Rhodium(III) Cage Compounds Based on Diphenylglycoluril
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Abstract: Metallo hosts containing an intramolecular cavity as well as a potentially active rhodium center have been synthesized from the concave building block tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5-(1H,3H)-dione (diphenylglycoluril, BB1) and its 1,3,4,6-bis(1,4-dihydroxy-2,3-xylene) derivative (BB2). To this end the ureylene nitrogen atoms of BB1 and the hydroxyl oxygen atoms of BB2 are provided with arms A, which are furnished with potential substrate binding sites and terminated with metal-binding groups X: BB-(A-X)4, A = ethylene glycol ether chain, X = 1-imidazolyl (1m), 1-benzimidazolyl (Benz), or 3-pyridyl (Py). Reaction of BB1-(A-X)4 (A = CH2(OCH2CH2)n (n = 1 and 2), X = Im) with RhCl3·3H2O results in the formation of complexes with general formula trans-[Rb(BB1-(A-X)4)Cl]Cl. These complexes have a cage structure with four imidazolyl groups in one plane with the rhodium center and two Cl ligands coordinated perpendicular to this plane. One of the trans-chloro atoms is located inside the cavity. When in BB1-(A-X)4, the arm A = CH2(OCH2CH2)3, a cis complex is formed with Rh(III). The corresponding benzimidazolyl complex (A = CH2(OCH2CH2)3, X = Benz), however, has the trans configuration. The origin of these different configurations is discussed. Complexes prepared from BB2-(A-X)4 (A = CH2(OCH2CH2)2n (n = 1 and 2), X = Benz and A = (CH2CH2O)2CH2, X = Py) and Rh(III) all have the trans configuration.

There is currently great interest in the important and very promising field of intramolecular inclusion chemistry.1 A principal theme in this field is the molecular design of inclusion catalysts that mimic nature's unsurpassed enzymes.2 When one realizes the great importance of metals in biocatalysis3 as well as current artificial catalysis,4 it is surprising to find that the development of "metallo inclusion catalysts" has lagged behind that of their organic counterparts. Besides some incidental examples,5 Busch, Mansuy, and Suslick have presented interesting studies that combine a metal ion's catalytic power and a cavity-containing molecule's ability to select and orient a substrate.6,7

An inclusion catalyst should contain binding and catalytic sites that converge on an enclosed guest molecule. Rebek concluded that the topology of most organic, cavity-containing hosts (cyclodextrins, crown ethers, and cyclophanes) do not fulfill this requirement because functional groups attached to the outer surface of these hosts point away from the enclosed substrates (see Figure 1, left).8

In this paper we describe the design, synthesis, and characterization of new macropolycyclic metallo cages containing relatively large cavities with a potentially active rhodium(III) center adjacent to a substrate binding site (see Figure 1, right). The metallo cages are based on the concave building block diphenylglycoluril, which was previously described by us.6 In addition, two new types of heterotopic tetrapodal ligands (tetrapodands), based on the novel concave building block 5, are presented.9 It will be demonstrated that our tetrapodands can introduce unexpected "macroligand effects".

Results and Discussion

Molecular Design. In a previous paper6 we introduced the metallo cage strategy for the preparation of a macropolycyclic metallo host: to a concave building block (BB) are attached four spacer units (A), comprising chains furnished with potential substrate binding sites, terminated with metal-binding groups (L) adjacent to a substrate binding site (see Figure 1, left). The metallo cages are based on the concave building block diphenylglycoluril, which was previously described by us.6 In addition, two new types of heterotopic tetrapodal ligands (tetrapodands), based on the novel concave building block 5, are presented.9

phenylimidazo[4,5-d]imidazole-2,5-(1H,3H)-dione (BB2, 5) as basic building blocks in our study. The latter is more concave

Chart I

<table>
<thead>
<tr>
<th>BB1-(A-X)4</th>
<th>BB2-(A-X)4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: A = H</td>
<td>5: A = H</td>
</tr>
<tr>
<td>2a: A = CH2(OCH2CH2)2, X = Im (= 1-imidazolyl)</td>
<td>6a: A = CH2CH2OCH2CH2, X = Cl</td>
</tr>
<tr>
<td>2b: A = CH2(OCH2CH2)3, X = Im</td>
<td>6b: A = CH2CH2OCH2CH2, X = Benz</td>
</tr>
<tr>
<td>3: A = CH2(OCH2CH2)2, X = Im</td>
<td>7a: A = CH2CH2OCH2CH2, X = Cl</td>
</tr>
<tr>
<td>4: A = CH2(OCH2CH2)3, X = Benz (= 1-benzimidazolyl)</td>
<td>7b: A = CH2CH2OCH2CH2, X = Benz</td>
</tr>
<tr>
<td>8: A = (CH2CH2O)2CH2, X = Py (= 3-pyridyl)</td>
<td>9: A = CH2CH2OCH2CH2CH2, X = Py</td>
</tr>
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</table>

1 University of Utrecht.
2 University of Nijmegen.
and more preorganized\textsuperscript{10} than the former as it contains two o-xylene side walls (see Figure 3).\textsuperscript{9} The spacer units attached to 1 and 5 consist of ethylene glycol ether chains or of a short trimethylene chain.

We have chosen Rh(III) as a metal center, because it is known to form kinetically stable octahedral complexes of the type trans-[Rh\textsubscript{L}X\textsubscript{2}]X (wherein L is an N-donating ligand, e.g. pyridine, pyrimidine, or thiazole, and X is a halogen).\textsuperscript{11} These complexes perfectly meet the requirements of the above formulated metallo cage strategy.

As a ligating group we have at first chosen imidazole. This aromatic heterocyclic five-membered ring contains a pyrrole-like nitrogen (N1), which can easily be alkylated (for attachment of a spacer), and a pyridine-like nitrogen (N3), which is able to stabilize various metal ions.\textsuperscript{3a} In this context it is of interest to mention that complexes of Rh(III) and 1-methylimidazole are almost as stable as their amine analogues.\textsuperscript{11} The robustness of the latter complexes ensures that photochemical reactions can be studied even under ambient conditions without interference from thermal reactions.\textsuperscript{12} For strategic reasons (vide infra) we later switched over to the imidazole derivative benzimidazole.

A pyridyl unit provides the third ligating group. First, one reason for this choice is that with this ligand complexes of the type trans-[Rh\textsubscript{L}X\textsubscript{2}]X, wherein L is a substituted pyridine, are easily accessible.\textsuperscript{11} Second, the (substitution) chemistry of rhodium(III)-pyridyl complexes has been studied relatively well. For instance, an interesting property of trans-[Rh(pyr)\textsubscript{4}Cl\textsubscript{2}]\textsuperscript{+} (pyr = pyridine) is the possibility to form, by reaction with BH\textsubscript{3}, the cationic trans-[Rh(pyr)\textsubscript{4}Cl\textsubscript{2}]\textsuperscript{+},\textsuperscript{13} a species that is supposed to act as a hydride-transfer agent. A metallo cage with a trans-[Rh(pyr)\textsubscript{4}Cl\textsubscript{2}]\textsuperscript{+} "roof" could, therefore, open up a new way to reduce a bound substrate regioselectively. The 3-position of the pyridine ring has been selected for the attachment of the spacer unit. The reason for this is architectural; CPK models demonstrate that position 3 is the most suitable one for building a cavity-containing metallo cage. Attachment via position 4 forces the groups to bend outward, and the 2-position is not suitable for steric reasons.

**Tetrapodands.** The tetrapodands 2b, 3, and 4 were synthesized in a way similar to that reported previously for tetrapodand 2a (see also the Experimental Part).\textsuperscript{6}

The reaction path for the tetrapodands 6b and 7b is outlined in Scheme I. Synthesis starts with the reaction of BB2-H\textsubscript{4} (5) with an ω-chlorotosylate. At room temperature, with DMSO as a solvent and solid KOH as a base, selective alkylation takes place with tosylate acting as a leaving group, yielding the tetrachlorides 6a and 7a. Subsequently, an in situ prepared benzimidazolate with tosylate acting as a leaving group, yielding the tetrachlorides 6a and 7a. Subsequently, an in situ prepared benzimidazolate nucleophile can be substituted for a chloride yielding the tetrapodands 6b and 7b. An advantage of this method over the one with a dichloro or ditosylate is that intramolecular bridge formation between the BB2-H\textsubscript{4} hydroxy oxygens is prevented.

Scheme II shows the route to the tetra-(3-pyridyl) podands. The first one, 8, has a trimethylene spacer; it is prepared by reacting building block 5 with the bromide 10-HBr. The second one, 9, has two CH\textsubscript{2}OCH\textsubscript{2} groups in each spacer unit. Its preparation starts with the reaction of BB2-H\textsubscript{4} (5) with an ω-chlorotosylate. At room temperature, with DMSO as a solvent and solid KOH as a base, selective alkylation takes place with tosylate acting as a leaving group, yielding the tetrachlorides 6a and 7a. Subsequently, an in situ prepared benzimidazolate nucleophile can be substituted for a chloride yielding the tetrapodands 6b and 7b. An advantage of this method over the one with a dichloro or ditosylate is that intramolecular bridge formation between the BB2-H\textsubscript{4} hydroxy oxygens is prevented.

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As we have seen, the reaction of BB2-H\textsubscript{4} (5) with ω-chlorotosylate is a versatile procedure that can be adapted to suit any desired podand. The synthetic opportunities provided by the metallo cage strategy have already been demonstrated in the preparation of a Rh(I) complex (Scheme II).

**Tetrapodand 7b.** The reaction of BB2-H\textsubscript{4} (5) with an ω-chlorotosylate is a versatile procedure that can be adapted to suit any desired podand. The synthetic opportunities provided by the metallo cage strategy have already been demonstrated in the preparation of a Rh(I) complex (Scheme II).
Table II. Molar Conductivities and d-d Transitions of Rhodium Complexes in Methanol

<table>
<thead>
<tr>
<th>compd</th>
<th>( \lambda_{mp} )</th>
<th>( \lambda_{max}(d-d) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[Rh(2a)Cl2]Cl</td>
<td>105</td>
<td>b</td>
</tr>
<tr>
<td>trans-[Rh(2b)Cl2]Cl</td>
<td>106</td>
<td>b</td>
</tr>
<tr>
<td>ex-cis-[Rh(3)Cl2]Cl</td>
<td>140</td>
<td>b</td>
</tr>
<tr>
<td>trans-[Rh(4)Cl2]Cl</td>
<td>108</td>
<td>419</td>
</tr>
<tr>
<td>trans-[Rh(6)Cl2]Cl</td>
<td>104</td>
<td>415</td>
</tr>
<tr>
<td>-</td>
<td>414'</td>
<td>414'</td>
</tr>
<tr>
<td>trans-[Rh(7b)Cl2]Cl</td>
<td>100</td>
<td>416</td>
</tr>
<tr>
<td>trans-[Rh(8)Cl2]Cl</td>
<td>90</td>
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<tr>
<td>trans-[Rh(12)Cl2]Cl</td>
<td>104</td>
<td>418</td>
</tr>
<tr>
<td>TEBA*</td>
<td>101</td>
<td></td>
</tr>
</tbody>
</table>

*At 25 °C and 10⁻³ M. The d-d transitions are masked by intense bands of the tetrapodands.

Figure 4. ¹³C NMR spectra (200 MHz, CD₂OD) in the region 125-135 ppm: (left) trans-[Rh(2a)Cl₂]Cl, (right) ex-cis-[Rh(3)Cl₂]Cl. The four peaks belonging to the phenyl carbon atoms are indicated; the other signals originate from the three imidazolyl carbon atoms.

Rhodium(III) Complexes Based on BB1. Reaction of tetrapodand 2a with RhCl₃·3H₂O in methanol as a solvent yields, after workup, a product with a FAB mass spectrum that can be assigned to the ion [Rh(2a)Cl₂]⁺. To make sure that in solution neither oligomeric nor polymeric networks were present, we applied gel permeation chromatography. The results (Table I) clearly show that the product consists of a compound having a molecular size of the same order of magnitude as that of the free tetrapodand, and it can thus be implied that the product is monomeric in solution.

The molar conductivity of the reaction product determined in methanol solution (Table II) is in the range expected for 1:1 electrolytes and agrees with the molecular formula [Rh(2a)Cl₂]Cl. Furthermore, the ¹H NMR data for this compound indicate that all four imidazolyl groups are coordinated to the rhodium center. Compared to those of the free tetrapodand, the resonances of the NCHN imidazolyl protons in the complex have shifted 0.65 ppm downfield. The appearance of all the imidazolyl protons at exactly the same chemical shift indicates that the imidazolyl groups are symmetrically coordinated to the Rh(III) center in a trans configuration. For a cis configuration, one would expect at least two resonance signals for the NCHN protons (one belonging to a set of ligands trans to a chloride and another one belonging to a set of mutually trans ligands). The presence of a fast (on the NMR time scale) ligand exchange, for which the two resonances would appear as a single peak, can be excluded since Rh(III) compounds are known to be kinetically inert.¹⁵

In the proton-decoupled ¹³C NMR spectrum (methanol-d₄; see Figure 4) the imidazolyl carbon atoms give rise to three sharp signals, indicating again that the four ligands are trans symmetrically bound to the Rh(III) center. Further support for the proposed trans-[Rh(2a)Cl₂]Cl structure is the similarity of the far-IR spectrum (375-250 cm⁻¹) of our product to that of the complex trans-[Rh(1-Melm)Cl₂]Cl.¹¹ A picture of the cage structure of [Rh(2a)Cl₂]Cl is given in Figure 5a.

As reported earlier,²⁴ tetrapodand 2a forms a cage compound with a Pd(II) metal center. We observed that the [Pd(2a)]²⁺ cage is unstable and collapses via a twisting motion, most likely as a result of intramolecular H bonding between the polar C(2)H bond of the imidazolyl groups and the CH₂OCH₂ functions in the spacers. The palladium(II) cage alternates between a left- and a right-twisted conformation. A consequence of the cage collapse is that the CH₃Im protons become diastereotopic and possess different chemical shifts.⁶ In the ¹H NMR spectrum (methanol-d₄) of trans-[Rh(2a)Cl₂]Cl the resonance pattern of these methaneylene groups is a normal AA'BB' pattern. This behavior is what one expects, because in the rhodium complex one of the chloro ligands is inside the cavity, making cage collapse impossible.

Tetrapodand 2b is equipped with spacers, each of which is one OCH₂CH₂ fragment shorter than those in 2a. It appears to be difficult to assemble a CPK molecular model of a metallo cage with 2b, similar to trans-[Rh(2a)Cl₂]Cl. The reason for this difficulty is that the internal chloro ligand touches the glycoluril unit causing strain in the molecule. The question arises as to whether this monomeric Rh(III) compound can actually be prepared. To find the answer to this question, we carried out the reaction of 2b with RhCl₃·3H₂O in methanol as a solvent. Gel permeation chromatography demonstrates that we are now dealing with a product that is smaller than trans-[Rh(2a)Cl₂]Cl (see Table I), and it can be concluded that the compound is monomeric. In agreement with this conclusion are the sharp signals present in the ¹H NMR spectrum (methanol-d₄). This spectrum shows only one peak for the NCHN imidazolyl protons at 8.1 ppm, i.e. a downfield chemical shift of 0.5 ppm compared to the free tetrapodand. This indicates that the Rh(III) ion is symmetrically surrounded by the imidazolyl ligands in a trans-chloro configuration (see above). The molar conductivity of the reaction product determined in methanol solution (Table II) is in the range expected for 1:1 electrolytes.¹⁴ These data confirm that the rhodium complex of tetrapodand 2b, trans-[Rh(2b)Cl₂]Cl, can actually be prepared.
of the metallo cage \([\text{Rh}(2a)\text{Cl}_2]\text{Cl}\) (see Figure 4), indicating of the product (Table II) lies between that of a 1:1 and a 2:1 carbons will be influenced. The \(^{13}\text{C}\) NMR spectrum of the electrolyte. \(^{14}\) of polymeric products, because gel permeation chromatography on the NMR time scale. However, since raising the temperature CPK models show this configuration to be possible with tetrapodand 3 but not with the shorter-chained 2a and 2b. To check this possibility, we applied \(^{13}\text{C}\) NMR spectroscopy. If the cavity is filled, one of the chloro ligands will be positioned close to the rhodium product of 3 has the \([\text{Rh}(3)\text{Cl}_2]\text{Cl}\), while resembling that of \([\text{Rh}(2b)\text{Cl}_2]\text{Cl}\). One difference is the broadness of the signals in the \(^1\text{H}\) NMR spectrum (methanol-\(d_4\)) of this new product; this could be due to the presence of various conformations that interconvert on the NMR time scale. However, since raising the temperature to 60 °C did not change the spectrum, such an explanation is unlikely. The origin of the broad signals cannot be the presence of polymeric products, because gel permeation chromatography revealed the complex to be monomeric (Table I). In agreement with this, the FAB mass spectrum showed an isotopic pattern that is attributable to the ion \([\text{Rh}(3)\text{Cl}_2]\text{Cl}\) + . The molar conductivity is not possible, because such a compound is unknown. Two structural isomers having a cis configuration are possible: one in which the two chloro ligands are outside the cavity; we call them the \(\text{ex-cis}\) conformer, while resembling that of \([\text{Rh}(2a)\text{Cl}_2]\text{Cl}\), while differing significantly from the spectrum of the rhodium product of 3. In particular, the intensities of the signals in the spectrum of the latter complex (see Figure 6; \(\nu(\text{Rh}-\text{Cl}) = 360-250\ \text{cm}^{-1}\), \(\nu(\text{Rh}-\text{N}) = 600-500\ \text{cm}^{-1}\)) are consistent with this being a cis complex. Direct comparison, however, with a cis- \([\text{Rh}_2\text{Cl}_4]\text{Cl}\) compound (wherein L is an N-alkylated imidazole) is not possible, because such a compound is unknown.

Two structural isomers having a cis configuration are possible: one in which the two chloro ligands are outside the cavity and one in which these ligands are inside the cavity; we call them the ex-cis and in-cis configurations, respectively (see Figure 7). The CPK model of the in-cis conformer is a strained molecule, whereas, in contrast, the ex-cis conformer is very easy to assemble. Ligand substitution reactions at Rh(III) centers most likely occur via an associative mechanism. \(^{17,18}\) Generally, this mechanism involves a transition state in which five ligands nearly remain in their original positions, forming a square pyramid. Two other ligands, the leaving and entering groups, occupy nearly equivalent positions under the base of the square pyramid, at much greater distances from the metal ion than the five former ligands. \(^{15}\) This transition state accounts for retention of configuration and geometry after a cis nucleophilic attack. \(^{15}\) To explain our results, we assume that the reaction intermediate \([\text{RhL}_2\text{Cl}_3]\text{L}\) has the 1,2,4-configuration, consistent with \(C_2\), local from its \(^{13}\text{C}\) NMR spectrum, which shows split and broadened signals for the imidazolyl carbon atoms (see Figure 4). Further support comes from the far-IR spectra. Around 350 cm\(^{-1}\) (where the rhodium–chloro vibrations are found), \(^{11,16}\) the spectrum of \([\text{Rh}(2a)\text{Cl}_2]\text{Cl}\), while resembling that of \([\text{Rh}(1-\text{MeIm})_2\text{Cl}_3]\text{Cl}\), differs significantly from the spectrum of the rhodium product of 3. In particular, the intensities of the signals in the spectrum of the latter complex (see Figure 6; \(\nu(\text{Rh}-\text{Cl}) = 360-250\ \text{cm}^{-1}\), \(\nu(\text{Rh}-\text{N}) = 600-500\ \text{cm}^{-1}\)) are consistent with this being a cis complex. Direct comparison, however, with a cis- \([\text{Rh}_2\text{Cl}_4]\text{Cl}\) compound (wherein L is an N-alkylated imidazole) is not possible, because such a compound is unknown.

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symmetry. This assumption is in line with literature data, which show that in rhodium(III) complexes with pyridine and various nitrites as N-donating ligands the 1,2,4-isomer appears to be more stable than the 1,2,3-isomer.\(^\text{19}\) The origin of the difference in behavior between 2 and 3 is probably due to steric constraints. In the case of tetrapodand 2a the free arm in [RhL\(_2\)Cl\(_4\)]\(_2\)Cl can easily substitute the chloro ligand in the xy plane, yielding trans-[Rh(2a)Cl\(_3\)]\(_2\)Cl (see Figure 8, left); the chloro ligand situated in the cavity along the z axis is sterically screened by the tetrapodand itself. In addition, the formation of a seven-coordinated transition state in the cavity along the z axis is unlikely, because of a lack of space. In the case of tetrapodand 3 the situation is different. The free arm in [RhL\(_3\)Cl\(_4\)]\(_2\)Cl can now fill the cavity that has arisen as a result the formation of ex-cis-[Rh(3)Cl\(_3\)]\(_2\)Cl (see Figure 8, right).

 Normally, a reaction between RhCl\(_3\)-3H\(_2\)O and an N-donating ligand L yields the trans product [RhL\(_2\)Cl\(_4\)]\(_2\)Cl.\(^\text{11}\) It is known, however, that 1-Melm behaves differently; the reaction of 4 equiv of 1-Melm with RhCl\(_3\)-3H\(_2\)O in aqueous ethanol always results in the formation of [Rh(1-Melm)\(_3\)Cl]Cl\(_2\) and this indicates that an N-alkylated imidazole is able to substitute a chloro ligand along the z axis of a Rh(III) center.

 In the foregoing discussion it has been explained why attempts to synthesize larger cavities by lengthening the spacer units of the tetrapodands are unsuccessful. To have a better chance of success, we modified our long-chain tetrapodand 3 by substituting benzimidazolyl ligands for the imidazolyl ligands to give tetrapodands 4. With CPK models the maximum number of benzimidazolyl ligands that can be placed around one metal center is four; this limit is imposed by steric factors. CPK models also show that a cis configuration in a complex of type [M(Benz)\(_4\)X\(_2\)]X is very unlikely.\(^\text{20}\)

 Prior to this work, no trans-[RhL\(_4\)Cl\(_3\)]\(_2\)Cl compounds in which L is an N-alkylated benzimidazole had been reported. Therefore, we studied the reaction of RhCl\(_3\)-3H\(_2\)O with the model ligand 1-methylbenzimidazole (12). With methanol as a solvent, this reaction indeed yielded the required trans-[Rh(12)Cl\(_3\)]\(_2\)Cl, in quantitative yield. The results of elemental analysis, conductivity, IR, and FABMS are consistent with the proposed molecular formula. The \(^1\)H NMR spectrum (CDC\(_1\)\(_2\)) of this model compound showed relatively broad signals. We ascribe this broadness to the following configurational behavior. CPK models suggest a four-bladed propellor-shaped configuration for trans-[Rh(12)Cl\(_3\)]\(_2\)Cl (see Figure 9). As benzimidazole is asymmetrical, different geometrical configurations are possible depending on the orientation of the o-phenylene nucleus. Moreover, in one configuration every proton possesses a site in which its chemical shift is influenced by anisotropy effects induced by neighboring ligands. It is difficult to foresee what kind of isomer distribution will occur. In this context it is worthwhile mentioning that asymmetrically substituted pyridines behave likewise. In particular, in the case of trans-[Ni(3,4-Me\(_2\!\!\!\!\!\text{pyr})\(_4\)](ClO\(_4\))\(_2\) an X-ray structure determination indicates that a statistical distribution of isomers is present.\(^\text{16}\)

 The UV-vis spectrum of the model compound showed a d-d transition at 418 nm (methanol), which is characteristic of a trans-[RhL\(_4\)Cl\(_3\)]\(_2\)Cl configuration. For substituted pyridines and imidazoles this transition occurs at 409 ±2 nm.\(^\text{16}\) The small red shift observed for trans-[Rh(12)Cl\(_3\)]\(_2\)Cl might be explained by assuming a tetragonal distortion of the octahedral Rh(III) complex. Presumably, the steric interaction between the o-phenylene nucleus and the chloro ligand causes the latter to be pushed away from the Rh(III) center; as a result the ligand field splitting becomes smaller. The presence of these steric interactions is shown in Figure 9.

 After having carried out the above-described model reaction, we allowed RhCl\(_3\)-3H\(_2\)O to react with the tetrakis(1-benzimidazolyl) ligand 4 in methanol as a solvent. The product was isolated as a yellow glassy material, which, according to elemental analysis, had the molecular formula Rh(4)Cl\(_4\)H\(_2\)O. The FAB mass spectrum showed a dominant ion with an isotopic pattern fitting the formula [Rh(4)Cl\(_4\)]\(_2\). In agreement with this finding, the molar conductivity of the complex in methanol (Table II) is in the range for 1:1 electrolytes.\(^\text{14}\) Gel permeation chromatography

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demonstrated that the product \([\text{Rh}(4)\text{Cl}_2]Cl\) is monomeric in solution (Table I).

In the UV–vis spectrum of \([\text{Rh}(4)\text{Cl}_2]Cl\) the highest wavelength \(d-d\) transition is found at 419 nm (Table II). This value is in good agreement with that for the model compound \([\text{Rh}(12)\text{Cl}_2]Cl\), indicating that both compounds have a similar octahedral Rh(III) surrounding with trans-sited chloro ligands.

The \(^1H\) NMR spectrum of \([\text{Rh}(4)\text{Cl}_2]Cl\) (CDC\(_12\)) is consistent with the proposed structure. As in trans-\([\text{Rh}(12)\text{Cl}_2]Cl\), the benzimidazolyl protons give rise to broad signals and the resonances of the NCHN protons show a downfield chemical shift (ca. 0.3 ppm relative to the free tetrapodand), which is indicative of a Rh(III)–benzimidazolyl interaction.

A mixture of geometrical isomers, as described above for the complex trans-\([\text{Rh}(12)\text{Cl}_2]Cl\), is not likely to occur in the case of trans-\([\text{Rh}(4)\text{Cl}_2]Cl\) since movement of the benzimidazolyl ligands is restricted as a consequence of their connection to the glycoluril building block. CPK models reveal that the configuration with three benzimidazolyl \(o\)-phenylene units directed outside and one inside the metallo cage contains much strain, especially in the spacer unit of the inside-directed ligand. The complex with all four benzimidazolyl ligands directed outside is by far the easiest one to assemble. In this complex one chloro ligand is situated inside the cage and surrounded by the Rh(III) center and four NCHN benzimidazolyl hydrogen atoms; the other one is situated outside the cage and is surrounded by the Rh(III) center and four \(o\)-phenylene groups of the benzimidazolyl ligands. Finally, the trans-\([\text{Rh}(4)\text{Cl}_2]Cl\) metallo cage can possess two enantiomeric configurations, a left-handed and a right-handed propellor.

Rhodium(III) Complexes Based on BB2. The reaction between RhCl\(_3\)-3H\(_2\)O and the tetrakis(1-benzimidazolyl) podands 6b and 7b yielded the metallo cages trans-\([\text{Rh}(6b)\text{Cl}_2]Cl\) and trans-\([\text{Rh}(7b)\text{Cl}_2]Cl\) (see Figure 5b). According to gel permeation chromatography, the compounds are monomeric (see Table I). The molecular conductivity of the two products is in the range for 1:1 electrolytes (see Table II). In both cases, the FAB mass spectrum displays the molecular ion (\(M - Cl\))^+. The UV–vis spectra are in agreement with a trans-\([\text{RhL}_4\text{Cl}_2]^+\) configuration.

The cage of trans-\([\text{Rh}(7b)\text{Cl}_2]Cl\) is the largest one we have made; in the open conformation it measures about 11 Å from the bottom (the central C–C bond of the glycoluril unit) to the top (the rhodium center). Compared to metallo cages based on building block BB1, the rigid character of building block BB2 makes a collapse of the cage, as occurs in \([\text{Pd}(2a)\text{Cl}_2]^4\) impossible.

Before studying the reaction of the tetra(3-pyridyl) podands 8 and 9 with RhCl\(_3\)-3H\(_2\)O, we performed a model reaction between RhCl\(_3\)-3H\(_2\)O and 4 equiv of 3-(\(^2\)chloro,5-dioxaheptyl)pyridine (11) in methanol as a solvent. The product of this reaction is a yellow compound. Elemental analysis and spectroscopic data are in agreement with a complex of the type trans-\([\text{RhL}_4\text{Cl}_2]Cl\). In particular, the UV–vis spectrum shows a \(\lambda_{max} (d-d)\) transition in the UV–vis spectrum, because it was broadened upon complexation; they are situated outside the metallo cage and do not “feel” the asymmetry introduced by the Rh(III) complexation.

Finally, we performed a reaction between RhCl\(_3\)-3H\(_2\)O and the tetra(3-pyridyl) podand 9. The yellow product was characterized (see Tables I and II and the Experimental Part) as \([\text{Rh}(9c)\text{Cl}_2]Cl\). This compound has a relatively large cavity with most likely a trans-\([\text{Rh}(Py)_4\text{Cl}_2]^+\) moiety as roof.

Monomer versus Polymer. It may be asked why monomeric instead of polymeric complexes are formed with the ligands we have used. Since the arms of our tetrapodands are relatively long the enthalpy of complexation to the metal will be similar for monomer and polymer. Thus, the entropy terms will be predominant. Accordingly, since the polymer, being a three-dimensional network with low flexibility, would have an entropy appreciably lower than that of the monomer, formation of the monomer will be preferred.

As Pd(II) forms kinetically labile complexes, the thermodynamically more stable monomer will be obtained. In contrast, complexes of the type \([\text{RhL}_4\text{Cl}_2]Cl\) are kinetically inert. This means that any kinetically formed polymer would not simply give monomers. The reason we obtain monomeric cages in good yields could be that the intermediate preceding cage formation, viz. \([\text{RhL}_4\text{Cl}_2]^+\), is kinetically labile.

Conclusion

Several cavity-containing Rh(III) compounds have been prepared and characterized. Unexpected from the point of view of “normal” coordination chemistry is the formation of the ex-cis-Rh(III) complex using the long-chain tetra(1-imidazolyl) podand 3, whereas the similar podands 2a and 2b, having shorter spacers, yield trans-\([\text{RhL}_4\text{Cl}_2]^+\) species. Tetrapodands in which the arms are terminated with 1-benzimidazolyl or 3-pyridyl ligating groups give the trans-\([\text{RhL}_4\text{Cl}_2]Cl\) complexes exclusively.

Experimental Part

General Procedures. \(^1H\) NMR spectra were recorded on Varian EM-360, Bruker AW-80, and Bruker WP-200 instruments. Chemical shifts (\(\delta\)) are reported downfield from internal (CH\(_3\))\(_2\)Si. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Infrared and UV–vis spectra were taken on Perkin-Elmer 283 and Perkin-Elmer 555 spectrophotometers, respectively. The far-IR data were measured via the transformation method using a Perkin-Elmer 1710 interferometer. FAB mass spectra were recorded on a VG ZAB 2F quadrupole mass spectrometer (argon: 70 eV; Cs: 130 eV). Conductivity measurements were carried out at 25.0 °C on a Philips PW 9501 conductivity meter. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Applied Chemistry TNO Zeist, The Netherlands. Melting points were determined on a Mettler FP5/FPS photoelectric melting point apparatus. Gel permeation chromatography was performed on a Sephadex LH-60 column (length 22 cm, diameter 1 cm) with methanol as eluent at a flow rate of 31 mL/h.

Unless otherwise indicated, commercial chemicals were used as received. DMSO, DMF, and methanol were dried over 3-A sieves prior to use. Diethyl ether and chloroform were distilled from benzophenone ketyl and CaCl\(_2\), respectively.

Compounds. Tetrahydro-3a,5a-diphenylimidazo[4,5-d]imidazole-2,5-(1H,3H)-dione (1). This compound was synthesized according to a literature procedure.\(^{24}\)
2.4,6-Tetraakis(7-(1-imidazolyl)-2,5-dioxahexyl)tetracydro-3a,6a-epidinylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (2a). The synthesis of this compound has been published previously.

2.4,6-Tetraakis(4-(1-imidazolyl)-2-oxobutyl)tetracydro-3a,6a-epidinylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (2b). The synthesis of this compound has been published previously.

2.4,6-Tetraakis(10-(1-imidazolyl)-2,5,8-trioxaeclyl)tetracydro-3a,6a-epidinylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (3). This compound has been described previously as a 3,6-dioxoaeostane instead of 1-chloro-5-hydroxy-3-oxapentane. The resulting tetrachloride is a light yellow syrup. Conversion with sodium acetate or weakly acidic water (the pH was adjusted to 5.5 for sodium acetate) afforded a 3,6-dioxoaeostane instead of 1-chloro-5-hydroxy-3-oxapentane.

2.4,6-Tetraakis(7-(1-imidazolyl)-2,5-dioxahexyl)-1,3:4,6-Bis(1,4-dihydroxy-2,3-xylylene)tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (5). This reaction mixture was added to aqueous sodium hydroxide solution, resulting in a white gummy substance. Its H NMR spectrum (CDCl3) as follows.

2.4,6-Bis[(4-chloro-1,4-dioxo-2-xylylene)tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (6a). Under a nitrogen atmosphere compound 5 (2.81 g, 5 mmol) dissolved in 56 ml of DMF. After adding 11.2 mL of l-tosyl-5-chloro-3-oxapentane (5.3 g, 30 mmol) in 25 ml of DMF. The solution was stirred at room temperature for 1 h, 1-tosyl-5-chloro-3-oxapentane (8.57 g, 30 mmol) was added. The mixture was stirred at room temperature for 10 h and thereafter added dropwise, while stirring vigorously, to a mixture of 400 mL of doubly distilled water and 50 mL of 10% aqueous HCl. The pH of the solution was kept between 5 and 7 by adding concentrated HCl. The precipitate was filtered, washed with water and diethyl ether (10x), and dried in vacuo: yield 3.6 g (74%) of 6a as a white solid; mp >210 °C (dec); IR (KBr) 1720 (C = O), 1130-1070 (COC); 'H NMR (CDCl3) δ 6.81 (br, 20 H, PhH), 6.5 (s, 4 H, XyH), 5.4 (d from AB q, 4 H, NCH2), 3.8 (m, 36 H, NCH2 and OCH3), 3.4 (m, 36 H, NCH2 and OCH3). Anal. Caled for C58H52N8O8: C, 72.41; H, 6.79; N, 12.38; O, 18.60. Found: C, 72.39; H, 6.72; N, 12.39; O, 18.60.

2.4,6-Bis[1,4-dihydroxy-2,3-xylylene]tetracydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (5). This compound was synthesized as described in literature.

2.4,6-Bis[1,4-8-(3-pyridyl)-1,4,7-tixoacetyl]-2,3-xylylene]tetracydro-3a,6a-epidinylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (9). Under a nitrogen atmosphere compound 5 dissolved in 32.6 mL of DMSO containing powdered KOH (5.92 g, 0.1 mmol) was dissolved in 50 mL of methanol and added instantaneously, while stirring vigorously, to a mixture of 400 mL of doubly distilled water and 100 mL of 10% aqueous HCl. The organic layer was concentrated in vacuo and added dropwise, while stirring vigorously, to 300 mL of ethyl acetate. The precipitate was filtered off, and the solvent was evaporated in vacuo. The residue was dissolved in CHCl3 and chromatographed over Sephadex LH-20, yielding another 120 mg (20%) of 9: total yield 75% of light yellow solid; mp >100 °C (dec); FABMS (M + H)+ m/e 1039; IR (KBr) 1720 (C = O) cm−1; 'H NMR (CDCl3) δ 8.6 (4 H, PhH), 7.3-6.5 (m, 18 H, PhH and PhH), 6.4 (s, 4 H, XyH), 5.5 (d from AB q, 4 H, NCH2), J = 16 Hz, 3.8 (m, 12 H, NHCH2 and OCH3), 2.8 (m, 8 H, CH2Py), 2.0 (m, 8 H, OCH3 and CH2Py). Anal. Caled for C59H60N8O8: C, 72.41; H, 6.07; N, 10.56; O, 18.60. Found: C, 72.39; H, 6.33; N, 10.46; O, 18.83.

3-(3-Bromopropyl)pyrididine Hydrogen Bromide (3H-BBB). This compound was prepared according to the literature procedure.

1-Chloro-7-(3-pyridyl)-3,6-dioxahexane (11). Under a nitrogen atmosphere compound 5 dissolved in 25 mL of DMF. The solution was stirred for 16 h. The KOH was filtered off, and the solvent was evaporated in vacuo. The residue was dissolved in a minimum amount of methanol and chromatographed over Sephadex LH-20: yield 1.48 g (40% of 9) as a yellow syrup; FABMS (M + H)+ m/e 1279; IR (NaCl disks) 1720 (COC) cm−1; 'H NMR (CDCl3) δ 8.4 (br, 8 H, PhH), 7.7-7.0 (m, 8 H, PhH), 6.9 (s, 10 H, PhH), 6.5 (s, 4 H, XyH), 5.5 (d from AB q, 4 H, NCH2), J = 16 Hz, 3.8 (m, 12 H, NHCH2 and OCH3), 3.4 (m, 36 H, NCH2), 3.2 (m, 36 H, NCH2 and OCH3). Anal. Caled for C59H60N8O8: C, 72.48; H, 6.72; N, 12.39; O, 18.64. Found: C, 72.35; H, 6.72; N, 12.39; O, 18.60.
Rhodium(III) Cages Based on Diphenylglycoluril

### Table III. FABMS Results of trans-[Rh(6b)Cl3]Cl

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative intensity, %</th>
<th>assignt</th>
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<tbody>
<tr>
<td>1315</td>
<td>100</td>
<td>(M - 3Cl - Rh + H)*</td>
</tr>
<tr>
<td>1415</td>
<td>17</td>
<td>(M - 3Cl - 2H)*</td>
</tr>
<tr>
<td>1452</td>
<td>41</td>
<td>(M - 2Cl)*</td>
</tr>
<tr>
<td>1487</td>
<td>49</td>
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<tr>
<td>1475</td>
<td>10</td>
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</tr>
<tr>
<td>1605</td>
<td>50</td>
<td>(M - 2Cl + NBA)*</td>
</tr>
</tbody>
</table>

*NBA = m-nitrobenzyl alcohol.

(KBr) 1720 (C=O), (trans-reflection) 338 (RhCl3); 1H NMR (CD2OD) δ 8.5-7.8 (br, 4 H, NCHN), 7.5-6.7 (br, 18 H, ArH and NCH(NH)), 5.1-4.5 (br, 8 H, NCH2O), 4.3 (t, br, 8 H, CH2I3m), 4.0-3.3 (m, 30 H, O(CH2CH2O)2CH2).

trans-[Rh(4)Cl3]Cl. RhCl3·3H2O (26.4 mg, 0.1 mmol) was dissolved in 50 mL of methanol and added instantaneously, while stirring vigorously, to a hot solution of tetrapodand 4 (134.2 mg, 0.1 mmol). The mixture was refluxed for 16 h, filtered over infusorial earth, and evaporated in vacuo, yielding the complex as a yellow solid in quantitative yield.

**trans-[Rh(6b)Cl3]Cl.**

This compound was synthesized from RhCl3·3H2O and 7b as described for trans-[Rh(4)Cl3]Cl: mp >245 °C (dec); FABMS (M - Cl)* m/e 1663; 1H NMR (CD2OD) δ 8.5-7.1 (br, 20 H, BenzH), 6.9 (s, 10 H, PhH), 5.9-5.1 (br, 4 H, NCH(H), 4.7-2.8 (br, 52 H, NCH/H and OCH2CH2OCH2CH2); IR (KBr) 1720 (C=O); 1110-1060 (COC) cm⁻¹. Anal. Calcld for C66H66N6O6Cl2Rh·(H2O): C, 55.17; H, 5.69; N, 9.20; O, 18.39. Found: C, 55.33; H, 5.80; N, 9.03; O, 17.90.

trans-[Rh(8)Cl3]Cl. This compound was synthesized from RhCl3·3H2O and 8 as described for trans-[Rh(4)Cl3]Cl: mp >240 °C (dec); FABMS (M - Cl)* m/e 1511; 1H NMR (CD2OD) δ 8.9-6.0 (br, 20 H, PyH and PhH), 7.0 (s, 10 H, PhH), 5.6 (br, 4 H, NCH2), 4.1-3.2 (br, 12 H, NCH/H and OCH2CH2OCH2); IR (KBr) 1720 (C=O). Anal. Calcld for C66H66N6O6Cl2Rh·(H2O): C, 55.17; H, 5.78; N, 10.34; O, 17.72. Found: C, 55.28; H, 5.88; N, 10.20; O, 17.72.

trans-[Rh(6b)Cl3]Cl. Procedure 1. This compound was synthesized from RhCl3·3H2O and 6b as described for trans-[Rh(4)Cl3]Cl: mp >170 °C (dec); FABMS (M - Cl)* m/e 1487. The FAB mass spectrum of trans-[Rh(6b)Cl3]Cl displays not only an intense isotope pattern belonging to the Rh-containing molecular ion (M - Cl)* m/e 1487 but, in addition, signal patterns at m/e 1575 and 1605. The isotope distribution for both patterns is similar to the one for (M - 2Cl)*. The difference in mass numbers between m/e 1605 and 1452 (for (M - 2Cl)*) is exactly the mass of a matrix molecule m-nitrobenzyl alcohol (see Table III).

Furthermore, the signal at m/e 1575 can be assigned to (M - 2Cl)* plus m-nitrobenzyl alcohol minus an NO fragment. Apparently, trans-[Rh(6b)Cl3]Cl forms a host-guest type adduct with a matrix molecule: 1H NMR (CD2OD) δ 8.5-7.2 (br, 20 H, BenzH), 7.0 (s, 10 H, PhH), 6.8-6.1 (br, 4 H, XyH), 5.9-5.1 (br, 4 H, NCH(H), 4.8-3.1 (br, 36 H, NCH/H and OCH2CH2OCH2CH2); IR (KBr) 1720 (C=O); 1110-1060 (COC) cm⁻¹. Anal. Calcld for C66H66N6O6Cl2Rh·(H2O): C, 52.39; H, 5.63; N, 9.65; O, 20.22. Found: C, 52.51; H, 6.51; N, 8.41; O, 20.76. The compound is very hygroscopic and rapidly becomes inhomogeneous; consequently, elemental analysis is difficult to perform.

trans-[Rh(6b)Cl3]Cl. Procedure 2. DMSO/ETH Reaction. Under a nitrogen atmosphere 6b (100 mg, 0.076 mmol) was dissolved in a mixture of 38 mL of DMSO and 38 mL of ethanol. To this reaction mixture was added RhCl3·3H2O (20 mg, 0.076 mmol). The solution was stirred and heated to 100 °C for 2 h. DMSO and ethanol were evaporated in vacuo, yielding the complex as a yellow solid in quantitative yield.

trans-[Rh(6b)Cl3]Cl. Procedure 3. DMSO/H2 Reaction. Under a nitrogen atmosphere 6b (50 mg, 0.038 mmol) was dissolved in 38 mL of DMSO. To this reaction mixture was added RhCl3·3H2O (10 mg, 0.038 mmol). The reaction mixture was stirred and molecular hydrogen was bubbled through the solution for 10 h at 20 °C. DMSO was evaporated in vacuo, yielding the complex as a yellow solid in quantitative yield.

trans-[Rh(7b)Cl3]Cl. This compound was synthesized from RhCl3·3H2O and 7b as described for trans-[Rh(4)Cl3]Cl: mp >245 °C (dec); FABMS (M - Cl)* m/e 1663; 1H NMR (CD2OD) δ 8.5-7.1 (br, 20 H, BenzH), 6.9 (s, 10 H, PhH), 5.9-5.1 (br, 4 H, NCH(H), 4.7-2.8 (br, 52 H, NCH/H and OCH2CH2OCH2CH2); IR (KBr) 1720 (C=O); 1110-1060 (COC) cm⁻¹. Anal. Calcld for C66H66N6O6Cl2Rh·(H2O): C, 55.17; H, 5.69; N, 9.20; O, 18.39. Found: C, 55.33; H, 5.80; N, 9.03; O, 17.90.

### Acknowledgment

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1, 101241-21-8; 3, 11875-66-5; 4, 11872-42-6; 5, 106319-02-2; 6a, 11875-67-6; 6b, 11875-68-7; 7a, 11875-69-8; 7b, 11875-70-1; 8, 11875-71-2; 9, 11875-72-3; 10-11b, 41038-63-5; 11, 11875-73-4; trans-[Rh(2a)Cl3]Cl, 101333-07-7; trans-[Rh(2b)Cl3]Cl, 11875-76-7; ex cis-[Rh(3)Cl3]Cl, 11875-77-8; trans-[Rh(4)Cl3]Cl, 11875-78-9; trans-[Rh(6b)Cl3]Cl, 106319-07-7; trans-[Rh(7b)Cl3]Cl, 11875-79-0; trans-[Rh(8)Cl3]Cl, 11875-80-3; trans-[Rh(9)Cl3]Cl, 11875-81-4; trans-[Rh(11)Cl3]Cl, 11875-82-5; trans-[Rh(12)Cl3]Cl, 11875-83-6; 1-chloro-8-hydroxy-3,6-dioxaoxactane, 5197-62-6; sodium imidazolide, 5587-42-8; 1-tosyl-5-chloro-3-oxapentane, 11875-74-5; sodium benzimidazolate, 1073-32-1; 1-tosyl-8-chloro-3,6-dioxaoxactane, 11875-75-6.