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Efficient Access to 5- and 5,6- Dibromophenanthroline Ligands

Anne Stumper,[a] Thomas David Pilz,[b] Markus Schaub,[a] Helmar Görls,[b] Dieter Sorsche,[a] Katrin Peuntinger,[c] Dirk Guldi[c] and Sven Rau*[a]

Abstract: Providing bromo functionalized precursor molecules is essential to generate desired target compounds utilizing cross coupling reactions. Here we show an improved synthetic route – feasible at low temperatures and affording high yields - for the ligands 5-bromo-1,10-phenanthroline (**1**) and 5,6-dibromo-1,10-phenanthroline (**2**). Corresponding Ruthenium complexes providing **2** in varying numbers are easily accessible in high yields and the analogue to tris-homoleptic $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine), $[Ru(\mathbf{2})_3]^{2+}$, is presented. Comparison of the X-ray diffraction analyses provides detailed information about the structures of the ligands and their corresponding metal complexes. The investigation of electrochemical properties generated detailed information about the ^{3}MLCT state localized on **2**. We show conversion of heteroleptic Ruthenium complexes of these ligands in Suzuki cross coupling reactions whereas the ligands did not undergo Suzuki coupling under the used conditions.

Introduction

In order to generate novel molecular systems chemists are dependent on suitable possibilities to link different substrates with one another. This is of great importance in a variety of research fields like energy conversion or biomedical applications. Compounds bearing bromo functionalities offer many suitable reaction pathways like substitution reactions, cross coupling[1] (Sonogashira,[2] Suzuki[3-5]) and elimination reactions to obtain sophisticated molecules.

Therefore it is desirable to have access to suitably derivatised bromo substituted building blocks. For example, a peptide hormone Ru(II) polypyridyl conjugate functioning as selective photodynamic therapeutic was generated using a synthetic pathway including a bromo intermediate, 4-bromo-2,2'-bipyridine.[6] In order to get to the bromo intermediate, however, one has to carry out a multiplicity (partly inefficient) syntheses. We hence investigated the possibility to use 1,10-phenanthroline based building blocks in order to improve the overall time and substance efficiency of synthetic pathways towards functional ligands and their Ru(II) complexes. Already in 1978 Dénes and Chira presented a synthetic strategy for multiple bromo substituted 1,10-phenanthrolines.[7] Since then many groups made use of those compounds and their properties albeit modifying the synthetic conditions.[8-10] For example Tor et al. used 3-bromo- or 3,8-dibromo substituted 1,10-phenanthrolines, their corresponding alkyne substituted ligands and the Ru(II) and Os(II) compounds[11] which are used for the design of hetero-nuclear metal complexes via coupling reactions. 5,6-dibromo-phenanthroline is used to build up a variety of compounds bearing thioether functionalities or *S,S*- coordination sites[12-15] or for the design of water oxidation catalysts,[16] whereas others use alkyne substituted phenanthroline Ruthenium (II) complexes for biological applications. Thereby, coupling was performed on the ligand scaffold with subsequent complexation.[17] In 2008 the group of Fujii presented Suzuki coupling on the chromophore core of 5-bromo-phenanthroline Ru(II) complexes.[18] They used common precursors like $[(2,2'\text{-bipyridine})_2RuCl_2]$ as well as $[(4,4'\text{-dimethyl-}2,2'\text{-bipyridine})_2RuCl_2]$ and introduced ligands such as 5-bromo-phenanthroline (**Figure 1**).

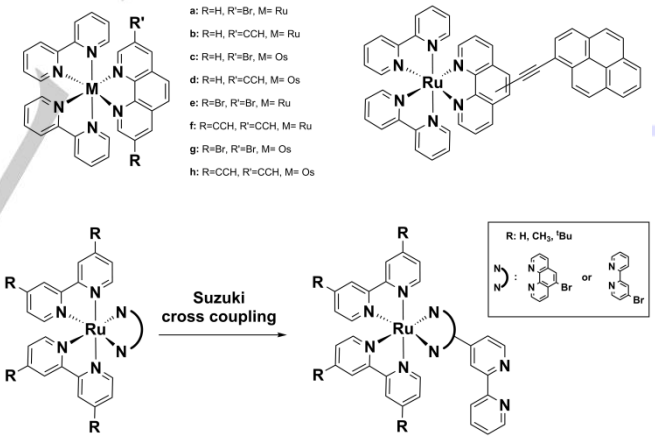

Figure 1. Complexes presented by the research groups Tor (top left), Thummel and McFarland (top right) and Fujii (bottom).

The yields for coupling reactions dropped significantly when complexes were converted whose precursor molecules bore substituted bipyridine units (yields: 53-54% (2,2'-bipyridine), 14-16% (4,4'-dimethyl-2,2'-bipyridine), 20% (4,4'-di-tertbutyl-2,2'-bipyridine)).[18] Comparing the literature known synthetic pathways of 4-bromo-2,2'-bipyridine[7] and 5-bromo-1,10-phenanthroline[7,8,18] both expose disadvantages. As the syntheses of 5-bromo- (**1**) and 5,6-dibromo-1,10-phenanthroline (**2**) are single step reactions, this ligand system offers significant time and resource profits compared to the bpy scaffold. However, for **1** and **2** very harsh conditions have to be applied. The reaction is carried out in pressure tubes at elevated

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temperatures (>120°C) in oleum. Therefore, an optimization of reaction protocols with milder conditions and high yields would be desirable. We optimized the required ligand syntheses which determine the yield and investigated the synthetic accessibility of Ru(II) complexes bearing either 5-bromo- or 5,6-dibromo-phenanthroline in varying numbers. Study of corresponding solid state structures as well as photophysical and electrochemical properties yielded crucial information on the effect of bromine substitution. Furthermore we analyzed the feasibility of Suzuki cross coupling utilizing these bromo functionalities. An overview of the investigated compounds is depicted in **Figure 2**.

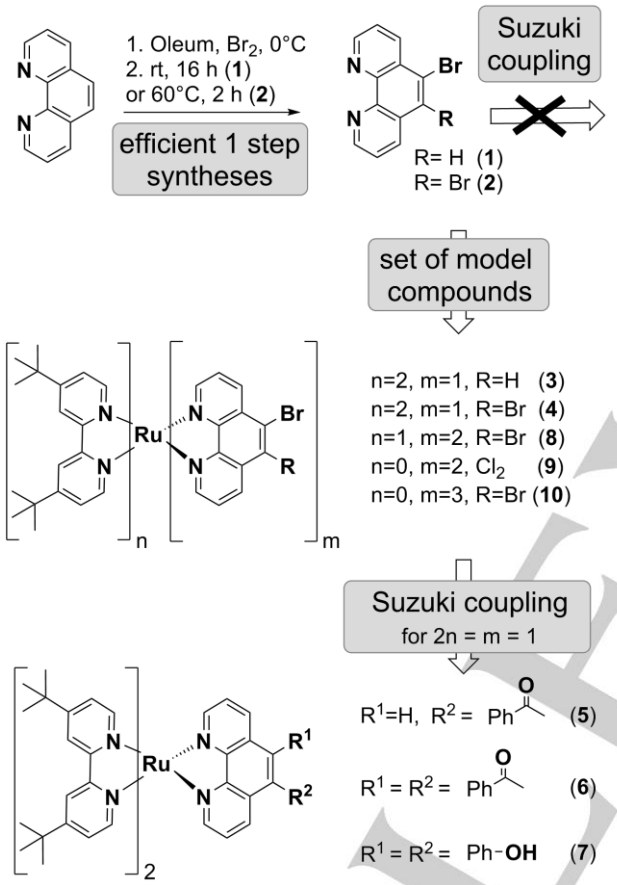

Figure 2. Schematic overview of investigated compounds and experiments.

Results and Discussion

Bromination of 1,10-phenanthroline (phen)

We were able to develop an improved synthesis procedure for 5-bromo-1,10-phenanthroline (**1**) and for 5,6-dibromo-1,10-phenanthroline (**2**). The literature known syntheses are carried out in pressure tubes at elevated temperatures in oleum (>120°C) with mostly low yields and time consuming work up procedures.[7,8,18] The group of Eisenberg obtained the best yield (90%) with 15% oleum in a pressure tube for 23 h at 135°C.[19] We have established a new synthetic protocol protocol using oleum (65%) at room temperature and normal pressure for 16 h (**1**), and at 60 °C for 2 h (**2**), respectively (**Figure 2**). Thereby elemental bromine is added in required equivalents to a solution of phen in oleum. After completion of the reaction, extraction with chloroform and recrystallization afforded pure compounds in good yields of 70% for **1** and 93% for **2**. Unreacted educt phenanthroline can be easily removed via stirring in ether for 12 hours. The successful reaction can be determined by losing signals for protons in 5- and 5,6-position in the ^{1}H-NMR spectrum. For **1** and **2** crystal structures (monoclinic, space group *P2*(1)/n) could be obtained via slow evaporation of chloroform solutions. The crystal lattice exhibits alternating orientation of the phen scaffolds and aromatic π-stacking can be observed. ("π-π" in **Table S1**, example depicted in **Figure S1**, ESI). The bromination had no significant effect on bond lengths and angles of the phen scaffold (**Table S1**, ESI).

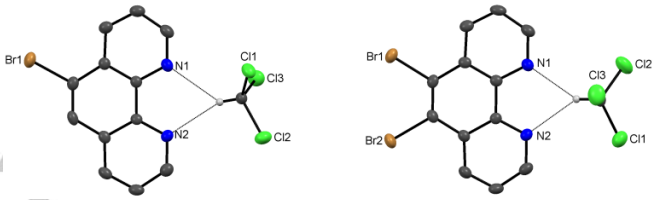

Figure 3. ORTEP representation of the molecular structures of **1** and **2**; coordination to chloroform via hydrogen bonds; ellipsoids were drawn at 50% probability level.

Synthesis of Ruthenium chromophores

To understand the effects arising from the bromination of the phen ligands the corresponding Ru(II) polypyridyl complexes were synthesized bearing either **1** or **2** in their periphery. Additionally, a series of Ru(II) polypyridyl complexes with varying numbers of **2** according to the formula $[(tbbpy)_{3-n}Ru(\mathbf{2})_m]^{2+}$ (with tbbpy= 4,4'-tert-butyl-2,2'-bipyridine and n = 0, 1, 2, m = 1, 2, 3) was prepared to verify the coordination of multiple halogenated phen ligands towards Ru(II) chromophore cores. It is known, that unequally halogenated tpphz derivatives tend to show low coordination affinity mediated by the electron withdrawing effect of these functional groups.[20,21] The synthesis of heteroleptic Ruthenium polypyridine complexes of the type $[(tbbpy)_2Ru(\mathbf{1/2})]^{2+}$ was performed using literature known conditions[10] and yielded $[(tbbpy)_2Ru(\mathbf{1})]^{2+}$ (**3**) and $[(tbbpy)_2Ru(\mathbf{2})]^{2+}$ (**4**) in high yields (>90%) and purity (see **Figure 4**). Initial structural characterization was performed with various NMR-spectroscopic methods as well as mass spectrometry. Recrystallization in acetone/water or MeCN/water solutions yielded appropriate single crystals for X-ray diffraction.

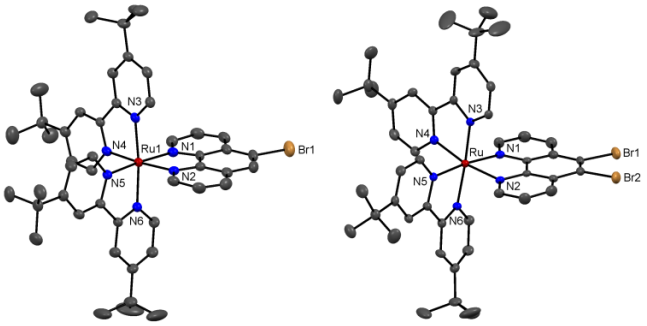

Figure 4. Solid state structures of **3** (left) and **4** (right); counter ions and hydrogen atoms were omitted for clarity; ellipsoids were drawn at 60% level in this ORTEP representation.

The synthesis of the complexes comprising more than one brominated ligand (**8** and **10**) required the preparation of the $[(\mathbf{2})_2RuCl_2]$ precursor derivative **9** (see **Figure 2**).

Reaction of the starting material $[Ru(cod)Cl_2]_n$[22] with **2** (2 eq) in refluxing DMF under inert conditions and microwave irradiation yielded in a blue, highly insoluble solid. After work up and characterization of the product by ^{1}H-NMR spectroscopy in CD_2Cl_2 exhibited two sets of three signals. The low solubility in various solvents made the product inaccessible for ^{13}C-NMR spectroscopy or mass spectrometry techniques. However, very careful recrystallization from CH_2Cl_2 yielded black single crystals suitable for X-ray diffraction (see **Figure 5**). Subsequent preparation of $[(tbbpy)Ru(\mathbf{2})_2]^{2+}$ (**8**) succeeded by conversion of tbbpy and **9** in a microwave reaction utilizing literature conditions.[24] For the detailed characterization of the product NMR, MS and X-ray diffraction experiments were performed. To obtain the tris-homoleptic derivative $[Ru(\mathbf{2})_3]^{2+}$ (**10**) three equivalents of **2** in moist DMF were converted in a microwave reaction chamber and after work up the red product was characterized via NMR and MS techniques. This is pleasing as previous attempts to convert the tetra-bromo derivative, 3,5,6,8-Br-**phen**, to yield a tris-homoleptic chromophore did not succeed.[9]

Comparing bond lengths and angles of the investigated Ru(II) complexes resulted in high structural similarity (**Table S2**, ESI). Free phen ligands compared to metal complexes did not show significant changes in bond lengths and angles either and as a result typical Ru-N1/N2 bond lengths (phen scaffold) and typical Ru- N3/N4/N5/N6 bond lengths (bpy backbone) are observed, which exactly match the known bond lengths of related compounds.[8,20,23]

In contrast, cisoidal chloro complex **9** exhibits slightly shortened Ru-N3 bond lengths which is in agreement with literature concerning reference compound cis-$[(tbbpy)_2RuCl_2]$.[24]

Obviously, 5-Bromo and -5,6-Dibromo-1,10-phenanthroline can be utilized as conventional *N,N'*-chelating ligands for the preparation of all kinds of $[(tbbpy)_n Ru(\mathbf{2})_m]^{2+}$ (n= 0, 1, 2; m = 1, 2, 3) complexes. This result indicates that for **2** a more conventional electronic properties may be expected in contrast to 3,5,6,8-Br-phen since this ligand could not be employed for similar reactions.

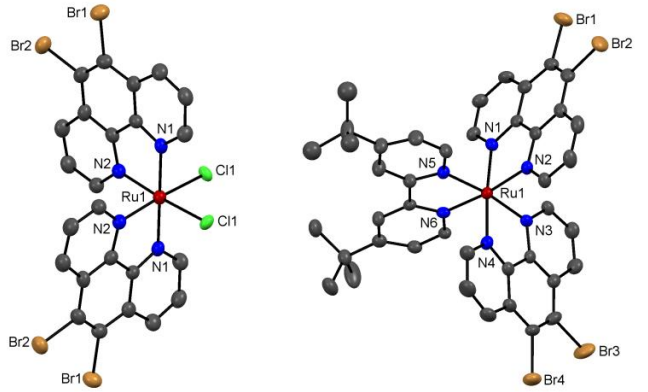

Figure 5. ORTEP representations of the molecular structures of precursor **9** (left) and resulting homologue **8** (right); counter ions and hydrogen atoms were omitted for clarity; ellipsoids were drawn at 50% level.

Photophysical Characterization of Metal Complexes

At first glance, the absorption and emission properties of the two series $[(tbbpy)_{3-n}$ Ru $(\mathbf{2})_n]^{2+}$ (n = 0, 1, 2, 3) and $[(tbbpy)_2Ru(phenBr_m)]^{2+}$ (m = 0, 1, 2, 4) (the precursor **9** was excluded) are typical for $[Ru(bpy)_3]^{2+}$ complexes. All substances exhibit the characteristic singlet metal to ligand charge transfer (^{1}MLCT) absorption band ranging from 400 to 500 nm as well as intense luminescence between 600 and 800 nm. A closer look reveals an increase in molar extinction coefficients as a function of the number n of **2** with values from $\epsilon_{(n=0)} \approx 16000$ Lmol^{-1}cm^{-1} in model compound $[Ru(tbbpy)_3]^{2+}$ to $\epsilon_{(n=3)} \approx 19000$ Lmol^{-1}cm^{-1} in **10** For acetonitrile and dichloromethane, the ^{1}MLCT is hysochromically shifted with increasing number of **2**. This is presumably due to the contribution of the bromo-substituted phen-centered ^{1}MLCT-absorption. A similar trend evolves when inspecting the emission of the $[(tbbpy)_{3-n}Ru(\mathbf{2})_n]^{2+}$-series in acetonitrile. In particular, a hypsochromically shifted and intensified emission band is detected with increasing number of phen ligands. Interestingly, the homoleptic model compound $[Ru(tbbpy)_3]^{2+}$ shows an emission maximum at 614 nm and an emission intensity which is in between **4**, **8** and **10**. Again, when going from n = 1 to 3 a successive hypsochromical shift of the emission maximum is discernable. In dichloromethane rather than acetonitrile, the emission doubles in intensity and shifts hypsochromically by 10 nm. For a better comparison of the characteristic absorptions and emissions of **3** and **4**, the data for reference complexes $[(tbbpy)_2Ru(\mathbf{phen})]^{2+}$ and $[(tbbpy)_2Ru(3,5,6,8\text{-Br-}\mathbf{phen})]^{2+}$ were taken from the literature[8,10, 25] As such, all complexes in this series exhibit absorption maxima around 450 nm with exception of $[(tbbpy)_2Ru(3,5,6,8\text{-Br-}\mathbf{phen})]^{2+}$. The latter shows a hypsochromically shifted absorption maximum at 441 nm. In contrast, the emission behavior is only slightly changed with increasing number of bromo functionalities comparing **3** and **4**. Emissions of these compounds are hypsochromically shifted when compared to the reference $[(tbbpy)_2Ru(3,5,6,8\text{-Br-phen})]^{2+}$ and bathochromically shifted when compared to $[(tbbpy)_2Ru(phen)]^{2+}$.

Table 1. UV/vis absorption and emission data of references, the series $[(tbbpy)_{3-n}Ru(phenBr_2)_n]^{2+}$ (n=0,1,2,3), $[(tbbpy)_2Ru(phenBr_m)]^{2+}$ (m=0,1,2,4) and Suzuki cross coupling products **5**, **6** and **7**.

compound	solvent	$\lambda_{max,abs}$ [nm]	$\varepsilon_{\lambda max}$ [L mol^{-1} cm^{-1}]	$\lambda_{max,em}$ [nm]
$[Ru(tbbpy)_3]^{2+}$	DCM	464	16 000	607
	MeCN	458	17 900	614
$[(tbbpy)_2Ru(\mathbf{phen})]^{2+}$[8,20]	DCM	455	19 000	602
	MeCN	454	16 000	610
$[(tbbpy)_2Ru(3,8\text{-Br-}\mathbf{phen})]^{2+}$[20]	DCM	440	18 000	638
$[(tbbpy)_2Ru(3,5,6,8\text{-Br-}\mathbf{phen})]^{2+}$[10,20]	DCM	440	19 000	657
	MeCN	441	15 000	672
$[Ru(\mathbf{phen})_3]^{2+}$[10]	DCM	448	17 000	578
	MeCN	450	18 200	593
$[Ru(3,8\text{-Br-}\mathbf{phen})_3]^{2+}$[26]	MeCN	424	8 700	599
3	DCM	451	13 500	621
	MeCN	449	17 800	630
4	DCM	452	17 500	621
	MeCN	449	14 300	631
5	MeCN	454		617
6	MeCN	455		619
7	MeCN	457		610
8	DCM	433	20 500	611
	MeCN	434	22 200	621
10	DCM	451	19 000	587
	MeCN	450	18 200	600

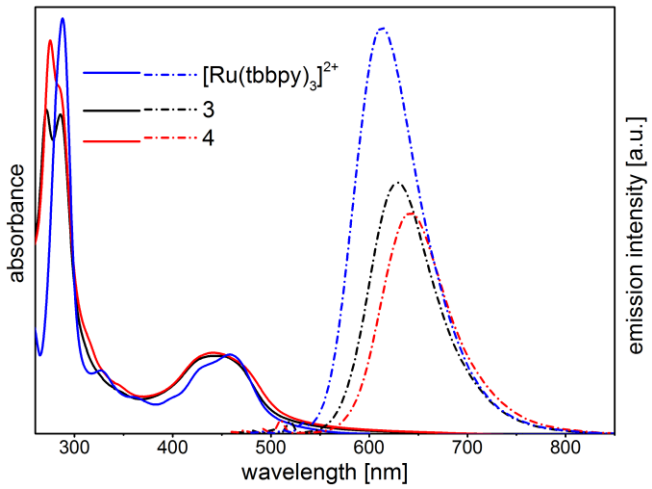

Figure 6. Exemplary UV/Vis and emission spectra of the standard complex $[Ru(tbbpy)_3]^{2+}$, **3** and **4**; measured in MeCN with same optical density at the ^{1}MLCT transition.

Emission Decay Dynamics

The emission dynamics of the ^{3}MLCT states of the complexes, as determined in acetonitrile and dichloromethane by means of time correlated single photon counting experiments (TCSPC) corroborated the steady-state emission data (**Table 2**). Generally, the lifetimes of **3** and **4** in aerated solutions of dichloromethane (450 ns) are enhanced compared to those in aerated acetonitrile solutions (140 ns). A different quencher concentration and / or a different viscosity in the more polar solvent might contribute to the differences. Nevertheless, in aerated solvents the lifetimes slightly changed dependent on the number of bromo substituents on the phen scaffold. Complexes **3** and **4** have a 40 ns longer lifetime, when compared to $[(tbbpy)_2Ru(3,5,6,8\text{-Br-}\mathbf{phen})]^{2+}$ (100 ns), and a 50 ns shortened lifetime, when compared to $[(tbbpy)_2Ru(\mathbf{phen})]^{2+}$ (211 ns). From these results can be concluded that substitution of the phen backbone with bromo substituents (-I/+M effect) exerts a remarkable influence on the ^{3}MLCT excited state lifetime of the corresponding Ru(II) complexes. Based on the emission data of the $[(tbbpy)_{3-n}Ru(\mathbf{2})_n]^{2+}$ (n=1, 2, 3) series substitution of the 5,6-positions only imperceptive influence on the excited state energy is observable, while the effect of the substitution in the 3,8-position is rather striking. The ordering of the lifetimes within this series is similar to the ordering of the relative luminescence intensities in dichloromethane. A direct correlation between short lifetime intensities points to the lack of other deactivating processes. Most notable is here the excited state quenching by oxygen.

Table 2. Life times (τ) of Ruthenium complexes in DCM and MeCN.

compound	solvent	$\tau_{aerated}$ [ns]	$\tau_{deaerated}$ [ns]
$[Ru(tbbpy)_3]^{2+}$	DCM	248[28]	609[28]
	MeCN	107[28]	730[28]
$[Ru(phen)_3]^{2+}$[10]	DCM	460	
	MeCN	150	
$[(tbbpy)_2Ru(phen)]^{2+}$[9,27]	DCM	272	
	MeCN	211	1423
3	DCM	452	
	MeCN	139	
4	DCM	438	
	MeCN	140	1347
$[(tbbpy)_2Ru(3,5,6,8\text{-Br-}phen)]^{2+}$[10,27]	DCM	591	
	MeCN	100	1336
8	DCM	573	
	MeCN	196	2190
10	DCM	353	
	MeCN	247	1380

Electrochemical Characterization

Interpretation of luminescence data yielded the assumption that functionalization in 5,6-position has less influence on the excited state energy compared to 3,8-position substitution. Thus, the electrochemical properties of $[(tbbpy)_{3-n}Ru(\mathbf{2})_n]^{2+}$ complexes (n = 0, 1, 2, 3) and $[Ru(tbbpy)_3]^{2+}$, **3**, **4** and $[(tbbpy)_2Ru(3,5,6,8\text{-Br-}\mathbf{phen})]^{2+}$ were determined and compared with literature[8,10] (**Table 3**).

Table 3. Selected redox potentials $E_{1/2}$ [V] of presented Ruthenium complexes and reference compounds; referenced vs. Fc/Fc^+ in a 0.1M solution of Bu_4NPF_6 in dry acetonitrile under argon atmosphere; $(LL)^x$: ligand centered reduction.

Compound/ potential	$E_{1/2}(LL)^3$ [V]	$E_{1/2}(LL)^2$ [V]	$E_{1/2}(LL)^1$ [V]	$E_{1/2}(Ru^{2+/3+})$ [V]
$[Ru(tbbpy)_3]^{2+}$[28]	-2.28	-2.02	-1.82	0.73
$[(tbbpy)_2Ru\text{-}(\mathbf{phen})]^{2+}$[8,10]	-2.23	-1.99	-1.80	0.78
$[(tbbpy)_2Ru(3,5,6,8\text{-Br-}\mathbf{phen})]^{2+}$[10]	-	-	-	0.92
3	-2.23	-1.98	-1.78 (-1.65, ir)	0.83
4	-2,32	-2.00	-1.79 (-1.68/ -1.58, ir)	0.85
8	-2.27	-1.99	-1.89 (-1.67 ir)	0.90
10	-2.18 (ir)	-1.79 (ir)	-1.54 (ir)	0.95

Interestingly, the series $[(tbbpy)_{3-n}Ru(\mathbf{2})_n]^{2+}$ (n=0, 1, 2, 3; compounds $[Ru(tbbpy)_3]^{2+}$, **4**, **8**, **10**) exhibited a shift of potentials referring to the oxidation process centered on the metal center ($E_{1/2}(Ru^{2+/3+})$). Thereby increasing numbers of n of **2** afforded higher potentials. Additionally, the complexes of this set (besides n=3) show three quasi reversible reduction potentials which can be assigned to the three ligand centered reductions ($(LL)^x$). With increasing number of bromo substituents the number of irreversible reductions also rose which likely can be attributed to reductions of bromine atoms under subsequent dehalogenation. The other series $[Ru(tbbpy)_3]^{2+}$, **3**, **4** and $[(tbbpy)_2Ru(3,5,6,8\text{-Br-}\mathbf{phen})]^{2+}$ exhibited an analogous shift for the potential of the metal centered oxidation ($E_{1/2}(Ru^{2+/3+})$). Based on the available data sets, the ground state redox properties of a general compound A and the emission properties (one electron potential according to the zero-zero excited state energy, $E_{0\text{-}0}$) permits a rough determination of the redox potentials of excited state couples according to the adjacent equations:[29]

$$E(A^+/A^*) \approx E(A^+/A) - E_{0\text{-}0}$$

$$E(A^*/A^-) \approx E(A/A^-) + E_{0\text{-}0}$$

Applying this for the series of Ruthenium complexes $[(tbbpy)_{3-n}Ru(\mathbf{2})_n]^{2+}$ (n = 0, 1, 2, 3) yields an comparative energy scheme (**Figure 7**). The excited state redox potential centered on the ligand does not change and values of about -1.1 V are obtained. For n = 1, 2, 3 the ground state metal centered redox potential is shifted from 0.73 to 0.95 V with increasing number of **2**. This effect is very interesting and has been applied by Thummel et al in tuning water oxidation catalysis. The highest activity was observed, when utilizing **2** (instead of phen or bpy) as ligand for the photosensitizer unit.[16] This is in agreement with our findings regarding the redox potentials of **2** compared to tbbpy or phen.

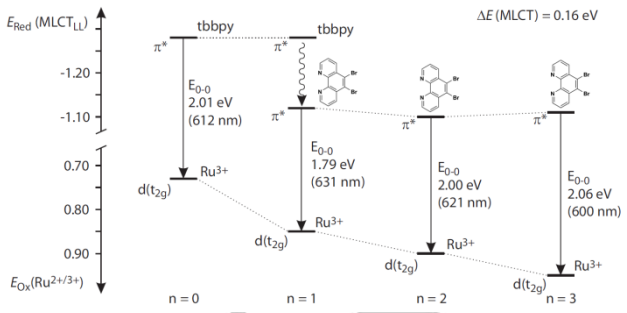

Figure 7. Compilation of the ^{3}MLCT excited state redox potentials that can be tapped (oxidative quenching mechanism, $E(A^+/A^*)$), the ground state redox potentials for the oxidation ($E(A^+/A)$) and the emission energies ($E_{0\text{-}0}$) of the series $[(tbbpy)_{3-n}Ru(\mathbf{2})_n]^{2+}$ (n=0, 1, 2, 3).

Additionally, all compounds in this set (besides n=3) exhibited three quasi reversible reduction potentials. They can be assigned to the three reductions centered on the ligands, respectively. Furthermore, a higher reduction potential (≈-0.16 V) for the excited state is observed for n=0. In conclusion this implies that the energy of the ^{3}MLCT-state centered on ligand **2** is irrespective of potential influences which result from other ligands coordinating the metal ion. Thus, the ^{3}MLCT-states located on **2** account for the emitting excited states (KASHA's rule) in compounds with n=1, 2, 3 as they exhibit reduction potentials about 0.16 eV lower in energy than the tbbpy centered ^{3}MLCT-states. This is in agreement with the previous discussion of the photophysical phenomena in terms of hypsochromically shifted absorption and bathochromically shifted emission. The analogous correlation for the set $[(tbbpy)_2Ru(phenBr_m)]^{2+}$ (m=0, 1, 2, 4) is shown in **Figure 8** and compares the influence of the number of bromine atoms coupled to the phen backbone to the introduced redox potentials.

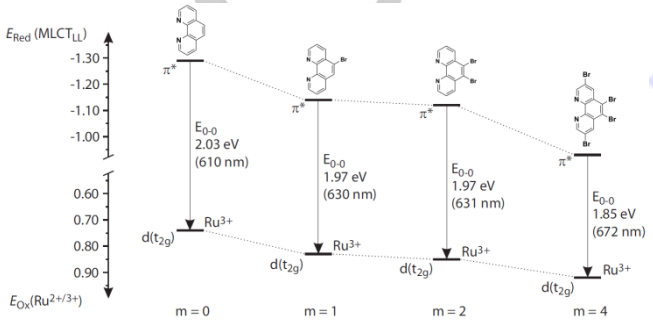

Figure 8. Compilation of the ^{3}MLCT excited state redox potentials of the that can be tapped (oxidative quenching mechanism, $E(A^+/A^*)$), the ground state redox potentials for the oxidation ($E(A^+/A)$) and the emission energies ($E_{0\text{-}0}$) of the series $[(tbbpy)_2Ru(phenBr_m)]^{2+}$ (m=1, 2, 4,) and $[(tbbpy)_2Ru\mathbf{phen}]^{2+}$.

Here, with increasing quantity of bromo substituents at the phen scaffold higher ground state metal centered oxidation potentials and a change in excited state oxidation potentials are observed. Multiple bromination of the phenanthroline ligand evidently reduces the excited state reduction potential. This results in a decreased energy for the $phenBr_m$-centered ^{3}MLCT leading to emission when relapsing from the excited to the ground state. Realizing this, the photochemical significance of the 5,6-position becomes clearly evident for redox and luminescence properties of corresponding Ruthenium chromophores.

Suzuki cross coupling of brominated complexes

In preliminary studies we investigated the suitability of the 5,6-dibromophenanthroline scaffold to function as a substrate for organometallic cross coupling reactions. For the free ligands no reactivity in Suzuki coupling could be observed. We evaluated the reactivity of $[(tbbpy)_2Ru(\mathbf{1})]^{2+}$ and $[(tbbpy)_2Ru(\mathbf{2})]^{2+}$ exemplary in Suzuki cross coupling reactions to receive compounds **5**, **6** and **7** (**Figure 9**). For the conversion of **3** with (4-acetylphenyl) boronic acid a very good yield of 97% was achieved. Product **5** was characterized *via* mass spectrometry, NMR spectroscopy and elemental analysis. Subsequently, we investigated if twofold Suzuki reactions are possible on the chromophore core utilizing **4** as starting material. The reactions were carried out with (4-acetylphenyl) boronic acid and (4-hydroxyphenyl) boronic acid to yield **6** (68%) and **7** (45%), respectively. The achieved yields for one and twofold Suzuki cross coupling reactions are higher compared to literature data where yields dropped

drastically (14-20%) when utilizing precursors bearing substituted (Me, tbbpy) ligands.[18] Characterization was performed *via* NMR spectroscopy, mass spectrometry and via X-ray diffraction (**Figure 10**).

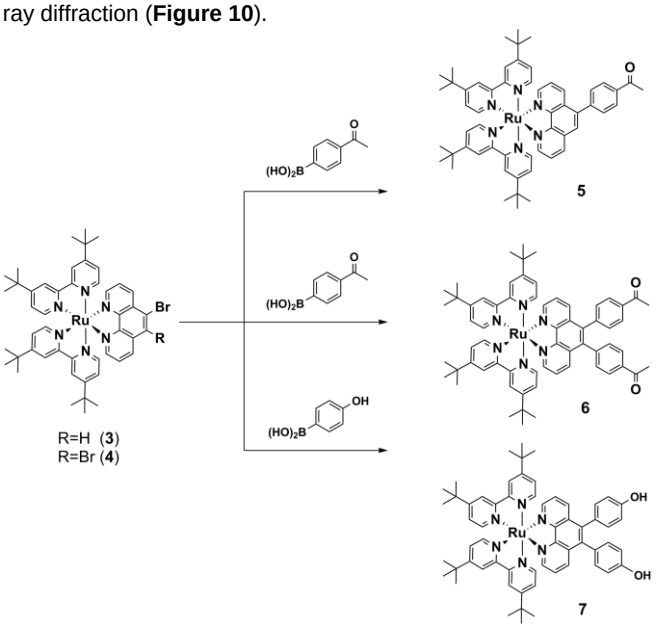

Figure 9. Products of bromo substituted complexes converted with boronic acids in Suzuki coupling; conditions: acetonitrile/water; 2M aqueous Na_2CO_3 solution; $Pd(PPh_3)_2Cl_2$.

Comparison of complexes **6** and **7** with precursor complex **4** reveals high similarity in measured bond lengths and angles (Compilation of selected bond lengths and angles is given in **Table S3**, ESI). The torsion of the phenyl ring for **6** leads to an almost orthogonal arrangement to the phen plane. Similar arrangement is found for **7**, were both phenyl rings are distorted for 78.3(4)° and respectively 76.1(4)° out of the phen plane. For **7**, two complexes are bridged via two water molecules.

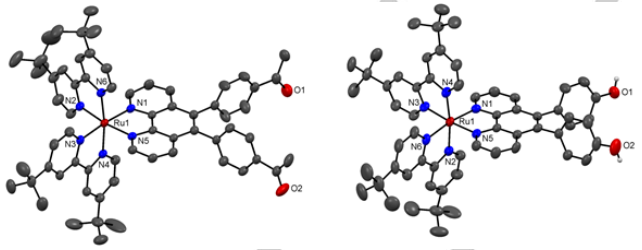

Figure 10. ORTEP representations of the molecular structures of **6** and **7**, counter ions and hydrogen atoms were omitted for clarity; ellipsoids were drawn at 50% level.

Thereby typical hydrogen bond lengths of 1.936(3) Å are observed between the hydrogen of the phenol moiety and an oxygen atom of the water molecule. Also the O-O distances of 2.829(4) Å are common for similar Ru(II) polypyridyl complexes which bear ligands like oxalamidines[30] or bibenzimidazoles.[31]

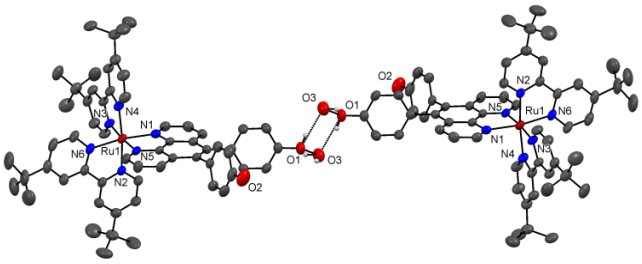

Figure 11. Depiction of hydrogen bonds of interacting OH groups within the solid state; counter ions, coordinated solvent and hydrogen atoms were omitted for clarity; ellipsoids were drawn at 50% level.

^{1}H-NMR spectra are informative to check if the coupling reaction was successful. Exemplary shift of the protons in 4,4' position and appearance for phenyl protons in the aromatic region of the spectrum are easy to follow. Exemplary depiction is given in **Figure 13**.

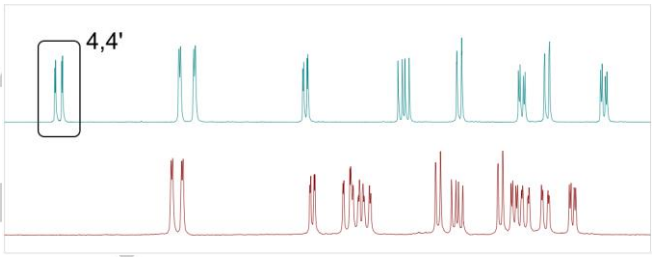

Figure 13. Aromatic region of the ^{1}H-NMR spectra of educt **4** (top) and Suzuki product **6** (bottom) in MeCN-d_3 showing the shift for protons in 4- and 4'-position (see ESI for description) and appearance of phenyl protons.

Suzuki coupling products show absorption and luminescence properties comparable to $[Ru(tbbpy)_3]^{2+}$. No bathochromic shift was observed which could be explained with the twisting of the substituted phenyl moieties possibly resulting in a reduced π-π-delocalization (see ESI).

Conclusions

Improved synthetic strategies for 5-bromo- and 5,6-dibromo-phenanthroline using low temperatures (room temperature, 60°C), normal pressure and short reaction times (2-16 h) with very good yields (70-93%) are presented. This provides access to a brominated ligand system which may undergo a variety of conversions. Henceforth, we prepared a series of bromo substituted Ru(II) complexes which generate a group of related complexes where structure property relations can be established All complexes introduced are easily accessible in high yields. It was possible to create a D_3 symmetric homoleptic Ru(II) complex which is terminated by six bromo functionalities. A detailed characterization of the components via X-ray diffraction provided important structural information. The comparison of the photophysical and electrochemical properties of these coordination compounds was performed and it could be shown, that the energy of the ^{3}MLCT-state centered on ligand **2** is

independent of possible influences which result from other ligands around the Ruthenium ion. Thus, the ^{3}MLCT-states localized on **2** represent the emitting excited states. It was shown that the reactivity of bromo functionalities at the phenanthroline in Suzuki cross coupling reactions scaffold can be influenced by coordination of the corresponding ligand to a metal center. Most interestingly, the free ligands showed no reactivity in Suzuki coupling reactions, whereas the Ruthenium bound 5-bromo- and 5,6-dibromophenanthrolines are facilely substituted by different aromatic building blocks.

Experimental Section

General

If not noted otherwise, all chemicals were commercially available and used without further purification. The following chemicals were prepared according to literature procedures: $[Ru(tbbpy)_2Cl_2]$[8], $[Ru(tbbpy)_3][PF_6]_2$[8], 4,4'-ditertbutyl-2,2'-bipyridine [32,33], $[Ru(cod)Cl_2]_n$[22]. The NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer, on a Jeol EX-270 DELTA and on a Jeol EX-400 DELTA spectrometer (270/400MHz), respectively. The chemical shifts δ are given in parts per million relative to tetramethylsilane (TMS, δ=0 ppm) referenced internally to the residual proton chemical shift in the deuterated solvent. Mass spectra were recorded with a SSQ 710 spectrometer (Finnigan MAT). Electrospray ionization spectra were recorded with a MAT 95 XL (Thermoquest-Finnigan MAT). Steady state absorption spectra were obtained using either a Perkin Elmer Lambda2 UV/vis two-beam spectrophotometer or a Jasco V-670 UV/Vis Spectrophotometer using a width of 2 nm and a scan rate of 480 nm/min. All spectra were recorded using a quartz glass cuvette of 10·10 mm. Steady state emission spectra were recorded using a Jasco FP-6200 spectrofluorometer or a Jasco Spectrofluorometer FP-8500 and a Horiba Jobin Yvon FluoroMax-3 spectrometer using a slitwidth of 2 nm for excitation and emission and an integration time of 0.5 s. The studies were performed in a 10·10 mm quartz glass cuvette. Electrochemical data were obtained by cyclic voltammetry using a conventional single-compartment three-electrode cell arrangement in combination with a potentiostate "AUTOLAB®, eco chemie". As auxiliary and reference electrode two Pt wires were used; working electrode: glassy carbon. The measurements were carried out in anhydrous and argon saturated acetonitrile. Tetrabutylammonium hexafluorophosphate ($c(TBAPF_6)$=0.1 M) was used as supporting electrolyte at ambient temperature (20 (±5)°C). All potentials are referenced to ferrocene/ferrocenium ($E(Fc/Fc^+)$ = 0.00V). Emission lifetimes were determined via time correlated single photon counting (TCSPC) on a Horiba Jobin Yvon FlouroLog-3 emission spectrometer with a Hamamatsu MCP photomultiplier (R3809U-58). For excitation a laser diode (NanoLED-405L, 403 nm, pulse width = 200 ps, maximum of repetition rate 100 kHz) was used. All measurements were performed in a 10·10mm quartz glass cuvette. Elemental analysis was performed on a Euro Vector Euro EA. Crystal structure intensity data for the compounds were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[34,35,36] The structures were solved by direct methods (SHELXS[37]) and refined by full-matrix least squares techniques against Fo2 (SHELXL-97[37]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen, non-disordered atoms were refined anisotropically.[37] Crystallographic data as well as structure solution and refinement details are summarized in **Table 4** (ESI). MERCURY was used for structure representations.[38] Supporting Information available: Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1451528 for 1, CCDC-1451529 for 2, CCDC-1451530 for 3, CCDC-1451531 for 4, CCDC-1451532 for 8, and CCDC-1451533 for 9. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

Ligand syntheses

5-Bromo-1,10-phenanthroline (1): 30ml of fuming sulfuric acid (65%) were added with cooling to 4.0 g (20.2 mmol) of 1,10-phenanthroline hydrate. After the 1,10-phenanthroline was dissolved a slight excess of bromine (0.6ml, 11.75mmol) was added to the solution in one portion. Upon stirring for 3 hours at room temperature the reaction mixture turned colorless due to the complete consumption of bromine. The reaction was not stopped until 16 hours later by pouring the solution on 250ml on ice and neutralization (pH=5) with ammonia. Extraction with small amounts of chloroform and drying of combined organic phases over Na_2SO_4 yielded a crude product after removal of the solvent. Redissolving in boiling toluene and hot filtration was used to remove impurities. A crude mixture of **1** and **2** with small traces of the starting material phenanthroline was obtained. Purification by column chromatography did not succeed. Starting material phenanthroline was removed by stirring in ether for 12 h and subsequent collection of the solids. Slow recrystallization from chloroform yielded the pure compound (**1**×$CHCl_3$) as colorless crystals in good yields (70%). ^{1}H-NMR ($CDCl_3$, 400MHz): δ = 9.1 (m, $2H_{(2/9)}$), 8.526 (dd, $1H_{(4)}$, ^3J = 8.4Hz, ^4J = 1.6Hz), 8.034 (dd, $1H_{(7)}$, ^3J = 8.1Hz, ^4J = 1.6Hz), 7.979 (s, $1H_{(6)}$), 7.624 (dd, $1H_{(3)}$, ^3J = 8.3Hz, ^3J = 4.4Hz), 7.520 (dd, $1H_{(8)}$, ^3J = 8.1Hz, ^3J = 4.3Hz) ppm. ^{13}C-NMR ($CDCl_3$, 100MHz): δ = 150.89, 150.68, 146.65, 145.67, 135.89, 135.06, 145.09, 129.64, 128.80, 124.00, 123.64, 120.78 ppm. Crystals suitable for X-ray diffraction were obtained from chloroform. Crystal data: $C_{12}H_7N_2Br$×$CHCl_3$, M_r = 378.47 g/mol, colorless crystal, size 0.065×0.065×0.05mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 6.9802(2), b = 20.3654(6), c = 9.8052(3) Å, α = 90.000, β = 92.768(2), γ = 90.000°, V = 1392.23(7)Å^3, T = -90(2)°C, Z = 4, $\rho_{calcd.}$ = 1.806 g/cm^3, $\mu_{(Mo\text{-}K\alpha)}$ = 35.13 cm^{-1}, F(000) = 744, 9838 reflections in h(-9/9), k(-25/26), l(-12/10) measured in the range 2.00° ≤ Θ ≤ 27.48°, completeness Φmax = 99.8%, 3182 independent reflections, R_{int} = 0.0449, 2576 reflections with $F_o > 4\sigma(F_o)$, 204 parameters, 0 restraints, $R_{obs.}$ = 0.0433, $wR^2_{obs.}$= 0.1016, R_{all}= 0.0583, wR^2_{all}= 0.1080, GOOF = 1.052, largest difference peak and hole: 0.914/-0.486 e/Å^3. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1451528.

5,6-Dibromo-1,10-phenanthroline (2): 30ml of fuming sulfuric acid (65%) were added with cooling to 4.0 g (20.2 mmol) of 1,10-phenanthroline hydrate. After the phenanthroline was completely dissolved (2 hours) an excess of bromine 1.7ml (33.3 mmol) was added to the solution. This mixture was heated to 60°C for two hours. This mixture was poured onto 200 ml of ice after the reaction time. Upon neutralization (pH=7) a precipitate formed, which was extracted with chloroform. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under vacuum. Then the crude product was dissolved in hot toluene, the insoluble dark impurities were filtered of and the solvent was removed under vacuum. Purification was achieved by recrystallization from chloroform. After drying at high-vacuum the pure compound was obtained as white powder (93%). ^{1}H-NMR ($CDCl_3$, 400MHz): δ = 9.232 (dd, $2H_{(2/9)}$, ^3J = 4.4 Hz, ^4J = 1.6 Hz), 8.778 (dd, $1H_{(4/7)}$, ^3J = 8.6Hz, ^4J = 1.6Hz), 7.739 (dd, $1H_{(3/8)}$, ^3J = 8.6Hz, ^3J = 4.4 Hz) ppm. ^{13}C-NMR ($CDCl_3$, 100MHz): δ = 150.92 ($2C_{(2/9)}$), 145.09 ($2C_{(10a/10b)}$), 137.56 ($2C_{(4a/6a)}$), 128.74 ($2C_{(4/7)}$), 125.27 ($2C_{(5/6)}$), 124.60 ($2C_{(3/8)}$) ppm.

MS: 338 m/z (100%, M^+). elemental analysis: calc.: C: 42.64%, H: 1.79%, N: 8.29%, Br: 47.28% found: C: 37.95%, H: 2.71%, N: 8.22%, Br: 46.17%. Crystals suitable for X-ray diffraction were obtained from chloroform. Crystal data: $C_{12}H_6N_2 \times CHCl_3$, M_r = 2071.08 g/mol, colorless cuboid, size 0.05 × 0.05 × 0.04mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 11.7492(4), b = 11.7577(4), c = 12.3256(4) Å, α = 90.000, β = 118.106(2), γ = 90.000°, V = 1501.92Å^3, T = -90(2)°C, Z = 4, $\rho_{calcd.}$ = 2.023 g/cm^3, $\mu_{(Mo\text{-}K\alpha)}$ = 5.920 cm^{-1}, F(000) = 880, 10426 reflections in h(-15/15), k(-14/15), l(-16/15) measured in the range 2.55° ≤ Θ ≤ 27.505°, completeness Φmax = 99.6%, 3429 independent reflections, R_{int} = 0.0311, 3429 reflections with $F_o > 4\sigma(F_o)$, 181 parameters, 0 restraints, $R_{obs.}$ = 0.0311, $wR^2_{obs.}$ = 0.0702, R_{all} = 0.0532, wR^2_{all} = 0.0786, GOOF = 0.959, largest difference peak and hole: 0.572 / -0.487 e/Å^3. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1451529.

Metal complex syntheses

Synthesis of [Ru(L)$_2$(L')]$^{2+}$-type complexes (method C1): One equivalent (~ 50-300mg) of the cis-[Ru(tbbpy)$_2$Cl$_2$] compound and one equivalent of the desired ligand were dissolved in 100ml of a mixture of ethanol/water (4:1 / v:v).This mixture was refluxed in the microwave for 60-300 minutes with a power of 150W. Ethanol was removed after cooling to precipitate impurities from the remaining aqueous solution. After filtration, 9 equivalents of NH_4PF_6 were added. The formed precipitate was collected after stirring for 30 minutes and was washed with water several times. Purification was either achieved by recrystallization from mixtures of acetone, acetonitrile or water, or by column chromatography with mixtures of acetonitrile/sat. solution of KNO_3/water. To remove water from the product, it was dissolved in dichloromethane, dried with Na_2SO_4 and filtered. After removal of the solvent under vacuum pure product compound [Ru(L)$_2$(L')][PF$_6$]$_2$ was obtained. Yield: (70-95%).

[(tbbpy)$_2$Ru(5-bromo-1,10-phenanthroline)][PF$_6$]$_2$ (3): According to **method C1**, 664 mg (936 μmol) of [Ru(tbbpy)$_2$Cl$_2$] and 355 mg (936 μmol) of **1** were reacted in the microwave for 90 minutes in 125ml of ethanol/water. After cooling, ethanol was removed and precipitated impurities were filtered off. Then 916 mg (5.62 mmol) NH_4PF_6 were added and the formed precipitate was filtered collected and was washed with water. Purification was achieved by recrystallization from acetone/water by slow evaporation. This yielded also crystals suitable for X-ray diffraction. After removal of water the pure **3** was obtained as red powder. The yield is 1.07 g (898 μmol, 96%). ^{1}H-NMR (CD_3CN, 400MHz): δ = 8.79 (dd, 1H$_{(4)}$, ^3J = 8.2Hz, ^4J = 1.2Hz), 8.61 (s, 1H$_{(6)}$), 8.51 (dd, 1H$_{(7)}$, ^3J = 8.2Hz, ^4J = 1.2Hz), 8.50 (m, 2H$_{(3\text{-}bpy)}$), 8.46 (m, 2H$_{(3'\text{-}bpy)}$), 8.11 (dd, 1H$_{(2)}$, ^3J = 4.8Hz, ^4J = 0.8Hz), 8.07 (dd, 1H$_{(9)}$, ^3J = 4.6Hz, ^4J = 1.2Hz), 7.83 (dd, 1H$_{(3)}$, ^3J = 8.4Hz, ^3J = 5.2Hz), 7.75 (dd,1H$_{(8)}$, ^3J = 8.3Hz, ^3J = 5.3Hz), 7.67 (dd, 2H$_{(6\text{-}bpy)}$, ^3J = 6.0Hz, ^3J = 3.0Hz), 7.45 (ddd, 2H$_{(5\text{-}bpy)}$, ^4J = 1.6Hz, ^4J = 1.8Hz, ^3J = 5.8Hz), 7.38 (dd, 2H$_{(6'\text{-}bpy)}$, ^3J = 5.8Hz, ^3J = 4.2Hz), 7.21 (m, 2H$_{(5'\text{-}bpy)}$), 1.43 (d, 18H$_{(8'\text{-}bpy)}$, ^3J = 1.0Hz), 1.35 (s, 18H$_{(8\text{-}bpy)}$) ppm. ^{13}C-NMR (CD_3CN, 100MHz): δ = 163,73 (2C$_{(4\text{-}bpy)}$), 163,59 (2C$_{(4'\text{-}bpy)}$), 158.05 (2C$_{(2\text{-}bpy)}$), 157.76 (2C$_{(2'\text{-}bpy)}$), 154.00 (1C$_{(2)}$), 153.67 (1C$_{(9)}$), 152.28 (2C$_{(6'\text{-}bpy)}$), 152.06 (2C$_{(6\text{-}bpy)}$), 149.73 (1C$_{(10)}$), 148.45 (1C$_{(1)}$), 137.05 (1C$_{(4)}$), 136.52 (1C$_{(7)}$), 132.08 (1C$_{(6)}$), 131.89 (1C$_{(5)}$), 131.44 (1C$_{(4')}$), 127.67 (1C$_{(3)}$), 127.61 (1C$_{(8)}$), 125.64 (2C$_{(5\text{-}bpy)}$), 125.45 (2C$_{(5'\text{-}bpy)}$), 122.72 (1C$_{(5)}$), 122.53 (2C$_{(3\text{-}bpy)}$), 122.44 (2 C$_{(3'\text{-}bpy)}$), 36.36 (2C$_{(7'\text{-}bpy)}$), 36.27 (2C$_{(7\text{-}bpy)}$), 30.52 (3C$_{(8'\text{-}bpy)}$), 30.44 (3C$_{(8\text{-}bpy)}$) ppm. Crystals suitable for X-ray diffraction were obtained from acetonitrile/water. Crystal data: $[C_{48}H_{55}N_6BrRu]^{2+}[PF_6]^-_2 \times 2CH_3CN$, M_r = 1269.01 g/mol, red-brown cuboid, size 0.06×0.06×0.05mm^3, triclinic, space group P$\bar{1}$ (No. 2), a = 12.5680(3), b = 13.9694(4), c = 16.9912(4) Å, α = 70.946(1), β = 75.702(1), γ = 89.332(2)°, V = 2724.56(12)Å^3, T = -90°C, Z = 2, $\rho_{calcd.}$ = 1.547 g/cm^3, $\mu_{(Mo\text{-}K\alpha)}$ = 11.65 cm^{-1}, F(000) = 1292, 19983 reflections in h(-16/15), k(-18/16), l(-22/21) measured in the range 2.37° ≤ Θ ≤ 27.49°, completeness Φmax = 99.1%, 12387 independent reflections, R_{int} = 0.0376, 8826 reflections with $F_o > 4\sigma(F_o)$, 699 parameters, 0 restraints, $R_{obs.}$ = 0.0605, $wR^2_{obs.}$ = 0.1585, R_{all} = 0.0951, wR^2_{all} = 0.1786, GOOF = 1.024, largest difference peak and hole: 2.767/-1.715 e/Å^3. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1451530.

[(tbbpy)$_2$Ru(5,6-dibromo-1,10-phenanthroline)][PF$_6$]$_2$ (4): 300mg (423 μmol) of [Ru(tbbpy)$_2$Cl$_2$] and 143mg (423 μmol) **2** were reacted in the microwave according to **method C1** in 60ml of ethanol/water for 90 minutes. After cooling and removal of ethanol impurities were filtered off. Then 415mg (2.54 mmol) NH_4PF_6 were added to precipitate the desired product. Purification was achieved by recrystallization from acetone/water by slow evaporation. This yielded also crystals suitable for X-ray diffraction. Water was removed by dissolving the crude product in dichloromethane and drying with Na_2SO_4 and removal of the precipitate and solvent. The yield was 466mg (398 μmol, 90%) of pure **4** as red powder. ^{1}H-NMR (CD_3CN, 400MHz): δ = 8.87 (dd, 2H$_{(4/4')}$, 3J = 8.6Hz, 4J = 1.2Hz), 8.50 (d, 2H$_{(3\text{-}bpy)}$, 4J = 1.8Hz), 8.45 (d, 2H$_{(3'\text{-}bpy)}$, 4J = 1.8Hz), 8.12 (dd, 2H$_{(2/2')}$, 3J = 5.3Hz, 4J = 1.2Hz), 7.81 (dd, 2H$_{(3/3')}$, 3J = 8.6Hz, 3J = 5.2Hz), 7.67 (d, 2H$_{(6\text{-}bpy)}$, 3J = 6.2Hz), 7.45 (dd, 2H$_{(5\text{-}bpy)}$, 3J = 6.1Hz, 4J = 2.0Hz), 7.32 (d, 2H$_{(6'\text{-}bpy)}$, 3J = 6.0Hz), 7.30 (dd, 2H$_{(5'\text{-}bpy)}$, 3J = 6.1Hz 4J = 2.0Hz), 1.43 (s, 18H$_{(t\text{-}Bu')}$), 1.35 (s, 18H$_{(t\text{-}Bu)}$) ppm. ^{13}C-NMR (CD_3CN, 100MHz): δ = 163.82 (2C$_{(4\text{-}bpy)}$), 163.67 (2C$_{(4'\text{-}bpy)}$), 157.95 (2C$_{(2\text{-}bpy)}$), 157.69 (2C$_{(2'\text{-}bpy)}$), 154.14 (2C$_{(2/9)}$), 152.36 (2C$_{(6'\text{-}bpy)}$), 152.02 (2C$_{(6\text{-}bpy)}$), 148.68 (2C$_{(10'/10'')}$), 138.08 (2C$_{(4/7)}$), 131.96 (2C$_{(4'/6')}$), 128.31 (2C$_{(3/8)}$), 127.22 (2C$_{(5,6)}$), 125.67 (2C$_{(5\text{-}bpy)}$), 125.44 (2C$_{(5'\text{-}bpy)}$), 122.57 (2C$_{(3\text{-}bpy)}$), 122.47 (C$_{(3'\text{-}bpy)}$), 36.36 (2C$_{(7'\text{-}bpy)}$), 36.27 (2C$_{(7\text{-}bpy)}$), 30.50 (3C$_{(8'\text{-}bpy)}$), 30.43 (3C$_{(8\text{-}bpy)}$) ppm. MS: 1120.9 m/z (100%, [M-PF$_6$]$^+$), 1120.9 m/z (10%, [M-PF$_6$-Br]$^+$). Crystals suitable for X-ray diffraction were obtained from acetone/water. Crystal data: $[C_{48}H_{54}N_6Br_2Ru]^{2+}[PF_6]^-_2 \times 2CH_3COCH_3$,$M_r$ = 1381.96 g/mol, red-orange crystal, size 0.04×0.04×0.04mm^3, triclinic, space group P$\bar{1}$ (No. 2), a = 10.5859(2), b = 11.7274(3), c = 24.0080(7) Å, α = 90.444(1), β = 94.113(2), γ = 92.976(2)°, V = 2968.59(13)Å^3, T = -90°C, Z = 2, $\rho_{calcd.}$ = 1.546 g/cm^3, $\mu_{(Mo\text{-}K\alpha)}$ = 17.46 cm^{-1}, F(000) = 1400, 20454 reflections in h(-13/13), k(-15/14), l(-31/28) measured in the range 2.05° ≤ Θ ≤ 27.47°, completeness Φmax = 98.1%, 13329 independent reflections, R_{int} = 0.0362, 10002 reflections with $F_o > 4\sigma(F_o)$, 728 parameters, 0 restraints, $R_{obs.}$ = 0.0507, $wR^2_{obs.}$ = 0.1164, R_{all} = 0.0797, wR^2_{all} = 0.1317, GOOF = 1.011, largest difference peak and hole: 1.029/-0.718 e/Å^3. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1451531.

[(tbbpy)$_2$Ru((4-(1,10-phenanthroline-5-yl)phenyl)ethan-1-one)][PF$_6$]$_2$ (5): Under Ar atmosphere 100 mg (0.08 mmol) of **3**, 60 mg (0.37 mmol) of 4-acetylphenylboronic acid and 10 mg (0.014 mmol) (Pd(PPh$_3$)$_2$Cl$_2$ were dissolved in 50 ml degassed MeCN and 25 ml of a degassed 2 M Na_2CO_3 solution. The solution was refluxed for 4 days and after cooling to room temperature filtrated. Solvents were removed under reduced pressure, the solid was dissolved in EtOH. The target compound was precipitated with aqueous NH_4PF_6 solution, filtrated and washed thoroughly with water and Et_2O. Pure complex **5** could be received via recrystallization by slow evaporation out of an acetone/water mixture. The yield was 100 mg (82 μmol, 97%). ^{1}H-NMR (CD_3CN, 400 MHz): δ = 8.60 (dd, J = 8.3, 1.1 Hz, 1H), 8.52 (d, J = 1.9 Hz, 2H), 8.48 (d, J = 1.9 Hz, 2H), 8.43 (dd, J = 8.6, 1.1 Hz, 1H), 8.23 (s, 1H), 8.21 (d, J = 8.4 Hz, 2H), 8.08 (7, m, 2H), 7.80 – 7.66 (m, 6H), 7.50 – 7.41 (m, 4H), 7.23 (dd, J = 7.9, 6.1, 2.0 Hz, 2H), 2.68 (s, 3H), 1.45 (s, 18H), 1.37 (s, 18H). MS (FD; ethanol): m/z= 1082 [M-PF$_6$]$^+$, 468 [M-2PF$_6$]$^{2+}$. Elemental analysis for $C_{56}H_{62}F_{12}N_6OP_2Ru$: calc.: C: 54.86, H: 5.10, N: 6.85. found: C: 54.69, H: 5.02, N: 6.55.

[(tbbpy)$_2$Ru((4,4'-(1,10-phenanthroline-5,6-yl)-bis(phenylen-ethan-1-one))][PF$_6$]$_2$ (6): Under Ar atmosphere 300 mg (0.24 mmol) **4**, 77.87 mg (0.48 mmol) of 4-acetylphenylboronic acid and 30 mg (0.042 mmol) ($Pd(PPh_3)_2Cl_2$ were dissolved in 50 ml degassed MeCN and 25 ml of a degassed 2 M Na_2CO_3 solution. The solution was refluxed for 10 days and after cooling to room temperature filtrated. Solvents were removed under reduced pressure, the solid was dissolved in EtOH. The target compound was precipitated with aqueous NH_4PF_6 solution, filtrated and washed thoroughly with water and Et_2O. Pure complex **6** could be received via recrystallization by slow evaporation out of an acetone/water mixture. The yield was 220 mg (16 μmol, 68%). ^{1}H-NMR (CD_3CN, 500 MHz): δ = 8.53 (d, *J* = 1.8 Hz, 2H), 8.49 (d, *J* = 1.8 Hz, 2H), 8.10 (dd, *J* = 5.2, 1.2 Hz, 2H), 7.99 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.94 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.93 (dd, J= 8.0, 1.5 Hz, 2H), 7.71 (d, *J* = 6.0 Hz, 2H), 7.65 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.52 (d, *J* = 6.0 Hz, 2H), 7.47 (dd, *J* = 6.1, 2.1 Hz, 2H), 7.44 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.38 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.30 (dd, *J* = 6.0, 2.0 Hz, 2H), 2.56 (s, 6H), 1.45 (s, 18H), 1.40 (s, 18H). ^{13}C-NMR (CD_3CN, 101 MHz): δ = 198.59 (2C), 163.52 (2C), 163.42 (2C), 157.92 (2C), 157.75 (2C), 153.02 (2C), 152.17 (2C), 151.92 (2C), 148.44 (2C), 141.49 (2C), 138.73 (2C), 137.53 (2C, 136.04 (2C), 132.00 (2C), 131.96 (2C), 131.58 (2C) , 129.01 (2C), 129.00 (2C), 127.03 (2C), 125.51 (2C), 125.33 (2C) , 122.45 (2C), 122.39 (2C), 36.24 (2C), 36.19 (2C), 30.39 (6C), 30.35 (6C),, 26.97 (2C). MS (HRM-ESI; acetonitrile): m/z= 1199 [M-PF_6]$^+$, 528 [M-2PF_6]$^{2+}$. Elemental analysis for $C_{64}H_{68}F_{12}N_6O_2P_2Rux1.25\ H_2O$: calc.: C: 56.24, H: 5.20, N: 6.15. found: C: 56.27, H: 5.17, N: 5.89. Crystal data: $C_{66}H_{71}F_{12}N_7O_2P_2Ru$, M_r=1385.30 g mol^{-1}, red fragment, crystal size 0.1558 x 0.1054 x 0.0746 mm^3, triclinic, space group *P* -1, a = 12.2062(3) Å, b = 15.1931(3) Å, c = 20.6095(5) Å, α = 102.6314(2)°, β= 99.352(2)°, γ = 103.924(2)°, V = 3525.33(15) Å^3, T = 180(2) K, Z = 2, $\rho_{calcd.}$ = 1.305 Mg/m^3, μ (Cu-Kα) = 2.895 mm^{-1}, F(000) = 1428, altogether 32893 reflexes up to h(-15/15), k(-18/13), l(-25/24) measured in the range of 7.412° ≤ Θ ≤ 73.757° , completeness Θ_{max} = 99.7 %, 13812 independent reflections, R_{int} = 0.0320, 13257 reflections with Fo > 4 σ(Fo), 812 parameters, 2 restraints, $R1_{obs}$ = 0.0481, $wR2_{obs}$ = 0.1351, $R1_{all}$ = 0.0550, $wR2_{all}$ = 0.1390, GOOF = 1.057, largest difference peak and hole: 1.047/-0.848 e·Å^{-3}. Residual electron densities could not be fitted to a reasonable structure. The Platon SQUEEZE routine was therefore applied. According to the respective residual electron count (81 e$^-$) and the corresponding void shape clearly indicates the presence of two molecules of heavily distorted acetonitrile. CCDC 1518486 contains 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

[(tbbpy)$_2$Ru((4,4'-(1,10-phenanthroline-5,6-yl)-bis(phenol))][PF$_6$]$_2$ (7): Under Ar atmosphere 150 mg (0.12 mmol) **4**, 50 mg (0.36 mmol) of 4-hydroxyphenylboronic acid and 20 mg (0.028 mmol) ($Pd(PPh_3)_2Cl_2$ were dissolved in 50 ml degassed MeCN and 25 ml of a degassed 2 M Na_2CO_3 solution. The solution was stirred for 7 days at room temperature. The solution was filtrated, solvents were removed under reduced pressure and the solid was dissolved in a small amount of EtOH. The target compound was precipitated with aqueous NH_4PF_6 solution, filtrated and washed thoroughly with water and Et_2O. Pure complex **7** could be received via recrystallization by slow evaporation out of an acetone/water mixture. The yield was 0.07g (0.054 mmol, 45%). ^{1}H-NMR (CD_3CN, 400 MHz): δ = 8.52 (d, *J* = 1.7 Hz, 2H), 8.49 (d, *J* = 2.0 Hz, 2H), 8.12 (dd, *J* = 8.5, 1.1 Hz, 2H), 8.03 (dd, *J* = 5.1, 1.1 Hz, 2 H), 7.71 (d, *J* = 5.9 Hz, 2H), 7.62 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.53 – 7.41 (m, 4H), 7.27 (dd, *J* = 6.0, 2.0 Hz, 2H), 7.17 – 6.97 (m, 4H), 6.86 – 6.75 (m, 4H), 1.45 (s, 18H), 1.3 (s, 18H). MS (HRM-ESI; MeCN): m/z= 1147.3802 [M-PF_6]$^+$, 501.2070 [M-2PF_6]$^{2+}$. Elemental analysis for $C_{64}H_{68}F_{12}N_6O_2P_2Rux0.25\ C_3H_6O$: calc.: C: 55.84, H: 5.05, N: 6.43. measured: C: 55.77, H: 4.99, N: 6.50. Crystal data: $C_{64}\ H_{76}\ F_{12}\ N_6\ O_4\ P_2$ Ru, M_r = 1384.31 g mol^{-1}, red hexagonal prism, crystal size 0.2158 x 0.1447 x 0.1353 mm^3, triclinic, space group *P* -1, a = 11.8547(3) Å, b = 14.0372(4) Å, c = 20.8266(4) Å, α = 91.470(2)°, β= 91.017(2)°, γ = 107.516(2)°, V = 3302.73(15) Å^3, T = 180(2) K, Z = 2, $\rho_{calcd.}$ = 1.392 Mg/m^3, μ (Mo-Kα) = 0.370 mm^{-1}, F(000) = 1432, altogether 39770 reflexes up to h(-14/14), k(-17/17), l(-25/26) measured in the range of 3.405° ≤ Θ ≤ 26.372° , completeness Θ_{max} = 99.7 %, 13472 independent reflections, R_{int} = 0.0482, 10349 reflections with Fo > 4 σ(Fo), 904 parameters, 7 restraints, $R1_{obs}$ = 0.0633, $wR2_{obs}$ = 0.1664, $R1_{all}$ = 0.0858, $wR2_{all}$ = 0.1837, GOOF = 1.051, largest difference peak and hole: 1.132/-0.678 e·Å^{-3}. OH distances in the single water molecule as well as C-C and C-O distances of diethyl ether were fixed using the DFIX and DANG commands. Short intermolecular distances reported in the checkcif report correspond to the distortion of terminal methyl groups of diethyl ether. CCDC 1518485 contains 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.

[(tbbpy)Ru(5,6-dibromo-1,10-phenanthroline)$_2$][PF$_6$]$_2$ (8): Following **method C1**, 105mg (124 μmol) of **9** and 33,2mg (124 μmol) of tbbpy were reacted in the microwave for 180 minutes in 100ml of ethanol/water. After cooling, ethanol was removed and dark precipitated impurities were filtered off. Then 121mg (720 μmol) of NH_4PF_6 were added and the formed precipitate was collected and washed with water. Purification was achieved by column chromatography using acetonitrile/water and subsequent recrystallization from acetonitrile/water. Careful washing of the obtained crystals with very small amounts of methylene chloride yielded pure product. This yielded as well crystals suitable for X-ray diffraction. After removal of water, pure **8** was obtained as red powder. The yield was 17mg (12.5 μmol, 10%). ^{1}H-NMR (CD_3CN, 400MHz): δ = 8.93 (dd, 2H$_{(4/4')}$, ^3J = 8.8Hz, ^4J = 0.8Hz), 8.83 (dd, 2H$_{(4/4')}$, ^3J = 7.6Hz, ^4J = 0.8Hz), 8.49 (d, 2H$_{(3\text{-}bpy)}$, ^4J = 1.8Hz), 8.21 (dd, 2H$_{(2/2')}$, ^3J = 5.3Hz, ^4J = 0.8Hz), 7.93 (dd, 2H$_{(2/2')}$, ^3J = 5.2Hz, ^4J = 0.8Hz), 7.87 (dd, 2H$_{(3/3')}$, ^3J = 8.8Hz, ^3J = 5.3Hz), 7.62 (dd, 2H$_{(3/3')}$, ^3J = 7.6Hz, ^3J = 5.2Hz), 7.48 (d, 2H$_{(6\text{-}bpy)}$, ^3J = 6.0Hz), 7.23 (dd, 2H$_{(5\text{-}bpy)}$, ^3J = 6.1Hz, ^4J = 2.0Hz), 1.37 (s, 18H$_{(t\text{-}Bu)}$) ppm. ^{13}C-NMR (CD_3CN, 100MHz): δ = 164.14 (2C$_{(4\text{-}bpy)}$), 157.82 (2C$_{(2\text{-}bpy)}$), 154.81 (2C$_{(2/9)}$), 154.53 (2C$_{(2/9)}$), 152.68 (2C$_{(6'\text{-}bpy)}$), 148.72 (2C$_{(10'/10'')}$), 148.49 (2C$_{(10'/10'')}$), 138.58 (2C$_{(4/7)}$), 138.45 (2C$_{(4/7)}$), 132.05 (2C$_{(4'/6')}$), 132.00 (2C$_{(4'/6')}$), 128.36 (2C$_{(3/8)}$), 128.18 (2C$_{(3/8)}$), 127.30 (2C$_{(5,6)}$), 127.21 (2C$_{(5,6)}$), 125.51 (2C$_{(5\text{-}bpy)}$), 122.65 (2C$_{(3\text{-}bpy)}$), 36.35 (2C$_{(7\text{-}bpy)}$), 30.47 (3C$_{(8\text{-}bpy)}$) ppm. MS (ESI): 1190.5 m/z (100%, [M-PF6]$^+$), 522.8 m/z (60%, [M-2PF6]$^{2+}$). Crystals suitable for X-ray diffraction were obtained from acetonitrile/water. Crystal data for **8**: $[C_{42}H_{36}N_6Ru]^{2+}[PF_6]^-_2 \times CH_3CN$, M_r = 1376.47 g/mol, red-brown crystal, size 0.05 × 0.05 × 0.04mm^3, triclinic, space group P $\bar{1}$ (No. 2), a = 12.0674(4), b = 13.6818(4), c = 16.1755(4) Å, α = 97.260(2), β = 93.727(2), γ = 98.202(2)°, V = 2612.73(13)Å^3, T = -90(2)°C, Z = 2, $\rho_{calcd.}$ = 1.750 g/cm^3, $\mu_{(Mo\text{-}K\alpha)}$ = 35.02 cm^{-1}, F(000) = 1348, 19732 reflections in h(-15/15), k(-17/17), l(-20/20) measured in the range 2.60° ≤ Θ ≤ 27.45°, completeness Φ_{max} = 99.3%, 11863 independent reflections, R_{int} = 0.0364, 8038 reflections with $F_o > 4\sigma(F_o)$, 659 parameters, 0 restraints, $R_{obs.}$ = 0.0545, $wR^2_{obs.}$ = 0.1422, R_{all} = 0.0935, wR^2_{all} = 0.1618, GOOF = 1.032, largest difference peak and hole: 1.730 / -0.919 e/Å^3. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1451532.

[Cl$_2$Ru(5,6-dibromo-1,10-phenanthroline)$_2$] (9): For this reaction, 280 mg (1.00mmol) of [Ru(COD)Cl$_2$]n and 676 mg (2.00mmol) of **2** were suspended in 50ml of dry DMF and heated for two hours at 150 W in the microwave. After cooling, the solvent was removed. The remaining solid was dissolved in a small amount of chloroform and heated to reflux very short. Addition of ethanol and recrystallization in the cold yielded a black precipitate. Removal of the side product **10** was achieved via extraction of the methylene chloride solution with water and by column

chromatography with acetone/DMF. After removal of the solvent 400mg (470 μmol) of a black and almost insoluble powder were obtained (yield = 47%). ^{1}H-NMR (CD_2Cl_2, 400MHz): δ = 9.250 (d, $2H_{(2/9)}$, ^{3}J = 4.2Hz), 8.237 (d, $4H_{(4/7)}$, ^{3}J = 8.4Hz), 7.687 (dd, $2H_{(2/9)}$, ^{3}J = 5.2Hz, ^{3}J = 8.4Hz) ppm. Crystals suitable for X-ray diffraction were obtained from dichloromethane. Crystal data: $[C_{24}H_{12}N_4Cl_2Br_4Ru]\times 3CH_2Cl_2$, M_r = 1101.76 g/mol, black crystal, size 0.06×0.06×0.03mm^3, monoclinic, space group C2/c (No. 15), a = 18.1042(8), b = 16.7210(13), c = 14.0302(9) Å, α = 90.000, β = 125.740(3), γ = 90.000°, V = 3447.4(4)A3, T = -90°C, Z = 4, $\rho_{calcd.}$ = 2.123 g/cm^3, $\mu_{(Mo\text{-}K\alpha)}$ = 57.39 cm^{-1}, F(000) = 2108, 11467 reflections in h(-23/22), k(-21/21), l(-14/18) measured in the range 1.93° ≤ Θ ≤ 27.46°, completeness Φ_{max} = 99.5%, 3929 independent reflections, R_{int} = 0.0634, 2688 reflections with $F_o > 4\sigma(F_o)$, 200 parameters, 0 restraints, $R_{obs.}$ = 0.0468, $wR^2_{obs.}$ = 0.1075, R_{all} = 0.0834, wR^2_{all} = 0.1232, GOOF = 1.040, largest difference peak and hole: 0.981/-0.738 e/Å^3. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1451533.

[Ru(5,6-dibromo-1,10-phenanthroline)$_3$][PF$_6$]$_2$ (10): For this reaction 131mg (468μmol) of $[Ru(cod)Cl_2]_n$ and 474mg (1.40mmol) of **2** were heated in a mixture of ethanol/water over night at reflux and afterwards for two hours in the microwave (150W). After removal of the solvent and the in water insoluble side products, NH_4PF_6 was added. Purification was achieved using column chromatography in acetonitrile/water. Recrystallization from acetonitrile gave the desired product in high purity. Yield: 17%, 109 mg, 31.2 μmol. ^{1}H-NMR ($CDCl_3$, 400MHz): δ = 8.876 (dd, $6H_{(4/7)}$, ^{3}J = 8.2Hz, ^{4}J = 1.2Hz), 8.526 (dd, $1H_{(2/9)}$, ^{3}J = 5.6Hz, ^{4}J = 1.2Hz), 8.034 (dd, $1H_{(3/8)}$, ^{3}J = 8.8Hz, ^{3}J = 5.2Hz) ppm. ^{13}C-NMR ($CDCl_3$, 100MHz): δ = 155.14 ($6C_{(4/7)}$), 148.49 ($6C_{(10'/10'')}$), 138.80 ($6C_{(2/9)}$), 131.99 ($6C_{(4'/6')}$), 128.21 ($6C_{(3/7)}$), 127.21 ($6C_{(5/6)}$) ppm. MS: (ESI) m/z = 1206.2 (100%, $[M\text{-}PF_6]^+$).

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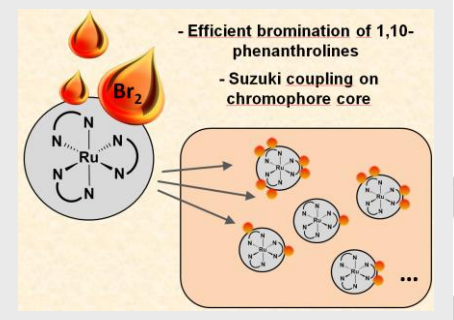
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Text for Table of Contents

Improved syntheses for 5-bromo and 5,6-dibromo-1,10-phenanthroline are presented. A series of corresponding Ru(II) polypyridine complexes are characterized in detail and converted in Suzuki cross coupling reactions. A detailed correlation is developed between the number of bromine substituents and photochemical and electrochemical properties of ruthenium complexes.



Efficient Bromination

*Anne Stumper, Thomas David Pilz, Markus Schaub, Helmar Görls, Dieter Sorsche, Katrin Peuntinger, Dirk Guldi Sven Rau**

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Efficient Access to 5- and 5,6-Dibromophenanthroline Ligands