Supporting Information

Cis-locked Ru(II)-dmsO precursors for the microwave-assisted synthesis of bis-heteroleptic polypyridyl compounds.

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The reactions of cis-[RuCl$_2$(dmso)$_4$] (1) with the model diimine chelating ligands phen and dppz

a) Reactions performed in refluxing chloroform.

Complex 1 was treated with one equiv. of phen in refluxing chloroform for 1h, i.e. in the conditions that, according to Grätzel and co-workers,$^1$ and Spiccia and co-workers,$^2$ are expected to afford selectively the mono-substituted complex cis,cis-[RuCl$_2$(dmso-S)$_2$(phen)] in good yield. Conversely, according to $^1$H NMR analysis (Figure S1), we obtained a ca. 1:1 mixture of the stereoisomers cis,cis-[RuCl$_2$(dmso-S)$_2$(phen)] (a) and trans,cis-[RuCl$_2$(dmso-S)$_2$(phen)] (b), together with a good amount of unreacted precursor 1 (Scheme S1).

![Figure S1](image-url) Aromatic region of the $^1$H NMR spectrum (CDCl$_3$) of: (top) complex trans,cis-[RuCl$_2$(dmso-S)$_2$(phen)] (b); (bottom) the reaction mixture obtained by treatment of 1 with one equiv. of phen in refluxing CHCl$_3$ for 1h.

![Scheme S1](image-url) The reactivity of cis-[RuCl$_2$(dmso)$_4$] (1) with 1 equiv. of phen in refluxing chloroform.
The NMR spectrum of the more symmetrical isomer b (four aromatic resonances, 2H each, and a singlet for two dmso-S ligands) is compatible also with the third stereoisomer cis,trans-[RuCl_2(dmso-S)_2(phen)] (c) (Figure S2).

For comparative purposes, the stereoisomer b was selectively prepared by treatment of trans-[RuCl_2(dmso-S)_4] (1t), the stereo and linkage isomer of 1, with phen at room temperature (its NMR spectrum is shown in Figure S1). Complex 1t, in fact, is known to replace selectively two adjacent dmso-S ligands leaving unchanged the geometry of the Ru(II) fragment (Scheme S2). We also found that, consistent with what previously observed for the corresponding bpy complex,^S3 compound b is not stable in chloroform solution at room temperature and within 24 hours isomerizes to a mixture of a and of the other symmetrical isomer c. From this solution we managed to get crystals of c suitable for X-ray analysis that afforded the molecular structure of the complex (Figure S3).

Figure S2. The three stereoisomers cis,cis-[RuCl_2(dmso-S)_2(phen)] (a), trans,cis-[RuCl_2(dmso-S)_2(phen)] (b), and cis,trans-[RuCl_2(dmso-S)_2(phen)] (c).

Scheme S2. Preparation of trans,cis-[RuCl_2(dmso-S)_2(phen)] (b) from trans-[RuCl_2(dmso-S)_4] (1t) in methanol at room temperature.
Figure S3. ORTEP representation (50% probability ellipsoids) of stereoisomer cis,trans-
[RuCl$_2$(dmso-S)$_2$(phen)] (c).

b) Reactions performed in refluxing ethanol.
Complex 1 was treated with one equiv. of phen in refluxing ethanol for 2h, i.e. in the conditions
that – with the similar ligand dppz – according to Burke and Keyes afforded selectively the mono-
substituted complex cis,cis-[RuCl$_2$(dmso-S)$_2$(dppz)] in good yield.$^4$ The orange product that
precipitated spontaneously from the cooled solution turned out to be, according to NMR analysis, a
c. 5:1 mixture of cis,cis-[RuCl$_2$(dmso-S)$_2$(phen)] (a) and cis,trans-[RuCl$_2$(dmso-S)$_2$(phen)] (c) (see
below Figure S4). The mother liquor, beside a and c, contained the disubstituted charged complex
cis-[RuCl(dmso-S)(phen)$_2$]Cl (d). The proton NMR spectrum of this species is characterized by two
singlets (3H each) for the residual dmso-S and sixteen resolved aromatic resonances for the two
inequivalent phen ligands (see below Figure S4). No resonances attributable to unreacted 1 were
detected.
Thus, the reactivity of 1 with phen in refluxing ethanol can be summarized as reported in Scheme
S3:
Scheme S3. The reactivity of cis-[RuCl₂(dmso)₄] (1) with 1 equiv. of phen in refluxing ethanol.

Very similar results were obtained, under the same conditions, using one equiv. of dppz in the place of phen.

The reaction of 1 with two equiv. of phen in refluxing ethanol (8h) afforded the same three main products a, c, and d as above, even though in different relative ratios. The first fraction was formed by a mixture of a and c (Figure S4), whereas the second fraction, obtained from the concentrated mother liquor, was almost pure d (Figure S4). To be noted that one methyl resonance of the dmso-S in d is shifted at very low frequencies. This singlet is attributed to the methyl that falls in the shielding cone of the adjacent phenanthrolines.

Figure S4. ¹H NMR spectra (CDCl₃) of the two fractions obtained from the reaction of 1 with two equiv. of phen in refluxing ethanol for 8h. Top: 1st fraction, which is a mixture of a and c; bottom: 2nd fraction, that consists of almost pure cis-[RuCl(dmso-S)(phen)]Cl (d).
Experimental section

cis-[RuCl₂(dmso)₄] (1) + 1 equiv of phen in refluxing chloroform.
A 50.0 mg amount of cis-[RuCl₂(dmso)₄] (1) (0.10 mmol) was dissolved in 10 mL of chloroform together with one equiv. of phen (18.7 mg). The pale yellow solution was heated to reflux for 1h. The final deep-orange solution was evaporated to an oil that, upon addition of acetone (5 mL), afforded a yellow solid that was removed by filtration, washed with acetone and diethyl ether, and dried under vacuum. According to its ¹H NMR spectrum this precipitate is a ca. 1:1 mixture of the stereoisomers a and b plus unreacted 1. Upon dropwise addition of diethyl ether to the concentrated mother liquor (ca. 2 mL) a pale yellow – creamy precipitate was obtained that, according to the ¹H NMR spectrum in CDCl₃, was mainly composed by unreacted 1. The estimated yield in the a + b mixture was lower than 50%.

trans-[RuCl₂(dmso-S)₄] (1t) + phen in methanol.
A 50.0 mg amount of trans-[RuCl₂(dmso-S)₄] (1t) (0.10 mmol) was dissolved in 5 mL of methanol together with one equiv. of phen (18.7 mg). The orange solution became progressively red and afforded a deep-orange precipitate formed. This was collected by filtration, washed with diethyl ether and dried under vacuum. According to its ¹H NMR spectrum this precipitate was pure cis,trans-[RuCl₂(dmso-S)₂(phen)] (b). Upon dropwise addition of diethyl ether to the concentrated mother liquor (ca. 2 mL) a second fraction of the same product was obtained. Total yield of b: 41.9 mg (80%).

cis-[RuCl₂(dmso)₄] (1) + 1 equiv of phen in refluxing ethanol.
A 50.0 mg amount of cis-[RuCl₂(dmso)₄] (1) (0.10 mmol) was dissolved in 10 mL of ethanol together with one equiv. of phen (18.7 mg) and heated to reflux for 2h. The final red-orange solution slowly afforded (72 h) at room temperature an orange precipitate, that was collected by filtration, washed with cold ethanol and diethyl ether, and dried under vacuum. According to its ¹H NMR spectrum this precipitate is a ca. 6:1 mixture of the stereoisomers a and c. Yield 25.3 mg (48%). Upon dropwise addition of diethyl ether to the concentrated mother liquor (ca. 4 mL) a second orange precipitate was obtained that, according to the ¹H NMR spectrum in CDCl₃, contained comparable amounts of a, c, and cis-[RuCl(dmso-S)(phen)₂]Cl (d).

cis-[RuCl₂(dmso)₄] (1) + 2 equiv of phen in refluxing ethanol.
A 101.6 mg amount of cis-[RuCl₂(dmso)₄] (1) (0.21 mmol) was dissolved in 15 mL of ethanol together with two equiv. of phen (74.8 mg) and heated to reflux for 8h. The final deep-red solution was concentrated to ca. half volume. Dropwise addition of diethyl ether until cloudiness afforded an orange precipitate, that was collected by filtration, washed with cold ethanol and diethyl ether,
and dried under vacuum. According to its $^1$H NMR spectrum this precipitate was a ca. 5:1 mixture of the stereoisomers $a$ and $c$. Yield 62.45 mg (59%). A small amount of a second fraction precipitated spontaneously from the mother liquor (containing also the diethyl ether from the washing). According to its $^1$H NMR spectrum it was almost pure $cis$-[RuCl(dmso-S)(phen)$_2$]Cl (d).

**NMR characterization of compounds a - d**

$cis,cis$-[RuCl$_2$(dmso-S)$_2$(phen)] (a) (C$_{16}$H$_{20}$Cl$_2$N$_2$O$_2$Ru$_2$, MW = 507.94). $^1$H NMR (CDCl$_3$) δ, ppm: 2.52, 3.17, 3.60, 3.63 (s, 3H, dmso-S), 7.79 (dd, 1H, H8), 7.98 (m, 3H, H3+H5+H6), 8.39 (dd, 1H, H4), 8.51 (dd, 1H, H7), 9.99 (dd, 1H, H2), 10.14 (dd, 1H, H9).

$trans,cis$-[RuCl$_2$(dmso-S)$_2$(phen)] (b) (C$_{16}$H$_{20}$Cl$_2$N$_2$O$_2$Ru$_2$, MW = 507.94). $^1$H NMR (CDCl$_3$) δ, ppm: 3.66 (s, 12H, dmso-S), 7.86 (m, 2H, H3,8), 7.99 (s, 2H, H5,6), 8.44 (dd, 2H, H4,7), 10.07 (dd, 2H, H2,9).

$cis,trans$-[RuCl$_2$(dmso-S)$_2$(phen)] (c) (C$_{16}$H$_{20}$Cl$_2$N$_2$O$_2$Ru$_2$, MW = 507.94). $^1$H NMR (CDCl$_3$) δ, ppm: 3.04 (s, 12H, dmso-S), 7.84 (dd, 2H, H3,8), 8.01 (s, 2H, H5,6), 8.37 (dd, 2H, H4,7), 9.89 (dd, 2H, H2,9).

$cis$-[RuCl(dmso-S)(phen)$_2$][Cl] (d) (C$_{26}$H$_{22}$Cl$_2$N$_4$ORuS, MW = 610.47). $^1$H NMR (CDCl$_3$) δ, ppm: 1.96 (s, 3H), 3.45 (s, 3H), 7.33 (dd, 1H), 7.56 (dd, 1H), 7.63 (dd, 1H), 8.02 (dd, 1H), 8.05 (dd, 1H), 8.09 (dd, 1H), 8.14 (dd, 1H), 8.25 (dd, 1H), 8.35 (dd, 1H), 8.41 (dd, 1H), 8.53 (dd, 1H), 8.62 (dd, 1H), 8.68 (dd, 1H), 9.17 (dd, 1H), 10.05 (dd, 1H), 10.56 (dd, 1H).
Spectral characterization of the new cis-locked precursors 6 and 7

Figure S5. $^1$H NMR spectrum (CDCl$_3$) of $\textit{fac}$-[RuCl(dms-S)$_3$(η$^2$-acac)] (6).
Figure S6. $^1$H NMR spectrum (CD$_3$NO$_2$) of $\textit{fac}$-[Ru(dmsO)(dmsO)$_3$(η$^2$-acac)] (7).
Reactions of the cis-locked precursors with bpy

Figure S7. $^1$H NMR spectra (aromatic region) in DMSO-$d_6$ of the raw product mixtures from the reactions between the cis-locked precursors 2 – 5 and bpy performed in a MW reactor. Color code: black = unreacted bpy, blue = the bis-bpy product, red = [Ru(bpy)$_3$]$^{2+}$. Reaction conditions: [Ru] = 390 mM, absolute ethanol, bpy/Ru = 2, MW, 120°C, 1h.

Table S1. Molar percentages determined by NMR integration in the raw product mixtures from the reactions between the cis-locked precursors 2 – 7 and bpy performed in a MW reactor. Reaction conditions: [Ru] = 390 mM, absolute ethanol, bpy/Ru = 2, 120°C, 1h.

| Complex | Free bpy% | Ru(bpy)$_2$(O–O)$^{n+}$ | Ru(bpy)$_3$$^{2+}$ |
|---------|-----------|-----------------------|-----------------|
| K[RuCl(dmso-S)$_3$(η$_2$-mal)] (2) | 34 | 18 | 48 |
| K[RuCl(dmso-S)$_3$(η$_2$-mal)] (3) | 10 | 64 | 26 |
| K[RuCl(dmso-S)$_3$(η$_2$-ox)] (4) | 97 | 2 | 1 |
| K[Ru(dmso-O)(dmso-S)$_3$(η$_2$-ox)] (5) | 24 | 14 | 62 |
| K[RuCl(dmso-S)$_3$(η$_2$-acac)] (6) | 46 | 38 | 15 |
| K[Ru(dmso-O)(dmso-S)$_3$(η$_2$-acac)][PF$_6$] (7) | n.d.* | 73 | 27 |

* In this case a precipitate is found in the vial at the end of the run, a mixture of [Ru(bpy)$_2$(η$_2$-acac)][PF$_6$] (8) and [Ru(bpy)$_3$][PF$_6$]$_2$. 
Figure S8. The $^1$H NMR spectra (aromatic region) in DMSO-$d_6$ show the effect of the concentration on the selectivity towards $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$ in the reaction between $\text{K}[\text{fac-RuCl(dmsos-S)}_3(\eta^2\text{-mal})]$ (2) and bpy performed in a MW reactor. Color code: black = unreacted bpy, blue = $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$, red-orange = $[\text{Ru(bpy)}_3]^{2+}$. Reaction conditions: absolute ethanol, bpy/Ru = 2, 120°C, 1h.

Table S2. The effect of the concentration on the selectivity towards $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$ in the reaction between $\text{K}[\text{fac-RuCl(dmsos-S)}_3(\eta^2\text{-mal})]$ (2) and bpy performed in a MW reactor. The % values are obtained by integrating the NMR spectra of Figure S8. Reaction conditions: absolute ethanol, bpy/Ru = 2, 120°C, 1h.

| [Ru] mM | Free bpy | $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$ | $[\text{Ru(bpy)}_3]^{2+}$ |
|---------|----------|--------------------------------------|-----------------|
| 390     | 34       | 18                                   | 48              |
| 97.5    | 32       | 38                                   | 30              |
| 6.1     | 43       | 51                                   | 6               |
| 1.5     | 59       | 51                                   | 3               |
Figure S9. The $^1$H NMR spectra (aromatic region) in DMSO-$d_6$ show the effect of the concentration on the selectivity towards [Ru(bpy)$_2$(η$_2$-ox)] in the reaction between [fac-Ru(dmso-O) (dmso-S)$_3$(η$_2$-ox)] (5) and bpy performed in a MW reactor. Color code: black = unreacted bpy, blue = [Ru(bpy)$_2$(η$_2$-ox)], red-orange = [Ru(bpy)$_3$]$_{2+}$. Reaction conditions: absolute ethanol, bpy/Ru = 2, 120°C, 1h.

Table S3. The effect of the concentration on the selectivity towards [Ru(bpy)$_2$(η$_2$-ox)] in the reaction between [fac-Ru(dmso-O)(dmso-S)$_3$(η$_2$-ox)] (5) and bpy performed in a MW reactor. The % values are obtained by integrating the NMR spectra of Figure S9. Reaction conditions: absolute ethanol, bpy/Ru = 2, 120°C, 1h.

| [Ru] mM | Free bpy | [Ru(bpy)$_2$(η$_2$-ox)] | [Ru(bpy)$_3$]$_{2+}$ |
|---------|----------|--------------------------|-----------------------|
| 390     | 26       | 13                       | 62                    |
| 97.5    | 22       | 41                       | 37                    |
| 24.3    | 36       | 42                       | 22                    |
| 6.1     | 43       | 44                       | 13                    |
**Figure S10.** The $^1$H NMR spectra (aromatic region) in DMSO-$d_6$ show the effect of the temperature on the selectivity towards $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$ in the reaction between K[$\text{fac-RuCl(dmoso-S)_3(\eta^2\text{-mal})}$] (2) and bpy performed in a MW reactor. Color code: black = unreacted bpy, blue = $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$, red-orange = $[\text{Ru(bpy)}_3]^{2+}$. Reaction conditions: absolute ethanol, [Ru] = 6.1 mM, bpy/Ru = 2, 1h.

**Table S4.** The effect of the temperature on the selectivity towards $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$ in the reaction between K[$\text{fac-RuCl(dmoso-S)_3(\eta^2\text{-mal})}$] (2) and bpy performed in a MW reactor. The % values are obtained by integrating the NMR spectra of Figure S10. Reaction conditions: absolute ethanol, [Ru] = 6.1 mM, bpy/Ru = 2, 1h.

| T (°C) | Free bpy | $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$ | $[\text{Ru(bpy)}_3]^{2+}$ |
|--------|----------|----------------------------------|-----------------|
| 100    | 26       | 13                               | 62              |
| 120    | 43       | 51                               | 6               |
| 150    | 16       | 77                               | 7               |
Figure S11. The $^1$H NMR spectra (aromatic region) in DMSO-$d_6$ show the effect of the temperature on the selectivity towards $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$ in the reaction between $[\text{fac-Ru(dmso-O)(dmso-S)}_3(\eta^2\text{-mal})]$ (3) and bpy performed in a MW reactor. Color code: black = unreacted bpy, blue = $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$, red-orange = $[\text{Ru(bpy)}_3]^{2+}$. Reaction conditions: absolute ethanol, $[\text{Ru}] = 6.1$ mM, bpy/Ru = 2, , 1h.

Table S5. The effect of the temperature on the selectivity towards $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$ in the reaction between $[\text{fac-Ru(dmso-O)(dmso-S)}_3(\eta^2\text{-mal})]$ (3) and bpy performed in a MW reactor. The % values are obtained by integrating the NMR spectra of Figure S11. Reaction conditions: absolute ethanol, $[\text{Ru}] = 6.1$ mM, bpy/Ru = 2, 1h.

| T ($^\circ$C) | Free bpy | $[\text{Ru(bpy)}_2(\eta^2\text{-mal})]$ | $[\text{Ru(bpy)}_3]^{2+}$ |
|--------------|----------|---------------------------------|-----------------|
| 120          | 27       | 46                              | 26              |
| 150          | 11       | 89                              | <1%             |
**Figure S12.** The $^1$H NMR spectra (aromatic region) in DMSO-$d_6$ show the effect of the concentration, temperature, and reaction time on the outcome of the reaction between [cis-RuCl$_2$(dmsO)$_4$] (1) and bpy performed in a MW reactor. See Figure S13 for peak assignments. Reaction conditions: absolute ethanol, bpy/Ru = 2, 1h.
Figure S13. Peak assignments in the $^1$H NMR spectrum (aromatic region) in DMSO-$d_6$ of the raw reaction mixture from the reaction between $[\textit{cis-RuCl}_2(\text{dms})_4]$ (1) and bpy performed in a MW reactor. Reaction conditions: absolute ethanol, [Ru] = 6.1 mM, T = 120°C, bpy/Ru = 2, 1h.
Spectral characterization of compounds 8 – 15

**Figure S14.** UV-vis spectrum in chloroform of [Ru(bpy)$_2$(η$^2$-acac)][PF$_6$] (8).

**Figure S15.** UV-vis spectrum in chloroform of [Ru(bpy)$_2$(η$^2$-mal)] (9).

**Figure S16.** UV-vis spectrum in CHCl$_3$ of [Ru(phen)$_2$(η$^2$-mal)] (10).
Figure S17. UV-vis spectrum in CHCl$_3$ of [Ru(phen)$_2$(η$^2$-ox)] (12).

Figure S18. UV-vis spectrum in MeOH of [Ru(dpphen)$_2$(η$^2$-ox)] (13).

Figure S19. UV-vis spectrum in CHCl$_3$ of [Ru(phen)$_2$(η$^2$-acac)]Cl (14).
**Figure S20.** UV-vis spectrum in CHCl₃ of [Ru(dpphen)₂(η²-acac)]Cl (15).

**Figure S21.** ¹H NMR spectrum (DMSO-𝑑₆) of [Ru(bpy)₂(η²-acac)][PF₆] (8) with labeling scheme.
**Figure S22.** $^1$H NMR spectrum (DMSO-$d_6$) of [Ru(bpy)$_2$(η$^2$-mal)] (9) with labeling scheme.

**Figure S23.** Downfield region of the H-H COSY spectrum (CDCl$_3$) of [Ru(bpy)$_2$(η$^2$-mal)] (9). See Figure S22 for the labeling scheme.
Figure S24. $^1$H NMR spectrum (DMSO-$d_6$) of [Ru(phen)$_2$(η$^2$-mal)] (10) with labeling scheme. In the insert the resonance of malonate.

Figure S25. Downfield region of the H-H COSY spectrum (DMSO-$d_6$) of [Ru(phen)$_2$(η$^2$-mal)] (10); see Figure S24 for the labeling scheme.
Figure S26. Downfield region of the HSQC spectrum (DMSO-$d_6$) of $[\text{Ru(phen)}_2(\eta^2-\text{mal})]$ (10); see Figure S24 for the labeling scheme.
Figure S27. $^1$H NMR spectrum (DMSO-$d_6$) of [Ru(dp phen)$_2$(η²-mal)] (11) with labeling scheme. In the insert the resonance of malonate. The peak of residual chloroform is marked with an *.

Figure S28. Downfield region of the H-H COSY spectrum (DMSO-$d_6$) of [Ru(dp phen)$_2$(η²-mal)] (11) see Figure S27 for the labeling scheme.
Figure S29. Downfield region of the HSQC spectrum (DMSO-$d_6$) of [Ru(dpphen)$_2$(η$^2$-mal)] (11) see Figure S27 for the labeling scheme.
**Figure S30.** $^1$H NMR spectrum (DMSO-$d_6$) of [Ru(phen)$_2$(η$^2$-ox)] (12) with labeling scheme.

**Figure S31.** H-H COSY spectrum (DMSO-$d_6$) of [Ru(phen)$_2$(η$^2$-ox)] (12); see Figure S30 for the labeling scheme.
Figure S32. HSQC spectrum (DMSO-$d_6$) of [Ru(phen)$_2$(η$^2$-ox)] (12); see Figure S30 for the labeling scheme.
Figure S33. $^1$H NMR spectrum (DMSO-$d_6$) of $\text{[Ru(dpphen)]}_2(\eta^2\text{-ox})$ (13) with labeling scheme.

Figure S34. H-H COSY spectrum (DMSO-$d_6$) of $\text{[Ru(dpphen)]}_2(\eta^2\text{-ox})$ (13) see Figure S33 for labeling scheme.
Figure S35. HSQC spectrum (DMSO-\textit{d}_6) of [Ru(dpphen)\textsubscript{2}(\eta\textsuperscript{2}-ox)] (13) see Figure S33 for the labeling scheme.
Figure S36. $^1$H NMR spectrum (DMSO-$d_6$) of [Ru(phen)$_2$(η$_2$-acac)]Cl (14) with labeling scheme.

Figure S37. H-H COSY spectrum (DMSO-$d_6$) of [Ru(phen)$_2$(η$_2$-acac)]Cl (14); see Figure S36 for the labeling scheme.
Figure S38. HSQC spectrum (DMSO-$d_6$) of [Ru(phen)$_2$(η$^2$-acac)]Cl (14); see Figure S36 for labeling scheme.
Figure S39. $^1$H NMR spectrum (DMSO-$d_6$) of [Ru(dpphen)$_2$(η$^2$-acac)]Cl (15) with labeling scheme.
Figure S40. H-H COSY spectrum (DMSO-$d_6$) of [Ru(dpphen)$_2$(η$^2$-acac)]Cl (15); see Figure S39 for the labeling scheme.
Figure S41. HSQC spectrum (DMSO-d$_6$) of [Ru(dpphen)$_2$(η$_2$-acac)]Cl (15); see Figure S39 for the labeling scheme.
Spectral characterization of the bis-heteroleptic complexes [Ru(phen)$_2$(bpy)][PF$_6$]$_2$ (16) and [Ru(bpy)$_2$(phen)][PF$_6$]$_2$ (17)

Figure S42. Spectral changes in the UV-vis spectrum during the reaction of [Ru(phen)$_2$(η$_2$-mal)] (10) (purple line) with one equiv. of bpy in refluxing EtOH + 10 equiv. of TFA to afford [Ru(phen)$_2$(bpy)]$^{2+}$ quantitatively in ca. 1h (orange line).

Figure S43. $^1$H NMR spectrum (CD$_3$CN) of [Ru(phen)$_2$(bpy)][PF$_6$]$_2$ (16) with labelling scheme (p stands for phen, b for bpy).
Figure S44. H-H COSY spectrum of (CD$_3$CN) of [Ru(phen)$_2$(bpy)][PF$_6$]$_2$ (16); see Figure S43 for labelling scheme.

Figure S45. Spectral changes in the UV-vis spectrum during the reaction of [Ru(bpy)$_2$(η$^2$-mal)] (9) (purple line) with one equiv. of phen in refluxing EtOH + 10 equiv. of TFA to afford [Ru(bpy)$_2$(phen)]$^{2+}$ quantitatively in ca. 1h (orange line).
**Figure S46.** $^1$H NMR spectrum (CD$_3$CN) of [Ru(bpy)$_2$(phen)][PF$_6$]$_2$ (17) with labelling scheme (p stands for phen, b for bpy).

**Figure S47.** H-H COSY spectrum of (CD$_3$CN) of [Ru(bpy)$_2$(phen)][PF$_6$]$_2$ (17); see Figure S46 for labelling scheme.
Table S6. Crystallographic data and refinement details for compounds fac-[RuCl(dmso-S)$_3$(η$^2$-acac)] (6), fac-[Ru(dmso-O)(dmso-S)$_3$(η$^2$-acac)][PF$_6$] (7), and cis,trans-[RuCl$_2$(dmso-S)$_2$(phen)] (c).

| Empirical Formula          | 6       | 7       | c       |
|---------------------------|---------|---------|---------|
| C$_{11}$H$_{25}$ClO$_5$RuS$_3$ |         |         |         |
| C$_{13}$H$_{31}$F$_6$O$_6$PRuS$_4$ |         |         |         |
| C$_{16}$H$_{20}$Cl$_2$N$_2$O$_2$RuS$_2$ |         |         |         |
| Formula weight (Da)        | 470.01  | 657.66  | 508.43  |
| Temperature (K)            | 100(2)  | 100(2)  | 100(2)  |
| Wavelength (Å)             | 0.700   | 0.700   | 0.700   |
| Crystal system             | monoclinic | monoclinic | monoclinic |
| Space Group                | P 21/n  | P 21/c  | P 21/c  |
| a (Å)                     | 8.356(2) | 12.435(3) | 16.164(7) |
| b (Å)                     | 14.6850(7) | 11.338(1) | 19.153(9) |
| c (Å)                     | 14.9920(6) | 17.750(1) | 13.189(3) |
| α (°)                     | 90       | 90      | 90      |
| β (°)                     | 95.60(1) | 91.79(2) | 107.54(2) |
| γ (°)                     | 90       | 90      | 90      |
| V (Å$^3$)                 | 1830.9(3) | 2501.3(8) | 3893(3) |
| Z                         | 4        | 4       | 8       |
| ρ (g·cm$^{-3}$)            | 1.705    | 1.746   | 1.735   |
| F(000)                    | 960      | 1336    | 2048    |
| μ (mm$^{-1}$)              | 1.285    | 1.036   | 1.237   |
| θ min, max (°)            | 1.916, 28.227 | 1.614, 29.998 | 1.301, 28.227 |
| Resolution (Å)            | 0.74     | 0.70    | 0.74    |
| Total refl. collctd       | 29469    | 89392   | 61622   |
| Independent refl.         | 4676     | 7573    | 9911    |
| Obs. Refl. [Fo>4σ(Fo)]    | 4673     | 7517    | 9898    |
| I/σ(I) (all data)         | 63.33    | 45.80   | 62.71   |
| I/σ(I) (max res)          | 49.75    | 34.68   | 53.01   |
| Completeness (all data)   | 0.985    | 0.988   | 0.982   |
| Rmerge (all data)          | 2.0%     | 4.0%    | 2.4%    |
| Rmerge (max res)           | 2.0%     | 3.5%    | 2.7%    |
| Multiplicity (all data)    | 6.2      | 11.5    | 6.1     |
| Multiplicity (max res)     | 6.1      | 9.7     | 5.8     |
| Data/restraint/parameters  | 4676/0/191 | 7573/0/291 | 9911/0/452 |
| GooF                       | 1.136    | 1.069   | 1.166   |
| R[I>2.0σ(I)]$^a$ wR2 [I>2.0σ(I)]$^a$ | 0.0230, 0.0561 | 0.0306, 0.0816 | 0.0216, 0.0554 |
| R (all data),$^a$ wR2 (all data)$^a$ | 0.0230, 0.0561 | 0.0308, 0.0818 | 0.0217, 0.0554 |
Table S6 contd. Crystallographic data and refinement details for compounds [Ru(phen)$_2$(η$^2$-mal)]·5H$_2$O (10·5H$_2$O), [Ru(dpphen)$_2$(η$^2$-mal)]·3.75H$_2$O (11·3.75H$_2$O), and [Ru(phen)$_2$(η$^2$-ox)]·H$_2$O (12·H$_2$O).

|                  | 10·5H$_2$O | 11·3.75H$_2$O | 12·H$_2$O   |
|------------------|------------|--------------|-------------|
| Empirical Formula| C$_{27}$H$_{18}$N$_4$O$_4$Ru·5H$_2$O | C$_{51}$H$_{34}$N$_4$O$_4$Ru·3.75H$_2$O | C$_{26}$H$_{16}$N$_4$O$_4$Ru·H$_2$O |
| Formula weight (Da) | 653.60     | 935.45       | 567.51      |
| Temperature (K)   | 100(2)     | 100(2)       | 100(2)      |
| Wavelength (Å)    | 0.700      | 0.700        | 0.700       |
| Crystal system    | triclinic  | triclinic    | triclinic   |
| Space Group       | P –1       | P –1         | P –1        |
| a (Å)             | 10.322(3)  | 12.765(5)    | 9.5710(7)   |
| b (Å)             | 10.569(2)  | 13.403(2)    | 11.3260(5)  |
| c (Å)             | 13.064(3)  | 26.445(3)    | 12.1490(5)  |
| α (°)             | 84.832(6)  | 102.828(8)   | 83.891(6)   |
| β (°)             | 76.176(8)  | 90.20(2)     | 74.856(4)   |
| γ (°)             | 72.432(5)  | 108.05(1)    | 72.743(6)   |
| V (Å$^3$)         | 1319.1(5)  | 4182.0(2)    | 1213.4(1)   |
| Z                 | 1          | 4            | 2           |
| ρ (g·cm$^{-3}$)   | 1.646      | 1.486        | 1.553       |
| F(000)            | 668        | 1926         | 572         |
| μ (mm$^{-1}$)     | 0.624      | 0.416        | 0.655       |
| θ min, max (°)    | 1.581, 28.227 | 0.780,24.014 | 2.484,28.224 |
| Resolution (Å)    | 0.74       | 0.74         | 0.74        |
| Total refl. collctd | 6720      | 127131       | 58712       |
| Independent refl. | 6720      | 13220        | 6156        |
| Obs. Refl. [Fo>4σ(Fo)] | 6575     | 11730        | 6087        |
| I/σ(I) (all data) | 46.09      | 30.10        | 100.64      |
| I/σ(I) (max res)  | 37.72      | 13.39        | 69.35       |
| Completeness (all data) | 0.989   | 0.960        | 0.977       |
| R$_{merge}$ (all data) | 3.2%     | 4.5%         | 1.7%        |
| R$_{merge}$ (max res) | 4.1%      | 14.7%        | 2.6%        |
| Multiplicity (all data) | 6.0        | 9.3          | 9.5         |
| Multiplicity (max res) | 5.6        | 8.8          | 9.1         |
| Data/restraint/parameters | 6720/17/327 | 13220/66/1081 | 6156/15/316 |
| GooF              | 1.072      | 1.047        | 1.095       |
| R[I>2.0σ(I)], a wR2 [I>2.0σ(I)] | 0.0459, 0.1531 | 0.0741, 0.1989 | 0.0366, 0.0936 |
| R (all data), a wR2 (all data) | 0.0464, 0.1536 | 0.0811, 0.2070 | 0.0368, 0.0938 |
Table S7. Selected coordination distances (Å) and angles (°) for $fac$-[RuCl(dmsos-S)$_3$(η$_2$-acac)] (6).

| Selected distances (Å)           |       |
|----------------------------------|-------|
| Ru1–Cl1                          | 2.4326(4) |
| Ru1–O1                           | 2.075(1)  |
| Ru1–O2                           | 2.064(1)  |
| Ru1–S1                           | 2.2516(5) |
| Ru1–S2                           | 2.2622(5) |
| Ru1–S3                           | 2.2650(4) |

| Selected angles (°)              |       |
|----------------------------------|-------|
| O1–Ru1–Cl1                       | 85.58(4)   |
| O1–Ru1–S1                        | 177.39(4)  |
| O1–Ru1–S2                        | 87.41(4)   |
| O1–Ru1–S3                        | 87.89(4)   |
| O2–Ru1–Cl1                       | 86.13(4)   |
| O2–Ru1–O1                        | 91.38(5)   |
| O2–Ru1–S1                        | 86.02(4)   |
| O2–Ru1–S2                        | 174.40(4)  |
| O2–Ru1–S3                        | 90.79(4)   |
| S1–Ru1–Cl1                       | 94.49(1)   |
| S1–Ru1–S2                        | 95.21(2)   |
| S1–Ru1–S3                        | 91.89(2)   |
| S2–Ru1–Cl1                       | 88.33(2)   |
| S2–Ru1–S3                        | 94.62(2)   |
| S3–Ru1–Cl1                       | 172.70(2)  |
Table S8. Selected coordination distances (Å) and angles (°) for \( \text{fac-}[\text{Ru(dmsO-O)(dmsO-S)}_3(\eta^2-\text{acac})][\text{PF}_6] \) (7).

| Selected distances (Å)                  |
|----------------------------------------|
| Ru1–O11 2.071(1)                        |
| Ru1–O12 2.066(1)                        |
| Ru1–O21 2.133(1)                        |
| Ru1–S31 2.2490(6)                       |
| Ru1–S41 2.2493(6)                       |
| Ru1–S51 2.2667(5)                       |

| Selected angles (°)                     |
|----------------------------------------|
| O11–Ru1–O21 86.50(5)                   |
| O11–Ru1–S31 90.73(4)                   |
| O11–Ru1–S41 174.52(4)                  |
| O11–Ru1–S51 87.03(4)                   |
| O12–Ru1–O11 90.61(5)                   |
| O12–Ru1–O21 82.15(5)                   |
| O12–Ru1–S31 90.52(4)                   |
| O12–Ru1–S41 90.68(4)                   |
| O12–Ru1–S51 174.84(4)                  |
| O21–Ru1–S31 172.13(4)                  |
| O21–Ru1–S41 88.40(4)                   |
| O21–Ru1–S51 93.11(4)                   |
| S31–Ru1–S41 94.58(2)                   |
| S31–Ru1–S51 94.10(2)                   |
| S41–Ru1–S51 91.25(2)                   |
Table S9. Selected coordination distances (Å) and angles (°) for *cis,trans*-\([\text{RuCl}_2(\text{dmso-S})_2(\text{phen})]\) (c).

| Selected distances (Å)         |
|-------------------------------|
| Ru1–Cl11 2.4292(9) Ru2–Cl21 2.4360(8) |
| Ru1–Cl12 2.4301(8) Ru2–Cl22 2.4286(8) |
| Ru1–N11  2.071(1)  Ru2–N21  2.078(1)  |
| Ru1–N12  2.062(1)  Ru2–N22  2.05591) |
| Ru1–S11  2.3170(8) Ru2–S21  2.3082(7) |
| Ru1–S12  2.3027(8) Ru2–S22  2.3177(7) |

| Selected angles (°)            |
|-------------------------------|
| Cl11–Ru1–Cl12  92.20(3) Cl21–Ru2–Cl22 91.86(4) |
| N11–Ru1–Cl11  94.07(4)  N21–Ru2–Cl21 172.89(3) |
| N11–Ru1–Cl12  173.67(3)  N21–Ru2–Cl22 95.22(5) |
| N11–Ru1–S11  89.81(4)  N21–Ru2–S21  92.07(4) |
| N11–Ru1–S12  91.82(4)  N21–Ru2–S22  89.23(4) |
| N12–Ru1–Cl11  173.94(3)  N22–Ru2–Cl21 92.86(5) |
| N12–Ru1–Cl12  93.56(4)  N22–Ru2–Cl22 175.24(3) |
| N12–Ru1–N11  80.14(5)  N22–Ru2–N21  80.06(6) |
| N12–Ru1–S11  88.31(3)  N22–Ru2–S21  90.27(4) |
| N12–Ru1–S12  92.63(3)  N22–Ru2–S22  91.99(4) |
| S11–Ru1–Cl11  89.90(2)  S21–Ru2–Cl21  88.70(2) |
| S11–Ru1–Cl12  89.30(3)  S21–Ru2–Cl22  89.31(2) |
| S12–Ru1–Cl11  89.32(2)  S22–Ru2–Cl21  90.27(2) |
| S12–Ru1–Cl12  89.15(3)  S22–Ru2–Cl22  88.51(2) |
| S12–Ru1–S11  178.24(1)  S22–Ru2–S21  177.56(1) |
**Table S10.** Selected coordination distances (Å) and angles (°) for [Ru(phen)$_2$(η$^2$-mal)]·5H$_2$O (10·5H$_2$O).

**Selected distances (Å)**

| Bond          | Distance (Å) |
|---------------|--------------|
| Ru1–N11       | 2.034(3)     |
| Ru1–N12       | 2.049(3)     |
| Ru1–N21       | 2.063(3)     |
| Ru1–N22       | 2.025(3)     |
| Ru1–O31       | 2.089(3)     |
| Ru1–O32       | 2.092(3)     |

**Selected angles (°)**

| Angle          | Angle (°)       |
|----------------|-----------------|
| N11–Ru1–N12    | 80.9(1)         |
| N11–Ru1–N21    | 95.5(1)         |
| N11–Ru1–O31    | 88.5(1)         |
| N11–Ru1–O32    | 171.4(1)        |
| N12–Ru1–N21    | 174.9(1)        |
| N12–Ru1–O31    | 86.5(1)         |
| N12–Ru1–O32    | 90.5(1)         |
| N21–Ru1–O31    | 97.0(1)         |
| N21–Ru1–O32    | 93.2(1)         |
| N22–Ru1–N11    | 95.1(1)         |
| N22–Ru1–N12    | 96.2(1)         |
| N22–Ru1–N21    | 80.4(1)         |
| N22–Ru1–O31    | 175.7(1)        |
| N22–Ru1–O32    | 86.2(1)         |
| O31–Ru1–O32    | 90.6(1)         |
Table S11. Selected coordination distances (Å) and angles (°) for [Ru(dpphen)$_2$(η$^2$-mal)]·3.75H$_2$O (11·3.75H$_2$O).

### Selected distances (Å)

| Bond                  | Distance (Å) |
|-----------------------|--------------|
| Ru1–N21               | 2.046(5)     |
| Ru2–N51               | 2.035(5)     |
| Ru1–N22               | 2.034(5)     |
| Ru2–N52               | 2.048(5)     |
| Ru1–N31               | 2.047(5)     |
| Ru2–N61               | 2.057(5)     |
| Ru1–O11               | 2.100(4)     |
| Ru2–O41               | 2.100(4)     |
| Ru1–O12               | 2.097(4)     |
| Ru2–O42               | 2.100(4)     |

### Selected angles (°)

| Bond                  | Angle (°) |
|-----------------------|-----------|
| N21–Ru1–N31           | 174.5(2)  |
| N21–Ru1–O11           | 91.6(2)   |
| N21–Ru1–O12           | 86.2(2)   |
| N22–Ru1–N21           | 80.5(2)   |
| N22–Ru1–N31           | 95.0(2)   |
| N22–Ru1–O11           | 171.8(2)  |
| N22–Ru1–O12           | 88.1(2)   |
| N31–Ru1–O11           | 93.1(2)   |
| N31–Ru1–O12           | 96.7(2)   |
| N32–Ru1–N21           | 97.3(2)   |
| N32–Ru1–N22           | 96.0(2)   |
| N32–Ru1–N31           | 80.2(2)   |
| N32–Ru1–O11           | 87.1(2)   |
| N32–Ru1–O12           | 175.0(2)  |
| O12–Ru1–O11           | 89.2(2)   |

O12–Ru2–O42 89.0(2)
**Table S12.** Selected coordination distances (Å) and angles (°) for [Ru(phen)$_2$(η$_2$-ox)]$^+$·H$_2$O (12·H$_2$O).

**Selected distances (Å)**

| Bond | Distance (Å) |
|------|--------------|
| Ru1–N21 | 2.057(2) |
| Ru1–N22 | 2.026(2) |
| Ru1–N31 | 2.040(2) |
| Ru1–N32 | 2.032(2) |
| Ru1–O11 | 2.081(2) |
| Ru1–O12 | 2.082(2) |

**Selected angles (°)**

| Angle | Angle (°) |
|-------|-----------|
| N21–Ru1–O11 | 93.13(7) |
| N21–Ru1–O12 | 85.37(7) |
| N22–Ru1–N21 | 80.54(8) |
| N22–Ru1–N31 | 95.05(8) |
| N22–Ru1–N32 | 95.37(8) |
| N22–Ru1–O11 | 171.41(8) |
| N22–Ru1–O12 | 93.82(8) |
| N31–Ru1–N21 | 175.37(7) |
| N31–Ru1–O11 | 91.11(7) |
| N31–Ru1–O12 | 93.54(7) |
| N32–Ru1–N21 | 101.26(8) |
| N32–Ru1–N31 | 80.48(8) |
| N32–Ru1–O11 | 91.55(7) |
| N32–Ru1–O12 | 169.44(7) |
| O11–Ru1–O12 | 79.80(7) |
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