Supporting Informations:

**Figure S1.** ORTEP diagram of ([1]ClO₄). Perchlorate anion is removed for clarity.

Ellipsoids are drawn at 50% probability. Hydrogen atoms, with exception of the N–bonded one, have been omitted for clarity.

**Figure S2.** ORTEP diagram of ([2]ClO₄). Perchlorate anion is removed for clarity.

Hydrogen atoms, with exception of the N–bonded one, have been omitted for clarity. Ellipsoids are drawn at 50% probability.

**Figure S3.** Packing diagrams of (a) trans–[Ru(acac)₂(Ⅱ)ClO₄ ([2]ClO₄) and (b) trans–Ru(acac)₂(Ⅱ)₂ (Ⅱ), viewed down the c– axis.

**Figure S4.** Intramolecular hydrogen bonding in (3).

**Figure S5.** Cyclic voltammograms of (1) (——), (2) (——) and (3) (••••) in acetonitrile.

**Figure S6.** Electronic spectra of (1) (——), ([1]ClO₄) (——), (2) (••••), ([2]ClO₄) (••••••••) and (3) (•••••••••) in acetonitrile.

**Figure S7.** EPR spectrum of ([1]ClO₄) in CHCl₃ at 77K. The inset shows the EPR spectrum of ([1]ClO₄) in the sold state at 77K.

**Figure S8.** Electrospray mass spectrum of (2) in CH₃CN.

**Figure S9.** Electrospray mass spectrum of (3) in CH₃CN.

**Figure S10.** Electrospray mass spectrum of ([2]ClO₄) in CH₃CN.

**Figure S11.** Electrospray mass spectrum of ([1]ClO₄) in CH₃CN.

**Table S1.** Intramolecular hydrogen bonding in (3).
Scheme S1. Suggested pathway for the simultaneous formations of $trans$ (2) and $cis$ (3) species.
Figure S4
Figure S5
Figure S6
Figure S7
Figure S10

- m/z 130.15
- m/z 471.05
- m/z 542.07
- m/z 642.13

$\{(\text{[2]} \text{ClO}_4)^-\text{ClO}_4^+\}$
Figure S11

471.06 \{[(1)\text{ClO}_4]-\text{ClO}_4\}^+$

(371.00, 299.98)
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[ 3655. ] = 3/2-x,1/2-y,z
where \( \equiv \), \( S = \text{CH}_3\text{CN} \), \( L \equiv 2,2'\text{-dipyridylamine} \)

**Scheme S1**