h \le 10$, $-13 \le k \le 13$, $0 \le l \le 16$	$-12 \le h \le 12$, $-19 \le k \le 27$, $-29 \le l \le 29$	$-14 \le h \le 14$, $-14 \le k \le 14$, $-15 \le l \le 14$
Reflections collected	2565	67884	24105
Independent reflections	2565 [R_{int} = ?, R_{sigma} = 0.0304]	21059 [R_{int} = 0.0348, R_{sigma} = 0.0347]	5844 [R_{int} = 0.0305, R_{sigma} = 0.0241]
Data/restraints/parameters	2565/0/147	21059/0/1623	5844/48/448
Goodness-of-fit on F^2	1.085	1.047	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0548, wR_2 = 0.1448	R_1 = 0.0359, wR_2 = 0.0869	R_1 = 0.0200, wR_2 = 0.0466
Final R indexes [all data]	R_1 = 0.0572, wR_2 = 0.1457	R_1 = 0.0442, wR_2 = 0.0936	R_1 = 0.0220, wR_2 = 0.0475
Largest diff. peak/hole / e Å^{-3}	2.22/–1.55	2.71/–0.86	0.67/–0.42

2. NMR spectra

[Cp*Ru(μ-$C_{10}H_8$)RuCp*] (1)

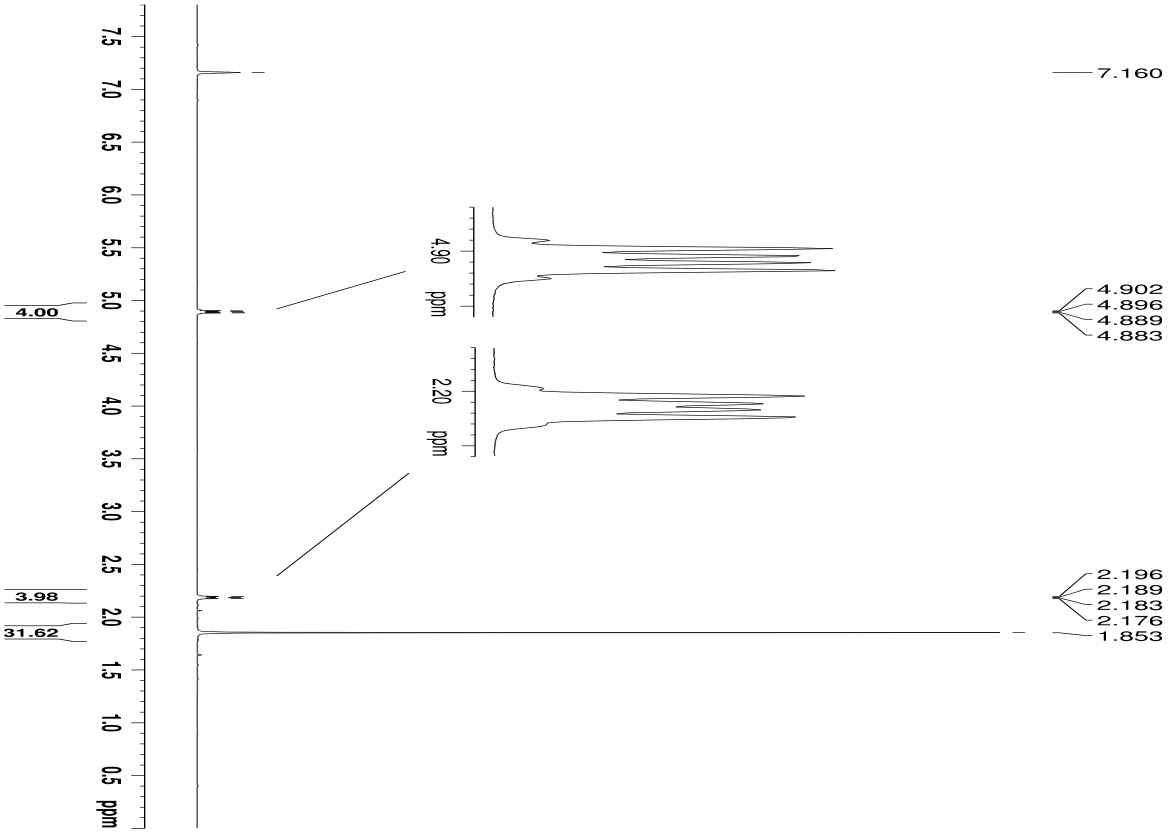

Figure S1. ^{1}H NMR spectrum of **1** (300 K, 300.13 MHz, C_6D_6).

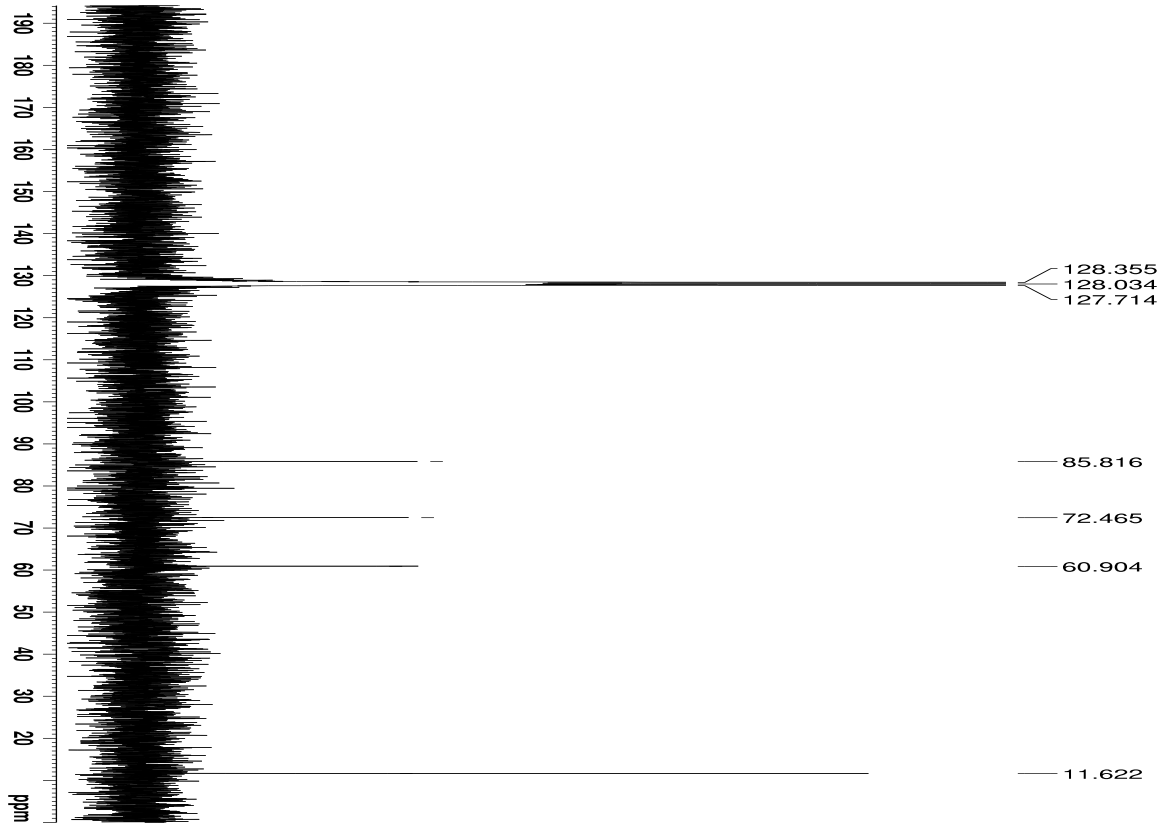

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1** (300 K, 75.47 MHz, C_6D_6).

[Cp*Ru(μ-$C_{10}H_8$)RuCp*]BAr^F_4 ([1]BAr^F_4)

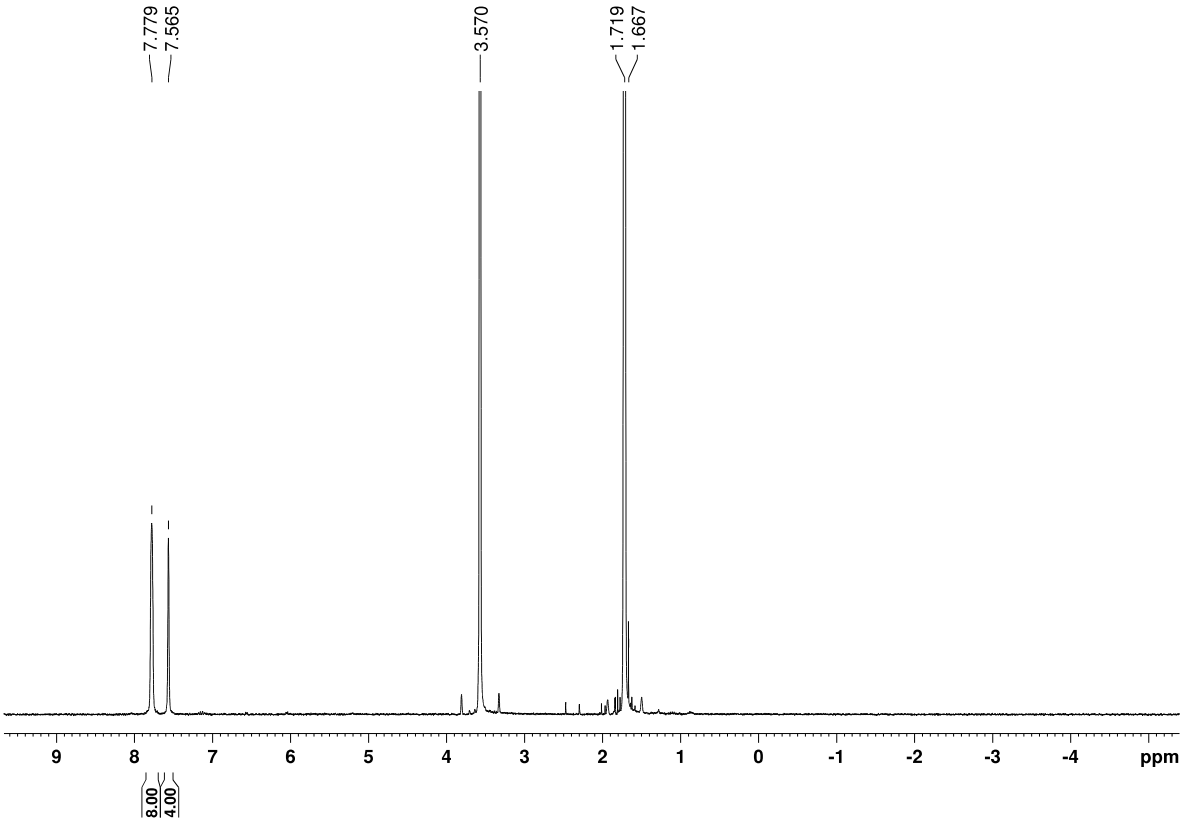

Figure S3. ^{1}H NMR spectrum of [**1**]BAr^F_4 (300 K, 300.13 MHz, THF-d_8).

[Cp*Ru(μ-$C_{10}H_8$)Ru(H)Cp*]BAr^F_4 ([3]BAr^F_4)

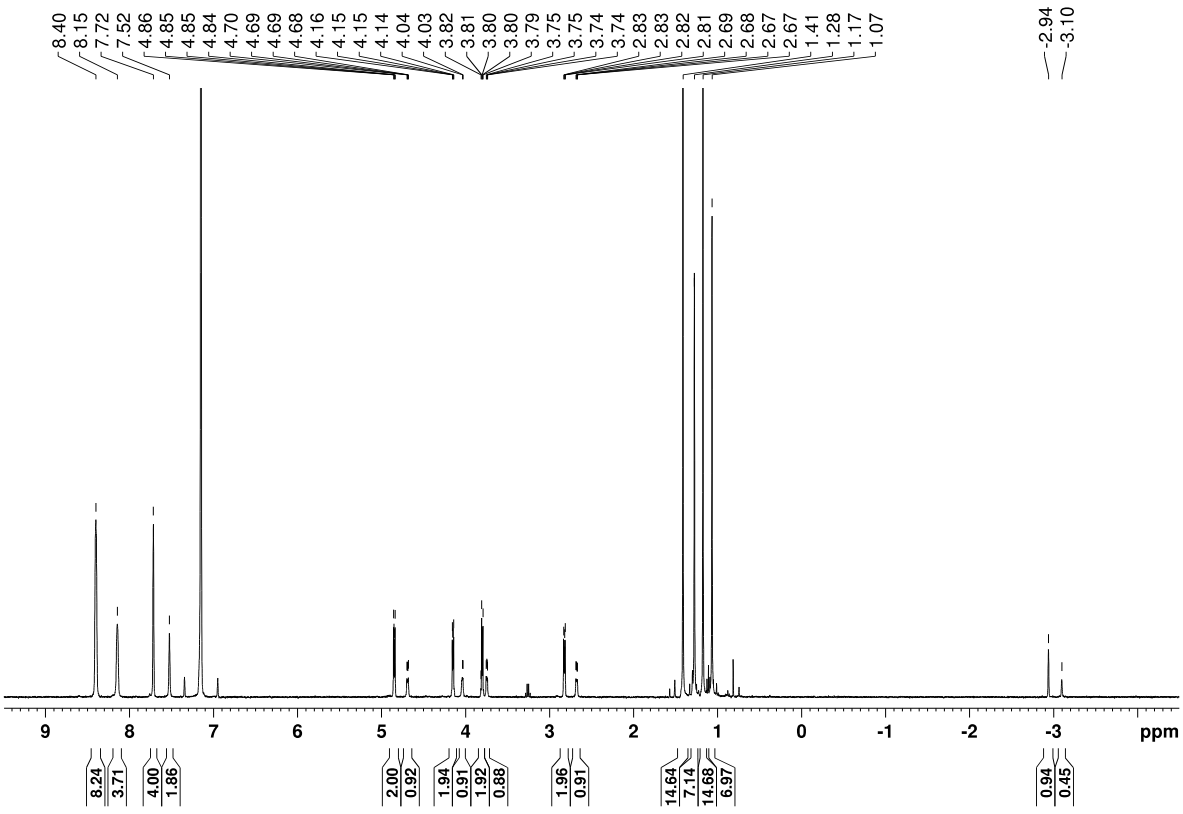

Figure S4. ^{1}H NMR spectrum of [**3**]BAr^F_4 (300 K, 400.13 MHz, C_6D_6).

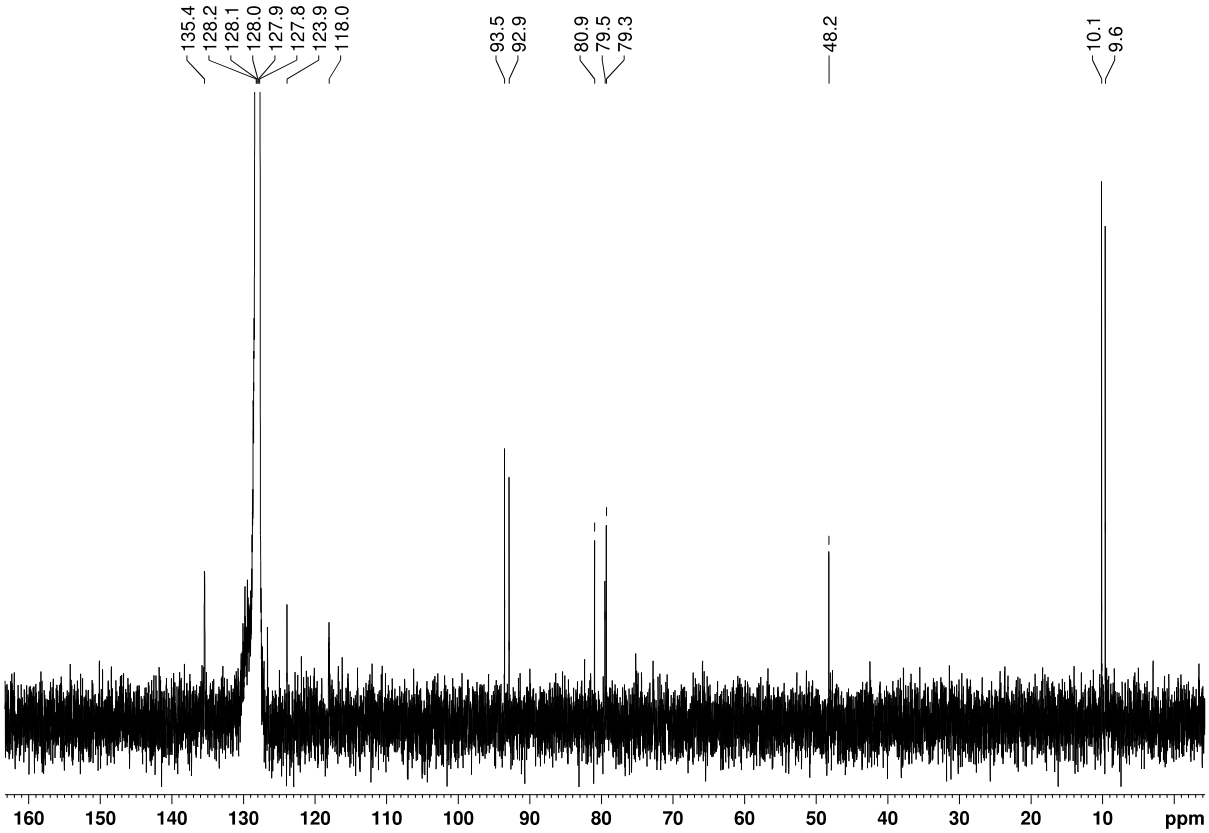

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of [**3**]BAr^{F}_{4} (300 K, 100.61 MHz, C_6D_6).

3. UV-vis spectra of [1] and [1]BAr^F_4

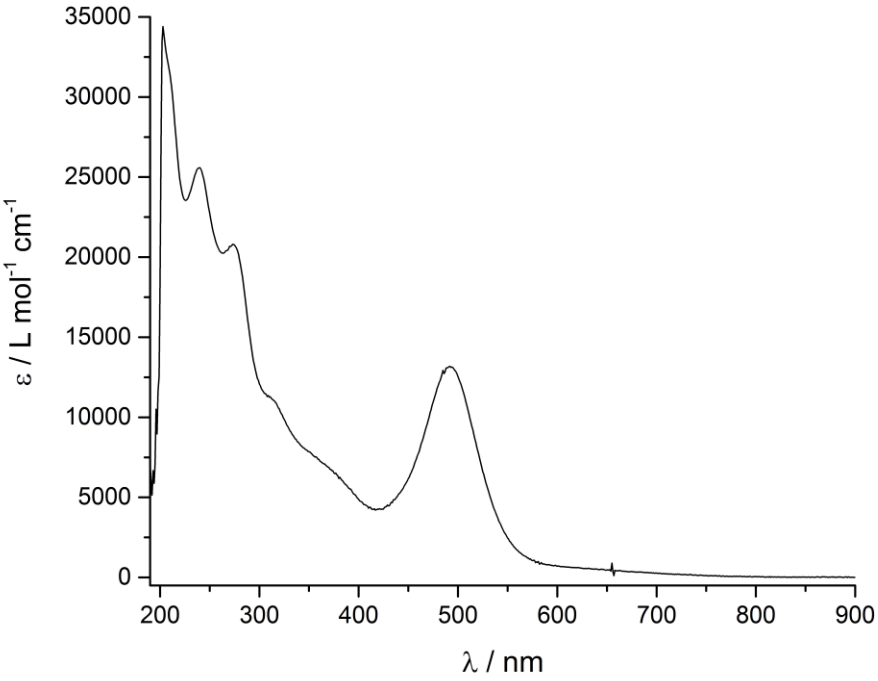

Figure S6. UV-vis spectrum of [**1**] in Et_2O ($c = 1.747 \cdot 10^{-5}$ mol L^{-1}).

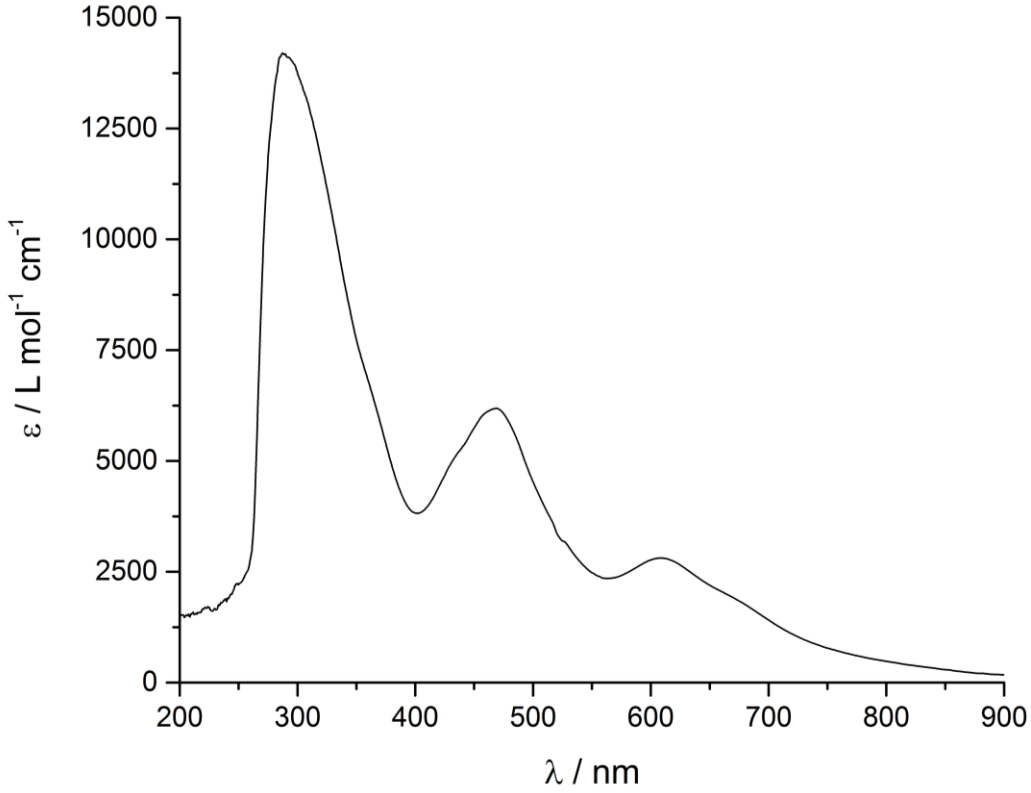

Figure S7. UV-vis spectrum of [**1**]BAr^F_4 in Et_2O ($c = 1.976 \cdot 10^{-4}$ mol L^{-1}).

4. DFT calculations

Computational methods

Geometry optimizations of [**1**], [**1**]$^{+}$, and [**3**] were performed with the Gaussian09 program package (Revision E.01).[1] The BP86 density functional[2] and the Ahlrichs def2-TZVP basis set[3] were employed for all atoms. Atom-pairwise dispersion correction to the DFT energy with Becke–Johnson damping (D3BJ) was applied.[4] The nature of the stationary points was verified by numerical frequency analyses. The calculation of the UV/Vis spectra was performed with the B3LYP hybrid functional,[5] and the def2-TZVP basis set for all atoms. Molecular orbitals were visualized with the program GaussView5.[5] The isosurface value is set to 0.05 for all figures.

Cartesian coordinates of [Cp*Ru($C_{10}H_8$)RuCp*] (**1**) optimized with Gaussian09 at the BP86-D3/def2-TZVP level of theory

Energy = -1356.84545318

Ru	2.49020000	-0.38900300	-0.00507100
C	4.68034300	-0.33869000	-0.05726000
C	4.21348800	0.29438400	1.15235500
C	0.06624600	-0.10942100	-0.71341100
C	0.06217600	-0.11927900	0.71993900
C	4.14899500	0.39987100	-1.17937800
C	3.39769500	1.43422500	0.77460100
C	3.36230500	1.50317900	-0.65732800
C	0.88508000	-1.05938600	-1.39753700
H	0.94382600	-1.00590100	-2.48583800
C	0.89488200	-1.07635500	1.38586200
H	0.96116600	-1.03527400	2.47424100
C	1.48014500	-2.17942400	-0.72542200
H	1.93379900	-2.99269500	-1.29211600
C	1.48393100	-2.18905300	0.69552600
H	1.94390500	-3.01094700	1.24451700
C	5.62878000	-1.49391000	-0.13982100
C	4.58438600	-0.08606700	2.55155400
Ru	-2.45077400	0.32590000	0.01173500
C	-0.78534500	0.84665500	-1.36952300
C	-0.77328700	0.83359400	1.39073500
C	4.44219000	0.14639000	-2.62441600
C	2.72394100	2.39235800	1.70598200
C	2.63660000	2.53606700	-1.46152100
H	5.46221400	-2.07840000	-1.05484600
H	6.67826600	-1.15068700	-0.14932000
H	5.50807600	-2.17103800	0.71673100
H	3.76646300	0.12920900	3.25297900
H	4.81594000	-1.15750400	2.62812400
H	5.47253100	0.47211200	2.89595700
C	-4.61569900	0.55482600	0.05753900
C	-4.23048500	-0.12686300	-1.15575600
C	-4.19237900	-0.25682100	1.17497900
C	-3.57542500	-1.36751000	-0.78235200
C	-3.55792500	-1.45173500	0.64644400
H	-0.83224200	0.78502200	2.47928000
H	-0.85366200	0.80404200	-2.45790100
C	-1.29820700	2.00070400	0.72781300
H	-1.70115400	2.83801500	1.29764200
C	-1.30247600	2.00850000	-0.69335800
H	-1.71383200	2.85140400	-1.24917200
H	3.60581700	0.46377100	-3.26285300
H	5.33888500	0.70016600	-2.95296900
H	4.62149100	-0.92074800	-2.81515800
H	2.50393200	1.92484500	2.67608400
H	3.35621400	3.27632600	1.89708100
H	1.76988700	2.73889900	1.28298900

H	2.32901100	2.13762000	-2.43820600
H	1.72559200	2.86627800	-0.94231800
H	3.26718000	3.42336500	-1.64423300
C	-5.39927300	1.82803900	0.14559900
C	-4.53651600	0.30703000	-2.55724700
C	-4.46510800	0.01471400	2.62064000
C	-3.08100600	-2.40438900	-1.74021200
C	-3.01960400	-2.58056200	1.46979900
H	-5.15327500	2.38157700	1.06220300
H	-6.48570000	1.63051000	0.15532500
H	-5.18861900	2.48636500	-0.70842400
H	-3.73264900	0.01354600	-3.24724800
H	-4.65429100	1.39734600	-2.63124500
H	-5.47124800	-0.15185600	-2.92475800
H	-3.68182700	-0.41305400	3.26141300
H	-5.42706900	-0.42646400	2.93620700
H	-4.51116200	1.09355700	2.82496400
H	-2.60260900	-1.94639600	-2.61760800
H	-3.91043800	-3.03605700	-2.10443800
H	-2.34110600	-3.06324700	-1.26745500
H	-2.53201800	-2.20568300	2.38101100
H	-2.27293400	-3.16599500	0.91768700
H	-3.82381400	-3.27194200	1.77948700

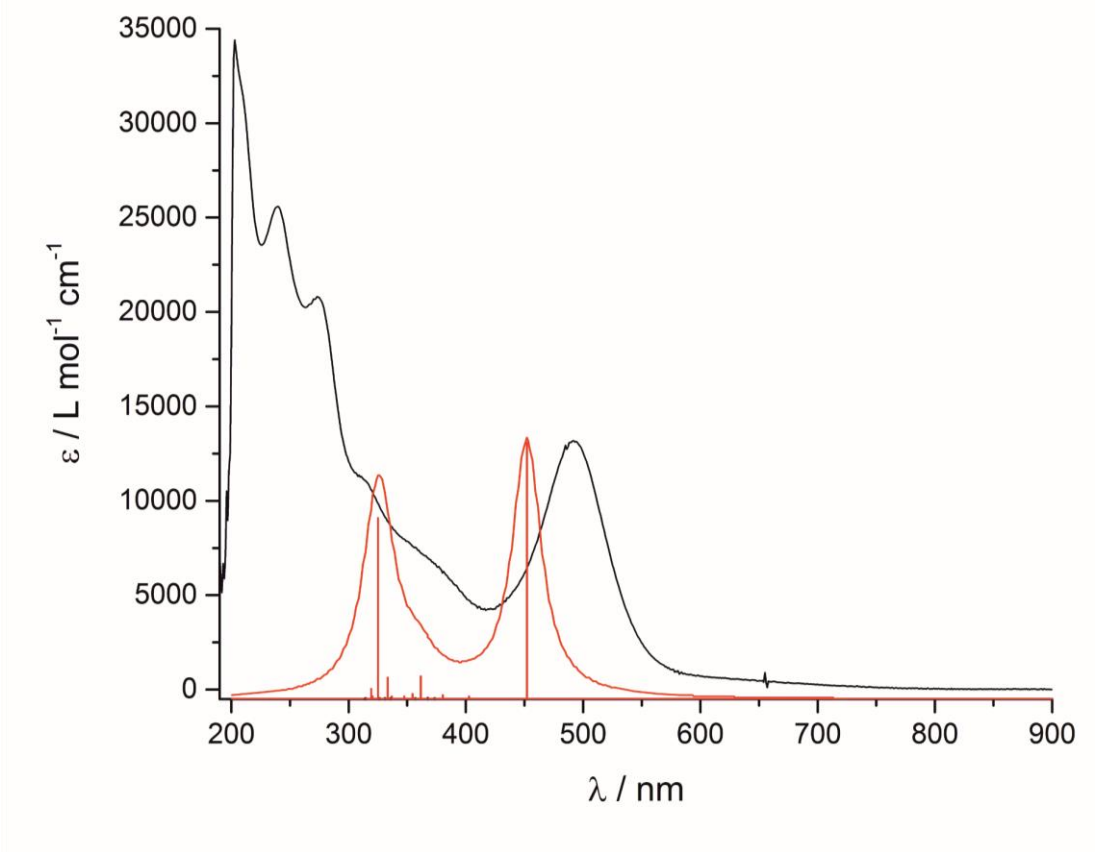

Figure S8. Experimental (black) and calculated (red) UV/Vis spectrum of **1** in Et_2O.

Table S2. Calculated electronic transitions of [**1**] on the B3LYP/def2-TZVP level of theory. The corresponding molecular orbitals are shown in Figure 9.

Nr.	*v* [nm]	*f*	%	Transition	Exp. *v* [nm]
1	452.25	0.426	17	HOMO−2 → LUMO	492
			65	HOMO → LUMO+1	
2	361.36	0.038	24	HOMO−1 → LUMO+1	370
			27	HOMO → LUMO+5	
			40	HOMO → LUMO+7	
3	333.70	0.037	29	HOMO−4 → LUMO	309
			40	HOMO−2 → LUMO	
			24	HOMO−1 → LUMO+1	
4	325.52	0.301	37	HOMO−4 → LUMO	309
			22	HOMO −4→ LUMO+3	
			19	HOMO → LUMO	
5	319.01	0.018	69	HOMO → LUMO+5	309

Cartesian coordinates of $[Cp^*Ru(C_{10}H_8)RuCp^*]^+$ (**1**$^+$) optimized with Gaussian09 at the BP86-D3/def2-TZVP level of theory

Energy = -1356.67910810

H	1.76989000	-2.94957200	-1.26133800
Ru	2.29145400	-0.32007900	-0.00003100
C	1.29171600	-2.13958300	-0.71149700
H	4.36211700	1.94850500	2.91005400
H	6.06909500	-1.00463800	1.80429500
H	4.36237100	1.94886900	-2.90970300
C	3.50551900	1.33438700	2.58741000
C	5.02743600	-1.30385000	1.60178200
C	3.50560700	1.33493500	-2.58715300
C	0.73024900	-1.03305900	-1.41241100
H	0.78290100	-0.99673400	-2.50040800
C	-0.00000500	0.00003600	-0.72649900
C	4.35755400	-0.29712800	0.72255400
C	1.29172400	-2.13965400	0.71125700
H	1.76990700	-2.94969700	1.26101100
C	3.67951600	0.90112700	1.16666400
C	3.27762400	1.65144300	0.00015900
C	0.73027500	-1.03319700	1.41228900
H	0.78293800	-0.99698300	2.50028800
C	4.35755000	-0.29698800	-0.72262100
C	3.67953200	0.90136300	-1.16649400

C	0.00000500	-0.00003600	0.72649500
Ru	-2.29145500	0.32007900	0.00002900
C	-0.73027600	1.03319600	-1.41229400
C	2.56556400	2.96467500	0.00030300
C	5.02742500	-1.30354200	-1.60204500
C	-0.73024800	1.03306000	1.41240700
C	-4.35755600	0.29712600	-0.72255200
H	-0.78290000	0.99673600	2.50040300
C	-1.29172500	2.13965400	-0.71126200
H	-1.76990800	2.94969700	-1.26101600
C	-3.67951900	-0.90113100	-1.16666000
C	-3.27762300	-1.65144300	-0.00015500
C	-1.29171500	2.13958300	0.71149300
H	-1.76988900	2.94957300	1.26133300
H	-0.78293900	0.99698200	-2.50029300
C	-4.35754800	0.29699000	0.72262300
C	-3.67952900	-0.90136000	1.16649800
H	4.51805300	-1.39993300	2.56979400
H	5.05402000	-2.29552800	1.13132600
H	3.44097500	0.47358400	3.26567600
H	1.92761600	3.07278300	-0.88703500
H	3.28345700	3.80166400	0.00050100
H	1.92745700	3.07249400	0.88756100
H	5.05401700	-2.29530600	-1.13177000
H	6.06908200	-1.00429200	-1.80452100
H	4.51802000	-1.39945300	-2.57006300
H	3.44079900	0.47428500	-3.26558800
H	2.59807800	1.93973300	-2.71487700
C	-5.02744000	1.30384400	-1.60178100
C	-3.50553000	-1.33439600	-2.58740500
C	-2.56556300	-2.96467500	-0.00029400
C	-5.02742300	1.30354600	1.60204500
C	-3.50559500	-1.33492600	2.58715700
H	-4.51805800	1.39992700	-2.56979400
H	-6.06909900	1.00463100	-1.80429300
H	-5.05402400	2.29552400	-1.13132800
H	-2.59783600	-1.93891500	-2.71527100
H	-4.36213700	-1.94850200	-2.91004700
H	-3.44097500	-0.47359700	-3.26567300
H	-1.92760700	-3.07277500	0.88703900
H	-3.28345500	-3.80166400	-0.00047900
H	-1.92746400	-3.07250100	-0.88755800
H	-5.05401400	2.29530900	1.13176800
H	-6.06908000	1.00429700	1.80452300
H	-4.51801700	1.39945900	2.57006200
H	-3.44080500	-0.47427300	3.26559100
H	-4.36234600	-1.94887900	2.90970900
H	-2.59805200	-1.93970400	2.71488200
H	2.59781400	1.93889100	2.71527700

Molecular orbitals of [**1**]$^{+}$

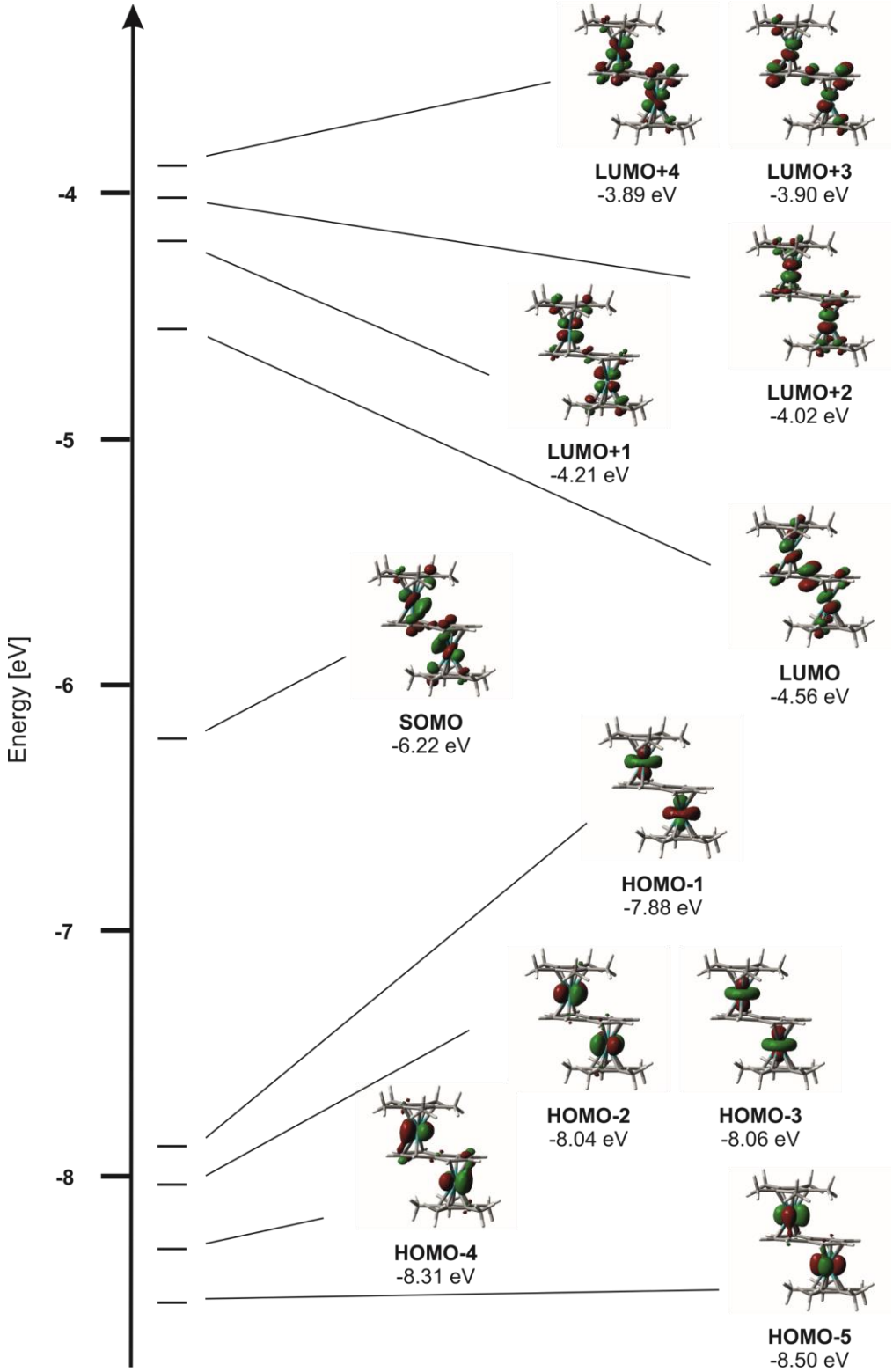

Figure S9. Molecular orbitals of [**1**]$^{+}$.

Cartesian coordinates of *endo*-[Cp*Ru(μ-$C_{10}H_8$)Ru(H)Cp*]$^+$ (*endo*-**3**$^+$) optimized with Gaussian09 at the BP86-D3/def2-TZVP level of theory

Energy = -1357.28740291

Ru	-2.55100600	-0.40156400	-0.01875100
C	-0.38935100	-0.75213200	-0.74184400
C	-0.39187900	-0.78888200	0.68916900
C	-3.01351700	1.70145800	-0.42530300
C	-3.89662200	0.85481000	-1.19419800
C	-1.30999300	-1.63022300	1.37053100
H	-1.34283000	-1.62285300	2.46038200
C	-3.23183700	1.41948700	0.97276800
C	-2.18666800	-2.44500000	-0.78285200
C	-4.25834000	0.40472000	1.07053500
C	-2.18904100	-2.48032600	0.63905100
H	-2.89348200	-3.12152100	1.16803200
C	-4.67157700	0.05966800	-0.27036000
C	-1.30579200	-1.55855100	-1.46822700
C	0.63447600	0.11503800	-1.34261800
C	0.63198400	0.04170700	1.33949500
C	-2.10307500	2.74740000	-0.97853600
C	-4.04997300	0.87262900	-2.68141100
C	-2.55271200	2.10183400	2.11582900
H	-2.88902900	-3.05952300	-1.34485000
C	-4.84764700	-0.13410500	2.33459700
C	-5.76514000	-0.89226800	-0.63400900
H	-1.33567000	-1.49583300	-2.55635900
Ru	2.41125100	-0.07044900	-0.00069400
C	0.96471800	1.34900300	-0.67947800
H	0.74201100	0.07422100	-2.42778600
H	0.73273900	-0.05935800	2.42121700
C	0.96243400	1.31132400	0.74703700
H	-1.26301600	2.94145400	-0.30127700
H	-2.65138100	3.69347700	-1.11861400
H	-1.69221100	2.45303100	-1.95317900
H	-3.10724400	1.13276300	-3.17986600
H	-4.80133400	1.62238200	-2.97890000
H	-4.38353900	-0.09999400	-3.06586800
H	-2.55526900	1.47496000	3.01689900
H	-3.06627100	3.04503900	2.36327600
H	-1.50897000	2.34186200	1.87284600
H	-5.20375400	-1.16436800	2.20479900
H	-5.70870700	0.47816900	2.64854200
H	-4.11950500	-0.12690900	3.15614400
H	-5.59790300	-1.34091400	-1.62177900
H	-6.73328500	-0.36633900	-0.66767000
H	-5.85637400	-1.70423800	0.09911800
C	4.27462800	1.19064400	-0.20407200
C	4.24544900	-0.87170100	0.88582700
H	1.27510300	2.23947600	-1.22612100
C	4.24573800	0.55561900	1.08973300

H	1.27519900	2.16906300	1.34314500
C	4.27598800	0.16524000	-1.21522800
C	4.27077000	-1.10997700	-0.54805000
H	1.93343400	-1.59729700	-0.04233100
C	4.34111500	2.66416500	-0.45155700
C	4.36845500	-1.91017400	1.95464800
C	4.31202100	1.24812500	2.41356200
C	4.37119400	0.37837300	-2.69173100
C	4.41874800	-2.43934300	-1.21893200
H	3.91264500	2.93348400	-1.42600600
H	5.38954700	3.00406100	-0.45003500
H	3.81383000	3.23384900	0.32568600
H	3.86519200	-1.59754000	2.87858000
H	5.42928800	-2.08994400	2.19559300
H	3.92954400	-2.86486600	1.63912000
H	3.87381100	2.25408400	2.36821000
H	5.35941000	1.35973600	2.73831900
H	3.78475800	0.67959900	3.19081300
H	3.86714000	-0.42463000	-3.24516900
H	5.42580400	0.39242400	-3.01264200
H	3.92306900	1.33434800	-2.99325100
H	4.01112800	-3.24979300	-0.60245900
H	5.48471400	-2.65429900	-1.39962700
H	3.90335200	-2.46005800	-2.18756500

Cartesian coordinates of *exo*-[Cp*Ru(μ-$C_{10}H_8$)Ru(H)Cp*]$^+$ (*exo*-**3**$^+$) optimized with Gaussian09 at the BP86-D3/def2-TZVP level of theory

Energy = -1357.08528620

Ru	2.45064300	0.34385300	0.00000700
C	0.19044400	0.35392600	-0.71466700
C	0.19042600	0.35409300	0.71463600
C	3.27104200	-1.71141500	-0.00030800
C	3.74163300	-1.00240500	-1.16868600
C	0.98997600	1.29817600	1.41735000
H	1.01909200	1.27449800	2.50775300
C	3.74119900	-1.00293600	1.16856300
C	1.72231900	2.30049300	-0.71148000
C	4.51082200	0.13898700	0.72388300
C	1.72229900	2.30067400	0.71099900
H	2.30437000	3.04017100	1.26096200
C	4.51110000	0.13930000	-0.72322600
C	0.99003200	1.29782100	-1.41759600
C	-0.72958900	-0.60648200	-1.34080400
C	-0.72962900	-0.60618100	1.34096900
C	2.53331100	-3.01425800	-0.00075400
C	3.57298800	-1.44590800	-2.58983800
C	3.57205600	-1.44703300	2.58946900
H	2.30444300	3.03984200	-1.26158500
C	5.27653400	1.07892600	1.60510600

C	5.27714000	1.07960600	-1.60376000
H	1.01917900	1.27386000	-2.50799500
Ru	-2.54179200	-0.55351300	0.00004500
C	-0.99181500	-1.86989100	-0.71937700
H	-0.84746400	-0.54112300	-2.42475600
H	-0.84751700	-0.54053800	2.42490100
C	-0.99182100	-1.86973300	0.71984200
H	1.89662100	-3.12110100	0.88724700
H	3.24597700	-3.85651400	-0.00094700
H	1.89676300	-3.12058500	-0.88891900
H	2.62193000	-1.97245600	-2.74376000
H	4.38336100	-2.14069500	-2.86782800
H	3.61335100	-0.60031400	-3.28904700
H	3.61201600	-0.60170100	3.28901900
H	4.38242200	-2.14180600	2.86750600
H	2.62100600	-1.97378200	2.74280800
H	5.39608200	2.06812400	1.14349900
H	6.28752800	0.68213100	1.79728400
H	4.78760200	1.21586200	2.57887500
H	4.78864000	1.21684700	-2.57770700
H	6.28824900	0.68294300	-1.79561800
H	5.39642000	2.06865400	-1.14176700
C	-4.80031600	-0.42185700	-0.00033200
C	-3.48058000	1.36635600	0.71591600
H	-1.21142500	-2.76719000	-1.29561600
C	-4.26874300	0.23068900	1.17298200
H	-1.21145600	-2.76688600	1.29629800
C	-4.26829100	0.23097000	-1.17327800
C	-3.48030700	1.36655400	-0.71561000
H	-3.23907600	-1.97570000	0.00009700
C	-5.84135000	-1.50088100	-0.00068000
C	-2.88487600	2.41443400	1.60630100
C	-4.65579000	-0.04933700	2.59333700
C	-4.65486000	-0.04868000	-2.59383500
C	-2.88426900	2.41489800	-1.60545500
H	-6.84331200	-1.03963900	-0.00085300
H	-5.77200600	-2.14041300	-0.88991500
H	-5.77239800	-2.14061700	0.88843800
H	-2.54176800	1.99147900	2.55982800
H	-3.64042300	3.18281400	1.84228500
H	-2.03594400	2.92601700	1.13352300
H	-4.88856600	-1.11118200	2.74778200
H	-5.55011500	0.53141000	2.87795400
H	-3.85401100	0.22236000	3.29288500
H	-3.85303700	0.22367700	-3.29307800
H	-5.54938700	0.53176000	-2.87843900
H	-4.88709400	-1.11057500	-2.74874700
H	-2.03517300	2.92596700	-1.13241500
H	-3.63955000	3.18365200	-1.84104700
H	-2.54128900	1.99233100	-2.55920300

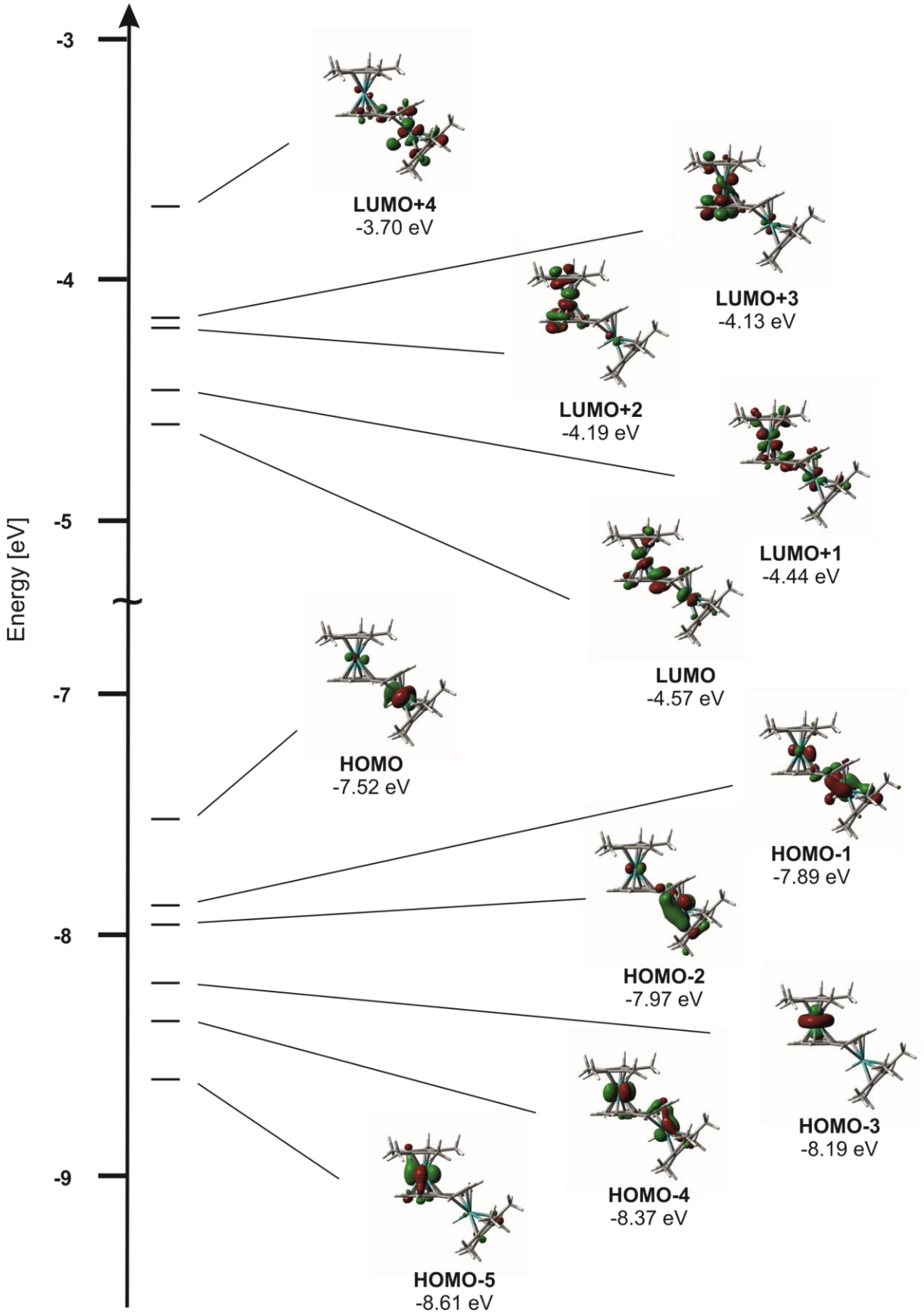

Figure S10. Molecular orbitals of *endo*-$\mathbf{3}^{+}$.

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