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Diastereoselective Formation of Metallamacrocyclic (Arene)Ru^{II} and Cp*Rh^{III} Complexes

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The reaction of $[(arene)RuCl_2]_2$ (arene = cymene, 1,3,5-$C_6H_3Me_3$) and $[Cp^*RhCl_2]_2$ half-sandwich complexes with tridentate heterocyclic ligands in the presence of base has been investigated. In all cases, the chloro-ligands were substituted to give metallacyclic products with ring sizes between 4 and 18 atoms. The cyclization occurs in a highly diastereoselective fashion with chiral recognition between the different metal fragments. The complexes were comprehensively characterized by elemental analysis, NMR spectroscopy, and single crystal X-ray crystallography. For 2-hydroxy-nicotinic acid and 2-amino-nicotinic acid, dinuclear structures were obtained (**15**–**17**) whereas for 2,3-dihydroxyquinoline, 2,3-dihydroxyquinoxaline, and 6-methyl-2,3-phenazinediol, trimeric assemblies were found (**19**–**22**), and for 4-imidazolecarboxylic acid, a tetrameric assembly (**18**) was found.

Introduction

Organometallic complexes are increasingly being used for the construction of polynuclear self-assembled structures.[1] The *fac*-Re(CO)$_3$X (X = Cl, Br) fragment, for example, was shown to be a versatile building block for the synthesis of rectangular metallamacrocycles,[2,3] some of which have found applications in sensing[4] or catalysis.[5] Half-sandwich complexes of ruthenium(II), rhodium(III), and iridium(III) are likewise very useful compounds for transition metal based self-assembly processes. They display a pseudotetrahedral geometry with three facial coordination sites available for complexation with neutral or anionic ligands. Using bidentate bridging ligands such as cyanide,[6] cyanamide,[7] diisocyano-

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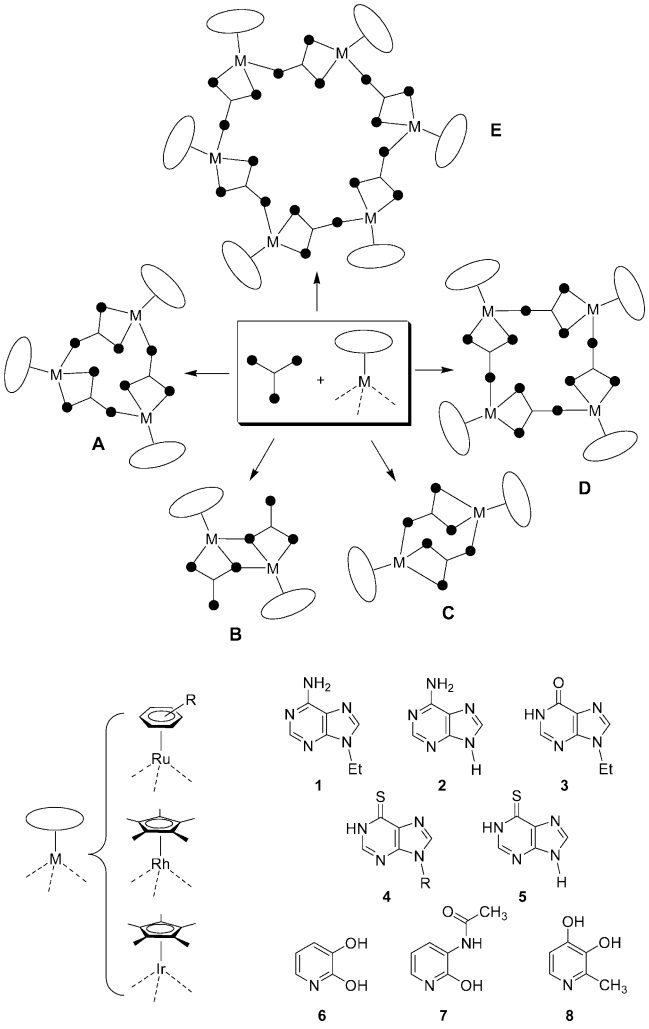
Scheme 1. Di-, Tri-, Tetra-, and Hexanuclear Metallamacrocycles (A−E) Obtained by Reaction of Half-Sandwich Complexes with Tridentate Ligands



compounds,[8] or diamino-compounds,[9] rectangular macrocycles and cage-structures have been obtained.

The geometries observed for tridentate ligands are schematically summarized in Scheme 1. Cationic, trinuclear complexes of type A have been synthesized by Fish et al. using adenine-derivatives such as **1** as the bridging ligand in combination with Cp^*Rh^{III} complexes.[10] Structurally related compounds with (arene)Ru^{II}, Cp^*Ir^{III}, and Cp^*Rh^{III} complexes were subsequently reported by Sheldrick[11,12] and Yamanari.[13]

Relatively small changes in the bridging ligand can give rise to large changes in the overall structure of the assembly: the free adenine-ligand **2** gives a tetranuclear complex of type D instead of the trinuclear metallomacrocycle found for **1**.[12] With 9-ethyl-hypoxanthine (**3**), a trimeric structure of type A was observed[14] whereas for the thio-derivative **4** a hexanuclear macrocycle of type E[15] was found and for the thio-derivative **5** a tetranuclear assembly of type "D" was found.[16]

Cationic trimers of type A were also obtained using amino acidate ligands.[17] Here, the metal fragments are connected via the two carboxylate O-atoms and the amino-group. Despite their simplicity, dinuclear complexes of type C have been described rarely.[18] If the tridentate ligand has a donor-group X with a high tendency to form direct M(μ-X)M bridges (e.g., aromatic thiolates), dinuclear structures of type B can be formed.[19] With very few exceptions, the above-mentioned assemblies are polycationic species. Consequently, they are often soluble in water. In terms of host−guest chemistry, this may be advantageous if hydrophobic interactions are the main driving force for guest inclusion.[10c] For the binding of cationic guests, however, these macrocyclic hosts are generally not very suited.

We have recently reported neutral metallamacrocycles of type A using the dihydroxypyridine ligands **6**,[20,21] **7**,[21] and **8**.[22] These compounds were obtained by reaction of the chloro-bridged complexes $[(\pi\text{-ligand})MCl_2]_2$ (π-ligand = Cp*, arene; M = Ru, Rh, Ir) with the respective ligands in the presence of base in excellent yields.[23] The macrocycles display a good solubility in a wide range of organic solvents

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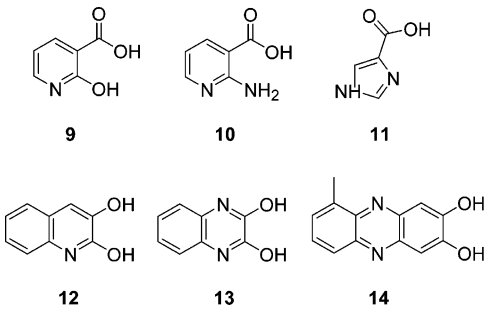
such as chloroform and benzene.[24] Their host−guest chemistry is very different from what was found for the cationic complexes described above. Trinuclear 3-oxy-pyridonate complexes of the general formula $[(\pi\text{-ligand})M(C_5H_3NO_2)]_3$ turned out to be very potent receptors for lithium and sodium salts.[20,21] The selectivity can be modulated by variation of the (π-ligand)M fragment. The complex $[(\eta^6\text{-}C_6H_5CO_2Et)\text{-}Ru(C_5H_3NO_2)]_3$, for example, was shown to have an extremely high selectivity for LiCl suggesting possible applications as a chemosensor.[25] A unique feature of these receptors is the fact that the lithium and sodium salts are bound as ion pairs. As a result, it was possible not only to isolate the unusual molecular forms of LiF[26] and Na_2SiF_6[27] but also to construct a highly specific chemosensor for the fluoride anion.[28]

In the following, we report the syntheses and the structures of di-, tri-, and tetranuclear (arene)Ru- and Cp*Rh-complexes, obtained in reactions with the heterocyclic compounds **9**−**14**. These ligands were chosen because they have at least three donor-atoms, two of which possess acidic protons. They can thus act as tridentate, dianionic ligands, an important prerequisite to obtain neutral metallamacrocycles.



Results and Discussion

The Carboxylic Acids 9−11 as Ligands. Upon reaction of $[(cymene)RuCl_2]_2$ or $[Cp^*RhCl_2]_2$ with 2-hydroxy-nicotinic acid (**9**) in the presence of NaOMe, the complexes **15** and **16** were isolated in good yield (Scheme 2). The NMR spectra of **15** and **16** were indicative of highly symmetrical structures with a ligand-to-metal ratio of 1:1. In the ^{1}H NMR spectrum of **15** ($CDCl_3$ or CD_3OD), two signals for the methyl-groups and four signals for the aromatic cymene CH-protons were observed (each signal appears as a doublet). This points to the fact that the pseudotetrahedral ruthenium atoms in **15** are stereogenic centers and configurationally stable on the NMR time scale.

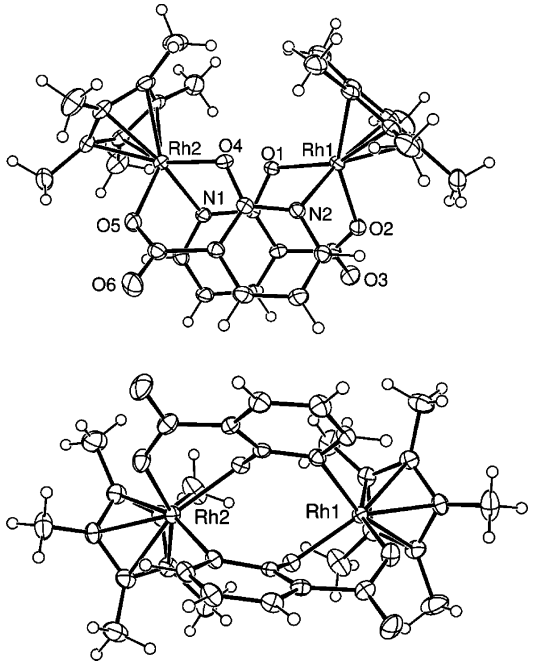
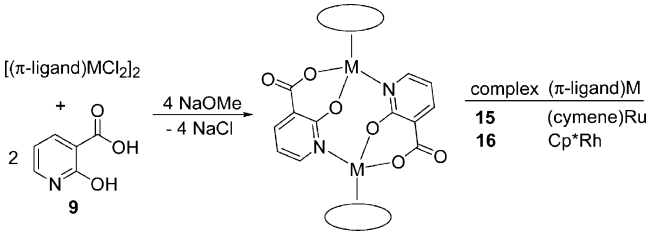


Figure 1. ORTEP drawings of the molecular structure of one enantiomer of **16** in the crystal (view from the side and from the bottom).

Scheme 2. Synthesis of the Dinuclear Complexes **15** and **16**



Since NMR spectroscopy is not a suited method to distinguish between the geometries A−E (Scheme 1), crystallographic investigations are of central importance. Single crystals of complex **16** were obtained by slow crystallization from dichloromethane/pentane. The molecular structure of one enantiomer of **16** is shown in Figure 1. A pseudo C_2-symmetric assembly of type C is observed. As expected, the dianionic ligand bridges the metal centers by coordination via two O-atoms forming a six-membered chelate ring (Rh1−O1 = 2.107(2) Å; Rh1−O2 = 2.108(3) Å; O1−Rh1−O2 = 85.21(9)°) and the pyridine N-atom (Rh1−N2 = 2.140(3) Å). The metal centers, which are 4.69 Å apart from each other, have the same absolute configuration. It is interesting to note that the exchange of the hydroxy group in **6** with a carboxy group in **9** is sufficient to drive the reaction entirely from the trimeric structure A[20,21] toward the dimeric structure C. Apparently, the additional flexibility of ligand **9** in combination with the slightly different coordinate vectors[29] allows the entropically favored structure C to be formed.

The reaction of $[Cp^*RhCl_2]_2$ with 2-amino-nicotinic acid (**10**) was performed under conditions as described above to give complex **17** (Scheme 3). On the basis of the spectroscopic data and the similarity of ligands **9** and **10**, a dinuclear

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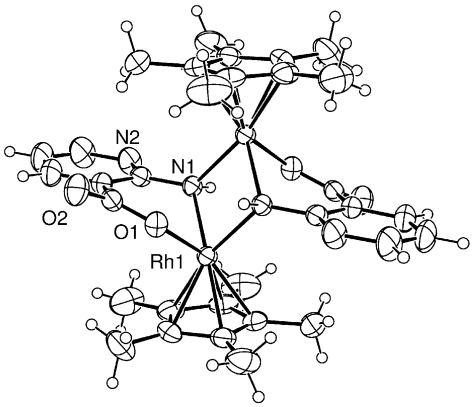
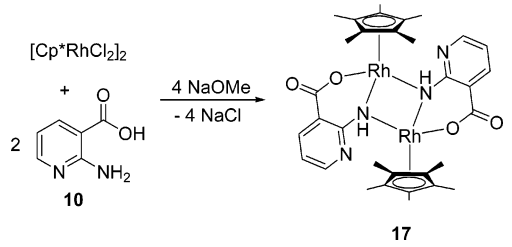


Figure 2. ORTEP drawings of the molecular structure of **17** in the crystal.

Scheme 3. Synthesis of the Dinuclear Complex **17**



structure of type C was expected. But the crystallographic analysis revealed that an amido-bridged complex of type B had formed (Figure 2).

The dianion of **10** is coordinated to the Rh atom via the carboxylate group and the deprotonated amine group forming a six-membered chelate ring (Rh1−O1 = 2.094(3) Å; Rh1−N1 = 2.104(3) Å; O1−Rh1−N1 = 83.47(11) Å). The pyridine N-atom is not coordinated to the transition metal. Both metals represent stereogenic centers and have the same absolute configuration. The planes defined by the Cp* rings and the planes defined by the pyridine rings deviate by only 6.9°. A structurally related CpRh* complex is formed upon reaction of $[Cp^*RhCl_2]_2$ with thiosalicylic acid in the presence of triethylamine.[30] But here the common Rh(μ-SR)$_2$Rh motive is observed. Dimeric Cp*Rh complexes with Rh(μ-NHR)$_2$Rh bridges, on the other hand, are rare.[31] Nevertheless, the amido bridge in **17** seems to be stable enough to prevent coordination of the free pyridine N-atom.

Similar to the 2-amino-nicotinic acid (**10**), the imidazole derivative **11** contains a carboxylic acid group, an acidic NH-group, and a neutral N-donor group. An important difference, however, is that ligand **11** is expected to form a five-membered N−O-chelate ring and not a six-membered one as for **9** and **10**. The smaller ring-size reduces the overall flexibility of the bridging ligand. It therefore appeared unlikely that the reaction of [(π-ligand)MCl_2]$_2$ complexes would yield dimeric structures as was found for **15**−**17**.

Initial attempts to synthesize macrocyclic complexes with ligand **11** and [(cymene)$RuCl_2$]$_2$ or $[Cp^*RhCl_2]_2$ using

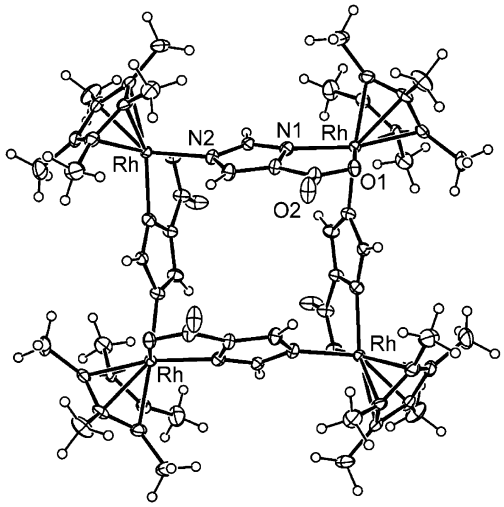
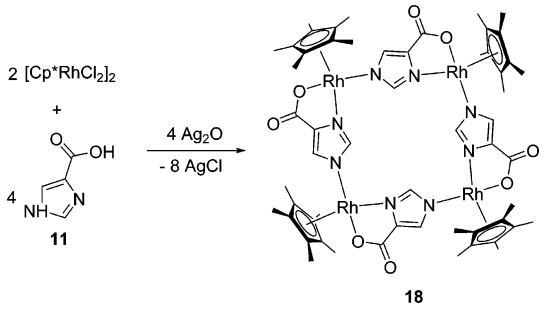


Figure 3. ORTEP drawings of the molecular structure of **18** in the crystal.

Scheme 4. Synthesis of the Tetranuclear Complex **18**



standard alkali metal bases such as LiOH were not successful. For the ruthenium complex, a mixture of products was obtained, and for the rather polar Cp*Rh complex, it turned out to be difficult to separate the LiCl side product in order to obtain the analytically pure product. Here, the utilization of Ag_2O as a base turned out to be the key to success[32] since the resulting AgCl can easily be separated by filtration (Scheme 4).

For complex **18**, the NMR spectra were indicative of a highly symmetrical complex of the formula [Cp*Rh-($C_4H_2N_2O_2$)]$_n$ showing only one set of signals for the Cp* and the bridging imidazole ligand. The aggregation number n was determined by single crystal X-ray crystallography, which revealed that complex **18** forms a tetrameric assembly of type D (Figure 3).

The twofold deprotonated ligand **11** acts as a $\mu,\eta^1{:}\eta^2$ bridge between two Cp*Rh fragments with Rh−N1 = 2.070(3) Å, Rh−N2 = 2.082(3) Å, and Rh−O1 = 2.109(2) Å. The five-membered N,O-chelate ring is nearly planar as evidenced by an dihedral angle of $\Theta_{N1RhO1C}$ = 5.35°. The rhodium atoms are 8.855(2) Å apart form each other. Overall, the complex displays S_4 symmetry. It is interesting to note that this is a feature that is found for all the tetrameric complexes of type D that have been characterized so far.[12,16]

2,3-Dihydroxyquinoline and 2,3-Dihydroxyquinoxaline as Ligands. As described above, 2,3-dihydroxypyridine (**6**)

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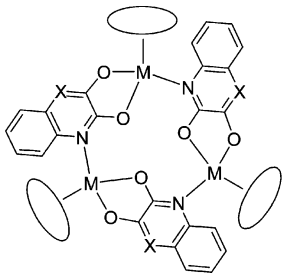
can be used as a ligand to obtain organometallic assemblies of type A.[20,21] 2,3-Dihydroxyquinoline (**12**) and 2,3-dihydroxyquinoxaline (**13**) are commercially available ligands that also contain the 2,3-dihydroxypyridine structural motif. The additional ring nitrogen atom of ligand **13**, however, makes the compound a potentially tetradentate ligand. In reactions with $[(\text{cymene})RuCl_2]_2$ or $[Cp^*RhCl_2]_2$ in the presence of Cs_2CO_3, the complexes **19**−**21** were obtained in good yield. The spectroscopic data (^{1}H, ^{13}C NMR) of the complexes were very similar and in agreement with a trimeric structure. For **19** and **20**, two signals can be observed for the diastereotopic methyl groups of the aromatic π-ligand. The reduced symmetry of the bridging quinoxaline ligands of complex **20** and **21** is manifested in the chemical shifts of the aromatic CH protons for which four sets of signals can be observed in the region between 6.9 and 8.2 ppm ($CHCl_3$).



complex	(π-ligand)M	X
19	(cymene)Ru	CH
20	(cymene)Ru	N
21	Cp*Rh	N

A determination of the molecular structure of **19** in the crystal confirmed that a trinuclear assembly of type A had formed with the dianionic 2,3-dioxyquinoline acting as a tridentate ligand (Figure 4). The catechol part of the ligand is coordinated in a slightly bent fashion to the ruthenium centers with dihedral angles Θ_{ORuOC} between 4.7° and 16.3°. The values indicate that the macrocyclic geometry is slightly strained because for monomeric ruthenium complexes with O,O′-bound hydroxypyridine ligands, the dihedral angle Θ_{ORuOC} is almost zero.[33] Likewise, the pyridine part of the ligand is not bound in a linear fashion with dihedral angles Θ_{RuNCO} between 5.4° and 6.4°. The ruthenium atoms are on average 5.28 ± 0.03 Å apart from each other; the diameter of the trimer is approximately 11 Å.

6-Methyl-2,3-phenazinediol as the Ligand. In order to obtain expanded macrocycles, we have synthesized the phenazinediol derivative **14** (Scheme 5). The coordinate vectors of **14** have the same relative orientation as those of ligand **13**, but the donor atoms are further apart from each other. Unfortunately, upon reaction with either $[(\text{cymene})RuCl_2]_2$ or $[Cp^*RhCl_2]_2$ in the presence of base, a mixture of products was obtained, even after purification by chromatography. We therefore investigated the reaction of **15** with the alternative (arene)Ru complex $[(1,3,5\text{-}C_6H_3Me_3)RuCl_2]_2$. After chromatography using basic alumina we were able to obtain a pure product (**22**) in 47% yield. The coordination to the (π-ligand)M fragment has a pronounced effect on the chemical shift of the ^{1}H NMR signals of the ligand. Whereas the signals of the aromatic protons of the free ligand **14** are confined to a region between 7.12 and 7.79 ppm (CD_3OD), the corresponding signals of complex **22** were found between 6.48 and 9.17 ppm.

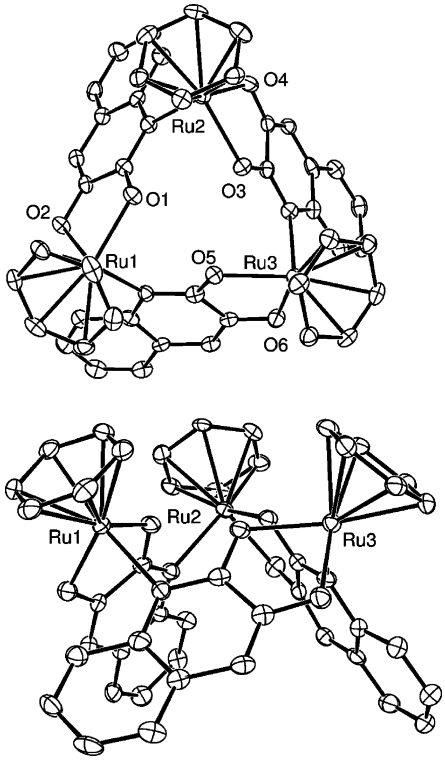
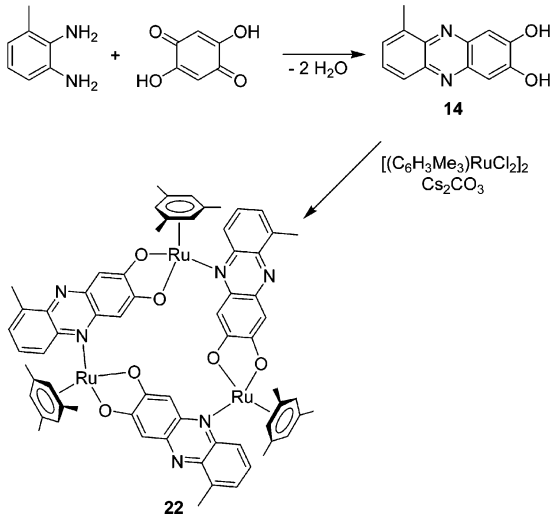


Figure 4. ORTEP drawings of the molecular structure of **19** in the crystal. Hydrogen atoms and the side chains of the aromatic π-ligands have been omitted for clarity.

Scheme 5. Synthesis of an Expanded Macrocycle of Type C Using the Dianion of 6-Methyl-2,3-phenazinediol as the Bridging Ligand



Crystals of **22** were obtained by slow evaporation of a solution of **22** in chloroform/methanol. As expected, the ligand **14** bridges the $(1,3,5\text{-}C_6H_3Me_3)Ru$ fragments by coordination via the two deprotonated hydroxy groups and one nitrogen atom (Figure 5). The sterically shielded nitrogen atom next to the methyl group is not involved in metal binding. The resulting metallomacrocycle has a ring size of 18 atoms with the metal atoms being 7.46 ± 0.02 Å apart from each other. Complex **22** thus represents one of the largest metallamacrocycles containing organometallic half-

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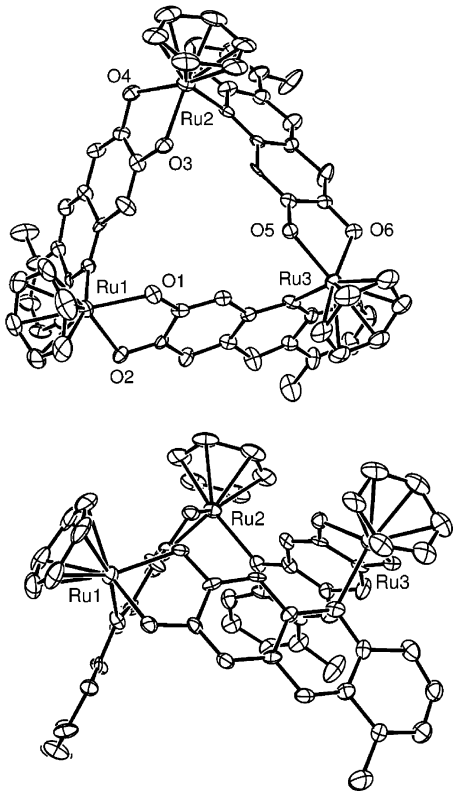


Figure 5. ORTEP drawings of the molecular structure of **22** in the crystal. Hydrogen atoms and the methyl groups of the aromatic π-ligands have been omitted for clarity.

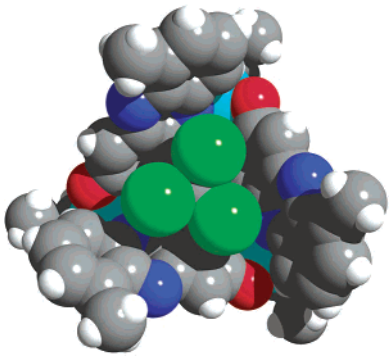


Figure 6. Space filling representation of the molecular structure of **22** in the crystal. The metallomacrocyle forms a large triangular cavity, which is occupied by a chloroform molecule.

sandwich complexes that has been described so far. Compared to what was found for the trimeric complex **19**, the macrocycle **22** displays an even more strained geometry. The catechol part of the ligand is coordinated to the ruthenium centers with dihedral angles Θ_{ORuOC} between 16.8° and 22.0°, and the N-donor atoms are coordinated in a very distorted fashion to the ruthenium atoms with dihedral angles Θ_{RuNCC} between 25.1° and 27.1°. It is conceivable that the strained geometry observed for this ligand may be responsible for the problems encountered during the synthesis with (cymene)Ru and Cp*Rh complexes.

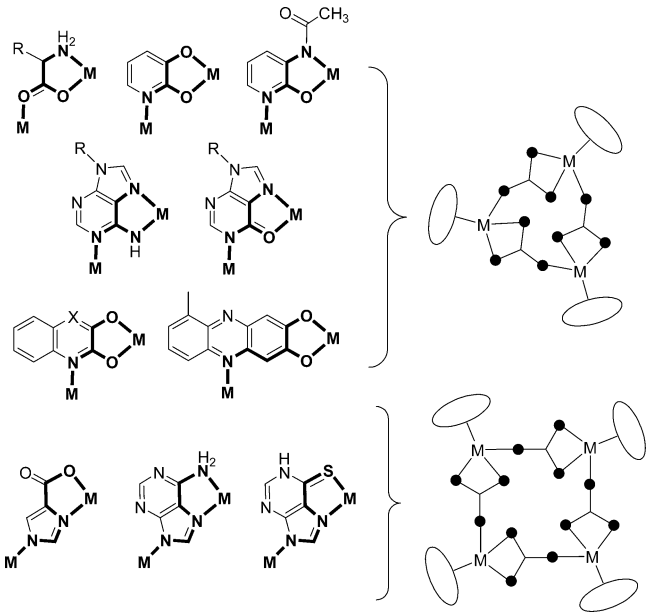
The three polyaromatic ligands, which are nearly perfectly orthogonal to each other, form a large triangular cavity with a maximum diameter of approximately 13 Å. In the crystal, the bottom of this cavity is occupied by a chloroform molecule, which is aligned to the 3-fold symmetry of the macrocycle (Figure 6).

Conclusion

Polynuclear organometallic complexes containing two, three, or four (arene)Ru and/or Cp*Rh fragments have been synthesized using tridentate O,O′,N- and O,N,N′-chelate ligands. The size of the resulting metallacycles was shown to depend decisively on the coordinate vectors[29] and the nature of the donor atoms of the bridging ligand. Relatively small modifications such as the exchange of an OH with an NH_2 group were shown to switch the geometry of the product. Alterations in the ligand periphery, on the other hand, did not affect the final structure. In most cases, the observed yields were very good. In view of the fact that metallamacrocycles of this kind are able to undergo exchange reactions under relative mild conditions,[34] it is assumed that the obtained products are formed by self-assembly under thermodynamic control. The metal atoms in these complexes represent stereogenic centers. In all cases, a single diastereoisomer was obtained indicating that there is strong chiral recognition between the metal fragments.

From the present study, taken together with previous results in this field, some guidelines for the construction of polynuclear metallamacrocyclic half-sandwich complexes can be deduced. First of all, it is essential to use multidentate ligands witch are rather rigid. Otherwise, entropically favored dimers such as **15**, **16**, and **17** are formed. For the synthesis of trimeric and tetrameric complexes, it is important to note that the coordinate vectors of the corresponding ligands are very similar for each class, regardless of the chemical nature of the ligand and the overall charge of the resulting macrocycle. This correlation is highlighted in Scheme 6. Ligands as diverse as amino acids,[17] 2,3-dihydroxypyridine,[20,21] 9-ethyladenine,[10] and 2,3-dihydroxyquinoxaline (this

Scheme 6. The Relative Arrangement of the Donor-Groups Determine the Geometry and the Aggregation Number of Macrocyclic Complexes with (Arene)Ru, Cp*Rh, or Cp*Ir Building Blocks



work) all give rise to trimeric complexes of type A which display a concave geometry. The three chiral half-sandwich complexes in these macrocycles always have the same absolute configuration. In reactions with the tridentate ligands 4-imidazolecarboxylic acid (this work), adenine,[12] and 6-purinethione,[16] on the other hand, tetrameric aggregates with S_4 symmetry are formed. Again the coordinate vectors are very similar.

It appears likely that this synthetic concept can be expanded. Other ligands, which have donor groups that are arranged in a fashion analogous to what is depicted in Scheme 6, will be good candidates for the formation of trimeric or tetrameric assemblies of type A and D. Given the size and the rigidity of the structures that are accessible in this fashion and given the interesting host−guest chemistry that has already been reported for this class of compounds (e.g., chiral shift reagents,[10d] selective binding of lithium,[24,25] or fluoride ions[28]), an increasing interest in metallamacrocycles containing half-sandwich complexes as building blocks can be expected for the future.

Experimental Section

General. The synthesis of all complexes was performed under an atmosphere of dry dinitrogen, using standard Schlenk techniques. $[Cp^*RhCl_2]_2$,[35] $[(cymene)RuCl_2]_2$,[36] and $[(1,3,5\text{-}C_6H_3Me_3)RuCl_2]_2$[37] were prepared according to literature procedures. 2-Amino-nicotinic acid, 2-hydroxy-nicotinic acid, 4-imidazolecarboxylic acid, 2,5-dihydroxy-1,4-benzoquinone, 2,3-diaminotoluene, and Cs_2CO_3 (99.9%) were purchased from Aldrich, 2,3-dihydroxypyridine was purchased form Fluka, and 2,3-dihydroxyquinoline was purchased from SPECS. The solution of NaOMe in MeOH was prepared by dissolving Na in MeOH. The concentration was subsequently determined by titration. The ^{1}H and ^{13}C spectra were recorded on a JEOL EX 400, a JEOL GSX 270, a Bruker Advance DPX 400, or a Bruker Advance 200 spectrometer using the residual protonated solvents (^{1}H, ^{13}C) as internal standards. All spectra were recorded at room temperature.

6-Methyl-2,3-phenazinediol (14). The synthesis of ligand **14** was performed in analogy to a method reported for structurally related 2,3-phenazinediols:[38] To a brown solution of 2,5-dihydroxy-1,4-benzoquinone (681 mg, 4.76 mmol) in glacial acetic acid (400 mL) was added a dark brown solution of 2,3-diaminotoluene (600 mg, 4.76 mmol) in glacial acetic acid (200 mL). The mixture, which soon turned dark red, was heated under reflux for 2 h. After cooling, the mixture was poured on to crushed ice. A brown powder precipitated immediately. After the volume of the solution was reduced in a vacuum, the product was filtered, washed with water, and dried under vacuum (yield: 956 mg, 83%). ^{1}H NMR (400 MHz, CD_3OD): 2.81 (s, 3 H, CH_3), 7.12 (s, br, 1 H, CH), 7.32 (s, 1 H, CH), 7.53 (d, ^3J = 7 Hz, 1 H, CH), 7.60 (dd, ^3J = 7 Hz, ^3J = 8 Hz, 1 H, CH), 7.79 (d, ^3J = 8 Hz, 1 H, CH). Anal. Calcd (%) for $C_{13}H_{10}N_2O_2\cdot 0.25CH_3COOH$: C 67.21, H 4.60, N 11.61. Found: C 67.03, H 4.33, N 11.67.

[(Cymene)Ru($C_6H_5NO_3$)]$_2$ (15). A suspension of $[(cymene)RuCl_2]_2$ (153 mg, 0.25 mmol) and 2-hydroxy-nicotinic acid (70 mg, 0.50 mmol) in degassed methanol (15 mL) was stirred at room temperature. After 10 min a solution of NaOMe in MeOH (500 μL, 2 M) was added. The resulting orange solution was stirred for 30 min. After evaporation of the solvent under reduced pressure, the product was extracted with dichloromethane (30 mL). Addition of hexane (20 mL) and evaporation of the solvent gave an orange powder (yield: 166 mg, 89%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.36 [d, ^3J = 7 Hz, 6 H, $CH(CH_3)_2$], 1.38 [d, ^3J = 7 Hz, 6 H, $CH(CH_3)_2$], 2.16 (s, 6 H, CH_3, cymene), 2.99 (sept, ^3J = 7 Hz, 2 H, $CH(CH_3)_2$], 5.13 (d, ^3J = 6 Hz, 2 H, CH, cymene), 5.37 (d, ^3J = 6 Hz, 2 H, CH, cymene), 5.57 (d, ^3J = 6 Hz, 2 H, CH, cymene), 5.63 (d, ^3J = 6 Hz, 2 H, CH, cymene), 6.09 (dd, ^3J = 6 Hz, ^3J = 7 Hz, 2 H, CH, pyridone), 7.25−7.50 (m, 4 H, pyridone). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 18.81, 22.36, 22.97, (CH_3), 31.14 [$CH(CH_3)_2$], 77.67, 78.86, 81.67, 83.38 (CH, cymene), 96.55, 101.12 (C, cymene), 112.83, 123.23, 140.87, 150.71 169.63, 173.75 (pyridone). Anal. (%) Calcd for $C_{32}H_{34}N_2O_6Ru_2\cdot 1.5CHCl_3$: C 43.55, H 3.87, N 3.03. Found: C 42.75, H 3.59, N 3.05.

[Cp*Rh($C_6H_5NO_3$)]$_2$ (16). A suspension of $[Cp^*RhCl_2]_2$ (155 mg, 0.25 mmol) and 2-hydroxy-nicotinic acid (70 mg, 0.50 mmol) in degassed methanol (15 mL) was stirred at room temperature. After 10 min a solution of NaOMe in MeOH (500 μL, 2 M) was added. The resulting orange solution was stirred for 30 min. After evaporation of the solvent under reduced pressure, the product was extracted with dichloromethane (30 mL). Addition of hexane (20 mL) and evaporation of the solvent gave an orange powder (yield: 161 mg, 86%). Crystals were obtained by vapor diffusion of pentane into a solution of **16** in chloroform. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.71 (s, 30 H, Cp*), 6.08 (dd, ^3J = 6 Hz, ^3J = 7 Hz, 2 H, CH, pyridone), 7.46 (dd, ^3J = 6 Hz, ^4J = 2 Hz, 2 H, CH, pyridone), 7.60 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 2 H, CH, pyridone). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 9.31 (Cp*), 91.69 [d, $^1J_{RhC}$ = 9 Hz, $C_5(CH_3)_5$], 112.20, 125.83, 140.55, 149.77, 171.07, 172.96 (pyridone). Anal. (%) Calcd for $C_{32}H_{36}N_2O_6Rh_2\cdot CHCl_3\cdot H_2O$: C 44.64, H 4.43, N 3.16. Found: C 44.53, H 4.95, N 3.30.

[Cp*Rh($C_6H_6N_2O_2$)]$_2$ (17). The complex was prepared analogous to that of **16** using 2-amino-nicotinic acid (69 mg, 0.50 mmol) instead of 2-hydroxy-nicotinic acid. Orange powder (yield: 125 mg, 67%) resulted. Crystals were obtained by vapor diffusion of pentane into a solution of **17** in chloroform. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (s, 30 H, Cp*), 6.91 (dd, ^3J = 5 Hz, ^3J = 7 Hz, 2 H, CH, pyridone), 8.17 (dd, ^3J = 5 Hz, ^4J = 2 Hz, 2 H, CH, pyridone), 8.43 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 2 H, CH, pyridone). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 8.08 (Cp*), 91.80 [d, $^1J_{RhC}$ = 8 Hz, $C_5(CH_3)_5$], 117.74, 121.58, 141.38, 148.90, 165.55, 171.34 (pyridone). Anal. (%) calcd for $C_{32}H_{38}N_4O_4Rh_2$: C 51.35, H 5.12, N 7.49. Found: C 50.65, H 5.02, N 7.28.

[Cp*Rh($C_4H_2N_2O_2$)]$_4$ (18). A mixture of $[Cp^*RhCl_2]_2$ (400.0 mg, 0.65 mmol), 4-imidazolecarboxylic acid (148.0 mg, 1.29 mmol), and Ag_2O (363.6 mg, 1.55 mmol) in degassed methanol (80 mL) was refluxed for 18 h. The mixture was filtered through Celite, which was subsequently washed with degassed methanol (60 mL). Evaporation of the solvent under reduced pressure gave a yellow powder (yield: 412 mg, 86%). Yellow crystals were obtained by slow diffusion of pentane into a solution of **18** in chloroform. ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) = 1.65 (s, 60 H, Cp*), 6.70 (s, 4 H, CH, imidazole), 7.23 (s, 4H, CH, imidazole). ^{13}C NMR (101 MHz, CD_3OD): δ (ppm) = 8.88 (Cp*), 95.07 (d, $^1J_{RhC}$ = 8 Hz, $C_5(CH_3)_5$), 130.75, 136.40, 140.75, 173.17 (CH + C, imidazole). Anal. Calcd (%) for $C_{56}H_{68}N_8O_8Rh_4\cdot 0.75CHCl_3$: C 45.98, H 4.67, N 7.56. Found: C 45.85, H 5.08, N 7.76.

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Table 1. Crystallographic Data for Complexes **16** and **17**

	16·2$H_2O$$CHCl_3$	**17**·4$CHCl_3$
empirical formula	$C_{33}H_{41}Cl_3N_2O_8Rh_2$	$C_{36}H_{42}Cl_{12}N_4O_4Rh_2$
mol wt [g mol^{-1}]	905.86	1225.96
cryst size	0.18 × 0.14 × 0.10	0.53 × 0.43 × 0.17
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a [Å]	9.6579(2)	10.0605(8)
b [Å]	11.8111(2)	23.730(5)
c [Å]	17.6881(3)	11.316(2)
α [deg]	107.7288(14)	90
β [deg]	90.3147(13)	113.949(11)
γ [deg]	109.5758(8)	90
V [Å^3]	1797.74(6)	2469.0(7)
Z	2	2
d [g cm^{-3}]	1.673	1.649
T [K]	200(2)	293(2)
abs coeff [mm^{-1}]	1.192	1.358
θ range [deg]	2.57−27.50	2.29−23.97
index ranges	−12 → 12	−11 → 10
	−15 → 14	−21 → 27
	−22 → 21	−10 → 12
reflns collected	16373	6170
indep reflns	7977 (R_{int} = 0.0328)	3839 (R_{int} = 0.0139)
abs correction	none	semiempirical
max and min transm		0.9992 and 0.9008
data/restraints/params	7977/6/457	3839/0/269
GOF on F^2	1.128	1.074
final R indices [$I > 2\sigma(I)$]	R1 = 0.0356	R1 = 0.0373
	wR2 = 0.0929	wR2 = 0.0907
R indices (all data)	R1 = 0.0505	R1 = 0.0431
	wR2 = 0.1076	wR2 = 0.0946
largest diff peak/hole [e Å^{-3}]	0.682/−1.141	0.650/−0.714

Table 2. Crystallographic Data for Complexes **18** and **19**

	18·$CHCl_3$	**19**·2$CHCl_3$·C_5H_{12}
empirical formula	$C_{64}H_{76}Cl_{24}N_8O_8Rh_4$	$C_{64}H_{71}Cl_6N_3O_6Ru_3$
mol wt [g mol^{-1}]	2347.77	1494.15
cryst size	0.17 × 0.17 × 0.17	0.23 × 0.20 × 0.17
cryst syst	tetragonal	orthorhombic
space group	$P\bar{4}2_1c$	$Pbca$
a [Å]	16.8483(6)	24.7004(17)
b [Å]	16.8483(6)	18.2764(17)
c [Å]	16.5554(8)	27.586(2)
α [deg]	90	90
β [deg]	90	90
γ [deg]	90	90
V [Å^3]	4699.5(3)	12453.1(17)
Z	2	8
d [g cm^{-3}]	1.659	1.594
T [K]	140(2)	140(2)
abs coeff [mm^{-1}]	1.423	1.029
θ range [deg]	3.00−25.03	3.50−25.03
index ranges	−20 → 16	−29 → 29
	−20 → 20	−19 → 19
	−19 → 19	−32 → 32
reflns collected	28053	73291
indep reflns	4141 (R_{int} = 0.0397)	10420 (R_{int} = 0.0604)
abs correction	empirical	empirical
max and min transm	0.8550 and 0.5340	0.8150 and 0.4410
data/restraints/params	4141/0/244	10420/9/739
GOF on F^2	1.039	1.105
final R indices [$I > 2\sigma(I)$]	R1 = 0.0243	R1 = 0.0531
	wR2 = 0.0602	wR2 = 0.1327
R indices (all data)	R1 = 0.0262	R1 = 0.0801
	wR2 = 0.0611	wR2 = 0.1529
largest diff peak/hole [e Å^{-3}]	0.552/−0.455	1.761/−0.615

[(Cymene)Ru($C_9H_5NO_2$)]$_3$ (19). A suspension of [(cymene)$RuCl_2$]$_2$ (120 mg, 0.20 mmol), 2,3-dihydroxyquinoline (63 mg, 0.39 mmol), and Cs_2CO_3 (320 mg, 0.98 mmol) in degassed methanol (40 mL) was stirred for 2 h 30 min at room temperature. During that time an orange product precipitated. After evaporation of the solvent under reduced pressure, the product was extracted with degassed dichloromethane (50 mL). Evaporation of the solvent under reduced pressure gave a brown powder, which was dissolved in degassed methanol (3 mL) and placed in a fridge (5 °C). After 12 h, the orange precipitate was collected and dried under vacuum (yield: 55 mg, 32%). Orange crystals were obtained by slow diffusion of pentane into a solution of **19** in chloroform. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.38 (d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$), 1.41 (d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$), 1.97 (s, 9 H, CH_3), 2.98 (sept, ^3J = 7 Hz, 3 H, CH(CH_3)$_2$), 5.15 (d, ^3J = 6 Hz, 3 H, CH, cymene), 5.43 (d, ^3J = 6 Hz, 3 H, CH, cymene), 5.66 (d, ^3J = 6 Hz, 6 H, CH, cymene), 5.84 (d, ^3J = 6 Hz, 6 H, CH, cymene), 6.28 (s, 3 H, CH, quinoline), 6.79 (t, ^3J = 7 Hz, 3 H, CH, quinoline), 6.88 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 3 H, CH, quinoline), 6.98 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 3 H, CH, quinoline), 8.41 (d, ^3J = 8 Hz, 3 H, CH, quinoline). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 18.79, 22.74, 23.85 (CH_3), 31.85 (CH(CH_3)$_2$), 76.40, 78.60, 83.03, 83.26 (CH, cymene), 97.52, 98.98 (C, cymene), 110.46, 120.73, 122.05, 123.49, 123.91, 127.35, 141.45, 156.47, 173.39 (quinoline). Anal. Calcd (%) for $C_{57}H_{57}Ru_3N_3O_6$·1.5CH_2Cl_2: C 53.61, H 4.61, N 3.20. Found: C 53.17, H 4.19, N 3.07.

[(Cymene)Ru($C_8H_4N_2O_2$)]$_3$ (20). Cs_2CO_3 (441 mg, 1.35 mmol) was given under stirring to a suspension of [(cymene)$RuCl_2$]$_2$ (164 mg, 0.27 mmol) and 2,3-dihydroxy-quinoxaline (87 mg, 0.54 mmol) in MeOH (50 mL). After 2 h the solvent was evaporated under reduced pressure, and the product was extracted with dichloromethane (50 mL). Evaporation of the solvent gave an orange powder (yield: 191 mg, 60%). Crystals can be obtained by crystallization from hot MeOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$), 1.43 (d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$), 2.23 (s, 9 H, CH_3, cymene), 3.03 (sept, ^3J = 7 Hz, 3 H, CH(CH_3)$_2$), 5.10 (d, ^3J = 6 Hz, 3 H, CH, cymene), 5.45 (d, ^3J = 6 Hz, 3 H, CH, cymene), 5.66 (d, ^3J = 6 Hz, 3 H, CH, cymene), 5.68 (d, ^3J = 6 Hz, 3 H, CH, cymene), 6.93 (t, ^3J = 8 Hz, 3 H, CH, quinoxaline), 7.03 (t, ^3J = 8 Hz, 3 H, CH, quinoxaline), 7.14 (d, ^3J = 8 Hz, 3 H; CH, quinoxaline), 8.18 (d, ^3J = 8 Hz, 3 H, CH, quinoxaline). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.98, 22.67, 23.60 (CH_3), 31.64 (CH(CH_3)$_2$), 78.68, 78,94, 82.29, 82.34 (CH, cymene), 97.67, 100.16 (C, cymene), 122.97, 123.10, 123.40, 124.84 (CH, quinoxaline), 137.47, 138.20, 162.09, 164.91 (C, quinoxaline). Anal. Calcd (%) for $C_{54}H_{54}Ru_3N_6O_6$·3CH_3OH·H_2O: C 52.65, H 5.27, N 6.46. Found: C 52.65, H 5.06, N 6.66.

[Cp*Rh($C_8H_4N_2O_2$)]$_3$ (21). A suspension of Cs_2CO_3 (262 mg, 0.80 mmol), [Cp*$RhCl_2$]$_2$ (99 mg, 0.16 mmol), and 2,3-dihydroxy-quinoxaline (52 mg, 0.32 mmol) in MeOH (50 mL) was stirred 3 h at room temperature. The solvent was evaporated under reduced pressure, and the product was extracted with dichloromethane (50 mL). Evaporation of the solvent gave an orange powder (yield: 137 mg, 87%). Crystals can be obtained by crystallization from a mixture of hot MeOH and chloroform. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (s, 45 H, Cp*), 6.86 (t, ^3J = 7 Hz, 3 H, CH, quinoxaline), 6.98 (t, ^3J = 7 Hz, 3 H, CH, quinoxaline), 7.13 (d, ^3J = 7 Hz, 3 H, CH, quinoxaline), 8.17 (d, ^3J = 7 Hz, 3 H, CH, quinoxaline). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 9.74 (Cp*), 91.57 (d, $^1J_{RhC}$ = 9 Hz, $C_5(CH_3)_5$), 122.60, 122.64, 123.45, 124.33 (CH, quinoxaline), 136.10, 138.89, 163.49, 165.50 (C, quinoxaline). Anal. Calcd (%) for $C_{54}H_{57}Rh_3N_6O_6$·2CH_3OH·$CHCl_3$: C 49.67, H 4.83, N 6.10. Found: C 50.10, H 5.01, N 5.83.

[(1,3,5-$C_6H_3Me_3$)Ru($C_{13}H_8N_2O_2$)]$_3$ (22). A suspension of 6-methyl-2,3-phenazinediol (220 mg, 0.97 mmol), Cs_2CO_3 (793 mg, 2.43 mmol), and [(1,3,5-$C_6H_3Me_3$)$RuCl_2$]$_2$ (284 mg, 0.49 mmol) in degassed methanol (120 mL) was stirred for 6 h at room temperature. During that time, an orange-brown solution was obtained.

Table 3. Crystallographic Data for Complex **22**

	22·2CHCl$_3$·3CH$_3$OH·H$_2$O
empirical formula	$C_{71}H_{76}Cl_6N_6O_{10}Ru_3$
mol wt [g mol^{-1}]	1689.29
cryst size	0.24 × 0.17 × 0.17
cryst syst	monoclinic
space group	*Ia*
a [Å]	17.0208(19)
b [Å]	17.3799(17)
c [Å]	24.390(3)
α [deg]	90
β [deg]	97.174(9)
γ [deg]	90
V [Å^3]	7158.6(13)
Z	4
d [g cm^{-3}]	1.567
T [K]	140(2)
abs coeff [mm^{-1}]	0.910
θ range [deg]	2.72 to 25.03
index ranges	−20 → 20 −18 → 20 −29 → 29
reflns collected	20583
indep reflns	12140 (R_{int} = 0.0965)
abs correction	empirical
max and min transm	0.5710 and 0.1060
data/restraints/params	12140/416/830
GOF on F^2	0.792
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0735 wR2 = 0.1613
R indices (all data)	R1 = 0.1394 wR2 = 0.1864
largest diff peak/hole [e Å^{-3}]	0.960/−0.607

After evaporation of the solvent under reduced pressure, the product was extracted with degassed dichloromethane (150 mL). Evaporation of the solvent under reduced pressure gave a red powder, which was purified by chromatography on basic aluminum oxide with chloroform/methanol (3:2). Evaporation of the solvent under reduced pressure gave a red powder (yield 260 mg, 49%). Crystals were obtained by slow evaporation of a solution of **22** in chloroform/methanol. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.91 (s, 27 H, CH_3, $C_6H_3Me_3$), 2.53 (s, 9 H, CH_3, phenazine), 4.76 (s, 9 H, CH, $C_6H_3Me_3$), 6.48 (s, 3 H, CH, phenazine), 7.14 (d, ^3J = 7 Hz, 3 H, CH, phenazine), 7.33 (dd, ^3J = 7 Hz, ^3J = 9 Hz, 3 H, CH, phenazine), 8.20 (s, 3 H, CH, phenazine), 9.17 (d, ^3J = 9 Hz, CH, phenazine). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 17.94 (CH_3, $C_6H_3Me_3$), 18.18 (CH_3, phenazine), 75.06 (CH, $C_6H_3Me_3$), 101.57 (CH, phenazine), 102.36 (C, $C_6H_3Me_3$), 103.60, 125.14, 125.57, 125.69, 135.72, 139.72, 141.68, 144.88, 147.75, 170.35, 175.04 (phenazine). Anal. Calcd (%) for $C_{66}H_{60}N_6O_6Ru_3$·2.5$CHCl_3$·H_2O: C 49.78, H 3.93, N 5.08. Found: C 49.66, H 3.95, N 4.84.

Crystallographic Investigations. The relevant details of the crystals, data collection, and structure refinement are listed in Tables 1−3. Diffraction data were collected using Mo Kα radiation on different equipment and at different temperatures: a 4-circle kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD (140 K; **18**, **19**, **22**), a Nonius kappa CCD (200 K; **16**), and a Nonius MACH3 (room temperature; **17**). Data reduction was performed with the following: CrysAlis RED 1.7.0[39] (**18**, **19**, **22**), DENZO-SCALEPACK,[40] (**16**) and MOLEN[41] (**17**). Absorption correction was applied to all data sets but **16**. For **17**, a semiempirical method (MULTI-SCAN)[42] has been employed, whereas an empirical method (DIFABS)[43] has been used for **18**, **19**, and **22**. Structure solutions were performed by the following: SIR97[44] (**16** and **22**), SHELXS-86[45] (**17**), DIRDIF99[46] (**18**), and SHELXS-97[47]-(**19**). All structures were refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model" with $U_{iso} = a^*U_{eq}$(C) (where *a* is 1.5 for methyl hydrogen atoms and 1.2 for others, and C is the parent carbon atom). Structure refinement and geometrical calculations were carried out on all structures with the SHELXL-97. Graphical representations of the molecular structures in the crystal were generated with the program ORTEP.[48] Some disorder problems have been encountered during the refinement of **19** and **22** concerning the solvent molecules (C_5H_{12} for **19** and $CHCl_3$, CH_3OH and H_2O for **22**). In the case of **19** some geometric constraints were applied while for **22** the whole structure underwent "rigid body" restraints and some solvent molecules were retained isotropic.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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