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Novel Ru^{II} Complexes with Bispidine-Based Bridging Ligands: Luminescence Sensing and Photocatalytic Properties

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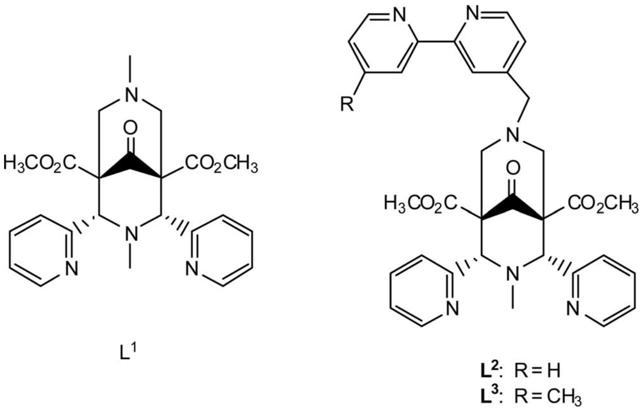
New ligands with a bidentate bipyridyl (bpy) and a tetradentate bispidine (bisp) subunit (bipyridyl = 2,2′-bipyridine derivative, bispidine = 3,7-diazabicyclo[3.3.1]nonane derivative) and their heterodinuclear {[Ru(bpy)$_3$]$^{2+}$-[M(bisp)]$^{2+}$} complexes (M = Cu^{2+}, Fe^{2+}) were prepared and characterized. The luminescence of the mononuclear Ru^{II} complexes (metal-free bisp subunit) is efficiently quenched in presence of Cu^{II}. An EPR spectroscopic study reveals that visible light irradiation does not alter the oxidation states of the two metal ions in {[Ru(bpy)$_3$]$^{2+}$-[Cu(bisp)]$^{2+}$}, i.e. there is energy rather than electron transfer. The heterodinuclear {[Ru(bpy)$_3$]$^{2+}$-[Cu(bisp)]$^{2+}$} complex shows a significant photocatalytic activity in the aziridination of styrene.

Introduction

Oligonuclear transition metal complexes capable of performing photoinduced energy or electron transfer are attracting much interest.[1–6] Due to the favorable photophysical properties such as long exited state lifetimes and high quantum yields of luminescence, many of these studies are devoted to systems containing Ru^{II} polypyridyl moieties as the photoactive component.[7–10] Therefore, the study of fundamental intramolecular energy transfer processes with Ru^{II} complexes[11–13] and the photophysics and photochemistry of the photo-induced reduction and oxidation of H_2O[14] have attracted considerable attention. However, there is only a limited number of examples, where the photochemical transformation of organic substrates induced by Ru^{II} complexes has been studied.[15–19] A central problem in this field is to find metal complexes with both high stability against photodecomposition and high reactivity.

Highly preorganized and rigid bispidine ligands (for example L^1, Scheme 1) form stable complexes with many transition metal ions and are selective for Cu^{II}.[20,21] Some show outstanding catalytic properties in processes such as the Cu-catalyzed aziridination[22–24] and the Cu- and Fe-induced oxygen activation.[25–28] Consequently, we have considered bispidine subunits as prospective building blocks for covalent bonding to a photoactive Ru^{II}-bipyridine site. Here we report the synthesis of the first examples of these bispidine-based bipyridine ligands, **L^2** and **L^3** (see Scheme 1), as well as the synthesis, redox and photophysical properties of the corresponding heterodinuclear Ru^{II}–Cu^{II} and Ru^{II}–Fe^{II} complexes. The possible application of the Ru^{II} complex as a luminescence sensor of Cu^{II} has been investigated and, as a first example of a photocatalytic process, the photoinduced Ru^{II}–Cu^{II}-catalyzed aziridination of styrene is also described.



Scheme 1.

Results and Discussion

Synthesis and Characterization of the Dinuclear Complexes

The ligands **L^2** and **L^3** were prepared by two consecutive Mannich condensation steps, leading to the piperidone precursor and the bispidones (Scheme 2).[29] Two different synthetic strategies were used to prepare the amino-bipyriyl derivatives, which are used in the second Mannich condensation step to produce the substituted bispidine ligands. The first method includes the synthesis of a nitrile-substituted bipyridine with a Negishi coupling (Scheme 2, a). The nitrile derivative is then reduced to afford 4-aminomethyl-2,2′-bipyridine. In the second method, a methyl-substituted

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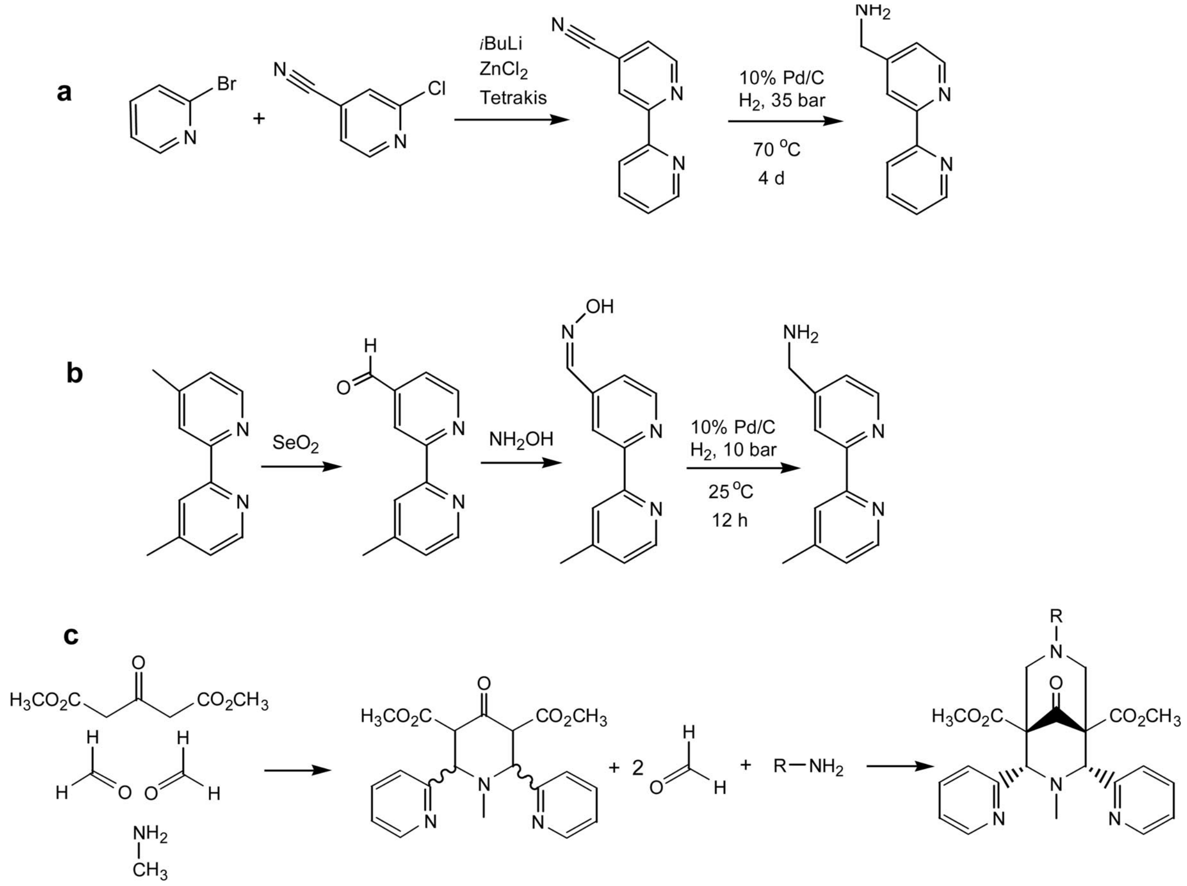


Scheme 2. Synthesis of bipyridine-substituted bispidine-type ligands.

bipyridine is used as the starting material. Oxidation of the methyl group leads to the aldehyde derivative, from which 4-methyl-2,2′-bipyridine-4′-carbaldoxime and 4-aminomethyl-4′-methyl-2,2′-bipyridine can be prepared in high yield (Scheme 2, b).

The metal-free ligands $\mathbf{L^2}$ and $\mathbf{L^3}$ were characterized by X-ray diffraction analysis. Both compounds crystallize with two independent molecules of similar structure in the unit cell. ORTEP diagrams of $\mathbf{L^2}$ and $\mathbf{L^3}$ are shown in Figure 1 and selected structural parameters are listed in Table 1. As expected,[20] in both ligands the rigid bispidine backbone has the desired *endo*-*endo* configuration with respect to the two pyridines. Due to lone-pair repulsion, in the metal-free ligands the pyridine groups at C2 and C4 (N1 and N2) are rotated away from the coordination site by approximately 180°.

Table 1. Selected experimental structural data of $\mathbf{L^2}$ and $\mathbf{L^3}$ (distances in Å, angles in degree, with estimated standard deviations in parentheses; values in square brackets refer to the second of the two independent molecules).

	$\mathbf{L^2}$	$\mathbf{L^3}$
N3···N7	2.943(2) [2.951(2)]	2.939(3) [2.871(3)]
N3–C2–C_{Ar}–N1	152.6(1) [152.1(1)]	164.3(2) [140.9(2)]
N3–C4–C_{Ar}–N2	–168.6(1) [–170.2(1)]	–139.7(3) [–148.7(3)]
N7–C25–C26–C27	–69.9(2) [–75.5(2)]	–121.6(3) [–109.5(3)]

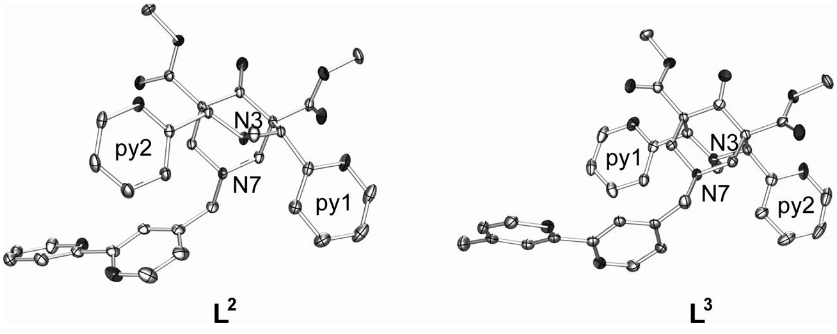


Figure 1. ORTEP plots of the dinucleating bispidine ligands $\mathbf{L^2}$ and $\mathbf{L^3}$ (ellipsoids shown at the 50% probability level; only one of the two independent molecules is shown in each case; hydrogen atoms are omitted for clarity).

The Ru^{II} complexes [(bpy)$_2$Ru(**L^2**)](PF$_6$)$_2$ (**1**) and [(bpy)$_2$-Ru(**L^3**)](PF$_6$)$_2$ (**2**) were obtained by the standard method for the synthesis of [Ru(bpy)$_3$]$^{2+}$ and similar complexes.[30] The reaction of **L^2** with Cu(ClO$_4$)$_2$·6H$_2$O leads to the formation of [Cu(**L^2**)](ClO$_4$)$_2$ (**3**), with Cu^{II} in the bispidine subunit. The heterodinuclear Ru^{II}–Cu^{II} complex [(bpy)$_2$-Ru(μ-**L^2**)Cu(Cl)$_2$](PF$_6$)$_2$ (**4**) was prepared by treatment of **3** with [Ru(bpy)$_2$(Cl)$_2$]. The mononuclear Ru^{II} precursor **2** reacts with iron dichloride to the heterodinuclear complex [(bpy)$_2$Ru(μ-**L^3**)Fe(Cl)$_2$](PF$_6$)$_2$ (**5**). The corresponding aqua complex [(bpy)$_2$Ru(μ-**L^3**)Fe(OH$_2$)$_2$](PF$_6$)$_4$ (**6**) was readily obtained by Cl$^-$ abstraction from **5** with AgPF$_6$. The reaction of **2** with a Cu^{II} salt leads to the formation of the heterodinuclear complex [(bpy)$_2$Ru(μ-**L^3**)Cu(NCCH$_3$)]-(PF$_6$)$_4$ (**7**). A three-dimensional model (molecular mechanics optimized) of a heterodinuclear complex ([(bpy)$_2$Ru(μ-**L^2**)M^{II}(X)$_2$]$^{n+}$) is given in Figure 2. All dinuclear Ru^{II}–Fe^{II} and Ru^{II}–Cu^{II} complexes are soluble in CH$_2$Cl$_2$, MeOH, and MeCN and are stable in day light at ambient temperature.

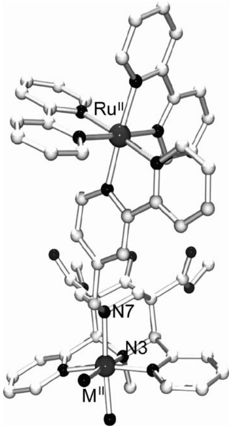


Figure 2. Plot of a structural model (optimized by molecular mechanics) of a heterodinuclear Ru^{II}–M^{II} complex of the dinucleating ligand **L^2**, [(bpy)$_2$Ru(μ-**L^2**)M^{II}(X)$_2$]$^{n+}$.

The redox potentials of **5**–**7** and some of the mononuclear precursors are listed in Table 2. In the CV of the mononuclear complex [(bpy)$_2$Ru(**L^3**)](PF$_6$)$_2$ (**2**), the single quasi-reversible wave is assigned to the metal-centered Ru^{II}/Ru^{III} oxidation process. The coordination of Fe^{II} to the bispidine coordination site does not lead to a significant shift of the Ru^{II}/Ru^{III} redox couple. The dinuclear Ru^{II}–Cu^{II} complex **7** has the Ru^{II}/Ru^{III} and Cu^{I}/Cu^{II} potentials slightly anodically shifted, probably due to partial electron density transfer from the Ru to the Cu center.

Electronic Absorption and Emission Spectroscopy

The UV/Vis spectra of the complexes were recorded in MeCN (see Table 3). The Ru^{II}-containing spectra are similar to those reported in the literature for [Ru(bpy)$_3$]$^{2+}$ and derivatives.[31] The intense absorption bands around 250 and 290 nm can be assigned to ligand-centered π-π* transitions. The relatively intense and broad bands in the visible region are assigned to spin-allowed d-π metal-to-ligand charge transfer (MLCT) transitions from the Ru^{II} center to the lowest-lying triplet of a bpy-type ligand [dπ(Ru) → π*(bpy)]. The weak d-d transitions centered at Fe^{II} or Cu^{II} were not observed due to superposition with the Ru^{II}-based charge transfer transitions.

The emission spectra of the complexes **2** and **5**–**7** were recorded in air-equilibrated MeCN solutions at room temperature and are shown in Figure 3. The spectra are from solutions of equal absorbance (0.13) at the 455 nm excitation wavelength. Compound **2** emits at 617 nm with a lifetime of 172 ns. The emission maxima and quantum yields are listed in Table 3. The quantum yield and spectral profiles are consistent with a ^{3}MLCT [dπ(Ru)→π*(bpy)] excited state (see above), being responsible for the emission. The significant decrease of luminescence intensity by substitution of the two chlorides with water in complex **5** may be due to a change in energy of the Fe^{II}-based electronic states. Efficient luminescence quenching of the Ru^{II} polypyridine chromophore is observed when Cu^{II} coordinates to the bispidine unit. The complexes [(bpy)$_2$Ru(**L^2**)](PF$_6$)$_2$ and [(bpy)$_2$Ru(**L^3**)](PF$_6$)$_2$ can therefore be considered as good on/off sensors for Cu^{II}. The addition of Zn^{II} to a solution of **1** did not affect the luminescence intensity (Table 4 and Figure 4). An effect of Ni^{II} coordination on the luminescence of **1** was apparent but significantly smaller than for Cu^{II}.

Table 2. Redox properties of mono- and dinuclear bispidine complexes.[a]

	$E_{1/2}$ (ΔE) /mV		
	Ru^{II}/Ru^{III}	Cu^{I}/Cu^{II}	Fe^{II}/Fe^{III}
[CuL^1(NCCH$_3$)](PF$_6$)$_2$	–	–474 (80)	–
[FeL^{1}Cl$_2$](PF$_6$)$_2$	–	–	+20 (73)
[FeL^1(H$_2$O)$_2$](PF$_6$)$_2$	–	–	+370 (irr.)
[(bipy)$_2$Ru**L^3**](PF$_6$)$_2$ (**2**)	+875 (133)	–	–
[(bipy)$_2$Ru(μ-**L^3**)Fe(Cl)$_2$](PF$_6$)$_2$ (**5**)	+867 (121)	–	+92 (91)
[(bipy)$_2$Ru(μ-**L^3**)Fe(OH$_2$)$_2$](PF$_6$)$_4$ (**6**)	+810 (88)	–	+350 (irr.)
[(bipy)$_2$Ru(μ-**L^3**)Cu(NCCH$_3$)](PF$_6$)$_4$ (**7**)	+966 (60)	–352 (66)	–
[(bipy)$_2$Ru**L^2**](PF$_6$)$_2$·2H$_2$O (**1**)	+986 (93)	–	–
[Cu**L^2**](ClO$_4$)$_2$·3H$_2$O (**3**)	–	–699 (irr.)	–
[(bpy)$_2$Ru(μ-**L^2**)Cu(Cl)$_2$](ClO$_4$)$_2$·5H$_2$O (**4**)	+991 (77)	–717 (irr.)	–

[a] The potentials are given vs. the Fc/Fc$^+$ couple in CH$_3$CN, with 0.1 TBAH as the supporting electrolyte.

Table 3. Electronic absorption and luminescence data.[a]

	MLCT absorption[b] λ_{max} /nm (ε /L M^{-1} cm^{-1})	λ_{max} /nm	Φ_{em}[c]
$[(bipy)_2Ru\mathbf{L^3}](PF_6)_2$ (**2**)	456 (13000)	617	0.0070
$[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Fe(Cl)_2](PF_6)_2$ (**5**)	456 (12800)	616	0.0068
$[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Fe(OH_2)_2](PF_6)_4$ (**6**)	456 (12700)	617	0.0027
$[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Cu(NCCH_3)](PF_6)_4$ (**7**)	456 (13100)	618	0.0019
$[(bipy)_2Ru\mathbf{L^2}](PF_6)_2$ (**1**)	453 (16100)	–	–
$[Cu\mathbf{L^2}](ClO_4)_2\cdot 3H_2O$	412 (3000)	–	–
$[(bpy)_2Ru(\mu\text{-}\mathbf{L^2})Cu(Cl)_2](ClO_4)_2\cdot 5H_2O$ (**4**)	453 (18100)	–	–

[a] Measured at 298 K in air-equilibrated acetonitrile. [b] Recorded at $c = 1.0 \times 10^{-5}$ M. [c] Determined with fluorescein as standard.

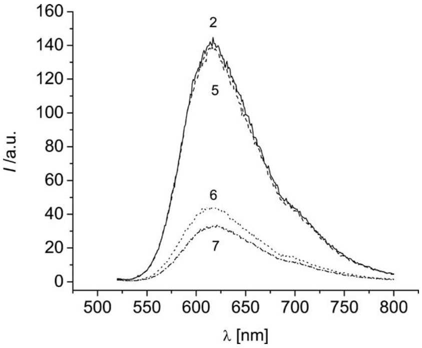


Figure 3. Emission spectra of the polypyridyl Ru^{II} complexes (1.0×10^{-5} M) in MeCN at 25 °C, excitation at 455 nm: $[(bipy)_2Ru(\mathbf{L^3})](PF_6)_2$ (**2**); $[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Fe(Cl)_2](PF_6)_2$ (**5**); $[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Fe(OH_2)_2](PF_6)_4$ (**6**); $[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Cu(NCCH_3)](PF_6)_4$ (**7**).

Table 4. Quenching of the $[(bpy)_2Ru(\mathbf{L^2})](PF_6)_2$ luminescence by the addition of metal ions.

	% Reduction of the luminescence intensity 1 equiv.	10 equiv.	100 equiv.
Cu^{2+}	40	53	70
Ni^{2+}	14	18	32
Zn^{2+}	2	4	5

EPR Spectroscopy

In order to understand the photomagnetic properties, $[(bpy)_2Ru(\mu\text{-}\mathbf{L^2})Cu(Cl)_2](PF_6)_2$ (**4**) was irradiated in the cavity of an EPR spectrometer with laser light of the wavelength of 442 nm. This wavelength is not exactly equal to that of the MLCT band of **4** but close enough to the absorption maximum to produce a significant luminescence. The irradiation of the probe leads to a small but significant and reversible decrease of the intensity of the EPR transitions (see Supporting Information). If Cu^{II} would be reduced to Cu^{I} by charge transfer from Ru^{II}, a transition due to Ru^{III} should appear. Since this was not observed, from the results of the EPR study it emerges that light irradiation of the dinuclear Ru^{II}–Cu^{II} complex does not lead to an electron transfer from the ruthenium(II) to the copper(II) site. The quenching of the ruthenium(II) excited state by copper(II) is therefore interpreted in terms of an energy transfer mechanism.

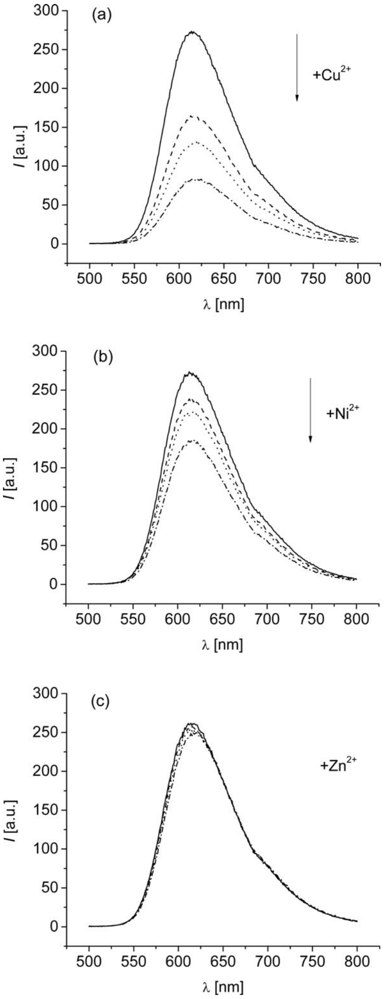
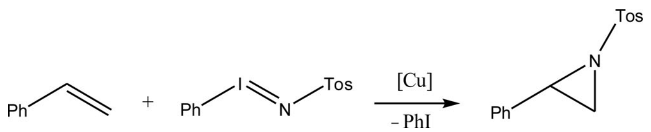


Figure 4. Emission spectra of $[(bpy)_2Ru(\mathbf{L^2})](PF_6)_2$ in H_2O at 25 °C, with excitation at 455 nm and addition of different metal ions: (a) Cu^{2+}, (b) Ni^{2+}, and (c) Zn^{2+}; the complex with the metal-free ligand (–), addition of 1 equiv. (- - -), 2 equiv. (· · ·), 100 equiv. (- · - ·).

Catalytic Aziridination

Bispidine-copper complexes catalyze the aziridination of styrene with [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane (PhINTs) (Scheme 3).[23] PhINTs is not soluble in MeCN, and the reaction is considered to be finished when a clear solution is observed. Therefore, the reaction time may be considered as a measure of the catalytic activity. The results of the aziridination of styrene, catalyzed by mono- and hetero-dinuclear complexes with bispidine-copper(II) subunits are listed in Table 5. The mononuclear Ru^{II} precursor **2** shows no catalytic activity in the aziridination reaction by light irradiation as well as in the dark. Light irradiation shows a small effect on the product yield when $[Cu(L^1)(NCMe)](PF_6)_2$ is used as the catalyst. With the heterodinuclear Ru^{II}–Cu^{II} complex **7** as catalyst (5 mol-% vs. PhINTs) the catalytic aziridination is considerably more efficient, even without light irradiation, i.e. there is a decrease of the reaction time from 7 h {observed for $[Cu(L^1)(NCMe)](PF_6)_2$} to 15 min, and the yield of product increases by a factor of more than two, compared with the mononuclear Cu^{II} bispidine complex.[22,23] The effect of light irradiation on the reaction rate was studied at lower concentrations of catalyst **7**. Illumination with visible light of a reaction mixture of complex **7** leads to a significant decrease of the reaction time, in comparison with the reaction in dark. A study of the redox potentials by cyclic voltammetry (CV) shows a small shift of the Cu^I/Cu^{II} redox couple in complex **7** compared to $[Cu(L^1)(NCMe)](PF_6)_2$ (122 mV, see Table 2). An increase of the electron density at the Cu^{II} center, measured by the more facile reduction of Cu^{II} to Cu^I, is probably responsible for the increased catalytic activity because the bispidine complex of Cu^I is considered as the catalytically active species.[22,23] However, this relatively small electronic effect cannot explain the drastic increase of the reaction rate. The additional increase of the reaction rate by light irradiation can be explained by a photo-induced energy transfer from the ruthenium polypyridyl subunit to the iodinane reactant at the copper site. That is, the catalytically active center gains some of the energy necessary to reach the transition state for the aziridination of styrene. Therefore, we consider the observed enhancement of the catalytic efficiency as an intramolecular sensitation.



Scheme 3. Copper-catalyzed aziridination of styrene with PhINTs.

Conclusions

Dinuclear Ru^{II}–Fe^{II} and Ru^{II}–Cu^{II} complexes with bispidine-based ligands have been synthesized and characterized. Electrochemical and photophysical studies indicate that the properties of the dinuclear species are related to those of the corresponding mononuclear Ru^{II} complexes $[(bpy)Ru(L^n)]^{2+}$. Efficient quenching of the Ru-based luminescence was observed by the formation of heterodinuclear Ru^{II}–Cu^{II} complexes. The heterodinuclear compound $[(bpy)_2Ru(\mu\text{-}\mathbf{L^3})Cu(NCCH_3)](PF_6)_4$ shows a high photocatalytic activity in the aziridination reaction of styrene.

Experimental Section

Methods and Materials: Commercially available chemicals and distilled solvents were used without further purification; solvents and chemicals for spectroscopy were of the highest possible grade and used as purchased. Styrene was degassed and kept for five minutes over molecular sieves (4 Å) before using in the aziridination experiments.

Electronic spectra were measured with a Jasco V-570 instrument. *Emission spectra* were recorded with a Varian Cary Eclipce fluorescence spectrophotometer. *Luminescence lifetime* measurements were performed with a FluoTime 100 (PicoQuant) instrument using time-correlated single-photon counting (TCSPC). A pulsed LED, emitting at 450 nm with a pulse width < 600 ps, operated at 10 MHz was used for excitation. *Luminescence quantum yields* were determined at an excitation wavelength of 455 nm with fluorescein (Φ_{em} = 0.95) as standard.[32] *NMR spectra* were recorded at 300 MHz (^1H) and 75.5 MHz (^{13}C) on a Bruker Avance DRX 300 instrument with the solvent as internal reference. *EPR measurements* were performed on a Bruker ELEXSYS E500 instrument at 4.9 K. For the *electrochemical measurements*, a BAS-100B workstation with a three-electrode setup, consisting of a glassy carbon working electrode, a Pt-wire as the auxiliary electrode and an $Ag/AgNO_3$ reference electrode [0.01 M Ag^+, 0.1 M $(Bu_4N)(PF_6)$ in MeCN], was used. The solutions were purged with N_2 before the measurement; scan rate 100 mV/s. Ferrocene was used as external standard. *FAB mass spectra* were measured on a Finnigan 8400 instrument with nibeol (4-nitrobenzyl alcohol) as a matrix. *Electrospray mass spectra* were recorded with a Finnigan TSQ 700 mass spectrometer. *Elemental analyses* were performed by the analytical laboratory of the chemical institutes at the University of Heidelberg.

Table 5. Aziridination of styrene, catalyzed by mono- and dinuclear bispidine complexes.

Complex	mol.-% cat. (vs. PhINTs)	Reaction time [h]	% Yield	TON	Light irradiation[a]
$[CuL^1(NCCH_3)](PF_6)_2$	5	7	52	10.3	no
$[CuL^1(NCCH_3)](PF_6)_2$	5	7	61	12.2	yes
$[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Cu(NCCH_3)](PF_6)_4$	5	0.25	96	19.1	no
$[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Cu(NCCH_3)](PF_6)_4$	5	0.25	99	19.8	yes
$[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Cu(NCCH_3)](PF_6)_4$	1	1	92	92	no
$[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Cu(NCCH_3)](PF_6)_4$	1	0.5	99	99	yes
$[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Cu(NCCH_3)](PF_6)_4$	0.25	5	82	326	no
$[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Cu(NCCH_3)](PF_6)_4$	0.25	2[b]	38	152	no
$[(bipy)_2Ru(\mu\text{-}\mathbf{L^3})Cu(NCCH_3)](PF_6)_4$	0.25	2	92	366	yes

[a] Tungsten lamp, 100 W. [b] Incomplete conversion.

Crystal Structure Determinations: Crystal data and details of the structure determinations are listed in Table 6. Intensity data were collected at 100 K with a Bruker AXS Smart 1000 CCD diffractometer (Mo-K_a radiation, graphite monochromator, λ = 0.71073 Å). Data were corrected for air and detector absorption, Lorentz and polarization effects;[33] absorption by the crystal was treated with a semiempirical multiscan method.[34–36] The structures were solved by direct methods with dual-space recycling ("shake-and-bake", **L**^{2}),[37,38] or by the charge flip procedure (**L**^{3})[39–42] and refined by full-matrix least-squares methods based on F^2 against all unique reflections.[43,44] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atom positions (except those of the methyl groups, which were calculated) were taken from difference Fourier syntheses and refined with isotropic temperature factors. The crystals of **L**^{3} were found to be twinned. Only single and composite reflections with contributions of the major twin individual were used for structure solution and refinement. Due to severe disorder and fractional occupancy, electron density attributed to solvent of crystallization (methanol and ethanol) was removed from the structure (and the corresponding F_{obs}) of **L**^{2} with the BYPASS procedure,[45] as implemented in PLATON (SQUEEZE).[46,47]

Table 6. Details of the crystal structure determination of **L**^{2} and **L**^{3}.

	L^2	**L**^{3}
Formula	$C_{34.5}H_{37}N_6O_6$	$C_{34}H_{34}N_6O_5$
Crystal system	triclinic	
Space group	$\bar{P}1$	
a /Å	10.058(5)	13.100(5)
b /Å	17.352(8)	14.524(6)
c /Å	19.395(9)	17.022(7)
α /°	110.287(6)	81.026(14)
β /°	92.305(6)	71.462(9)
γ /°	95.566(14)	79.728(13)
V /Å^3	3150(2)	3004(2)
Z	4	4
M_r	631.70	606.67
F(000)	1336	1280
d_c /Mgm^{-3}	1.332	1.341
μ (Mo-$K\alpha$) /mm^{-1}	0.093	0.092
max./min. transmission factors	0.8623/0.8110	0.86202/0.79354
θ range /°	1.1 to 30.5	1.8 to 25.0
Index ranges (indep. set) h,k,l	–14...14, –24...23, 0...27	–14...15, –16...17, 0...20
Reflections measured	76740	39714
Reflections unique [R_{int}]	19187 [0.0460]	10642 [0.1281]
Reflections observed [$I \geq 2\sigma(I)$]	12804	6155
Parameters refined	799	951
GooF on F^2	1.074	0.998
R indices [$F > 4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0493, 0.1260	0.0600, 0.1147
R indices (all data) $R(F)$, $wR(F^2)$	0.0870, 0.1424	0.1220, 0.1314
Largest residual peaks /eÅ^{-3}	0.531, –0.258	0.490, –0.287

CCDC-753113 (for **L**^{2}) and -753112 (for **L**^{3}) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Aziridination Experiments: The catalyst and styrene (1 mL, 8.7 mmol) were dissolved in dry MeCN (2 mL), before PhINTs (0.15 g, 0.4 mmol) was added. The reaction mixture was stirred at 25 °C under argon. In photocatalytic studies, a thermostatted Schlenk tube (20 mm diameter) was placed at a distance of 5 cm from a visible light source (tungsten lamp, 100 W). When the reaction mixture became clear (the corresponding reaction times are given in Table 5), it was passed through a short silica column. The column was washed with ethyl acetate (25 mL), and the solvents were removed under reduced pressure. Anthron (38.8 mg, 0.2 mmol) was added as internal standard to the resulting solid and the yield was determined by ^{1}H-NMR spectroscopy.[23]

Syntheses: 4-Aminomethyl-2,2′-bipyridine was synthesized according to published methods.[32,48,49] 4-Methyl-2,2′-bipyridine-4′-carboxaldehyde was prepared in a slightly modified way with respect to the published method.[50] The piperidon pL dimethyl (4′-oxo-1′,2′,3′,4′,5′,6′-hexahydro-[2,2′;6′,2′′]terpyridine-3′,5′-dicarboxylate), the bispidine ligand L^1 and its copper(II) complex [Cu(L^1)(NCCH$_3$)](PF$_6$)$_2$ were synthesized as reported in the literature.[51]

4-Methyl-2,2′-bipyridine-4′-carboxaldehyde: Selenium dioxide (4.42 g, 37.05 mmol) was dissolved in 1,4-dioxane (20 mL; containing 4% H$_2$O). To the solution of SeO$_2$, was added 5.25 g (28.5 mmol) of 4,4′-dimethyl-2,2′-bipyridyl dissolved in 200 mL of 1,4-dioxane. The reaction mixture was heated at gentle reflux for 24 h and then filtered through celite while hot. The celite was washed with 50 mL of EtOH, and the EtOH phase was combined with the filtrate; the solvent was removed by rotary evaporation. The residue was suspended in a saturated solution of NaHCO$_3$ (50 mL) and extracted with CH$_2$Cl$_2$ (5× 50 mL). The combined organic phase was dried with MgSO$_4$, and the CH$_2$Cl$_2$ was removed by rotary evaporation. The solid residue was suspended in a solution of 0.3 M sodium metabisulfite (100 mL) and stirred for 0.5 h. The solid was filtered and then suspended again in 50 mL of 0.3 M sodium metabisulfite solution. The suspension was stirred for 0.5 h and filtered. The combined filtrates were washed with ethyl acetate (2× 25 mL). Solid sodium hydrogen carbonate (18 g) was added to the Na$_2$S$_2$O$_5$ solution and the product was extracted with CH$_2$Cl$_2$ (20× 40 mL). The CH$_2$Cl$_2$ was dried with MgSO$_4$ and removed by rotary evaporation to yield 4-methyl-2,2′-bipyridine-4′-carboxaldehyde as a white solid; yield 1.95 g (9.84 mmol), 35%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.25 (s, 3 H), 6.99 (d, $^3J_{HH}$ = 4.8 Hz, 1 H), 7.51 (d, $^3J_{HH}$ = 4.8 Hz, 1 H), 8.06 (s, 1 H), 8.37 (d, $^3J_{HH}$ = 4.8 Hz, 1 H), 8.61 (s, 1 H), 8.68 (d, $^3J_{HH}$ = 4.8 Hz, 1 H), 9.97 ppm (s, 1 H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 20.9 (1 C, -*C*H$_3$), 120.3, 120.8, 121.7, 125.0, 142.3, 148.0, 148.8, 149.9, 154.3, 157.8 (10 C, bpy-*C*H), 191.4 ppm (1C, -H*C*=O). MS-FAB (nibeol) *m*/*z*: 199.2 [M + H]$^+$. C$_{12}$H$_{10}$N$_2$O (198.22): calcd. C 72.71, H 5.08, N 14.13; found C 72.61, H 5.10, N 14.11.

4-Methyl-2,2′-bipyridine-4′-carbaldoxime: A solution of 1.54 g (22.1 mmol) of hydroxylamine hydrochloride and 4.07 g (29.5 mmol) of K$_2$CO$_3$ in H$_2$O (15 mL) was added to a solution of 1.46 g (7.37 mmol) of 4-methyl-2,2′-bipyridine-4′-carboxaldehyde in MeOH (15 mL). The reaction mixture was stirred at 80 °C for 1 h. After cooling to room temperature the mixture was poured into 100 mL of ice cold H$_2$O. A white precipitate was filtered, washed with 10 mL of cold H$_2$O and dried in vacuo; yield 1.35 g (6.33 mmol), 86%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.44 (s, 3 H), 7.17 (d, $^3J_{HH}$ = 4.9 Hz, 1 H), 7.38 (d, $^3J_{HH}$ = 5.0 Hz, 1 H), 8.18 (s, 1 H), 8.52 (d, $^3J_{HH}$ = 4.9 Hz, 1 H), 8.58 (d, $^3J_{HH}$ = 4.8 Hz, 1 H), 8.76 (d, $^3J_{HH}$ = 4.9 Hz, 1 H), 11.90 ppm (s, 1 H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 21.3 (1 C, -*C*H$_3$), 118.7, 121.8, 123.0, 125.0 (4 C, bipy-*C*H), 141.8 (1 C, -H*C*=N-OH), 147.3, 148.5, 149.2, 149.7, 155.6, 156.3 ppm (6C, bipy-*C*H). MS-FAB (nibeol) *m*/*z*: 214.1 [M + H]$^+$. C$_{12}$H$_{11}$N$_3$O (213.24): calcd. C 67.59, H 5.20, N 19.71; found calcd. C ; found C7.50, H 5.25, N 19.76.

4-Aminomethyl-4′-methyl-2,2′-bipyridyl: A solution of 4-methyl-2,2′-bipyridine-4′-carboldoxime (1.0 g, 4.69 mmol) in MeOH

(70 mL) with 150 g of 10% Pd on charcoal was placed into a hydrogenator. The pressure was fixed to 10 bar, and the reaction was stirred overnight. The solution was filtered through celite and the solvent was removed by rotary evaporation. The white solid residue was dried in vacuo to yield 4-methylamino-4′-methyl-2,2′-bipyridyl as hemihydrate; yield 0.83 g (3.99 mmol), 85%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.13 (s, 3 H), 3.65 (s, 2 H), 6.83 (d, $^3J_{HH}$ = 4.8 Hz, 1 H), 6.97 (d, $^3J_{HH}$ = 4.2 Hz, 1 H), 7.97 (s, 1 H), 8.08 (s, 1 H), 8.25 (d, $^3J_{HH}$ = 4.9 Hz, 1 H), 8.32 (d, ^3J = 4.9 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 20.5 (-*C*H$_3$), 44.8 (-*C*H$_2$-NH$_2$), 118.7, 121.3, 124.1, 147.4, 148.3, 148.4, 148.5, 152.5, 155.2, 155.6 (bpy -*C*H) ppm. MS-FAB (nibeol) *m*/*z*: 200.1 [M + H]$^+$. $C_{12}H_{13}N_3$ (199.25): calcd. C 69.21, H 6.78, N 20.18; found C 68.86, H 6.94, N 19.98.

Dimethyl 3-Methyl-9-oxo-7-(2,2′-bipyridin-4-ylmethyl)-2,4-di(pyridin-2-yl)-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate (L^2): The piperidon pL (9.97 g, 26.02 mmol), 37% formaldehyde solution (5.15 g, 62.64 mmol) and 4-aminomethyl-2,2′-bipyridine (6.26 g, 33.82 mmol) were suspended in MeOH (50 mL) and heated under reflux for 1 h. The resulting dark reaction mixture was concentrated in vacuo to half of the volume and placed into a refrigerator (4 °C). After one night, a white crystalline precipitate was formed, filtered, washed with a small amount of cold MeOH and dried in vacuo; yield 4.49 g (7.57 mmol), 29%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.94 (s, 3 H, CH$_3$-N), 2.63 (d, $^2J_{HH}$ = 12.1 Hz, 2 H, H6/H8 equatorial, CH$_2$), 3.04 (d, $^2J_{HH}$ = 12.2 Hz, 2 H, H6/H8 axial, CH$_2$), 3.38 (s, 2 H, -CH$_2$-bpy), 3.74 (s, 6 H, -OCH$_3$), 4.63 (s, 2 H, H2/H4, CH), 7.02–7.06 (m, 2 H, Ar-H), 7.21–7.30 (m, 2 H, Ar-H), 7.40–7.46 (m, 2 H, Ar-H), 7.79 (dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 0.8 Hz, 1 H, Ar-H), 7.84 (d, $^2J_{HH}$ = 8.0 Hz, 2 H Ar-H), 8.37 (d, $^3J_{HH}$ = 4.1 Hz, 2 H, Ar-H), 8.50 (s, 1 H, Ar-H), 8.60 (d, $^3J_{HH}$ = 4.9 Hz, 1 H, Ar-H), 8.66 ppm (d, 1 H, $^3J_{HH}$ = 4.1 Hz, Ar-H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 42.3 (CH$_3$-N), 51.6 (OCH$_3$), 57.9 (N-CH$_2$-bipy) 60.4 (CH$_2$-N), 61.3 (C-CO), 72.5 (2 C, CH-N), 120.1, 121.6, 122.0, 122.5, 123.0, 123.9, 135.3, 136.1, 145.9, 148.2, 148.3, 148.4, 154.9, 155.4, 157.2, (20 C, C$_{Ar}$), 167.5 (2 C, COOCH$_3$), 202.3 (1 C, C=O) ppm. MS-FAB (nibeol) *m*/*z*: 593.5 [M + H]$^+$. $C_{33}H_{32}N_6O_5$ (592.64): calcd. C 66.88, H 5.44, N 14.18; found C 65.58, H 5.56, N 14.04.

Dimethyl 3-Methyl-7-(4′-methyl-2,2′-bipyridinyl-4-ylmethyl)-9-oxo-2,4-di(pyridin-2-yl)-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate (L^3): To a suspension of 2.67 g of the piperidone pL (6.98 mmol) in MeOH (25 mL), was added at room temperature 1.26 mL of a 37% aqueous formaldehyde solution (16.75 mmol). Finally, a solution of 1.89 g of 4-methylamino-4′-methyl-2,2′-bipyridyl hemihydrate (9.07 mmol) in MeOH (10 mL) is added to the reaction mixture and refluxed for 1 h. The resulting dark brown reaction mixture was cooled with the flask open to air. After one night a white solid precipitated, which was filtered, washed with EtOH and dried in vacuo; yield 1.02 g (1.68 mmol), 24%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.93 (s, 3 H, CH$_3$-bpy), 2.37 (s, 3 H, CH$_3$-N), 2.60 (d, $^2J_{HH}$ = 12.3 Hz, 2 H, H6/H8 equatorial, CH$_2$), 2.99 (d, $^2J_{HH}$ = 12.3 Hz, 2 H, H6/H8 axial, CH$_2$), 3.33 (s, 2 H, -CH$_2$-bpy), 3.71 (s, 6 H, -OCH$_3$), 4.63 (s, 2 H, H2/H4, CH), 7.00–7.04 (m, 2 H, py-H), 7.08 (d, $^3J_{HH}$ = 4.8 Hz, 2 H, bpy-H), 7.18 (d, $^3J_{HH}$ = 4.8 Hz, 2 H, bpy-H), 7.39–7.44 (m, 2 H, py-H), 7.84 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, py-H), 8.23 (s, 1 H, bpy-H), 8.34 (d, $^3J_{HH}$ = 4.8 Hz, 2 H, py-H), 8.49 (br. s, 2 H, bpy-H), 8.53 (d, $^3J_{HH}$ = 4.8 Hz, 1 H, bpy-H) ppm. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 21.0 (CH$_3$-bipy), 43.1 (CH$_3$-N), 52.3 (OCH$_3$), 58.8 (N-CH$_2$-bipy) 61.1 (CH$_2$-N), 62.0 (C-CO), 73.3 (2 C, CH-N), 121.6, 122.5, 122.7, 123.2, 124.6, 124.7, 136.0, 146.6, 148.0, 148.9, 148.0, 155.4, 156.3, 158.0 (20 C, C$_{Ar}$), 168.3 (2 C, COOCH$_3$), 203.2 (1 C, C=O) ppm. MS-FAB (nibeol) *m*/*z*: 607.2 [M + H]$^+$. $C_{34}H_{34}N_6O_5$ (606.67): calcd. C 67.31, H 5.65, N 13.85; found C 66.91, H 5.70, N 13.79.

[(bpy)$_2$Ru(L^2)](PF$_6$)$_2$·2H$_2$O (1): A solution of **L^2** (0.59 g, 1.00 mmol) and [Ru(bpy)$_2$Cl$_2$]·2H$_2$O (0.42 g, 0.80 mmol) in EtOH/H$_2$O (30 mL; 95:5, v/v) was refluxed overnight under Ar. The solution was concentrated by rotary evaporation to a half of the initial volume and treated with an aqueous solution of 10% NH$_4$PF$_6$ (10 mL). The resulting red precipitate was collected by filtration and washed with water. The crude product was recrystallized from a H$_2$O/MeOH solution; yield 0.18 g (17%). UV/Vis (CH$_3$CN), λ (nm), ε (L mol^{-1} cm^{-1}): 453 (16100). $C_{53}H_{52}F_{12}N_{10}O_7P_2Ru$ (1332.04): calcd. C 47.79, H 3.93, N 10.52; found C 47.99, H 3.96, N 10.16.

[(bpy)$_2$Ru(L^3)](PF$_6$)$_2$ (2): A solution of **L^3** (0.74 g, 1.22 mmol) and [Ru(bpy)$_2$Cl$_2$]·2H$_2$O (0.5 g, 0.98 mmol) in EtOH/H$_2$O (40 mL; 95:5, v/v) was refluxed overnight under Ar. The solution was concentrated by rotary evaporation (rest volume of ca. 5 mL) and treated with an aq. solution of 10% NH$_4$PF$_6$ (10 mL). The precipitate was collected by filtration and washed with H$_2$O. The crude product was dried in vacuo and then purified by column chromatography (Al$_2$O$_3$; 2× 30 cm; CH$_2$Cl$_2$/CH$_3$OH, 9:1). The main red band was collected, solvent was removed by rotary evaporation, and the resulting solid was dried in vacuo; yield 0.76 g (59%). MS-ESI (CH$_3$OH), *m*/*z*: 1165.27 [M – PF$_6$]$^+$, 510.15 [M – 2PF$_6$]$^{2+}$. UV/Vis (CH$_3$CN), λ (nm), ε (L mol^{-1} cm^{-1}): 248 (27500), 286 (34700), 456 (13000). $C_{54}H_{50}F_{12}N_{10}O_5P_2Ru$ (1310.04): calcd. C 49.51, H 3.85, N 10.69; found C 49.68, H 4.09, N 10.45.

[Cu(L^2)](ClO$_4$)$_2$·3H$_2$O (3): To a suspension of **L^2** (1.0 g, 1.64 mmol) in MeOH (10 mL), a solution of Cu(ClO$_4$)·6H$_2$O (0.67 g, 1.80 mmol) in MeOH/H$_2$O (1:1, 20 mL) was added. The resulting blue-green solution was heated under reflux for 12 h. The solution was concentrated under reduced pressure to a half of the initial volume and placed into a refrigerator (4 °C). The green precipitate was filtered and dried in vacuo; yield 1.04 g (1.14 mmol), 70%. UV/Vis (CH$_3$CN), λ (nm), ε (L mol^{-1} cm^{-1}): 412 (3000). $C_{33}H_{38}Cl_2CuN_6O_{16}$ (909.14): calcd. C 43.60, H 4.21, N 9.24; found C 43.88, H: 4.35, N 8.99.

[(bpy)$_2$Ru(μ-L^2)CuCl$_2$](ClO$_4$)$_2$·5H$_2$O (4): [CuL^2](ClO$_4$)$_2$·3H$_2$O (0.45 g, 0.5 mmol) and [Ru(bpy)$_2$Cl$_2$] (0.24 g, 0.5 mmol) were dissolved in EtOH (80 mL) and heated under reflux for 12 h. The resulting suspension was concentrated to a half of the initial volume and filtered. The resulting red-brown powder was dried in vacuo; yield 0.43 g (0.30 mmol), 60%. UV/Vis (CH$_3$CN), λ (nm), ε (L mol^{-1} cm^{-1}): 453 (18100). $C_{53}H_{58}Cl_4CuN_{10}O_{18}Ru$ (1429.51): calcd. C 44.53, H 4.09, N 9.80; found C 44.51, H 4.01, N 9.39.

[(bpy)$_2$Ru(μ-L^3)FeCl$_2$](PF$_6$)$_2$ (5): To a solution of 0.68 g (0.52 mmol) [(bpy)$_2$Ru(**L^3**)](PF$_6$)$_2$ in dry MeCN (10 mL) was added 0.07 g of FeCl$_2$ (0.55 mmol). The reaction mixture was stirred overnight under Ar. Then, the solvent was removed under reduced pressure. The solid residue was purified by column chromatography (Al$_2$O$_3$; 2× 20 cm; CH$_2$Cl$_2$/CH$_3$OH, 9:1). The main red-brown band was collected, the solvent was removed by rotary evaporation and the resulting solid was dried in vacuo; yield 0.60 g (66%). MS-ESI (CH$_3$OH), *m*/*z*: 1291.14 [M – PF$_6$]$^+$. UV/Vis (CH$_3$CN), λ (nm), ε (L mol^{-1} cm^{-1}): 248 (26800), 285 (32000), 456 (12800). $C_{54}H_{50}Cl_2F_{12}FeN_{10}O_5P_2Ru$ (1436.79): calcd. C 45.14, H 3.51, N 9.75; found C 45.74, H 4.24, N 9.68.

[(bpy)$_2$Ru(μ-L^3)Fe(H$_2$O)$_2$](PF$_6$)$_4$ (6): Silver hexafluorophosphate (0.187 g, 0.738 mmol) was added to a solution of [(bpy)$_2$Ru(μ-**L^3**)-FeCl$_2$](PF$_6$)$_2$ (0.530 g, 0.369 mmol) in MeCN (10 mL). After stirring overnight, the AgCl formed was removed by filtration. The solvent was removed from the filtrate under reduced pressure to afford $[(bpy)_2Ru(\mu\text{-}\mathbf{L}^3)Fe(H_2O)_2](PF_6)_4$ as a red solid; yield 0.52 g (84%). UV/Vis (CH_3CN), λ (nm), ε ($L\,mol^{-1}\,cm^{-1}$): 248 (26500), 285 (32600), 456 (12700). $C_{54}H_{54}F_{24}FeN_{10}O_7P_4Ru$ (1691.84): calcd. C 38.34, H 3.22, N 8.28; found C 38.33, H 3.75, N 8.23.

$[(bpy)_2Ru(\mu\text{-}L^3)Cu(NCCH_3)](PF_6)_4$ (7): To a solution of 1.0 g (0.76 mmol) $[(bpy)_2Ru\mathbf{L}^3](PF_6)_2$ in MeOH (20 mL) was added 0.24 g of $Cu(BF_4)_2\cdot 4H_2O$ (0.78 mmol). The reaction mixture was stirred overnight. Then, the solution was concentrated by rotary evaporation (rest volume of ca. 5 mL) and treated with an aqueous solution of 10% NH_4PF_6 (50 mL). The precipitate was collected by filtration and washed with H_2O. The crude product was dried in vacuo and purified by column chromatography (Al_2O_3; 2 × 20 cm; CH_2Cl_2/CH_3CN, 1:1). The main brown band was collected, the solvent was removed by rotary evaporation and the resulting solid was dried in vacuo; yield 0.67 g (0.39 mmol) 51%. MS-ESI (CH_3OH), *m/z*: 1391.17 $[M - CH_3CN, - 2PF_6^-, + F^-]^+$. UV/Vis ($CH_3CN$), λ (nm), ε ($L\,mol^{-1}\,cm^{-1}$): 248 (22400), 287 (33400), 456 (13100). $C_{56}H_{53}CuF_{24}N_{11}O_5P_4Ru$ (1704.56): calcd. C 39.46, H 3.13, N 9.04; found C 39.28, H 3.25, N 8.90.

Supporting Information (see also the footnote on the first page of this article): EPR spectrum of compound **4** (before and during irradiation) and UV/Vis spectra of compounds **1**–**7**.

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