Electronic Supplementary Information (ESI) for Chemical Communication

Isolation and Structural Characterization of a Mainly Ligand-Based Dimetallic Radical

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Experimental Section

General Procedures

All experiments were carried out under a nitrogen atmosphere by using standard Schlenk techniques and a glovebox. Solvents were dried prior to use. $Ru_3(CO)_{12}$ (Acros) was purchased and used upon arrival. $Ag[Al(OR_F)_4]$,[1] $[Ph_3C]^+[Al(OR_F)_4]^-$,[2] and $Ru_2Cp^*_2(\mu\text{-}CO)_2(CO)_2$ （**1**）[3] were synthesized according to the literature methods. EPR spectra were obtained using Bruker EMX plus-6/1 variable-temperature apparatus. UV-Vis spectra were recorded on the Lambda 750 spectrometer. Infrared spectra were collected on VECTOR22 FT-IR spectrometer. The ^1H NMR spectra were performed using a Bruker DRX-400 and 500 spectrometers in ppm downfield from Me_4Si. Element analyses were performed at Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences. X-ray crystal structures were obtained by using a Bruker APEX DUO CCD detector.

Synthesis of $\mathbf{1}^{\cdot+}[Al(OR_F)_4]^-$. Under anaerobic and anhydrous conditions, a mixture of **1** (0.109 g, 0.187 mmol) and $Ag[Al(OR_F)_4]$ (0.201 g, 0.187 mmol) in CH_2Cl_2(≈ 60 ml) protected from light was stirred at room temperature overnight. The resultant dark brown solution was filtered to remove the gray precipitate (Ag metal). The filtrate was then concentrated and stored at around -25 °C for 1 day to afford X-ray-quality crystals of $\mathbf{1}^{\cdot+}[Al(OR_F)_4]^-\bullet CH_2Cl_2$. Isolated yield: 0.029 g, 10% (crystals); mp > 320 °C; Elemental analysis calcd (%) for $C_{41}H_{32}O_8AlRu_2F_{36}Cl_2$: C 30.09, H 1.97; Found: C 30.97, H 1.96.

Synthesis of $[\mathbf{1}\text{-}H]^+[Al(OR_F)_4]^-$. Under anaerobic and anhydrous conditions, a mixture of **1** (0.147 g, 0.252 mmol) and $[Ph_3C]^+[Al(OR_F)_4]^-$ (0.305 g, 0.252 mmol) in CH_2Cl_2(≈ 30 ml) protected from light was stirred at room temperature overnight. The resulting orange solution was then concentrated and stored at around -30 °C for 1 day to afford X-ray-quality crystals of $[\mathbf{1}\text{-}H]^+[Al(OR_F)_4]^-$. Isolated yield: 0.073 g, 19% (crystals); mp 202°C (decomp); Elemental analysis calcd (%) for $C_{40}H_{29}O_8AlRu_2F_{36}$: C 30.98, H 1.89; Found: C 30.92, H 1.80. ^1H NMR (400 MHz, $CDCl_3$): $[\mathbf{1}\text{-}H]^+[Al(OR_F)_4]^-$ δ 1.25 (s, 2H), 1.54 (s, 6H), 1.99 (s, 15H), 2.28 (s, 6H).

Computational details

All the geometry optimizations were performed with the *ω*B97X-D functional. SDDAll ECP was applied for Ru atom and basis set 6-31G(d,p) for the rest of the atoms. Frequency calculations were carried out to confirm that all optimized geometries correspond to energy minima. The UV-vis absorption spectrum was calculated using time-dependent DFT (TD-DFT) method at the *ω*B97X-D/6-31G(d,p)//SDDAll, and polarized continuum model (PCM) was adopted to consider solvent (CH_2Cl_2) effects. Molecular orbital composition and Mayer bond order analysis was done by the Multiwfn program.[4] All calculations were performed with the Gaussian 09 program suite.

References:

1 I. Krossing, *Chem. —Eur. J.* **2001**, 7, 490.

2 I. Krossing, *J. Fluorine Chem.* **2001**, *112*, 83.

3 R. B. King, M. Z. Iqbal, *J. Organomet. Chem.* **1979**, *71*, 53.

4 T. Lu, F. Chen, *J. Comp. Chem*. **2012**, *33*, 580.

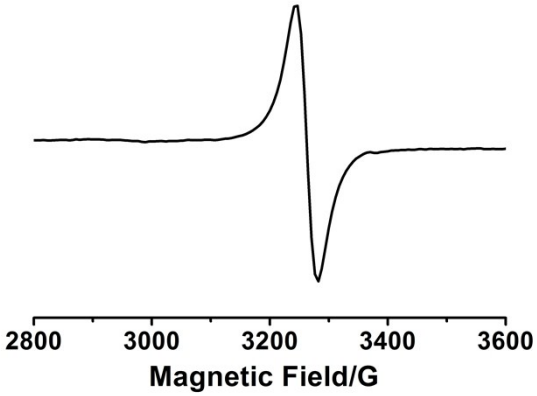


Fig. S1 Solution EPR spectrum of $\mathbf{1}^{\bullet+}$ in CH_2Cl_2 (1×10^{-2} M) at 298 K.

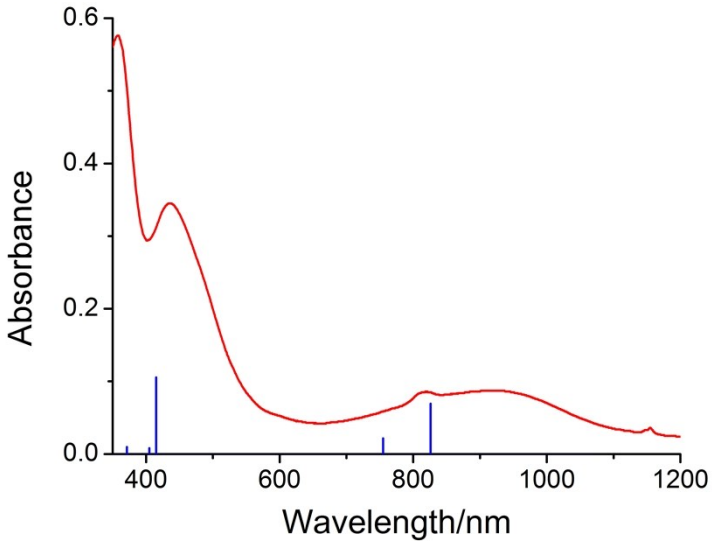
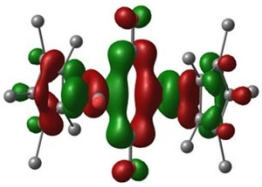


Fig. S2 The experimental (curve) and calculated (bars) UV-vis absorption spectra of $\mathbf{1}^{\bullet+}$.

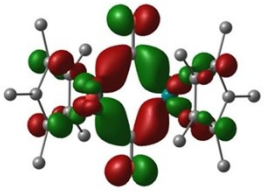
Table S1. TD-DFT calculated absorption wavelengths (λ), oscillator strengths (f), and assignments for seven highest electronic transition configurations.[a]

No.	λ (nm)	f	Assignment
1	1069.6	0	HOMO(β)→LUMO(β) (94%), H-8(B)→LUMO(β) (2%), H-3(β)→LUMO(β) (3%)
2	825.4	0.0472	**H-1(β)→LUMO(β) (92%)**, H-6(β)→LUMO(β) (5%)
3	754.4	0.0154	**H-2(β)→LUMO(β) (94%)**, HOMO(α)→LUMO(α) (2%)
4	610.5	0	H-3(β)→LUMO(β) (87%), H-8(β)→LUMO(β) (7%), H-2(β)→L+4(β) (2%), HOMO(β)→LUMO(β) (2%)
5	552.7	0	H-4(β)→LUMO(β) (88%), H-7(β)→LUMO(β) (7%), H-1(β)→L+4(β) (2%)
6	425.3	0.0002	H-9(β)→LUMO(β) (14%), H-5(β)→LUMO(β) (76%), HOMO(β)→L+4(β) (4%)
7	414.8	0.0713	H-6(β)→LUMO(β) (87%), H-1(α)→LUMO(α) (3%), H-7(β)→L+4(β) (2%), H-1(β)→LUMO(β) (5%)

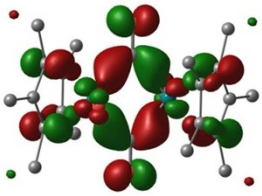
[a] H represents HOMO and L represents LUMO.



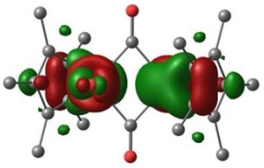
LUMO (α)



LUMO (β)



HOMO (α)



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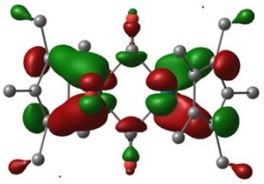
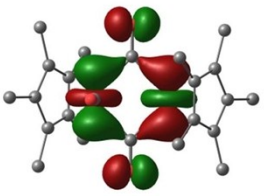


HOMO-1(β)



HOMO-2(β)

Fig. S3 Selected frontier molecular orbitals of $\mathbf{1}^{\bullet+}$.

Table S2. Molecular orbital compositions of $\mathbf{1}^{\cdot+}$ based on Mulliken population analysis.

Molecular orbital	Composition (%)			
LUMO(α)	Ru: 49.3%;	μ-CO: 17.2%;	Terminal-CO: 3.1%;	Cp*: 20.3%
HOMO(α)	Ru: 18.1%;	μ-CO: 35.0%;	Terminal-CO: 6.7%;	Cp*: 40.2%
HOMO-2(β)	Ru: 64.3%;	μ-CO: 27.7%;	Terminal-CO: 2.5%;	Cp*: 5.5%
HOMO-1(β)	Ru: 45.1%;	μ-CO: 7.4%;	Terminal-CO: 9.9%;	Cp*: 37.6%
LUMO(β)	Ru: 27.4%;	μ-CO: 34.5%;	Terminal-CO: 7.5%;	Cp*: 30.6%

Table S3. Mayer bond order of $\mathbf{1}^{\cdot+}$.

	Mayer bond order
Ru−μ-CO	0.67
Ru−Terminal-CO	0.98
Ru−Cp*[a]	0.33

[a] Calculated as the average value of the bond order of Ru with the carbon atoms on the Cp*ring.

Coordinates for calculated geometries

1:

C	-0.532846000	1.522975000	-2.589816000
C	-1.258639000	2.757267000	-2.148265000
H	-1.500545000	3.380644000	-3.016322000
H	-0.658550000	3.355515000	-1.460974000
H	-2.195194000	2.504498000	-1.645202000
C	0.884556000	1.317978000	-2.602693000
C	1.937900000	2.294593000	-2.175909000
H	2.769049000	1.784973000	-1.681871000
H	1.543670000	3.040596000	-1.484293000
H	2.337362000	2.820618000	-3.049984000
C	1.150185000	0.040815000	-3.195165000
C	2.512715000	-0.519222000	-3.468230000
H	2.974066000	-0.020137000	-4.327997000
H	2.463172000	-1.588215000	-3.686097000
H	3.167408000	-0.389453000	-2.602552000
C	-0.116321000	-0.546879000	-3.537832000
C	-0.306166000	-1.832767000	-4.286646000
H	-1.272600000	-2.288158000	-4.061534000
H	0.468993000	-2.559326000	-4.034791000
H	-0.260563000	-1.648505000	-5.365190000
C	-1.159404000	0.374448000	-3.173352000
C	-2.630297000	0.225540000	-3.417866000
H	-2.953702000	0.863498000	-4.248143000
H	-3.201882000	0.502788000	-2.528006000
H	-2.886540000	-0.806648000	-3.665682000
C	-1.481992000	0.222440000	0.019312000
C	-0.335582000	-2.150077000	-1.017577000
O	-2.655776000	0.395836000	0.031460000
O	-0.505700000	-3.292335000	-0.908782000
Ru	-0.065940000	-0.337552000	-1.326516000

C	0.532846000	-1.522975000	2.589816000
C	1.258639000	-2.757267000	2.148265000
H	1.500545000	-3.380644000	3.016322000
H	0.658550000	-3.355515000	1.460974000
H	2.195194000	-2.504498000	1.645202000
C	-0.884556000	-1.317978000	2.602693000
C	-1.937900000	-2.294593000	2.175909000
H	-2.769049000	-1.784973000	1.681871000
H	-1.543670000	-3.040596000	1.484293000
H	-2.337362000	-2.820618000	3.049984000
C	-1.150185000	-0.040815000	3.195165000
C	-2.512715000	0.519222000	3.468230000
H	-2.974066000	0.020137000	4.327997000
H	-2.463172000	1.588215000	3.686097000
H	-3.167408000	0.389453000	2.602552000
C	0.116321000	0.546879000	3.537832000
C	0.306166000	1.832767000	4.286646000
H	1.272600000	2.288158000	4.061534000
H	-0.468993000	2.559326000	4.034791000
H	0.260563000	1.648505000	5.365190000
C	1.159404000	-0.374448000	3.173352000
C	2.630297000	-0.225540000	3.417866000
H	2.953702000	-0.863498000	4.248143000
H	3.201882000	-0.502788000	2.528006000
H	2.886540000	0.806648000	3.665682000
C	1.481992000	-0.222440000	-0.019312000
C	0.335582000	2.150077000	1.017577000
O	2.655776000	-0.395836000	-0.031460000
O	0.505700000	3.292335000	0.908782000
Ru	0.065940000	0.337552000	1.326516000

1$^{\cdot+}$:

C	-1.556656000	0.016485000	0.004071000
C	-0.011887000	-1.075795000	2.198281000
C	-0.746983000	-2.567889000	-1.434346000
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C	-0.044591000	-3.535379000	0.562991000
C	-1.203533000	-3.137222000	-0.184014000
C	-1.639757000	-2.149729000	-2.560718000
H	-1.914537000	-3.030045000	-3.151090000
H	-1.149589000	-1.440392000	-3.228890000
H	-2.562734000	-1.696162000	-2.194231000
C	1.572496000	-2.188263000	-2.566194000
H	1.832530000	-3.076805000	-3.150860000
H	2.503056000	-1.747333000	-2.203276000
H	1.093526000	-1.475335000	-3.238669000
C	2.542840000	-3.476122000	0.160907000
H	2.846355000	-4.412456000	-0.319221000
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H	3.218843000	-2.688097000	-0.175348000
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H	-0.070080000	-5.372173000	1.635165000
H	-0.929463000	-4.064166000	2.455979000
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O	-0.009317000	-1.010448000	3.346731000
Ru	-0.018549000	-1.328163000	0.327345000
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C	0.011887000	1.075795000	-2.198281000
C	0.746983000	2.567889000	1.434346000
C	-0.673796000	2.584610000	1.436657000
C	-1.120854000	3.164856000	0.188077000
C	0.044591000	3.535379000	-0.562991000
C	1.203533000	3.137222000	0.184014000
C	1.639757000	2.149729000	2.560718000
H	1.914537000	3.030045000	3.151090000
H	1.149589000	1.440392000	3.228890000
H	2.562734000	1.696162000	2.194231000
C	-1.572496000	2.188263000	2.566194000
H	-1.832530000	3.076805000	3.150860000
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H	-3.218843000	2.688097000	0.175348000
C	0.051705000	4.299533000	-1.851591000
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H	0.929463000	4.064166000	-2.455979000
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C	2.631255000	3.413232000	-0.170830000
H	2.961463000	4.340110000	0.309960000
H	3.288313000	2.607104000	0.160155000
H	2.760308000	3.528974000	-1.248208000
O	2.724766000	-0.037083000	-0.003489000
O	0.009317000	1.010448000	-3.346731000
Ru	0.018549000	1.328163000	-0.327345000