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Controlled Formation of Mixed-Metal Macrocycles Using Dynamic Exchange Processes and Steric Constraints

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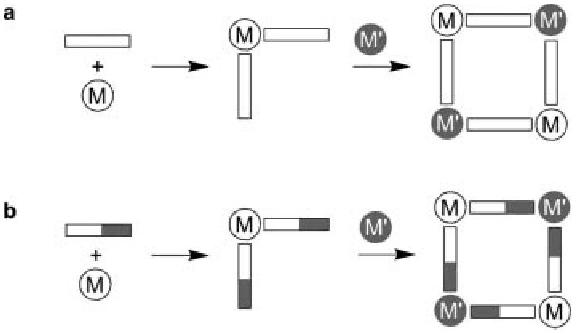
The exchange reaction of the trinuclear macrocycles $[(C_6H_3iPr_3)Ru(C_5H_3NO_2)]_3$ (**AAA**) and $[(cymene)Ru(C_5H_3NO_2)]_3$ (**BBB**) has been studied. It was found that the equilibration proceeds in two steps and that the final mixture is completely dominated by the mixed-metal macrocycles $[\{(C_6H_3iPr_3)Ru\}_2\{(cymene)Ru\}(C_5H_3NO_2)_3]$ (**AAB**) and $[\{(C_6H_3iPr_3)Ru\}\{(cymene)Ru\}_2(C_5H_3NO_2)_3]$ (**ABB**). The results are rationalized by assuming unfavorable steric interactions between adjacent $(C_6H_3iPr_3)Ru$ fragments. It is shown that interactions of this kind can be used to bias scrambling processes in such a way that mixed-metal macrocycles are obtained in over 80 % yield. The structures of $[\{(C_6Me_6)Ru\}\{(C_6H_6)Ru\}_2(C_5H_3NO_2)_3]$ and $[(Cp^{*}Rh)\{(C_6H_6)Ru\}_2(C_5H_3NO_2)_3]$ have been determined by single-crystal X-ray analysis.

Introduction

Transition metal-based self-assembly processes have been used extensively to build macrocyclic compounds with diverse structures and functionalities.[1] In the majority of these cases, metal complexes M with available coordination sites were combined with bridging ligands L to give symmetrical macrocycles of the type M_nL_n. These reactions are typically performed in a single step under thermodynamic control. Macrocycles containing two different metal fragments M and M′, however, are generally constructed in a two-step procedure.[2,3] For mixed-metal squares and rectangles, this is illustrated in Scheme 1. In a first step, a ditopic ligand is coordinated to a metal M. The resulting complex ML_2 is then reacted with a metal M′ to give the tetranuclear complex $M_2M'_2L_4$. Usually, the preformed metal complex ML_2 is kinetically inert under the reaction conditions employed in the second step (Scheme 1, a).[2] This avoids scrambling reactions, which would lead to mixtures of assemblies with variable M-M′ content and position. Alternatively, the formation of mixed-metal assemblies can be favored by the utilization of ligands having two distinct donor sites, each of which with a pronounced selectivity for the respective metal fragment M or M′, respectively (Scheme 1, b).[3] Additional specificity can be achieved by template effects. For the latter case, one-step syntheses of heterometallic macrocycles under thermodynamic control have been reported.[4]



Scheme 1. Stepwise synthesis of tetranuclear macrocycles containing two different metal fragments M and M′.

Over the last few years, we have reported in a number of publications the synthesis and host–guest chemistry of trinuclear metallamacrocycles comprised of (arene)Ru^{II} or (cyclopentadienyl)M^{III} (M = Rh, Ir) complexes and bridging 2,3-dihydroxypyridine ligands.[5] These complexes represent organometallic analogues of 12-crown-3 and show an outstanding affinity for lithium ions, even in aqueous solutions.[6] During the course of our studies we observed that in polar solvents, these metallacrown complexes undergo exchange reactions. This was used to create dynamic combinatorial libraries[7] of macrocycles and to investigate the adaptive behavior of such mixtures.[8] In the following we show that steric interactions can be used to guide the scrambling process in such a fashion that a defined mixed-metal macrocycle can be obtained in synthetically interesting yields.

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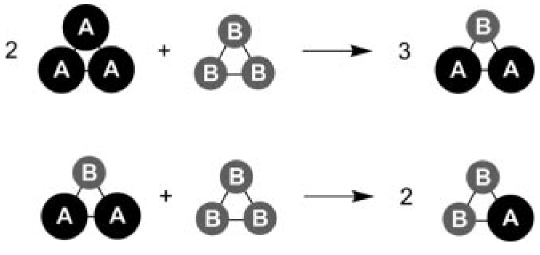
Results and Discussion

In a first experiment, we investigated the scrambling reaction of the two trimeric (arene)Ru complexes $[(C_6H_3i\text{Pr}_3)\text{Ru}(C_5H_3NO_2)]_3$ (**AAA**) and $[(\text{cymene})\text{Ru}(C_5H_3NO_2)]_3$ (**BBB**) (Scheme 2). The complexes were mixed in a 1:1 ratio in CD_3OD, with an initial concentration of 5.0 mM each. To accelerate the exchange process, the solution was gently heated to 40 °C. The reaction was followed by ^1H NMR spectroscopy and the time course is shown in Figure 1.



Scheme 2. The equilibration of $[(C_6H_3i\text{Pr}_3)\text{Ru}(C_5H_3NO_2)]_3$ (**AAA**) and $[(\text{cymene})\text{Ru}(C_5H_3NO_2)]_3$ (**BBB**) proceeds in two steps. First, the sterically encumbered **AAA** is converted into **AAB**. This is followed by a second, much slower transformation, in which **ABB** is formed.

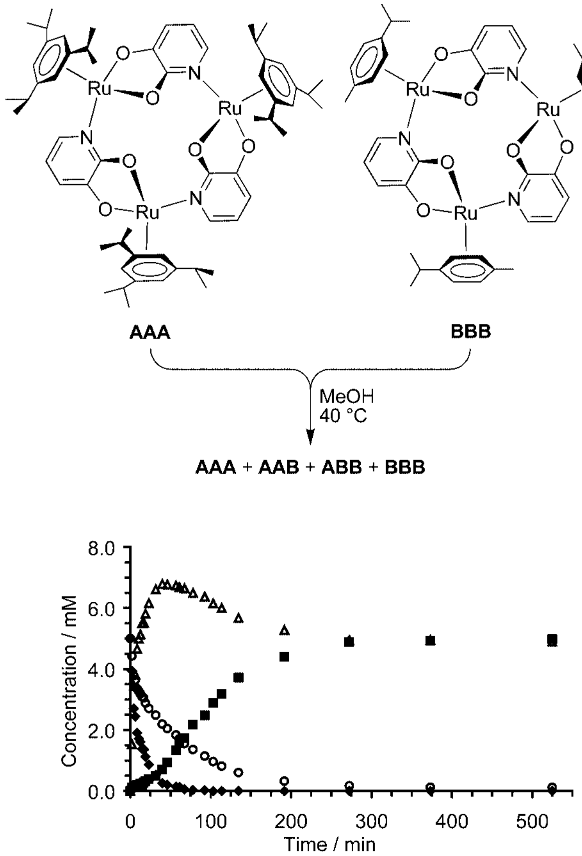


Figure 1. Time course of the reaction between $[(C_6H_3i\text{Pr}_3)\text{Ru}(C_5H_3NO_2)]_3$ (**AAA**; ♦) and $[(\text{cymene})\text{Ru}(C_5H_3NO_2)]_3$ (**BBB**, ○) to give the mixed-metal macrocycles **AAB** (Δ) and **ABB** (■) as determined by ^1H NMR spectroscopy. The reaction was performed in CD_3OD at 40 °C with initial concentrations of [**AAA**] = [**BBB**] = 5.0 mM.

The beginning of the reaction was marked by a fast decrease of **AAA** and a rapid increase of **AAB**. The formation of **ABB** was almost negligible in the first 15 min. During this period, the decrease of **AAA** was almost twice as fast as the decrease of **BBB**. After 40 min, a turning point was reached. The concentration of **AAB** was at its maximum and represented 68% of the total trimer concentration. Subsequently, a decrease of **AAB** and a concomitant increase of **ABB** were observed. Accordingly, the concentration-time profile of **ABB** shows a sigmoidal form. After six hours, the mixture was at equilibrium and only the two mixed complexes **AAB** and **ABB** were present in significant amounts.

For equally stable macrocycles, a statistical mixture of **AAA/AAB/ABB/BBB** = 1:3:3:1 would be expected. At first glance, the complete dominance of **AAB** and **ABB** after equilibration might suggest a preferential stabilization of the mixed complexes with respect to the homotrimers **AAA** and **BBB** (situation a, Figure 2). But there is another explanation for such a distribution: the B-rich species **ABB** and **BBB** are stabilized and the homotrimer **AAA** is significantly destabilized (situation b, Figure 2). For $\Delta\Delta G1 = \Delta\Delta G2 = 1/2\ \Delta\Delta G3$, the two situations result in the same equilibrium distribution with equal amounts of heterotrimers being the dominant species in solution. It is interesting to note that for the situation described in Figure 2 (b), the concentration of the stable homotrimer **BBB** is as low as that of the disfavored **AAA**. A more detailed discussion of this phenomenon can be found in a recent theoretical study.[9]

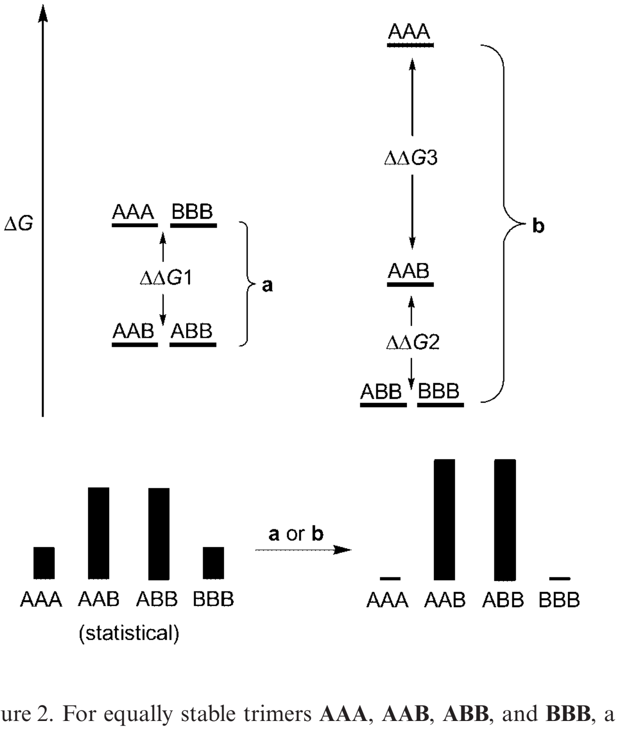


Figure 2. For equally stable trimers **AAA**, **AAB**, **ABB**, and **BBB**, a statistical 1:3:3:1 distribution is expected. The energetic situations shown in **a** and **b** both result in selective formation of the mixed trimers **AAB** and **ABB**.

An energy distribution similar to what is described in Figure 2 (b) is more likely to account for the dynamic mixture described above. Complex $[(C_6H_3iPr_3)Ru(C_5H_3NO_2)]_3$ (**AAA**) has three sterically demanding triisopropylbenzene ligands. The π-ligands approach each other and destabilize the aggregate. For the mixed trimer **AAB**, only one unfavorable A···A interaction is found, whereas the aggregates **ABB** and **BBB** display no intramolecular A···A contacts at all. The kinetic data support this picture. The sterically encumbered trimer **AAA** rapidly reacts with the smaller cymene complex **BBB** to give **AAB**. This first reaction is followed by a second, much slower reaction, in which **AAB** is converted into **ABB** (Scheme 2). It should be noted that the sequential formation of first **AAB** and then **ABB** excludes a simple bimolecular reaction mechanism in which two trimers **AAA** and **BBB** exchange fragments.

An interesting consequence from an asymmetric free energy distribution is the possibility to bias the equilibration process in favor of a certain species. For a dynamic mixture of equally stable trimers **AAA**, **AAB**, **ABB**, and **BBB**, the relative concentration of the mixed trimer **ABB** after equilibration can be increased from 37.5% to a maximum theoretical value of 44.3% by using two equivalents of **BBB** and only one equivalent of **AAA**. For a system such as the one described in Figure 2 (b), the maximum relative concentration of a mixed trimer after equilibration can be much higher.

To demonstrate this point, we have investigated the scrambling reaction of $[(C_6H_3iPr_3)Ru(C_5H_3NO_2)]_3$ (**AAA**) and $[(C_6H_6)Ru(C_5H_3NO_2)]_3$ (**CCC**) (Figure 3). The small benzene complex **CCC** was chosen to further accentuate the difference between the π-ligands. This time, the complexes were mixed in a 1:2 ratio with initial concentrations of [**AAA**] = 2.0 mM and [**CCC**] = 4.1 mM. The time course of the reaction is shown in Figure 3. The beginning of the equilibration process was again marked by the fast formation of the mixed complex **AAC** comprised of two large $(C_6H_3iPr_3)Ru$ moieties and the simultaneous rapid decrease of **AAA**. After 26 min, more than 95% of the initial amount of complex **AAA** was converted and the concentration of **AAC** reached its maximum. Then, its concentration decreased in favor of **ACC**. The equilibrium was reached after 10 h, after which the heterotrimer **ACC** completely dominated the mixture (83 ± 2%). Only minor amounts of **AAC** (7 ± 2%) and **CCC** (10 ± 2%) were found in the solution.

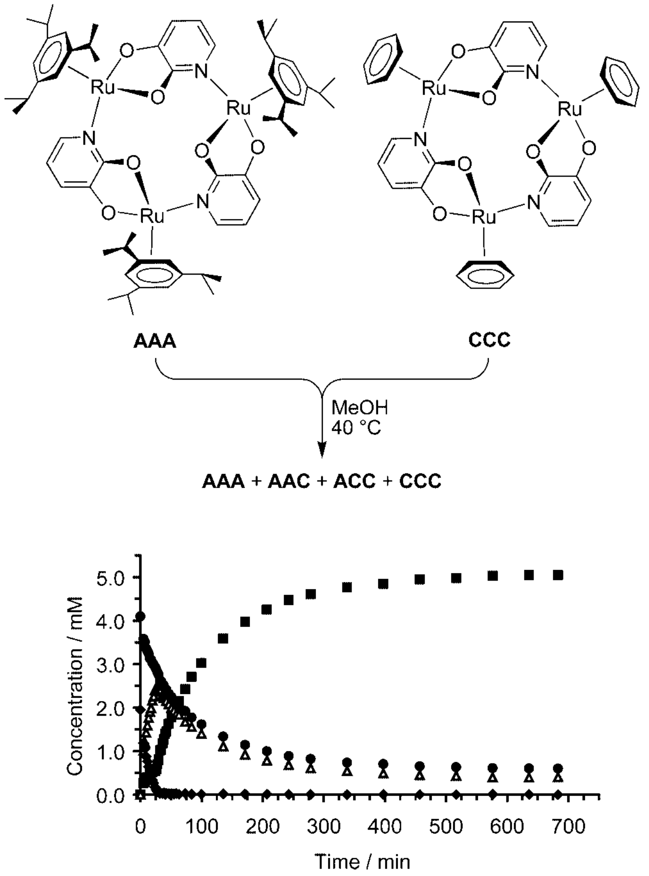


Figure 3. Time course of the reaction between $[(C_6H_3iPr_3)Ru(C_5H_3NO_2)]_3$ (**AAA**; ♦) and $[(C_6H_6)Ru(C_5H_3NO_2)]_3$ (**CCC**, ●) to give the mixed-metal macrocycles **AAC** (Δ) and **ACC** (■) as determined by ^1H NMR spectroscopy. The reaction was performed in CD_3OD at 40 °C with initial concentrations of [**AAA**] = 4.1 mM and [**CCC**] = 2.0 mM.

The results described above suggest that equilibration processes with 2:1 stoichiometries of complexes having significantly different π-ligands can be used for the controlled formation of mixed-metal macrocycles in preparative amounts. The following results show that this is indeed the case. Solutions containing two equivalents of the small benzene complex $[(C_6H_6)Ru(C_5H_3NO_2)]_3$ (**CCC**) and one equivalent of the trimers $[(C_6Me_6)Ru(C_5H_3NO_2)]_3$ (**DDD**) or $[Cp^*Rh(C_5H_3NO_2)]_3$ (**EEE**), both of which have sterically demanding π-ligands, were tempered in CD_3OD at 45 °C overnight. Similar to what was found in experiments with **AAA**, the mixed-metal complexes **DCC** and **ECC** were formed almost exclusively (>80%) as evidenced by ^1H NMR spectroscopy.

The complexes **ACC**, **DCC**, and **ECC** can not only be obtained by scrambling of preformed homotrimers but also directly from appropriate amounts of the respective building blocks. Thus, when two equivalents of the dimer $[(C_6H_6)RuCl_2]_2$,[10] one equivalent of $[(C_6H_3iPr_3)RuCl_2]_2$, $[(C_6Me_6)RuCl_2]_2$, or $[Cp^*RhCl_2]_2$ and six equivalents of the 2,3-dihydroxypyridine ligand were reacted in methanol in the presence of Cs_2CO_3, the products **ACC**, **DCC**, and **ECC** could be isolated with yields of ca. 60% and in good purity. It was also possible to obtain mixed-metal trimers with two large metal fragments and one small fragment. This was corroborated by the synthesis of complex **AAC** using two equivalents of $[(C_6H_3iPr_3)RuCl_2]_2$ and one equivalent of $[(C_6H_6)RuCl_2]_2$. It should be noted that exchange processes were found to be significantly slower in less polar solvents such as benzene and chloroform as compared to methanol. This allowed the characterization of the mixed-metal trimers in pure form.

The ^1H NMR spectroscopic data of all three products were in agreement with the anticipated structure: three sets of signals were observed for aromatic protons of the bridging pyridonate ligands and two singlets were found for the chemically distinct benzene π-ligands. The complexes **DCC** and **ECC** were also characterized by a single-crystal X-ray analysis (Figure 4, Figure 5, and Figure 6).

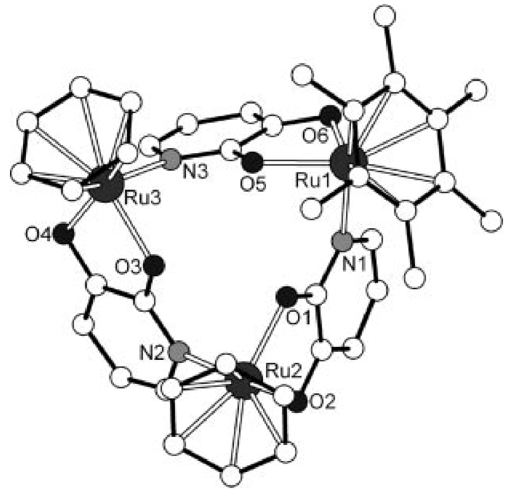


Figure 4. Ball-and-stick representation of the molecular structure of **DCC** in the crystal. The hydrogen atoms and the solvent molecules (2CHCl$_3$) are omitted for clarity. Selected bond lengths [Å]: Ru1–N1 2.130(6), Ru1–O5 2.086(4), Ru1–O6 2.065(5), Ru2–O1 2.060(5), Ru2–O2 2.069(5), Ru2–N2 2.118(6), Ru3–O3 2.069(5), Ru3–O4 2.073(5), Ru3–N3 2.139(6).

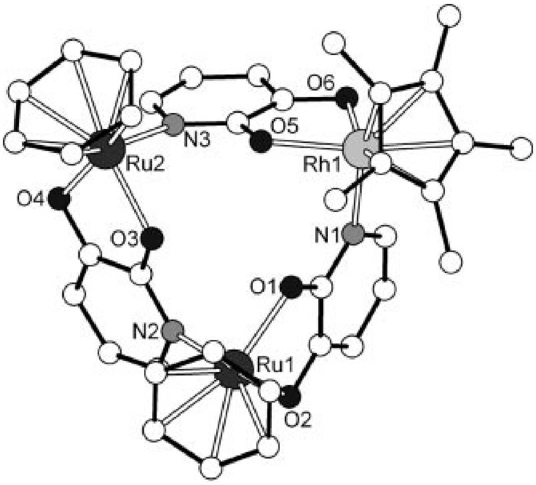


Figure 5. Ball-and-stick representation of the molecular structure of **ECC** in the crystal. The hydrogen atoms and the solvent molecules (H$_2$O, MeOH, C$_6$H$_5$CH$_3$) are omitted for clarity. Selected bond lengths [Å]: Rh1–O5 2.080(7), Rh1–O6 2.088(8), Rh1–N1 2.122(9), Ru1–O2 2.067(6), Ru1–O1 2.078(7), Ru1–N2 2.106(8), Ru2–O3 2.072(6), Ru2–O4 2.076(7), Ru2–N3 2.104(9).

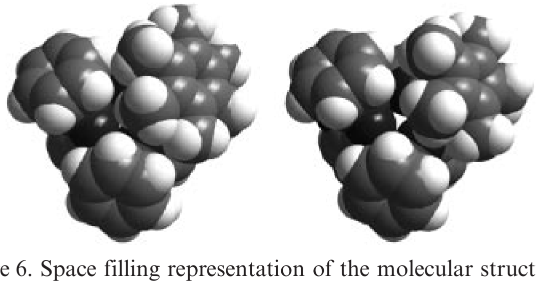


Figure 6. Space filling representation of the molecular structure of **DCC** (left) and **ECC** (right) in the crystal. The solvent molecules have been omitted for clarity.

The bond lengths and angles found for the macrocyclic core of **DCC** and **ECC** are comparable to what has been observed for the corresponding homotrimeric complexes.[5] Additional structural anisotropy due to the presence of different half-sandwich complexes was not observed. Indirect evidence for the reduced steric strain of the mixed-metal macrocycles **DCC** and **ECC** is the fact that their average metal–metal distances (**DCC**: 5.26 Å; **ECC**: 5.26 Å) are shorter than what has been observed for the homotrimers **DDD** (5.46 Å) and **EEE** (5.35 Å).[5g] The importance of the size of the π-ligand for the stability of the trimeric aggregates is also evident from the space filling representations of **DCC** and **ECC** (Figure 6).

Conclusions

The synthesis of metallamacrocycles containing two different metal fragments M and M′ is mostly performed in two or more steps under kinetic control. We have shown that steric interactions can be used to bias dynamic exchange processes in such a way that mixed-metal macrocycles are obtained in over 80% yield under thermodynamic control. The results are conceptually related to work on *mixed-ligand* metallamacrocycles and cages. Navarro and Romero et al. have shown that scrambling of symmetrical (en)Pd^{II}-based macrocycles with bridging 4,7-phenanthroline and 2-pyrimidinolate ligands can lead to the dominant formation of a single product given that appropriate stoichiometries are employed;[11] and Fujita et al. and James et al. have used steric interactions between ligands to achieve the quantitative formation of macrocycles and coordination cages containing two different heterocyclic ligands.[12,13] It should be noted that rather small differences in free energy of the various aggregates can be sufficient to bias dynamic mixtures of metallamacrocycles (or cages) towards the formation of a defined product. For the system described in Figure 2 (b), for example, a difference of $\Delta\Delta G2 = 1/2\ \Delta\Delta G3 = 3.0\ \mathrm{kcal\,mol^{-1}}$ results in an increase of the relative concentration of mixed product **ABB** from 44.3% (statistical) to 91.6% (for $[\mathbf{AAA}]_{\mathrm{initial}} = 1/2\ [\mathbf{BBB}]_{\mathrm{initial}}$).[14] In view of the fact that asymmetric metallamacrocycles may display interesting functional differences (host–guest chemistry etc.) when compared to their symmetrical M$_n$L$_n$ counterparts, the strategy discussed above should be regarded as an attractive alternative to step-wise synthetic procedures.

Experimental Section

General: All reactions were performed under dry dinitrogen. The complexes [(C$_6$H$_3$*i*Pr$_3$)Ru(C$_5$H$_3$NO$_2$)]$_3$ (**AAA**),[8c] [(cymene)-Ru(C$_5$H$_3$NO$_2$)]$_3$ (**BBB**),[5h] [(C$_6$H$_6$)Ru(C$_5$H$_3$NO$_2$)]$_3$ (**CCC**),[5g] [(C$_6$Me$_6$)Ru(C$_5$H$_3$NO$_2$)]$_3$ (**DDD**),[5g] [Cp*Rh(C$_5$H$_3$NO$_2$)]$_3$ (**EEE**),[5g] [(C$_6$H$_3$*i*Pr$_3$)RuCl$_2$]$_2$,[15] [(C$_6$Me$_6$)RuCl$_2$]$_2$,[16] [Cp*Rh-Cl$_2$]$_2$[17] and [(C$_6$H$_6$)RuCl$_2$]$_2$[18] were prepared according to literature procedures. 2,3-Dihydroxypyridine (95%) was purchased from Fluka and Cs$_2$CO$_3$ (99.9%) was purchased from Aldrich. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Advance DPX

400 spectrometer with the residual protonated solvent as internal standard. All spectra were recorded at room temperature.

Synthesis of Complex [{(C_6H_3iPr$_3$)Ru}{(C_6H_6)Ru}$_2$($C_5H_3NO_2$)$_3$] (ACC): A suspension of [(C_6H_3iPr$_3$)RuCl$_2$]$_2$ (75 mg, 0.10 mmol), [(C_6H_6)RuCl$_2$]$_2$ (110 mg, 0.22 mmol), 2,3-dihydroxypyridine (69 mg, 0.60 mmol), and Cs_2CO_3 (489 mg, 1.50 mmol) in degassed MeOH (25 mL) was stirred overnight at 45 °C. After evaporation of the solvent under reduced pressure, the product was extracted with CH_2Cl_2 (30 mL). A small amount of precipitate was observed after addition of hexane (60 mL), which was removed by filtration. The clear solution was concentrated to 15 mL and the resulting precipitate was filtered off and dried in vacuo. The mixed trimer was obtained as an orange powder in 60% yield (126 mg, 0.12 mmol) and 96% purity. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 [d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$], 1.44 [d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$], 2.81 [sept, br, ^3J = 7 Hz, 3 H, CH(CH$_3$)$_2$], 4.97 (s, 3 H, C$_6H_3i$Pr$_3$), 5.44 (s, 6 H, C_6H_6), 5.45 (s, 6 H, C_6H_6), 5.62–5.69 (m, 3 H, pyridone), 6.08 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, pyridone), 6.12 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, pyridone), 6.16 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, pyridone), 6.60 (dd, ^3J = 6 Hz, ^4J = 1 Hz, 1 H, pyridone), 6.63 (dd, ^3J = 6 Hz, ^4J = 2 Hz, 1 H, pyridone), 6.67 (dd, ^3J = 6 Hz, ^4J = 1 Hz, 1 H, pyridone) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 22.60, 23.28 (CH_3), 31.51 (CH), 71.09 (C_6H_3iPr$_3$), 81.60, 81.66 (C_6H_6), 107.10 (C_6H_3iPr$_3$), 109.99, 110.24, 110.30, 114.82, 115.09, 115.33, 132.11, 132.81, 133.11, 156.05, 156.28, 157.43, 171.06, 171.07, 171.62 (pyridone) ppm. $C_{42}H_{45}N_3O_6Ru_3\cdot 2CH_3OH$ (1055.12): calcd. C 50.09, H 5.06, N 3.98; found C 49.84, H 4.89, N 4.08.

Synthesis of Complex [{(C_6Me_6)Ru}{(C_6H_6)Ru}$_2$($C_5H_3NO_2$)$_3$] (DCC): A suspension of [(C_6Me_6)RuCl$_2$]$_2$ (67 mg, 0.10 mmol), [(C_6H_6)RuCl$_2$]$_2$ (110 mg, 0.22 mmol), 2,3-dihydroxypyridine (69 mg, 0.60 mmol), and Cs_2CO_3 (489 mg, 1.50 mmol) in degassed MeOH (25 mL) was stirred overnight at 45 °C. After evaporation of the solvent under reduced pressure, the product was extracted with CH_2Cl_2 (30 mL). A small amount of precipitate was observed after addition of hexane (60 mL), which was removed by filtration. The clear solution was concentrated to 15 mL and the resulting precipitate was filtered off and dried in vacuo. The mixed trimer was obtained as an orange powder in 50% yield (113 mg, 0.10 mmol) and 92% purity. The complex was crystallized from $CHCl_3$/pentane. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 18 H, C_6Me_6), 5.46 (s, 6 H, C_6H_6), 5.48 (s, 6 H, C_6H_6), 5.60 (dd, ^3J = 7 Hz, ^3J = 6 Hz, 1 H, pyridone), 5.67 (t, ^3J = 7 Hz, 1 H, pyridone), 5.71 (dd, ^3J = 7 Hz, ^3J = 6 Hz, 1 H, pyridone), 6.03 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, pyridone), 6.16 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, pyridone), 6.17 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, pyridone), 6.47 (dd, ^3J = 6 Hz, ^4J = 2 Hz, 1 H, pyridone), 6.60 (dd, ^3J = 6 Hz, ^4J = 2 Hz, 1 H, pyridone), 6.60 (dd, ^3J = 6 Hz, ^4J = 2 Hz, 1 H, pyridone) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 15.71 (CH_3), 81.47, 81.62 (C_6H_6), 89.11 (C_6Me_6), 109.51, 110.14, 110.53, 113.38, 114.73, 115.05, 131.36, 132.23, 132.21, 156.10, 156.13, 158.39, 170.28, 171.19, 171.76 (pyridone) ppm. $C_{39}H_{39}N_3O_6Ru_3\cdot 2CH_2Cl_2$ (1118.82): calcd. C 44.01, H 3.87, N 3.76; found C 44.27, H 4.53, N 3.95.

Synthesis of Complex [{Cp*Rh}{(C_6H_6)Ru}$_2$($C_5H_3NO_2$)$_3$] (ECC): A suspension of [Cp*RhCl$_2$]$_2$ (62 mg, 0.10 mmol), [(C_6H_6)RuCl$_2$]$_2$ (150 mg, 0.30 mmol), 2,3-dihydroxypyridine (69 mg, 0.60 mmol), and Cs_2CO_3 (489 mg, 1.50 mmol) in degassed MeOH (25 mL) was stirred overnight at 45 °C. After evaporation of the solvent under reduced pressure, the product was extracted with CH_2Cl_2 (30 mL). A small amount of precipitate was observed after addition of hexane (60 mL), which was removed by filtration. The clear solution was concentrated to 15 mL and the resulting precipitate was filtered off and dried in vacuo. The mixed trimer was obtained as brown-red powder in 59% yield (114 mg, 0.12 mmol) and 83% purity. The complex was crystallized from toluene/pentane. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (s, 18 H, Cp*), 5.45 (s, 6 H, C_6H_6), 5.46 (s, 6 H, C_6H_6), 5.65 (t, ^3J = 7 Hz, 1 H, pyridone), 5.69 (t, ^3J = 7 Hz, 1 H, pyridone), 5.79 (t, ^3J = 7 Hz, 1 H, pyridone), 6.10 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, pyridone), 6.19 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, pyridone), 6.23 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, pyridone), 6.62 (dd, ^3J = 6 Hz, ^4J = 1 Hz, 1 H, pyridone), 6.64 (dd, ^3J = 6 Hz, ^4J = 1 Hz, 1 H, pyridone), 6.73 (dd, ^3J = 6 Hz, ^4J = 1 Hz, 1 H, pyridone) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.26 (CH_3), 81.57, 81.77 (C_6H_6), 90.32 (d, ^1J(C,Rh) = 8 Hz, C, Cp*), 109.72, 110.24, 110.96, 113.99, 115.12, 115.21, 131.76, 131.84, 132.38, 156.25, 156.63, 157.93, 169.95, 171.22, 171.88 (pyridone) ppm. $C_{37}H_{36}N_3O_6RhRu_2\cdot CH_3OH\cdot H_2O$ (973.80): calcd. C 46.87, H 4.35, N 4.32; found C 46.57, H 4.59, N 4.29.

Synthesis of Complex [{(C_6H_3iPr$_3$)Ru}$_2${(benzene)Ru}($C_5H_3NO_2$)$_3$] (AAC): A suspension of [(C_6H_3iPr$_3$)RuCl$_2$]$_2$ (151 mg, 0.20 mmol), [(C_6H_6)RuCl$_2$]$_2$ (50 mg, 0.1 mmol), 2,3-dihydroxypyridine (69 mg, 0.60 mmol), and Cs_2CO_3 (489 mg, 1.50 mmol) in degassed MeOH (25 mL) was stirred overnight at 45 °C. After evaporation of the solvent under reduced pressure, the product was extracted with CH_2Cl_2 (30 mL). After addition of hexane (60 mL), the solution was concentrated to 15 mL and the resulting precipitate filtered off and dried in vacuo. The mixed trimer was obtained as a brown powder in 45% yield (100 mg, 0.09 mmol) and 90% purity. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 [d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$], 1.33 [d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$], 1.38 [d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$], 1.52 [d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$], 2.81 [sept, ^3J = 7 Hz, 3 H, CH(CH$_3$)$_2$], 3.22 [sept, ^3J = 7 Hz, 3 H, CH(CH$_3$)$_2$], 4.86 (s, 3 H, C$_6H_3i$Pr$_3$), 4.90 (s, 3 H, C$_6H_3i$Pr$_3$), 5.39 (s, 6 H, C_6H_6), 5.56 (t, ^3J = 7 Hz, 1 H, pyridone), 5.61 (t, ^3J = 7 Hz, 1 H, pyridone), 5.65 (t, ^3J = 7 Hz, 1 H, pyridone), 6.01 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, pyridone), 6.03 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, pyridone), 6.12 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, pyridone), 6.57 (dd, ^3J = 6 Hz, ^4J = 2 Hz, 1 H, pyridone), 6.63 (dd, ^3J = 6 Hz, ^4J = 2 Hz, 1 H, pyridone), 6.64 (dd, ^3J = 6 Hz, ^4J = 1 Hz, 1 H, pyridone) ppm. ^{13}C NMR (1010 MHz, $CDCl_3$): δ = 21.48, 22.42, 22.73, 24.19 (CH_3), 30.85, 31.64 (CH), 69.27, 69.87 (C_6H_3), 81.41 (C_6H_6), 107.96, 108.25 (C_6H_3), 109.55, 109.63, 110.14, 113.75, 114.12, 114.84, 132.03, 132.92, 133.09, 156.02, 156.64, 157.65, 171.02, 171.47, 171.29 (pyridone) ppm. $C_{51}H_{63}N_3O_6Ru_3\cdot 2CH_2Cl_2$ (1287.13): calcd. C 49.46, H 5.25, N 3.26; found C 49.07, H 5.41, N 3.61.

X-ray Crystallography: Details for the crystals and their structure refinement are listed in Table 1 whereas some relevant geometrical parameters are included in the picture captions. Data collection was performed at 140(2) K by means of a Mar345 imaging plate detector. Data reduction was carried out with CrysAlis RED, release 1.7.0.[19] Absorption correction has been applied to both data sets. Structure solution and refinement were performed with the SHELXTL software package, release 5.1.[20] The structures were refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined except the toluene molecule of complex **ECC**, which has been retained as isotropic with a fixed geometry. H atoms were placed in calculated positions using the riding model.

CCDC-617057 and -617058 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.

Table 1. Crystallographic data for the complexes **DCC** and **ECC**.

	DCC·2CHCl$_3$	**ECC**·MeOH·C$_7$H$_8$·H$_2$O
Empirical formula	$C_{41}H_{41}Cl_6N_3O_6Ru_3$	$C_{45}H_{50}N_3O_8RhRu_2$
Molecular weight [g mol^{-1}]	1187.68	1065.93
Crystal size [mm^3]	0.20 × 0.12 × 0.09	0.17 × 0.17 × 0.13
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a [Å]	9.2537(14)	13.273(5)
b [Å]	12.040(3)	18.718(5)
c [Å]	20.007(5)	18.668(4)
α [°]	85.44(2)	90
β [°]	80.731(16)	110.09(3)
γ [°]	88.110(16)	90
Volume [Å^3]	2192.5(8)	4356(2)
Z	2	4
Density [g cm^{-3}]	1.799	1.625
Temperature [K]	140(2)	140(2)
Absorption coeff. [mm^{-1}]	1.436	1.115
Θ range [°]	3.09 to 25.03	2.73 to 25.03
Index ranges	$-10 \le 10, -14 \le 14, -23 \le 23$	$-15 \le 15, -22 \le 22, -21 \le 22$
Reflections collected	14091	26761
Independent reflections	7271 (R_{int} = 0.0439)	7694 (R_{int} = 0.0626)
Absorption correction	semi-empirical	semi-empirical
Max. and min. transmission	0.9528 and 0.7704	0.8564 and 0.7350
Data / restraints / parameters	7271 / 0 / 533	7694 / 3 / 492
Goodness-of-fit on F^2	1.08	0.998
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0638, wR_2 = 0.1757	R_1 = 0.0688, wR_2 = 0.1885
R indices (all data)	R_1 = 0.0769, wR_2 = 0.1941	R_1 = 0.1118, wR_2 = 0.2197
Large diff. peak/hole [e·Å^{-3}]	1.152 and –1.076	0.946 and –0.957

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