



Photophysical Properties

Emissive Ruthenium–Bisdiimine Complexes with Chelated Thioether Donors

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Abstract: The photophysical properties of ruthenium(II) complexes of bidentate 2-[(alkylthio)methyl]pyridine (N,S) ligands have been systematically investigated. The co-ligands in the heteroleptic complexes were diimines (N,N ligands, e.g., bpy, phen) or tripodal tetradentate tris(2-pyridylmethyl)amine (tpa). Their X-ray structures revealed little variation in the Ru–S (2.31–2.33 Å) and Ru–N (2.06–2.11 Å) bond lengths. Despite this, considerable variation can be observed in the electrochemistry and spectroscopy measurements. The presence of the thioether sul-

Introduction

Ru complexes are widely used in coordination chemistry, for photosensitizing and photocatalytic purposes, and as metalloenzyme models and building blocks for synthesizing complex organic molecules and supramolecular constructs.^[1] The σ -donating and π -accepting properties of a ligand will impact both the photophysical and electrochemical properties of the resulting complex. If a long-lived excited state is required for photosensitizing or probing purposes, chromophoric ligands become a necessity. $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) is the prototype example with a prominent singlet metal-to-ligand charge-transfer (¹MLCT) electronic absorption band in the visible region, long-lived (1 µs) ³MLCT emission, and reversible electrochemical properties.^[1a,1b] The properties are routinely fine-tuned by substitutions on the ligand backbone, for example, with electron-donating or -withdrawing groups.^[1a,1b] The synthesis of heteroleptic complexes, that is, complexes with different ligands, provides an ability to further adjust the electronic properties and add functionality to a complex.^[1a,1b] In addition to the electronic effects, the geometric structure will also have an impact on important properties. For example, bulky ligands may preclude the formation of homoleptic complexes or destroy emission properties by increased nonradiative decay

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fur donor results in a shift to a more positive potential of the Ru²⁺/Ru³⁺ process, and the absorption maxima are consequently blueshifted in [Ru(N,N)₂(N,S)]²⁺ complexes compared with the [Ru(N,N)₃]²⁺ analogues. The [Ru(N,N)₂(N,S)]²⁺ complexes display strong room-temperature emission from ³MLCT states, governed by the N,N donors. This is corroborated by low-temperature steady-state emission studies, which revealed typical ³MLCT emission profiles and excited-state lifetimes of around 5–10 µs.

rates.^[2] Although it is relatively easy to predict the properties of homoleptic complexes based on the electronic properties of the ligand, Lever's electrochemical series, and the spectrochemical series, there are still many types of ligands the overall impact of which on properties is not yet well understood,^[3] for example, thioether ligands. Numerous reports of Ru complexes with thioether motifs can be found in the literature, but very few of those include a full photophysical characterization.^[4] Because thioethers are potential building blocks for further synthesis and as model compounds, it is important to establish an understanding of their steric and electronic properties and the subsequent impact on their photophysical and -chemical properties.

In this paper we describe the use of a bidentate mixed N,Sdonor chelate, consisting of a pyridine and a thioether motif, to form Ru^{II} complexes. The properties of the N,S ligands were studied in homo- and heteroleptic complexes built by the coordination of one N,S donor and two chromophoric bipyridine ligands. We also synthesized complexes with the nonchromophoric tripodal ligand tris(2-pyridylmethyl)amine (tpa), which features both a σ -donating central amine and π -accepting pyridines.^[1d,5] Crystal structures revealed that the coordination of the N,S ligand results in slightly irregular octahedral geometries. Spectroscopic studies at room temperature and 80 K proved that the small deviations from ideal geometries have little impact on the emissive properties, but that the nonradiative decay rates are slightly increased.

Results and Discussion

Synthesis

In this study we combined diimine (N,N) ligands [2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmb), or 1,10-phenanthrol-

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ine (phen)] with a chelating bidentate thioether-pyridine ligand (N,S), namely 2-[(methylthio)methyl]pyridine (**1**; Scheme 1), for the preparation of heteroleptic tris complexes of the form $[Ru(N,N)_2(N,S)]^{2+}$. To enable comparisons of the physical properties in the presence and absence of the chromophoric diimine ligands, a homoleptic $[Ru(N,S)_3]^{2+}$ complex of **1** was prepared as well as the heteroleptic complex $[Ru(tpa)(1)]^{2+}$, in which tpa is the tripodal tetradentate ligand tris(2-pyridylmethyl)amine. In addition, an extended version of ligand **1**, 2-[(ethyl-thio)methyl]pyridine (**2**), was synthesized and used to form homoleptic complexes.



Scheme 1. Ligands used to form the Ru complexes reported herein.

The heteroleptic Ru complexes were prepared from $[RuCl_2(dmso)_4]$ according to the procedure^[5b] shown in Scheme 2. In the first step, two dmso ligands were selectively replaced by the bidentate N,S chelates to give the isolable complexes $[RuCl_2(dmso)_2(N,S)]$.^[5a] In the second step, the remaining

dmso and chloride ligands were replaced by two bidentate diimine ligands or tpa. Microwave irradiation was used to speed up the reaction. All the complexes were isolated as hexafluorophosphate salts. The synthesis of the tris-homoleptic $[Ru(N,S)_3]^{2+}$ complexes followed the same basic procedure, however, 3 equivalents of the respective ligand were added and they were precipitated as perchlorate salts. The syntheses reported here differ from the majority of preparations of mononuclear ruthenium complexes with diimine ligands. Most begin with the in situ reduction of $RuCl_3$, subsequent reaction with the diimine ligand to give intermediate $[Ru(N,N)_2Cl_2]$ complexes, followed by substitution of the chloride ligands.^[6] This procedure avoids the use of silver salts for the removal of chloride.^[5b] Under the conditions reported here, no scrambling or loss of N,S ligands was detected.

Structures

Crystals suitable for X-ray crystallography were obtained for $[Ru(dmb)_2(1)](PF_6)_2$, $[Ru(phen)_2(1)](PF_6)_2$, and $[Ru(2)_3](ClO_4)_2$ (Figures 1 and 2). Selected bond lengths and angles are summarized in Tables 1 and 2. In $[Ru(2)_3](ClO_4)_2$, the bidentate ligands are arranged in a facial conformation and the Ru–S bond lengths are slightly shorter (Ru–S, 2.31 Å vs. 2.33 Å) compared with in the $[Ru(N,N)_2(N,S)]^{2+}$ complexes. In contrast the Ru–N bond lengths are longer (2.12 Å) in $[Ru(2)_3](ClO_4)_2$ than any Ru–N bond in the $[Ru(N,N)_2(N,S)]^{2+}$ complexes. The coordination



Scheme 2. Synthetic route employed to form the mono-thioether complexes.



Figure 1. Crystal structures of $[Ru(dmb)_2(1)](PF_6)_2$ (left) and $[Ru(phen)_2(1)](PF_6)_2$ (right). Anisotropic displacement parameters are drawn at the 30 % probability level. Hydrogen atoms have been omitted for clarity.







Figure 2. Crystal structures of $[Ru(tpa)(1)](PF_6)_2$ (left) and $[Ru(2)_3](CIO_4)_2$ (right). Unlabelled atoms are related by symmetry. Anisotropic displacement parameters are drawn at the 30 % probability level. Hydrogen atoms have been omitted for clarity.

geometries are irregular octahedral for all complexes, with angles for *trans* ligands ranging between 163 and 178°, with the corresponding angles for *cis* ligands being 79 to 100°. The Ru–S bond lengths are also similar to those reported for other Ru(N,N)₂-thioether complexes.^[4a-4c,4e,7] Crystals were also produced for [Ru(tpa)(1)](PF₆)₂ (Table 1, Figure 2) in which the sulfur donor of **1** is located *cis* to the tpa amine N. The longest Ru–N_{py} bond length in this complex is observed *trans* to the sulfur donor. The Ru–N bond lengths in [Ru(tpa)(1)](PF₆)₂ (2.07–2.11 Å) are longer than those reported for neutral [Ru(tpa)Cl₂]

Table 1. Selected bond lengths [Å] and angles [°] for $[Ru(dmb)_2(1)](PF_6)_{2/2}$ $[Ru(phen)_2(1)](PF_6)_{2/2}$, and $[Ru(tpa)(1)](PF_6)_{2/2}$.

	$[Ru(dmb)_2(1)](PF_6)_2$	$[Ru(phen)_2(1)](PF_6)_2$	$[Ru(tpa)(1)](PF_6)_2$
Ru–S1	2.3262(8)	2.3280(16)	2.3347(10)
Ru–N1	2.095(3)	2.100(5)	2.101(3)
Ru–N2	2.077(3)	2.061(4)	2.078(3)
Ru–N3	2.062(3)	2.072(5)	2.072(3)
Ru–N4	2.067(3)	2.072(4)	2.110(3)
Ru–N5	2.075(3)	2.086(4)	2.058(3)
N1-Ru-S1	82.03(7)	83.95(14)	81.51(9)
N1-Ru-N2	98.86(10)	96.56(18)	97.51(13)
N1-Ru-N3	176.95(10)	175.61(17)	178.05(14)
N1-Ru-N4	93.78(10)	91.61(17)	100.23(12)
N1-Ru-N5	89.08(10)	85.88(18)	98.46(12)
S1–Ru–N2	89.24(7)	91.98(13)	90.55(9)
S1–Ru–N3	98.42(8)	95.00(13)	97.24(10)
S1-Ru-N4	172.28(7)	171.25(12)	169.99(10)
S1–Ru–N5	94.73(8)	92.36(14)	89.27(10)
N2-Ru-N3	78.14(10)	79.19(18)	80.97(13)
N2-Ru-N4	97.84(10)	96.02(17)	98.95(13)
N2-Ru-N5	171.56(10)	175.22(18)	163.82(12)
N3-Ru-N4	86.12(10)	89.98(17)	81.26(13)
N3-Ru-N5	93.89(10)	98.44(18)	83.00(13)
N4-Ru-N5	78.67(10)	79.78(18)	80.73(13)

(2.03-2.06 Å) and the dicationic [Ru(tpa)(MeCN)₂]²⁺ (2.04-2.07 Å).^[5g] Kojima et al. reported crystal structures of [Ru(tpa)(N,N)]²⁺-type complexes in which the N,N ligands appear to cause more severe steric hindrance than the N,S ligand used here, manifested in larger differences in bond lengths and more distorted octahedral geometries.^[5f] Another interesting comparison for [Ru(tpa)(1)]²⁺ is [Ru(tpa)(dmso)(Cl)]⁺, in which the dmso is located either cis or trans to the amine N.^[1d,5a,5d] When dmso is cis to the N_{amine}, the Ru-S bond length is reported to be either 2.24^[5a] or 2.25 Å,^[5d] whereas for the *trans* isomer it is 2.27 Å.^[1d] These values are shorter than that observed for the thioether-Ru bond in $[Ru(tpa)(1)](PF_6)_2$ (2.31 Å). The reasons for the discrepancies in bond lengths are most likely a combination of steric effects (mono- vs. bidentate ligands and ligand size) as well as differences in electronic properties and possibly crystal packing forces.^[4a,8] The crystal structures reported here suggest no large impact on the photophysical properties caused by steric effects (see below).

Table 2. Selected bond lengths [Å] and angles [°] for [Ru(2)₃](ClO₄)₂.

	[Ru(2) ₃](ClO ₄) ₂	
Ru–S1	2.3141(19)	
Ru1–N1	2.119(6)	
N1–Ru–S1	82.87(15)	
N1-Ru-N1'	92.0(2)	
N1-Ru-S1'	171.90(15)	
N1-Ru-N1″	92.0(2)	
N1-Ru-S''	94.44(15)	
51–Ru–N1′	94.44(15)	
S1–Ru–S′	91.25(7)	
51-Ru-N1″	171.90(15)	







Figure 3. Electronic absorption spectra of $[Ru(bpy)_2(1)]^{2+}$, $[Ru(dmb)_2(1)]^{2+}$, $[Ru(phen)_2(1)]^{2+}$, $[Ru(tpa)(1)]^{2+}$, $[Ru(1)_3]^{2+}$, and $[Ru(2)_3]^{2+}$ with associated molar absorptivities measured in MeCN.

Electronic Absorption Spectroscopy

The electronic absorption data obtained in four different solvents at room temperature are summarized in Table 3, and the spectra in acetonitrile are shown in Figure 3. The $[Ru(N,S)_3]^{2+}$ complexes exhibit almost identical absorption spectra between 200 and 800 nm, with no appreciable absorption in the visible region. Their lowest-energy absorption bands display maxima at around 325 nm ($\varepsilon = 10000 \text{ M}^{-1} \text{ cm}^{-1}$). This band is not present in the spectra of the free ligands and is thus attributed to a metal-to-ligand charge-transfer (MLCT) process. The peak at around 245 nm has been attributed to a π - π * intraligand transition based on previous assignments^[4a] and the free ligand spectra (see Figure S1 in the Supporting Information).

Table 3. Electronic absorption and electrochemical data for the complexes at room temperature. $^{\left[a\right] }.$

	<i>E</i> _{ox} ^[b] [V]	λ _{max} [nm]		λ _{max} [nm]	
	vs. Fc ^{0/+}	($\varepsilon \ [M^{-1} \ cm^{-1}]$) in MeCN	MeOH	CH_2CI_2	H ₂ O
[Ru(bpy) ₂ (1)] ²⁺	1.05	432 (8.8)	434	433	437
[Ru(dmb) ₂ (1)] ²⁺	1.01	432 (9.0)	432	433	435
[Ru(phen) ₂ (1)] ²⁺	1.04	416 (12.1)	415	417	417
[Ru(tpa)(1)] ²⁺	0.89	371 (13.1)	370	370	370
[Ru(1) ₃] ²⁺	1.16	324 (9.9)	325	330	323
[Ru(2) ₃] ²⁺	1.24	325 (9.9)	325	326	324
[Ru(bpy) ₃] ^{2+[c]}	0.91 ^[d]	452 (13.0)	452	452	453
[Ru(dmb) ₃] ^{2+[c]}	0.71 ^[d]	450 (17.0)	459	459	455
[Ru(phen) ₃] ^{2+[c]}	1.02 ^[d]	442 (18.4)	-	447	448
[Ru(tpa)(dmso)Cl] ⁺	0.58 ^[e]	≈370 ^[e]	-	≈370 ^[e]	-

[a] Absorption wavelength maximum (λ_{max}) are reported in four solvents and molar absorptivities (ε) at the absorption band maxima in MeCN. [b] Electrochemical potentials (E_{ox}) are reported vs. the ferrocenium couple. [c] Data from Juris et al. unless otherwise noted.^[1b] [d] The original data were reported vs. SCE, 380 mV has been subtracted to align with the ferrocene reference system. [e] From Weisser et al.^[5a]

 $[Ru(tpa)(1)]^{2+}$ exhibits its lowest-energy maximum at 371 nm ($\varepsilon = 13100 \text{ m}^{-1} \text{ cm}^{-1}$) and a high-energy shoulder at 310–320 nm, a spectral shape very similar to that reported for $[Ru(tpa)(MeCN)_2]^{2+}.^{[5g]}$ These findings also appear consistent with the spectrum of the above-mentioned *S*-bonded $[Ru(tpa)(dmso)(Cl)]^+$ when the Cl⁻ is located *trans* to the tpa amine nitrogen. Interestingly, when the dmso is located *trans* to the amine nitrogen, the absorption band is significantly red-

shifted.^[5a] A comparison between $[Ru(tpa)(1)]^{2+}$ and $[Ru(tpa)(bpy)]^{2+}$ revealed that the bpy ligand induces a broader absorption with a pronounced shoulder in the visible region.^[5b,5f]

 $[{\rm Ru}({\sf N},{\sf N})_2({\sf N},{\sf S})]^{2+}$ complexes exhibit the expected ligand-centered transitions in the UV region^[1b] and MLCT bands in the visible region (λ_{max} = 416–432 nm). They are blueshifted by around 0.15 eV with respect to the parent $[{\rm Ru}({\sf N},{\sf N})_3]^{2+}$ complexes,^[1b] but redshifted compared with the data reported by Connick and co-workers for a set of complexes with bis-thioether ligands combined with phenanthroline derivatives.^[4a] This suggests that the higher the number of S donors, the more blueshifted the absorption spectra. This observation is also consistent with the results for $[{\rm Ru}({\sf N},{\sf S})_3]^{2+}$ complexes. The molar absorptivities are somewhat lower than the prototype $[{\rm Ru}({\sf N},{\sf N})_3]^{2+}$ complexes, in line with what has previously been observed for related complexes.^[4a,4d]

Electrochemistry

The metal-centered $Ru^{2+/3+}$ oxidation process can be accessed through electrochemical measurements and is expected to correlate with the MLCT absorption such that a more blueshifted absorption should correspond to a more positive oxidation potential.

This is indeed what is observed here (Table 3). The [Ru(N,S)₃]²⁺ complexes revealed quasireversible redox behavior in acetonitrile, in which the expected metal-based oxidation occurs at +1.16 and +1.24 V versus the ferrocenium couple $(Fc^{0/+})$ for $[Ru(1)_3]^{2+}$ and $[Ru(2)_3]^{2+}$, respectively. As suggested by the absorption data, the Ru^{2+/3+} potentials for the $[Ru(N,N)_2(N,S)]^{2+}$ complexes are lower than those of $[Ru(N,S)_3]^{2+}$ but higher than the values for the analogous $[Ru(N,N)_3]^{2+}$ complexes, all of which is consistent with Lever's electrochemical series. However, for the phen complex, the difference between $[Ru(phen)_2(1)]^{2+}$ and $[Ru(phen)_3]^{2+}$ is too small to be judged significant, at variance with the typical UV/Vis absorption/oxidation potential correlation. However, if we instead compare what Connick and co-workers observed for their Ru bis-thioether complexes, we observe a redshifted absorption and less positive Ru^{2+/3+} oxidation potentials, in general agreement with







Figure 4. Cyclic voltammograms recorded in MeCN (0.1 \mbox{M} TBAPF₆) for [Ru(phen)₂(1)](PF₆)₂ and [Ru(2)₃](ClO₄)₂ vs. Fc^{0/+}. Ag/Ag⁺ (0.01 \mbox{M} AgNO₃) was used as the reference electrode and 0.1 \mbox{M} butylammonium hexafluorophosphate in MeCN was used as the supporting electrolyte. The scan speed was 0.1 V/s for [Ru(2)₃](ClO₄)₂ and 0.05 V/s for [Ru(phen)^[2] (1)](PF₆)₂.

the expected correlation between absorption and electrochemical properties.^[4a]

The Ru^{2+/3+} wave for $[Ru(tpa)(1)]^{2+}$ is observed at 0.89 V versus Fc^{0/+}, which is more positive than the values reported for $[Ru(tpa)(dmso)(Cl)]^+$ complexes^[5a] (0.58 V vs. Fc^{0/+}) and slightly more positive than the 0.71 V reported for $[Ru(tpa)(bpy)]^{2+}$,^[5b] which can again be understood in terms of the electrochemical series.^[3]

The reduction potentials of Ru-polypyridine complexes typically provide valuable information about the lowest unoccupied molecular orbital (LUMO), which governs not only the reduction potentials, but also, to a large extent, the excited-state properties.^[1b,4a] Ouasireversible or irreversible waves were observed for all complexes when the negative potential range was scanned. The unexpected irreversibility (possibly due to small amounts of moisture in the solvents used) precludes a conclusive assignment of which ligand is easiest to reduce, and therefore is also most likely to host a MLCT excited state. However, an estimate can be obtained by comparing the CV data for $[Ru(2)_3]^{2+}$ with those obtained for $[Ru(N,N)_2(N,S)]^{2+}$ complexes and with the reported values for the [Ru(N,N)₃]²⁺ reference complexes (Figure 4).^[1b] The result of such a comparison is that the difference in energy is rather small. That, together with the uncertainty associated with converting potentials reported versus a different reference electrode, precludes a conclusive assignment of the first reduced ligand. However, one can easily

imagine that the extra electron can be more easily accommodated on the N,N ligands than on the N,S ligand. Thus, we conclude that an *N*,*N*-localized ³MLCT state is the most probable lowest excited state. This notion is also corroborated by the observed emission spectra (see below).

Emission Properties

Visible-light excitation in deoxygenated MeCN, MeOH, H₂O, and CH_2CI_2 revealed intense emission from all the $[Ru(N,N)_2(N,S)]^{2+}$ complexes, whereas the homoleptic complexes and $[Ru(tpa)(1)]^{2+}$ were nonemissive (see Figure 5 and Table 4). The maximum emission wavelengths consistently agree well with those reported for the corresponding $[Ru(N,N)_3]^{2+}$ complexes, and thus the broad, unstructured emission observed has been attributed to a diamine-localized ³MLCT state, consistent with the electrochemical observations.^[1b] The emission guantum yields, determined by using [Ru(bpy)₃]²⁺ as reference, are typically somewhat lower than those of the corresponding [Ru(N,N)₃]²⁺ complexes. This is corroborated by time-resolved emission experiments that revealed single-exponential excitedstate lifetimes of a few hundred nanoseconds, shorter than those of the tris-N,N analogues, but long enough to support the assignment of a ³MLCT state. The maximum emission wavelength for $[Ru(phen)_2(1)]^{2+}$ in acetonitrile is in good agreement with what Al-Rawashdeh et al. have observed for bis-phen bis-



Figure 5. Steady-state emission spectra of $[Ru(bpy)_2(1)](PF_6)_2$, $[Ru(dmb)_2(1)](PF_6)_2$, and $[Ru(phen)_2(1)](PF_6)_2$ at room temperature in neat MeCN (left) and in MeOH/EtOH (1:4, v/v) glass at 80 K (right).



thioether complexes.^[4a] However, their reported excited-state lifetimes are shorter than those observed here, which suggests that the nonradiative decay is higher in the bis-thioether complexes.^[4a]

Table 4. Electronic emission data for complexes in four different solvents at 298 K (n.a.: not available).

	λ_{\max} [nm]	τ [ns]	Φ	k _r [10 ⁴ s ⁻¹]	$k_{nr} \ [10^6 \ s^{-1}]$
MeCN					
[Ru(bpy) ₂ (1)] ²⁺	618	701	0.032	4.6	1.4
[Ru(dmb) ₂ (1)] ²⁺	627	653	0.015	2.3	1.5
$[Ru(phen)_2(1)]^{2+}$	598	444	0.016	3.6	2.2
[Ru(bpy) ₃] ^{2+[a]}	611	890	0.059	6.6	1.1
[Ru(dmb) ₃] ^{2+[b]}	625	777	0.041	5.3	1.2
[Ru(phen) ₃] ^{2+[a]}	604	460	0.028	6.1	2.1
MeOH					
[Ru(bpy) ₂ (1)] ²⁺	612	448	0.021	4.7	2.2
[Ru(dmb) ₂ (1)] ²⁺	624	627	0.030	4.8	1.6
$[Ru(phen)_2(1)]^{2+}$	595	222	0.010	4.5	4.5
[Ru(bpy) ₃] ^{2+[a]}	609	720	0.045	6.3	1.3
[Ru(dmb) ₃] ^{2+[c]}	640	950	0.086	9.1	0.96
[Ru(phen) ₃] ^{2+[a]}	595	450	0.019	4.2	2.2
CH_2CI_2					
[Ru(bpy) ₂ (1)] ²⁺	595	466	0.028	6.0	2.1
[Ru(dmb) ₂ (1)] ²⁺	612	515	0.034	6.6	1.9
$[Ru(phen)_2(1)]^{2+}$	582	133	0.009	6.8	7.5
[Ru(bpy) ₃] ^{2+[d]}	606	488	0.029	5.9	2.0
$[Ru(dmb)_3]^{2+[a]}$	618	931	0.12	13	0.95
[Ru(phen) ₃] ²⁺	n.a.	n.a.	n.a.	n.a.	n.a.
H ₂ O					
[Ru(bpy) ₂ (1)] ²⁺	624	570	0.030	5.3	1.7
[Ru(dmb) ₂ (1)] ²⁺	636	328	0.016	4.9	3.0
$[Ru(phen)_2(1)]^{2+}$	602	925	0.054	5.8	1.0
[Ru(bpy) ₃] ^{2+[d]}	626	630	0.043	6.8	1.5
$[Ru(dmb)_3]^{2+[a]}$	631	335	0.014	4.5	2.9
[Ru(phen) ₃] ^{2+[a]}	604	900	0.058	6.4	1.1

[a] Data from Juris et al. unless noted otherwise.^[1b] [b] Data from Ross et al.^[10] [c] In MeOH/EtOH. [d] Data from Caspar and Meyer.^[11]

The radiative and nonradiative rate constants for the complexes studied in this paper were calculated from the excitedstate lifetimes and quantum yields (Table 4). The radiative decay rates are unremarkable, whereas the nonradiative decay rates are consistently higher than those of the reference complexes.



A lower emission energy should manifest itself in a higher radiative decay, as postulated in the energy gap law.^[9] However, the small differences observed here seem to suggest a minor perturbation of the photophysical properties by the N,S-donor ligand itself rather than an emission energy dependence.

The low-temperature (80 K) emission experiments (Table 5 and Figure 5) revealed the expected well-resolved vibronic structure and blueshift of the maximum emission wavelengths compared with at room temperature.^[1b] Temperature-dependent lifetime measurements (80-160 K) were performed for $[Ru(bpy)_2(1)]^{2+}$ and $[Ru(dmb)_2(1)]^{2+}$ and revealed the expected behavior, that is, small differences in lifetime as long as the samples are in a solid glass matrix, and once the glass-fluid transition has occurred, the temperature dependence becomes more pronounced (see Figures S2 and S3 in the Supporting Information). Visible-light excitation of $[Ru(1)_3]^{2+}$ in an MeOH/ EtOH glass at 80 K resulted in a very weak emission signal centered at around 570 nm that lasted for several µs. Owing to the weak signal, it was not possible to determine the nature of the weakly emissive state, however, the results are not inconsistent with a very weakly emissive ³MLCT state.

Table 5. Emission data obtained at low temperature and spectral fitting parameters.

	$[Ru(bpy)_2(1)]^{2+}$	$[Ru(dmb)_2(1)]^{2+}$	$[Ru(phen)_2(\textbf{1})]^{2+}$	$[Ru(bpy)_3]^{2+[a]}$
λ _{Em} [nm]	573	591	562	582 ^[b]
τ [µs]	6.54	5.72	11.1	5.1 ^[b]
E_{00} [cm ⁻¹]	17800	17250 ^[c]	17870	17200
$v_{1/2}$ [cm ⁻¹]	620	795 ^[c]	723	650
$v_{\rm m}$ [cm ⁻¹]	1375	1350 ^[c]	1300	1350
S _M	0.95	0.85 ^[c]	0.63	0.87
$v_{\rm L} [{\rm cm}^{-1}]$	450	400 ^[c]	420	N/A
SI	1.46	1.42 ^[c]	0.57	0.97

[a] Data from Hammarström et al. unless otherwise noted.^[12c] [b] Data from Watts et al.^[15] [c] Simulated data, for an explanation see the text.

One way to gain more information about the factors governing the nonradiative deactivation of the ³MLCT state is to perform a spectral shape analysis (Table 5, Figure 6, and Figure S4 in the Supporting Information). This provides information about vibrational modes coupled to the transition and geometric differences between the ground and excited state. Following the approach of Meyer and co-workers,^[9c,11b,12] the low-tempera-



Figure 6. Emission spectra for $[Ru(bpy)_2(1)]^{2+}$ (left) and $[Ru(phen)_2(1)]^{2+}$ (right) in MeOH/EtOH (1:4) at 80 K with the result of spectral analysis according to Equation (1) overlaid.





ture emission spectra can be fitted to a series of Gaussian shapes, see Equation (1).

$$I(E) = \sum_{n_{M}} \sum_{n_{L}} \left(\frac{E_{00} - n_{M} v_{M} - n_{L} v_{L}}{E_{00}} \right)^{3} \left(\frac{S_{M} n_{M}}{n_{M}!} \right) \left(\frac{S_{L} n_{L}}{n_{L}!} \right) \times \left\{ \exp \left(-4 \ln 2 \left(\frac{E - E_{00} + n_{M} v_{M} + n_{L} v_{L}}{v_{1/2}} \right)^{2} \right) \right\}$$
(1)

E is the emission energy, *I*(*E*) is the emission intensity, E_{00} is the wavenumber of the 0–0 electronic transition, $v_{\rm M}$ and $v_{\rm L}$ are the wavenumbers of relevant medium and low frequency vibrational transitions, respectively, $n_{\rm M}$ and $n_{\rm L}$ are the corresponding vibrational-state quantum numbers, $v_{1/2}$ is the full width at half maximum (fwhm) of the Gaussians, and S_M and S_L are the Huang–Rhys factors quantifying the nuclear distortion between the ground and excited states, with $S_i = \lambda_i / v_i$ in which λ_i is the reorganization energy and v_i is the vibrational quantum (Table 5). The details of the fitting procedure are outlined in the Exp. Sect.

The extracted E_{00} values are, as expected from Figure 5, very similar. The values are also similar to that previously reported for [Ru(bpy)₃]²⁺.^[12c] The distortion between ground and excited states can be assessed by means of Huang-Rhys factors, which should be smaller when the excess electron density is localized over a larger ligand,^[13] which suggests that S_M should be lower for $[Ru(phen)_2(1)]^{2+}$ than for $[Ru(bpy)_2(1)]^{2+}$ with $[Ru(dmb)_2(1)]^{2+}$ in between, and this is indeed what was observed. The fact that the value of $S_{\rm M}$ for $[{\rm Ru}({\rm bpy})_2(1)]^{2+}$ is higher than that for [Ru(bpy)₃]²⁺ further supports the conclusion that the N,S donor causes the minor perturbation that increases the nonradiative decay (see above). Furthermore, the similarity in $\nu_{1/2}$ for $[Ru(bpy)_2(1)]^{2+}$ and $[Ru(bpy)_3]^{2+}$ also corroborates the previous assignments of a bpy-localized ³MLCT state. No reasonable fit could be generated for $[Ru(dmb)_2(1)]^{2+}$ due to a high-energy shoulder present in the 80 K spectrum. Instead, a simulation (see the Exp. Sect. for details) was performed. The high-energy band could be well fitted to a Gaussian shape, 670 cm^{-1} higher in energy and with a fwhm of 650 cm^{-1} , narrower than the vibrational bands (795 cm⁻¹) in $[Ru(dmb)_2(1)]^{2+}$. This is consistent with the high-energy band arising from a 1–0 transition.[14]

The low-temperature data and the spectral fitting combined corroborates the preliminary conclusions from the electrochemical and photophysical data obtained at room temperature; the mixed N,S chelate is nonchromophoric but induces minor perturbation to the diamine-localized emissive ³MLCT state such that the nonradiative decay is slightly increased compared with the N,N complexes.

Conclusions

We have prepared heteroleptic Ru^{II} complexes by using either a mixed N,S donor ligand and chromophoric diimine ligands or the N,S ligand and a tetradentate aminopyridine ligand. Crystal structures revealed slightly distorted octahedral geometries with unremarkable bond lengths. The complexes absorb visible light but at higher energies than typical Ru–polypyridine-type complexes, and they exhibit strong ³MLCT emission at room temperature as well as at 80 K. Comparison with well-known homoleptic Ru^{II} complexes suggest that the absorption properties observed can be attributed to electronic differences rather than steric effects. This is further manifested in the electrochemical properties, which follow the trends that can be expected based on Lever's electrochemical series. The nonradiative decay rates were analyzed and it could be concluded that the inclusion of the N,S donor induces a somewhat higher nonradiative decay rate compared with typical polypyridine–Ru complexes.

Experimental Section

Synthesis, Purification, and Analysis: 2-(Mercaptomethyl)pyridine,^[16] [RuCl₂(dmso)₄),^[17] [RuCl₂(dmso)₂(**1**)],^[18] and tpa^[5e] were prepared according to previously reported methods. All other chemicals were purchased from Sigma–Aldrich and used without further purification. The ligand composition was determined by ¹H and ¹³C NMR spectroscopy.

Caution! Although no problems were encountered during the synthesis of these complexes, perchlorate salts are potentially explosive and should be handled with care and only prepared in small amounts.

Physical Methods: ESI-MS spectra were recorded with a Bruker microTOF-QII spectrometer. Solution ¹H and ¹³C NMR spectra were recorded with a Bruker 400 MHz spectrometer using tetramethylsilane as internal standard. IR spectra were recorded with a Perkin– Elmer Spectrum 65 spectrometer equipped with a universal ATR sampling accessory. Cyclic voltammetry was carried out in dry solvents using an Autolab PGSTAT 10 electrochemical system with a platinum wire as the auxiliary electrode and Ag/Ag⁺ (0.01 M AgNO₃) as the reference electrode. *tert*-Butylammonium hexafluorophosphate (0.1 M) was used as electrolyte and all potentials are given versus the ferrocene/ferrocenium (Fc^{0/+}) redox couple ($E_{1/2}$ = 88 mV vs. Ag/Ag⁺, ΔE = 75–80 mV). Scan rates were either 0.1 or 0.05 V/s. Elemental microanalyses were performed at the Department of Chemistry, University of Copenhagen, Denmark.

X-ray Crystallography: Single-crystal diffraction data were measured by using a Bruker Nonius X8 KAPPA APEX II CCD diffractometer using graphite-monochromatized Mo- K_{α} radiation ($\lambda = 0.71073$ Å, 50 kV, 30 mA, sealed tube). Data were collected and processed by using the APEX2^[19] suite of programs with applied multi-scan absorption correction using SADABS.^[20] Initial models were obtained with SHELXS-2013 by using direct methods and further refined against F^2 by full-matrix least-squares methods using SHELXL-2013.^[21] Hydrogen atoms were placed at calculated positions and allowed to ride during refinement with C–H = 0.950–0.990 Å and $U_{\rm iso}(\rm H) = 1.2$ or $1.5U_{\rm eq}(\rm C)$. Selected crystallographic data and refinement details are presented in Table 6.

Photophysical Characterization: Spectrophotometric-grade acetonitrile (>99.5 %, Sigma–Aldrich), methanol (>99.9 % Sigma–Al-





Table 6	V row	cn/ctallographic	data for ID	(dmb) (1)(DE)	[Du(nhon)	(1)1/DE)	[Du(too)(1)](DE)	and $[P_{ij}(3)]$ $(C O_j)$	complayor
Table 0.	∧-iay	crystanographic		$u(u(u))_{2}(1)(1)_{6}(2)_{7}$	[hu(phen);	$(I)(\Gamma \Gamma_6)_2$	[nu(ipa)(I)](Fr ₆) ₂	and $[nu(\mathbf{Z})_3](CiO_4)_2$	complexes.

	$[Ru(dmb)_2(1)](PF_6)_2$	$[Ru(phen)_2(1)](PF_6)_2$	[Ru(tpa)(1)](PF ₆) ₂	$[Ru(2)_3](CIO_4)_2$
Empirical formula	$C_{31}H_{33}F_{12}N_5P_2RuS$	$C_{31}H_{25}F_{12}N_5P_2RuS$	$C_{25}H_{27}F_{12}N_5P_2RuS$	$C_{24}H_{33}Cl_2N_3O_8RuS_3$
M [g/mol]	898.69	890.63	820.58	759.68
Temperature [K]	150.0	150.0	150.0	100.0
Crystal system	triclinic	monoclinic	monoclinic	trigonal
Space group	РĪ	P21/n	P2 ₁ /n	P3c1
a [Å]	7.8801(6)	9.8508(6)	12.9686(4)	10.5556(3)
b [Å]	11.7985(9)	15.5970(9)	18.7961(6)	10.5556(3)
c [Å]	19.6163(15)	21.2508(14)	13.1345(5)	15.225(1)
α [°]	76.240(3)	90	90	90
β [°]	83.984(3)	93.431(4)	100.348(2)	90
γ [°]	87.489(3)	90	90	120
Volume [Å ³]	1761.4(2)	3259.2(3)	3149.58(19)	1469.11(13)
Z	2	4	4	2
$\rho_{calcd.}$ [mg/mm ³]	1.695	1.815	1.731	1.717
Abs. coefficient	0.691	0.746	0.764	0.981
F(000)	904.0	1776.0	1640.0	776.0
Crystal color/shape	Red/plate	Red/plate	Red/block	Yellow/block
Crystal size [mm ³]	0.47 imes 0.28 imes 0.05	$0.25 \times 0.10 \times 0.05$	0.50 imes 0.20 imes 0.20	$0.23 \times 0.10 \times 0.08$
2θ range for data collection [°]	7.062-52.744	7.296-52.744	7.228-52.744	4.456-60.998
Index ranges	$-9 \leq h \leq 8,$	$-12 \leq h \leq 11$,	$-16 \leq h \leq 13$,	$-15 \leq h \leq 14,$
	$-14 \le k \le 14,$	$-19 \le k \le 17,$	$-22 \leq k \leq 23,$	$-15 \leq k \leq 15,$
	<i>−</i> 22 ≤ <i>l</i> ≤ 24	-26 ≤ <i>l</i> ≤ 26	–16 ≤ <i>l</i> ≤ 16	-21 ≤ <i>l</i> ≤ 21
Reflections collected	31047	109905	34195	38396
Independent reflections (R _{int})	7014 (0.0327)	6532 (0.1171)	6369 (0.0283)	2982 (0.0336)
Data/restraints/parameters	7014/0/474	6532/0/470	6369/0/416	2982/1/125
GooF on F ²	1.083	0.932	1.126	1.363
Final $R_1(F)^{[a]} [I > 2\sigma(I)]/wR_2(F^2)^{[b]}$	0.0407/0.0958	0.0576/0.1339	0.0459/0.1016	0.0439/0.0982
$R_1^{[a]}/wR_2(F^2)^{[b]}$ (all data)	0.0518/0.1031	0.1267/0.1660	0.0604/0.1111	0.0451/0.0986
Flack parameter	_	_	-	0.018(11)
Largest diff. peak/hole [e/Å ³]	0.95/-0.78	1.02/-0.70	0.0604/0.1125	0.85/-0.73

[a] $R_1(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

drich), and dichloromethane (>99.5 % Sigma–Aldrich) were used as received. Water was filtered through a Milli-Q water purification system (Millipore) to a resistance of 18 M Ω /cm. The Ar gas used for deoxygenation purposes was obtained from AGA Gas AB Sweden.

UV/Vis absorption spectra between 200 and 800 nm were recorded with a Varian Cary 5000 UV/Vis-NIR spectrophotometer. Molar absorptivities were determined by linear regression from a set of 10 samples with different concentrations.

Steady-state emission experiments were carried out by using a SPEX Fluorolog-3 spectrofluorimeter (Jobin–Yvon Spex) with a R928 photomultiplier tube. Excitation light of 450 nm was obtained by using a 450 W xenon lamp and the emission spectra were recorded between 460 and 840 nm with absorbance adjusted to around 0.1 at the excitation wavelength. Emission quantum yields, Φ , were calculated in the wavenumber domain with [Ru(bpy)₃]Cl₂ in acetonitrile as reference by using Equation (2).

$$\Phi = \Phi_{\text{Ref}} \times A_{\text{Ref}} / A \times \int I(\nu) d\nu / \int I_{\text{Ref}}(\nu) d\nu \times \eta^2_{\text{Ref}} / \eta^2$$
(2)

A is the absorbance at the excitation wavelength, $\int I(\nu) d\nu$ is the emission intensity, and η is the refractive index. Time-resolved emission experiments were carried out by using a time-correlated single photon counting (TC-SPC) set-up. The excitation light was provided by a 405 nm diode laser (model LDH-P-C-405) and a PDL 800B pulsed diode driver (Picoquant, GmbH Germany), which was triggered by using a DG645 digital delay generator (Stanford Research Instruments). The emitted photons were collected by a thermoelectrically cooled microchannel plate photomultiplier tube (R3809U-50, Hamamatsu). The signal was digitalized by using a multichannel analyzer (SPC-300, Edinburgh Analytical Instruments) with 1024, 2048, or

4096 channels depending on the count rate to reduce count time and avoid potential photodegradation. The emission was recorded at the corresponding emission intensity maximum (λ_{em}) determined from the steady-state emission experiments until 10000 counts were collected in the top channel. The emission decay curves of the samples were fitted by using the FlouFit^[23] software. Low-temperature TC-SPC were recorded until 2000 counts in the top channel were recorded over a time window of 50 µs with 512 channels at a repetition rate of 20 kHz. All low-temperature absorption and emission spectroscopic analyses were performed in a liquid-nitrogencooled cryostat (Optistat, Oxford instruments) controlled by an intelligent temperature controller (ITC4, Oxford instruments). All the above spectroscopic measurements were performed in 1×1 cm quartz cells at room temperature, unless otherwise noted. Samples for steady-state and time-resolved emission measurements were purged with argon for 15 min prior to experiments, and the absorption spectra were recorded prior and subsequent to excitation to ensure the integrity of the sample. Radiative (k_r) and nonradiative (k_{nr}) rate constants were calculated by using the following relationships: $k_r = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$.

Spectral Fitting: The spectral fitting was carried out by using an in-house Matlab[®] program with nonlinear multidimensional minimization of the difference between the experimental and calculated spectra. From visual inspection of the spectra, a good initial approximation of several parameters can be extracted: $v_{\rm M}$ is taken as the spacing in the vibrational structure of the emission spectra, $S_{\rm M}$ is reasonably represented by dividing the intensity of the first and second vibrational feature, and E_{00} is approximately at the highenergy end at fwhm of the first vibrational peak. These parameters were extracted by the program and used as initial guesses, allowing



them to float by a factor of +/-1.25, whereas $\nu_{\rm L}$ was constrained between 400–500 cm⁻¹ and S_L between 0–4, as seen for other diimine complexes in the literature.^[14,22]

2-(Methylthiomethyl)pyridine (1): 2-(Mercaptomethyl)pyridine (15.5 g, 0.12 mol) and Et₃N (1.1 equiv., 0.13 mol, 13.8 g, 19.2 mL) were dissolved in MeCN (25 mL) and cooled to 0 °C whereupon a solution of MeI (1.1 equiv., 0.13 mol, 19.4 g, 8.5 mL) in MeCN (20 mL) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight whereupon the solvent was evaporated under reduced pressure leading to a mixture of 2-(methylthiomethyl)pyridine and triethylamine hydroiodide. The mixture was triturated with EtOAc (100 mL) and filtered to remove Et₃N·HI. The solvent was evaporated under reduced pressure to give a yellow oil, which was dissolved in CH₂Cl₂ (100 mL) and washed with dilute agueous NaOH (50 mL, 0.4 M). The organic phase was separated, dried with MgSO₄, and evaporated to yield 2-(methylthiomethyl)pyridine as a clear liquid, which was further purified by vacuum distillation (12.10 g, 0.09 mol, 70.10 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.49 (dq, J = 4.9 Hz, 1 H), 7.61 (td, J = 7.7, 1.9 Hz, 1 H), 7.31 (ddd, J = 7.8, 4.8, 1.2 Hz, 1 H), 7.11 (t, J = 7.2 Hz, 1 H), 3.75 (s, 2 H), 2.01 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 158.62, 149.29, 136.69, 123.00, 121.89, 40.10, 15.17 ppm.

2-(Ethylthiomethyl)pyridine (2): Synthesized analogously to compound **1** but by using ethyl iodide. Purified by short-path vacuum distillation to yield a colorless liquid (42.8 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.47 (d, *J* = 5.0 Hz, 1 H), 7.59 (td, *J* = 7.7, 1.8 Hz, 1 H), 7.32 (d, *J* = 7.1 Hz, 1 H), 7.10 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1 H), 3.79 (s, 2 H), 2.46 (q, *J* = 7.4 Hz, 2 H), 1.18 (t, *J* = 7.4 Hz, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 159.02, 149.23, 136.66, 123.00, 121.81, 38.83, 25.61, 14.45 ppm.

[Ru(bpy)₂(1)](PF₆)₂: [RuCl₂(dmso)₂(1)] (100.0 mg, 0.21 mmol) and 2,2'-bipyridine (66.8, 0.43 mmol, 2 equiv.) were suspended in glycerol (10 mL) and the reaction mixture was irradiated in a microwave at 200 °C for 20 min. The resulting dark-red solution was immediately poured over ice-cold saturated aqueous NH₄PF₆ (5 mL). The precipitate was collected by centrifugation, re-suspended in H₂O (5 mL) followed by filtration and additional washing with H₂O (5 mL) to remove residual NH₄PF₆. To remove residual glycerol the product was purified by dissolution in CH₃CN followed by careful addition of EtOH. The product was precipitated at -40 °C and filtered through a glass frit funnel, washed with abs. EtOH, and airdried to give the product as a red/brown powder to give a redorange powder (138.2 mg, 0.16 mmol, 78.1 %). FTIR (ATR diamond anvil): $\tilde{v} = 1466$ (w), 1447 (w), 836 (s), 763 (m), 732 (w), 557 (m) cm⁻¹. MS (ESI, MeCN, pos. mode): calcd. (found) m/z = 269.03 (269.03, $[Ru(bpy)_{2}(1 - CH_{3})]^{2+}$, $C_{27}H_{25}F_{12}N_{5}P$, 60%), 276.55 (276.54, [Ru(bpy)₂(1)]²⁺, C₂₇H₂₅N₅RuS, 20 %), 285.05 (285.05, [{Ru(bpy)₂(1)}³⁺ + OH⁻]²⁺, C₂₇H₂₆N₅RuSO, 100 %), 572.07 (572.08, [{Ru(bpy)₂(**1** – $(CH_3)\}^{3+} + 2OH^{-}]^{+}, C_{26}H_{24}N_5O2, 22 \%), 698.05$ (698.04. $[{Ru(bpy)_2(1)}^{2+} + PF_6^-]^+, C_{27}H_{25}F_6N_5PRuS, 27\%), 715.05$ (715.07, $[\{Ru(bpy)_2(\textbf{1})\} + OH^- + PF_6^-]^+, C_{27}H_{26}F_6N_5OPRuS, 66 \%).$ C₂₇H₂₅F₁₂N₅P₂RuS (842.59): calcd. C 38.49, H 2.99, N, 8.31; found C 39.88, H 2.69, N 8.89.

 $\begin{aligned} & [\text{Ru}(dmb)_2(1)](\text{PF}_6)_2\text{-}(\text{CH}_3)_2\text{CO:} & \text{Prepared analogously to} \\ & [\text{Ru}(\text{bpy})_2(1)](\text{PF}_6)_2 \text{ but by using } 4,4'\text{-dimethyl-2,2'-bipyridine to give} \\ & \text{the product as an orange powder (153.5 mg, 0.16 mmol, 76.4 \%).} \\ & \text{Recrystallization from acetone gave X-ray quality single crystals.} \\ & \text{FTIR (ATR diamond anvil): } \tilde{v} = 1618 (m), 1480 (w), 1239 (w), 820 (s, br), 554 (s), 526 (m) cm^{-1}. \text{ MS (ESI, MeCN, pos. mode): calcd. (found)} \\ & m/z = 297.07 (297.06, [\text{Ru}(dmb)_2(1 - \text{CH}_3)]^{2+}, \text{C}_{30}\text{H}_{30}\text{N}_5\text{RuS}, 20 \%), \\ & 304.58 (304.57, [\text{Ru}(dmb)_2(1)]^{2+}, \text{C}_{31}\text{H}_{33}\text{N}_5\text{RuS}, 18 \%), 327.06 (327.10, \\ & [\{\text{Ru}(dmb)_2(1) - \text{H}\} + 2\text{Na}^{+}]^{2+}, \text{C}_{31}\text{H}_{32}\text{N}_5\text{Na}_2\text{RuS}, 88 \%), 754.11 \end{aligned}$



$$\begin{split} & [\textbf{Ru(phen)}_2(1)](\textbf{PF}_6)_2: \mbox{ Prepared analogously to } [Ru(bpy)_2(1)](\textbf{PF}_6)_2 \\ & but by using 1,10-phenanthroline to give an orange powder \\ & (132.0 mg, 0.15 mmol, 70.6 %). \mbox{ Recrystallization from acetone gave } \\ & X-ray quality single crystals. FTIR (ATR diamond anvil): <math>\tilde{v} = 1427 \ (w), \\ & 835 \ (s, br), 776 \ (w), 722 \ (w), 556 \ (m) \ cm^{-1}. \ MS \ (ESI, \ MeCN, \ pos. mode): calcd. (found) <math>m/z = 321.05 \ (321.05, \ [\{Ru(phen)_2(1)\} + H_2O + Na^+]^{2+}, \ C_{31}H_{27}N_5NaORuS, 98 \ %), \ 497.06 \ (497.01, \ [\{Ru(phen)(1)\} + H_2O + MeCN + OH^-]^+, \ C_{21}H_{23}N_4O_2RuS, \ 100 \ \%), \ 515.07 \ (515.02, \ [\{Ru(phen)(1)\} + 2H_2O + MeCN + OH]^+, \ C_{21}H_{25}N_4O_3RuS, \ 74 \ \%), \\ & 787.08 \ (787.07, \ [\{Ru(phen)_2(1)\} + MeCN + PF_6^-]^+, \ C_{33}H_{28}F_6N_6PRuS, \ 78 \ \%). \ C_{31}H_{25}F_{12}N_5P_2RuS \ (890.64): calcd. C \ 41.81, \ H \ 2.83, \ N \ 7.86; \ found C \ 42.46, \ H \ 2.69, \ N \ 7.66. \end{split}$$

$$\begin{split} & [\text{Ru}(\text{tpa})(1)](\text{PF}_6)_2: \text{Prepared analogously to } [\text{Ru}(\text{by})_2(1)](\text{PF}_6)_2 \text{ but} \\ & \text{by using tris}(2-\text{pyridylmethyl})\text{amine to give an olive-green powder} \\ & (138.2 \text{ mg}, 0.17 \text{ mmol}, 80.2 \%). \text{ Recrystallization from acetone gave} \\ & \text{X-ray quality single crystals. FTIR (ATR diamond anvil): } \tilde{v} = 1606 (w), \\ & 1480 (w), 1448 (m), 1161 (w), 992 (w), 829 (s), 768 (s), 558 (s), 508 \\ & (m) \text{ cm}^{-1}. \text{ MS (ESI, MeCN, pos. mode): calcd. (found) } m/z = 258.04 \\ & (258.04, [\text{Ru}(\text{tpa})(1 - \text{CH}_3^-)]^{2+}, \text{ } C_{24}\text{H}_{24}\text{N}_5\text{Ru}\text{S}, 72 \%), 265.55 \\ & (265.55, [\text{Ru}(\text{tpa})(1)]^{2+}, \text{ } C_{25}\text{H}_2\text{N}_5\text{Ru}\text{S}, 43 \%), 550.09 \\ & (550.10, [\text{Ru}(\text{tpa})(1 - \text{CH}_3^-) + 20\text{H}^-]^+, \text{ } C_{24}\text{H}_{26}\text{N}_5\text{O}_2\text{Ru}\text{S}, 100 \%), 676.07 \\ & (676.06, [\{\text{Ru}(\text{tpa})(1)\} + \text{PF}_6^-]^+, \text{ } C_{25}\text{H}_2\text{F}_6\text{N}_5\text{PRuS}, 19 \%), 736.08 \\ & (736.13, [\text{Ru}(\text{tpa})(1 - \text{CH}_3^-) + \text{MeCN} + 20\text{H}^- + \text{PF}_6^-]^+, \\ & C_{26}\text{H}_{29}\text{F}_6\text{N}_6\text{O}_2\text{PRu}\text{S}, 17 \%). \text{ } C_{25}\text{H}_2\text{F}_1\text{N}_5\text{P}_2\text{Ru}\text{S} \\ & \text{ } 8.53; \text{ found C } 37.00, \text{ H } 3.15, \text{N} 8.55. \end{split}$$

[Ru(1)₃](ClO₄)₂·H₂O: [RuCl₂(dmso)₄] (345.2 mg, 0.71 mmol) and 2-(methylthiomethyl)pyridine (300.0 mg, 2.14 mmol, 3 equiv.) were dissolved in abs. EtOH (75 mL). AgNO₃ (255.6 mg, 1.50 mmol, 2.1 equiv.) was added and the reaction mixture was heated at reflux for 2 h followed by stirring at room temperature for 48 h. The precipitated AgCl was removed by filtration through Celite and the solvent was removed in vacuo to give an orange oil, which was dissolved in H₂O (15 mL). The product was precipitated by the slow addition of a saturated aqueous solution of NaClO₄, collected by filtration, and washed with ice-cold H_2O (3 \times 5 mL) to give a tanyellow powder after drying (220.0 mg, 0.29 mmol, 42.1 %). FTIR (ATR diamond anvil): $\tilde{v} = 1603$ (w), 1473 (w), 1435 (m), 1075 (s, br), 975 (m), 767 (m), 753 (m), 623 (s) cm⁻¹. MS (ESI, MeCN, pos. mode): calcd. (found) m/z = 252.01 (252.01, [{Ru(1)₃} - CH₃]²⁺, C₂₀H₂₄N₃RuS₃, 100 %), 259.52 (259.52, [Ru(**1**)₃]²⁺, C₂₁H₂₇N₃RuS₃, 75 %), 348.94 (348.94, $[{Ru(1 - CH_3)_2} - H]^+$, $C_{12}H_{11}N_2RuS_2$, 9 %), 363.96 (363.97, [{Ru(1)(1 - CH₃)} - H]⁺, C₁₃H₁₄N₂RuS₂, 37 %), 478.94 $(478.94, [{Ru(1)_2} + CIO_4^-]^+, C_{14}H_{18}CIN_2O_4RuS_2, 12\%), 501.93$ (502.02, [{Ru(1)₂} + ClO₄⁻ + Na⁺]⁺, C₁₄H₁₈ClN₂NaO₄RuS₂, 6 %), 517.93 $(518.03, [{Ru(1)_2} + CIO_4^- + Na^+ + O]^+, C_{14}H_{18}CIN_2NaO_5RuS_2, 5\%),$ 617.88 $(617.99, [{Ru(1)_2} + CIO_4^- + Na^+ + OH^-]^+,$ C₁₄H₁₉Cl₂N₂NaO₉RuS₂, 6 %). C₂₁H₂₉Cl₂N₃O₉RuS₃ (735.63): C 34.29, H 3.97, N 5.71; found C 33.91, H 3.38, N 5.62.

[Ru(2)₃](ClO₄)₂·H₂O: [RuCl₂(dmso)₄] (309.9 mg, 0.64 mmol) and 2-(ethylthiomethyl)pyridine (294.0 mg, 1.92 mmol, 3 equiv.) were dissolved in abs. EtOH (50 mL). AgNO₃ (228.3 mg, 1.34 mmol, 2.1 equiv.) was added and the reaction mixture was heated at reflux for 2 h followed by stirring at room temperature for an additional 48 h. The precipitated AgCl was removed by filtration through Celite and the solvent was removed in vacuo to give a red oily mass, which was dissolved in H₂O (10 mL). The product was precipitated by the addition of a saturated aqueous solution of NaClO₄, collected by filtration, washed with H₂O (2 × 5 mL), and air-dried (323.7 mg,





0.41 mmol, 65.0 %). Recrystallization from acetone gave X-ray quality single crystals. FTIR (ATR diamond anvil): $\tilde{v} = 1602$ (w), 1475 (w), 1440 (w), 1162 (w), 1083 (s, br), 762 (m), 712 (w), 623 (s), 440 (w) cm⁻¹. MS (ESI, MeCN, pos. mode): calcd. (found) m/z = 251.51 (251.50, [{Ru($2 - CH_3$)($2 - CH_2CH_3$)} + H⁺]²⁺, C₂₀H₂₃N₃RuS₃, 40 %), 266.03 (266.02, [{Ru(2)($2 - CH_3$)₂} + H⁺]²⁺, C₂₂H₂₈N₃RuS₃, 100 %), 280.55 (280.54, [Ru(2)]²⁺, C₂₄H₃₃N₃RuS₃, 45 %), 350.02 (349.96, [{Ru(2)} + 3H₂O + MeCN]⁺, C₁₀H₂₀N₂O₃RuS, 27 %), 507.00 (506.97, [{Ru($2 - CH_3$)($2 - CH_2CH_3$)₂} + H⁺ + H₂O]⁺, C₁₉H₂₃N₃ORuS₃, 9 %), 530.05 (530.05, [{Ru($2 - CH_2CH_3$)(2) - 2H⁺]⁺, C₂₂H₂₆N₃RuS₃, 7 %), 560.08 (560.08, [{Ru(2)₃} - H⁺]⁺, C₂₄H₃₂N₃RuS₃, 3 %), 660.04 (660.03, [{Ru(2)₃} + CIO₄⁻]⁺, C₂₄H₃₃CIN₃O₄RuS₃, 5 %). C₂₄H₃₅CI₂N₃O₉RuS₃ (777.71): C 37.07, H 4.54, N 5.40; found C 36.68, H 3.97, N 5.40.

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