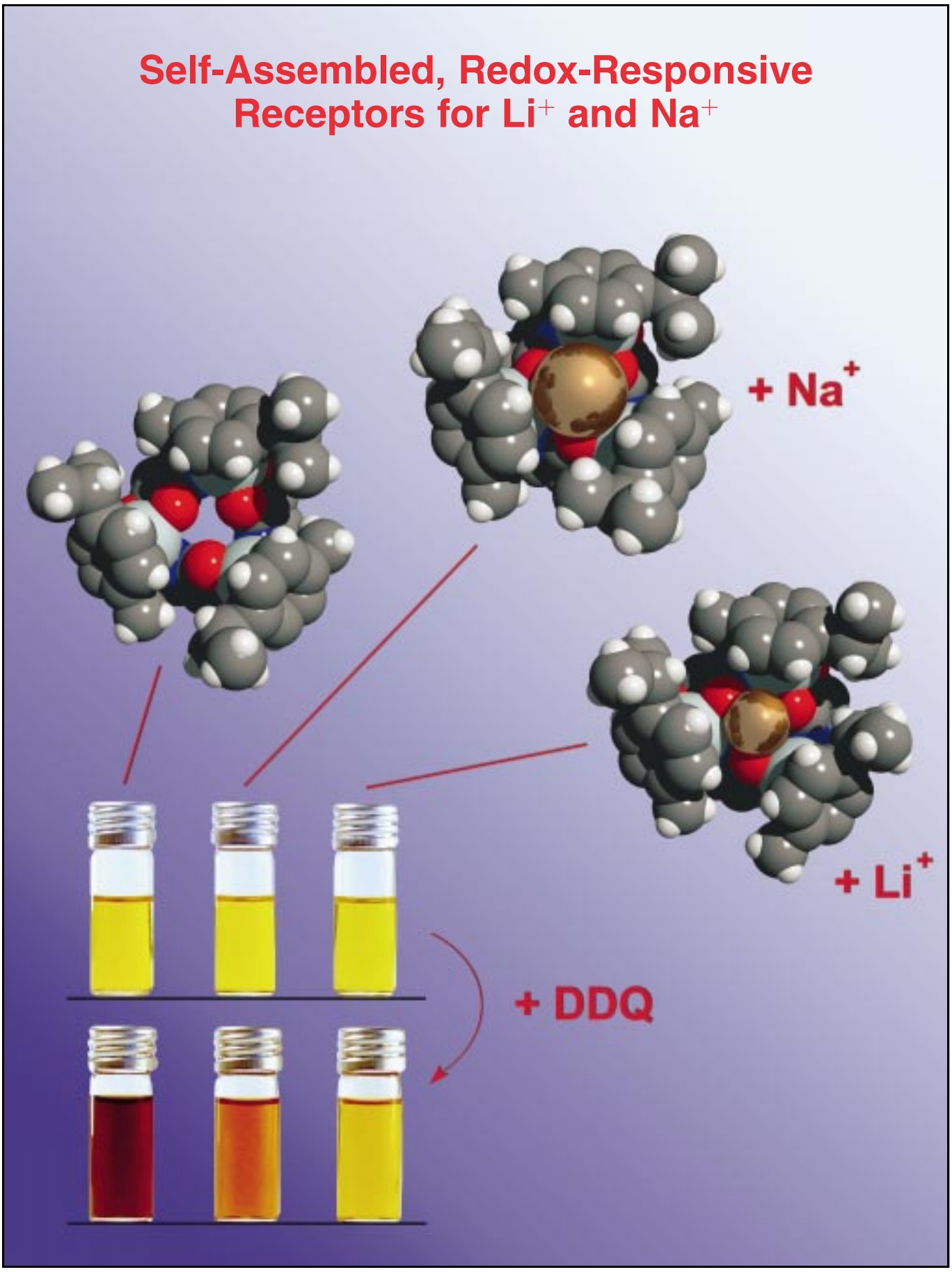

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Self-Assembled Organometallic [12]Metallacrown-3 Complexes

Holger Piotrowski,[b] Gerhard Hilt,[b] Axel Schulz,[b] Peter Mayer,[b] Kurt Polborn,[b] and Kay Severin*[a]

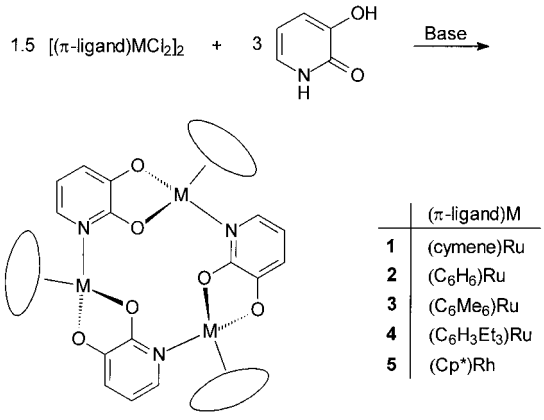
Abstract: The reaction of [(arene)-$RuCl_2]_2$ (arene = C_6H_6, cymene, $C_6H_3Et_3$, or C_6Me_6) or $[Cp^*RhCl_2]_2$ with 3-hydroxy-2-pyridone in the presence of Cs_2CO_3 gives trinuclear metallamacrocyclic complexes. The self-assembly process was shown to be completely diastereoselective, and a racemic mixture of complexes with $M_RM_RM_R$ or $M_SM_SM_S$ (M = Ru, Rh) configuration was obtained. Plausible mononuclear intermediates of the formula [(arene)-$RuCl(C_5H_4NO_2)$] (arene = cymene, C_6Me_6) have been isolated and characterized. A structurally related trimer was synthesized by using [(cymene)-$RuCl_2]_2$ and 3-acetamido-2-pyridone instead of 3-hydroxy-2-pyridone. The macrocycles were shown to be highly potent ionophores for Na^+ and/or Li^+ with negligible affinities for the larger cation K^+. The selectivities of the receptors depend on the π-ligand present: whereas the $(C_6H_6)Ru$– and (cymene)-Ru complexes bind both Li^+ and Na^+, the $(C_6Me_6)Ru$–, $(C_6H_3Et_3)Ru$–, and Cp*Rh complexes bind exclusively Li^+. For all receptors, the presence of alkali metal ions can be detected electrochemically: the peak potential is shifted by > 300 mV toward anionic potential upon binding. This behavior was utilized to detect Li^+ and Na^+ colorimetrically. Single crystal X-ray analyses have been carried out on eight complexes, four of which are bound to an alkali metal halide ion pair. Structural parameters, which affect the affinity and selectivity are discussed. A computational study on [{MX}[12]crown-3] complexes (M = Li, Na; X = Cl, Br, I) was performed in order to compare relevant bond lengths and angles of the energy-minimized structures with those of the organometallic receptors.

Keywords: ionophores · lithium · macrocycles · receptors · self-assembly

Introduction

Beginning with the work of Pedersen,[1] the synthesis of macrocyclic ionophores has been a very active field of research for more than 30 years. Today, a multitude of structurally very diverse compounds with high affinities and selectivities are known.[2, 3] Synthetic ionophores have found applications in ion selective sensors, as phase-transfer catalysts, and in membrane transport, amongst others.[3] A major drawback, however, is that the synthesis often requires substantial effort, especially for ionophores with tailor-made selectivities. An attractive alternative is the utilization of self-assembly processes.[4] In this context, the transition metal based assembly of macrocyclic ionophores[5] is of special interest since this approach offers a variety of advantages: the synthesis can often be accomplished in a single step with excellent yields. Furthermore, the unique properties of the resulting metallacrowns can possibly be used to facilitate the detection of guest molecules.

In a preliminary communication we have reported the synthesis of the redox-responsive receptor **1**, which was obtained in good yield by reaction of $[(cymene)RuCl_2]_2$ with 3-hydroxy-2-pyridone in the presence of base (Scheme 1).[6]



Scheme 1. Synthesis of trinuclear metallacrowns by self-assembly of half-sandwich complexes with 3-hydroxy-2-pyridone in the presence of base.

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This organometallic analogue of [12]crown-3 was shown to be a highly potent ionophore with a remarkable affinity for Li^+ and Na^+ and an almost perfect selectivity for Na^+ over K^+. Here we describe the synthesis of structurally related trinuclear (arene)Ru^{II} or Cp*Rh^{III} complexes. The variation of the bridging metal fragment affects not only the solubility and the redox behavior but also the selectivity of the organometallic receptor. Consequently, we were able to develop redox-responsive ionophores with extremely high selectivity for Li^+. The synthetic results are supplemented by a comprehensive crystallographic and computational study, performed to unravel the factors which control the host properties of our receptors.

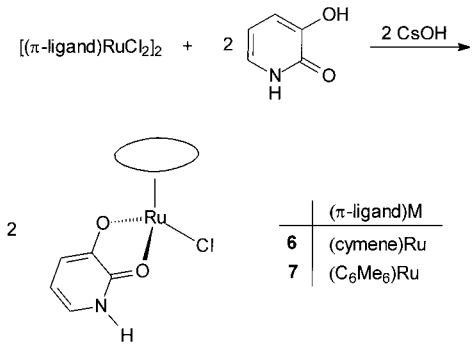
Results and Discussion

Synthesis of metallamacrocyclic receptors: The synthesis of two- and three-dimensional macrocyclic metal complexes by self-assembly is a flourishing field in modern inorganic chemistry.[7] Most complexes are based on classical coordination compounds (e.g. $Pd(en)^{2+}$), but organometallic fragments such as $M(CO)_3$ (M = Re, Mo), Cp*Rh, and CpCo are increasingly used to build these structures.[7, 8] In 1992, Fish et al. described a triangular metallamacrocycle with Cp*Rh^{III} corners and bridging nucleobase ligands.[9] Structurally related *tricationic* compounds with half-sandwich complexes at the corner were subsequently reported by Carmona,[10] Beck,[11] Sheldrick,[12] and Fish.[13] We have described *neutral* organometallic triangles, which were obtained by self-assembly of 3-oxy-2-methyl-4-pyridone complexes of Cp*Ir^{III} and (cymene)Ru^{II}.[14] In order to investigate whether other pyridonate ligands can be employed to build polynuclear organometallic structures we have examined the reaction of $[Cp^*RhCl_2]_2$ and various $[(arene)RuCl_2]_2$ complexes with 3-hydroxy-2-pyridone in the presence of base (Cs_2CO_3). In all cases cyclic trimers (**1**–**5**) were obtained in mostly good yields (Scheme 1).

The elemental analyses of the isolated products were indicative of a 1:1 ratio of (arene)Ru (or Cp*Rh) and the pyridonate ligand. The formation of trinuclear structures was suggested by the FAB mass spectra, which showed peaks at the expected *m*/*z* ratio along with peaks corresponding to di- and mononuclear species. The NMR (^1H, ^{13}C) spectra of **1**–**5** are in accordance with a C_3 symmetrical structure: only one set of signals is observed for the pyridonate as well as the arene ligands. Significant upfield shifts ($\delta \leq 0.96$) are found for the pyridonate ligands. The stereochemistry of the self-assembly process was of special interest since three stereogenic metal centers are formed. The presence of only one isomer, as suggested by the NMR spectra, was indicative of a highly diastereoselective reaction. Since no additional source of chiral induction was present during the synthesis, the macrocycles are obtained as a racemic mixture. For **1** and **4** the chirality of the complex was clearly evident in the ^1H NMR spectra: diastereotopic protons were found for the cymene ligand (**1**) and the methylene group of the 1,3,5-triethylbenzene ligand (**4**).

Pronounced differences were observed for the solubility of **1**–**5**: as expected[15] the $(C_6H_6)Ru$ complex **2** displayed a rather low solubility in common organic solvents such as dichloromethane. The (cymene)Ru, $(C_6Me_6)Ru$, and Cp*Rh complexes **1**, **3**, and **5**, on the other hand, can be dissolved in nonpolar solvents such as benzene and toluene, and complex **4** is even soluble in hot hexane.

In order to investigate the mechanism of the self-assembly process we carried out the reaction of $[(cymene)RuCl_2]_2$ and $[(C_6Me_6)RuCl_2]_2$ with 3-hydroxy-2-pyridone in the presence of only one equivalent of base (with respect to the ligand). In both cases, a mononuclear pyridonate complex (**6**, **7**) could be isolated in good yield. The spectroscopic data are in agreement with an O,O′-coordinated pyridonate ligand as depicted in Scheme 2, but a N,O-chelate as observed for some (arene)Ru complexes with 2-oxypyridinate ligands (arene = cymene, benzene)[16] cannot be excluded. Structurally related half-sandwich complexes with O,O′-coordinated 3-oxy-4-pyridonate ligands have previously been described by Davies[17] and by us.[14, 18] In contrast to **1** and **3**, the mononuclear complexes **6** and **7** are soluble in water. It seems likely, that in this solvent the chloro ligand is substituted by water to give a cationic "solvento" complex. The compounds **6** and **7** are plausible intermediates in the formation of the trinuclear complexes **1** and **3**. Base-induced macrocyclization could occur by deprotonation and replacement of the labile chloro ligand with the resulting pyridine ligand.



Scheme 2. Synthesis of mononuclear half-sandwich complexes.

The synthesis of **1**–**5** demonstrates that triangular structures can be obtained with various half-sandwich complexes of Ru^{II} and Rh^{III}. This flexibility is important for modifying the solubility and selectivity (see below) of the receptors. But furthermore, we were interested whether alterations in the bridging ligand can be tolerated in our synthetic approach. Among the possible variations of the 3-hydroxy-2-pyridone ligand, the substitution of the 3-hydroxy group with an *N*-acyl group seemed promising since ruthenium half-sandwich complexes with chelating ligands having anionic amide groups have previously been described.[19] And indeed, upon reaction of $[(cymene)RuCl_2]_2$ with 3-acetamido-2-pyridone in the presence of Cs_2CO_3 the trimeric complex **8** was isolated and structurally characterized. Reactions with other potentially tridentate ligands such as 2-hydroxy nicotinic acid were less successful, and the reactions gave rise to dinuclear complexes, which will be described elsewhere.

The isolation of the amide complex **8** suggests that the synthesis of trinuclear receptors with different *N*-acyl-3-

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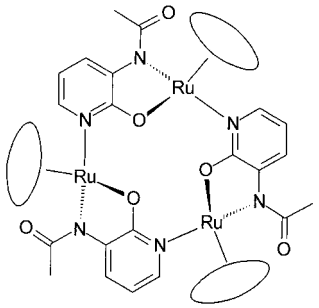

8

(π-ligand)M = (cymene)Ru

amino-2-pyridonate ligands can be accomplished. Thus, the preparation of metallamacrocyclic receptors having additional functional groups seems feasible. Of special interest would be complexes with acrylamide groups which could be used to incorporate such receptors in a polymeric matrix. Research along these lines is currently being pursued in our laboratory.

Host–guest chemistry: The macrocycle **1** has turned out to be an extremely potent ionophore for Li^+ and Na^+ with affinities in chloroform that are far superior to those of standard crown ethers such as [18]crown-6 and [12]crown-4 and comparable to those of cryptands.[6] The stability of $\mathbf{1}\cdot Li^+$ is so high that even LiCl can be extracted from water into chloroform. This characteristic is shared only by very few ionophores such as the highly preorganized spherands described by Cram.[20] Complex **1** displays no detectable affinity for K^+. This was explained by the steric requirements of the cymene ligands, which are placed around the donor O-atoms of the receptor.[6] It was therefore of special interest whether a different selectivity would be obtained for the ruthenium and rhodium complexes **2**–**5** having smaller (**2**) and larger (**3**–**5**) π-ligands. Especially the latter complexes seemed promising candidates for one of our main goals: the development of a lithium selective receptor. In recent years, there has been a considerable interest in synthetic ionophores with high selectivity for Li^+.[21, 22] Since lithium compounds are increasingly used in medicine and technology, methodologies to separate and determine Li^+ are highly desirable. For this purpose, ionophores have been considered early on, but the synthesis of compounds with a high selectivity for Li^+ remains a challenging task.

The affinity of the receptors **1**–**5** toward Li^+, Na^+, and K^+ was examined in extraction experiments: a solution of the respective metallacrown in methanol was stirred with an excess of MCl (M = Li, Na, K). After evaporation of the solvent the mixture was extracted with $CDCl_3$ and examined by ^1H NMR spectroscopy. The binding of alkali metal halides results in a significant downfield shift of the ^1H NMR signals of the pyridonate and the arene protons. Since the exchange of the alkali guest is slow on the NMR timescale,[23] the free and the complexed receptor can easily be distinguished. An all or nothing situation was encountered: either the respective adduct or the free receptor was obtained in quantitative yield. Therefore, these extraction experiments are also a good indicator of the selectivity of the receptors. In no case was KCl incorporated. The (benzene)Ru complex **2** displayed a behavior similar to that of **1**: LiCl as well as NaCl was extracted. This was not unexpected since the *p*-alkyl groups of the cymene ligands may adopt a conformation, in which they point away from the alkali metal binding site (Figure 10). Thus, a similar selectivity was expected for **1** and **2**. Remarkably, the macrocycles **3**–**5** are all selective for Li^+. Apparently, the Cp*, the hexamethylbenzene, as well as the 1,3,5-triethylbenzene ligands are sufficiently large to inhibit the binding of Na^+ ions.

The stability constants of alkali metal halide complexes are generally solvent dependent with lower K_a values in more polar solvents.[2c–e] A similar trend is found for the NaX (X = Cl, Br, I) complexes of **1** and **2**. If $\mathbf{1}\cdot$NaX or $\mathbf{2}\cdot$NaX is dissolved in $CDCl_3$ (10 mM) only the host–guest complex can be detected by ^1H NMR spectroscopy. In CD_3OD (10 mM), on the other hand, the free receptor can also be observed. Thus, a direct calculation of K_a is possible by integration of suitable ^1H NMR signals. The following values were obtained: $K_a(\mathbf{1}\cdot NaCl) = 3.5 \pm 0.5 \times 10^3\ L\,mol^{-1}$; $K_a(\mathbf{1}\cdot NaBr) = 1.5 \pm 0.3 \times 10^3\ L\,mol^{-1}$; $K_a(\mathbf{1}\cdot NaI) = 3.4 \pm 0.4 \times 10^2\ L\,mol^{-1}$; $K_a(\mathbf{2}\cdot NaCl) = 1.1 \pm 0.5 \times 10^2\ L\,mol^{-1}$. These data show that the stability of the Na^+ complexes is dependent on the nature of the halide anion, with K_a increasing in the series I < Br < Cl. The crystallographic analyses (see below) as well as the fact that the ^1H NMR spectra of $\mathbf{1}\cdot$NaCl (Figure 1), $\mathbf{1}\cdot$NaBr, and $\mathbf{1}\cdot$NaI are distinguishable suggest that the alkali metal halide is bound as an ion pair not only in $CDCl_3$ but also in CD_3OD. Therefore, the decreased stability of $\mathbf{1}\cdot$NaI as compared with $\mathbf{1}\cdot$NaCl may partially be attributed to steric repulsion between the large iodide anion and the cymene ligands.

The difference of the K_a value in CD_3OD and $CDCl_3$ is striking: whereas in $CDCl_3$ the affinity of **1** for NaCl is far superior to those of crown ethers such as [15]crown-5 or [18]crown-6 and comparable to those of cryptands,[6] in

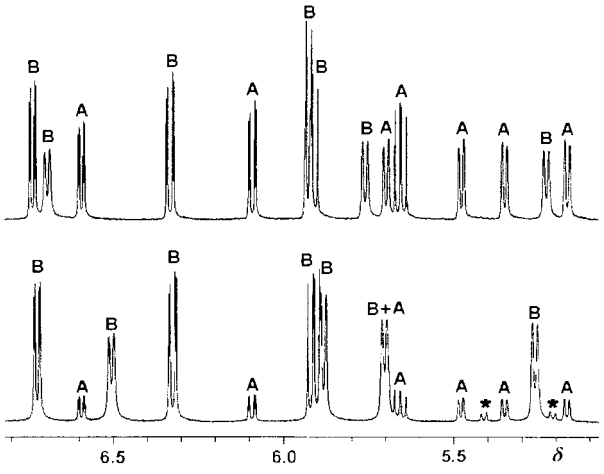

Figure 1. Aromatic region of the ^1H NMR spectrum of $\mathbf{1}\cdot$NaCl (bottom) and $\mathbf{1}\cdot$NaI (top) in CD_3OD (10 mM). The signals corresponding to the free receptor **1** are labeled with "A"; the signals of the Na^+ complexes are labeled with "B". Note that the relative amount of the free host "A" is larger for the NaI complex, and that the chemical shifts of the "B" signals are not identical.

CD_3OD the association constant of K_a (**1**·NaCl) $= 3.5 \pm 0.5 \times 10^3$ L mol^{-1} is similar to that of [15]crown-5.[2e] This behavior may also be the result of the simultaneous binding of the cation and the anion within the cavity of the macrocyclic host. Consequently, "naked" halide anions which are energetically unfavored in less polar organic solvents such as $CDCl_3$ are avoided. In CD_3OD, on the other hand, this advantage is less pronounced.

In contrast to the Na^+ complexes, the LiCl adducts of the receptors **1**–**5** are so stable that even in CD_3OD (10 mM) only the host–guest complex can be detected by ^1H NMR spectroscopy. Given that the concentration of the free receptor is less than 3%, the association constants in CD_3OD must be higher than 10^5 L mol^{-1}. In this context, it is interesting to note that an enhanced affinity for Li^+ as compared with Na^+ and K^+ was also observed for [12]metallacrown-4 compounds prepared by Pecoraro.[5a] The relative affinity of **1**–**5** towards LiCl was determined in competition experiments with equimolar amounts of two receptors. These experiments have revealed the following trend: K_a(**2**·LiCl) > K_a(**1**·LiCl) > K_a(**4**·LiCl) > K_a(**5**·LiCl) > K_a(**3**·LiCl).
Among the receptors which are specific for Li^+ (**3**–**5**), the (1,3,5-triethylbenzene)Ru complex **4** shows the highest affinity for LiCl. To quantify the stability of **4**·LiCl, we performed competition experiments with cryptand-2,1,1,[24] which is one of the most potent Li^+ ionophores commercially available. These experiments have shown that in $CDCl_3$ the affinity of **4** for LiCl is at least one order of magnitude higher than that of cryptand-2,1,1. This value represents just the lower limit. After several hours of tempering at 55 °C, the relative amount of **4**·LiCl as compared with free **4** was still slightly increasing, which indicated slow exchange kinetics. In CD_3OD, on the other hand, the stability of cryptand-2,1,1·LiCl is approximately ten times higher than that of **4**. From that data, a stability constant of K_a(**4**·LiCl) $= 10^7$ L mol^{-1} in CD_3OD can be estimated.[25] In contrast to receptor **1** which was able to quantitatively extract LiCl from water, with receptor **4** only small amounts (<10%) were extracted under otherwise identical conditions. This is most likely due to the reduced stability of **4**·LiCl as compared with **1**·LiCl.

In recent years, there has been a considerable interest in macrocyclic ionophores that contain transition metal redox centers.[26, 27] Systems of this kind are potentially useful to detect the guest molecules electrochemically, a prerequisite for amperometric molecular sensor devices. We investigated the redox behavior of the metallacrowns **1**–**5** by cyclic voltammetry. For all receptors three oxidation states are observed in a mixture of dichloromethane and acetonitrile (1:1). The peak potential of the first oxidation is found between 315 mV (**3**) and 634 mV (**2**). For the ruthenium complexes **1**–**4**, an indirect correlation is observed between the number of the electron-donating alkyl substituents on the arene ligand and the first peak potential. Upon binding of LiCl or NaCl, the cyclic voltammogram changes significantly. Importantly, the first peak potential is shifted by more than 300 mV toward anodic potential. Unfortunately the three oxidation states for the Li^+ and the Na^+ adducts are not as clearly resolved as for the free receptors, especially for the complexes **2**·LiCl, **2**·NaCl, **3**·LiCl, and **5**·LiCl. Thus, an exact determination of ΔE was not possible. It should be noted, however, that the values of $\Delta E = 357$ mV for **1**·LiCl (Table 1) and $\Delta E = 385$ mV for **4**·LiCl (Figure 2) are large compared with what is found for ferrocene containing crown ethers and cryptands.[27a, c, d]

Table 1. Peak potentials for the oxidation of the complexes **1**–**5** and the corresponding alkali metal halide adducts ($TBABF_4$; CH_2Cl_2/CH_3CN, 1:1).[a]

	E_1 [mV]	E_2 [mV]	E_3 [mV]
1	583	893	1125
1·LiCl	940 sh	1210	1426
1·NaCl	900 sh	1215	–
2	634	895	1070
2·LiCl	1127 sh	–	–
2·NaCl	1177	–	–
3	315	640	926
3·LiCl	1175 sh	–	–
4	480	795	1042
4·LiCl	865	1155	1402
5	536	772	984
5·LiCl	1180 sh	–	–

[a] sh = shoulder.

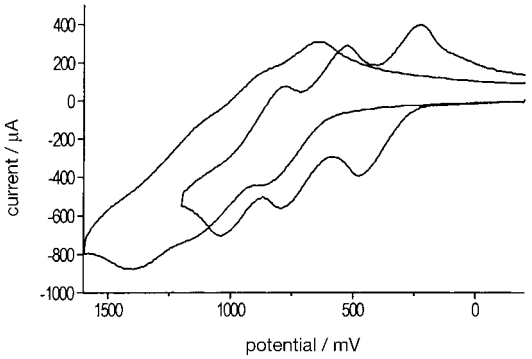

Figure 2. Cyclic voltammograms of the receptor **4** and the corresponding Li^+ complex **4**·LiCl in CH_2Cl_2/CH_3CN (1:1) measured against a Ag/AgCl reference electrode by using a glassy carbon working electrode at a scan rate of 4015 mV sec^{-1}. Upon complexation of Li^+ a pronounced shift of the first peak potential towards anodic potential is observed.

The large differences of the redox potentials of the free receptors and the corresponding MX adducts prompted us to search for an appropriate reagent to selectively oxidize the uncomplexed macrocycle. The idea behind that was that if the oxidation reaction is accompanied by a color change then the presence of Li^+ or Na^+ could be detected colorimetrically. For this purpose, DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) proved to be ideally suited. If a yellow solution of **1** in chloroform is treated with DDQ, a dark brown solution is immediately obtained. Under otherwise identical conditions only slight color changes are observed for the respective Li^+ and Na^+ complexes (Figures 3a and b). If the same reaction is carried out in a mixture of methanol and chloroform even the Na^+ and the Li^+ complex can be distinguished (Figure 3c). Similar behavior is observed for the Li^+ specific receptor **4**: upon reaction with DDQ, a dark brown solution is obtained, whereas for the Li^+ complex an orange solution is observed.

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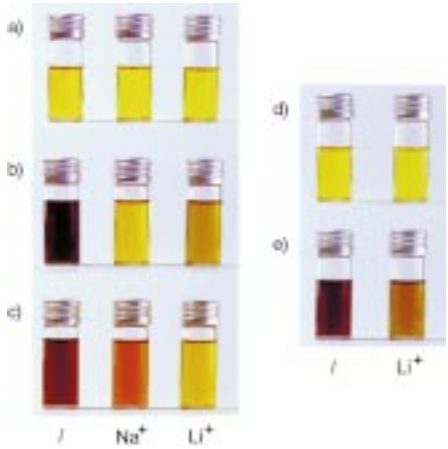


Figure 3. a) Solutions of **1** (left), **1**·NaCl (middle), and **1**·LiCl (right) in $CHCl_3$ (1.4 mL; concn = 650 μM); b) Upon addition of DDQ in $CHCl_3$ (300 μL; 6.7 mM) the free receptor is oxidized (left), whereas for the alkali metal complexes only slight changes are observed; c) The same experiment in a mixture of MeOH and $CHCl_3$ (7:3); the Na^+ complex (middle) and the Li^+ complex (right) can clearly be distinguished; d) Solutions of **4** (left) and **4**·LiCl (right) in $CHCl_3$ (1.4 mL; concn = 650 μM); e) Upon addition of DDQ in $CHCl_3$ (100 μL; 6.7 mM), a pronounced difference between the free receptor (left) and the Li^+ complex (right) is observed. The photos were taken approximately 1 min after addition of DDQ.

These experiments show that the redox-responsive macrocycles **1** and **4** can be employed to detect Li^+ and Na^+ ions in a simple colorimetric test. Given the very high selectivity and affinities of these receptors, various analytical applications can be envisioned.

Structural and theoretical investigations: In order to understand the structural parameters which affect the affinity and selectivity of our receptors, we have performed a comprehensive crystallographic analysis of the macrocyclic complexes with and without guest molecules. In this context, it should be noted that so far there are only very few metallacrowns for which structural data are available for both the neutral host and the corresponding host–guest complex.[5c, 5j] Similar to **1**,[6] the trinuclear complexes **2**, **3**, and **5** show a pseudo C_3 symmetrical geometry with three tetrahedral (arene)Ru^{II} or Cp*Rh corners connected by 3-oxo-2-pyridonate ligands (Figures 4, 5, and 6). The catechol part of the ligand is coordinated in a slightly bent fashion to the metal centers with dihedral angles Θ_{MOCC} between 8.2 and 15.1° (Table 2). Likewise, the pyridine part of the ligand is not bound in a linear fashion with dihedral angles Θ_{MNCC} between 5.2 and 9.8°. Overall, the bond lengths and angles of the metal-pyridonate skeleton of all receptors are very similar. Nevertheless, the receptors show some flexibility which is manifested in the differences of the M–M′ distances of up to 0.20 Å. Notably, the Ru–Ru distance (5.46 Å) as well as the O–O′ distance (3.21 Å) of the hexamethylbenzene complex **3** is larger than those found for **1**, **2**, and **5** (Ru–Ru = 5.32–5.38 Å; O–O′ = 3.04–3.10 Å). Presumably, this is due to repulsion between the bulky arene ligands. Similarly, the M–M′ distances are lengthened (compared with the free receptor) if sterically demanding guest molecules are present such as in **1**·NaI (ΔRu–Ru′ = 0.04 Å) and in **2**·NaBr (ΔRu–Ru′ = 0.07 Å). A related situation is encountered for **5**: upon coordination of LiCl the Cp* ligands and also the Rh atoms move apart (ΔRh–Rh′ = 0.12 Å).

The structure of the amide complex **8** (Figure 7) in the crystal is similar to those of the 3-oxy-2-pyridonate complexes. Again, a pseudo C_3 symmetrical structure is observed with all amide donor groups having a *cis* Ru–N–C–O configuration. The coordinating amide is markedly nonplanar with an averaged dihedral angle of $\Theta_{RuNCO} = 27.8°$.

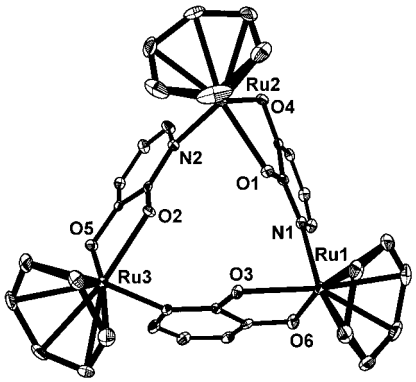


Figure 4. Molecular structure of receptor **2** in the crystal. The hydrogen atoms are omitted for clarity.

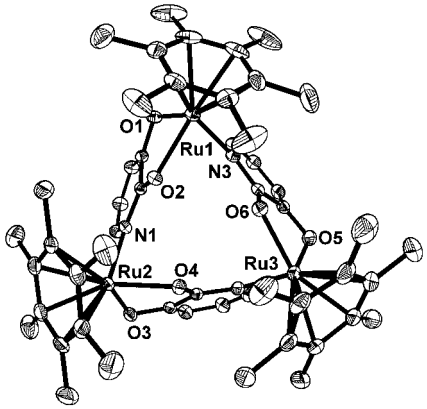


Figure 5. Molecular structure of receptor **3** in the crystal. The hydrogen atoms are omitted for clarity.

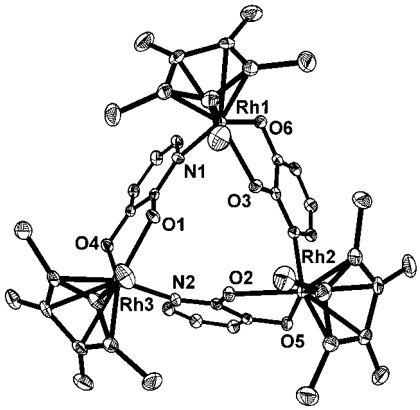
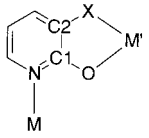


Figure 6. Molecular structure of receptor **5** in the crystal. The hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for the macrocyclic receptors **1**, **2**, **3**, **5**, and **8**.[a]



X = O, $NCOCH_3$
M = Ru, Rh

	M–N	M–O	M–X	O–M–X	M–O–C1–C2	M–N–C1–C2	O–O′	M–M′	Θ[c]
1	2.13	2.08	2.05	79.41	11.1	7.6	3.09	5.38	43.9
1·NaCl[b]	2.14	2.09	2.04	79.29	11.6	7.8	3.11	5.36	43.9
1·NaI	2.15	2.10	2.05	79.20	12.3	8.5	3.14	5.42	45.6
1·LiCl[b]	2.14	2.10	2.06	79.51	8.8	9.2	2.97	5.36	41.8
2	2.13	2.08	2.07	79.66	8.2	5.2	3.04	5.32	41.6
2·NaBr	2.14	2.11	2.06	79.1	10.8	5.7	3.11	5.39	44.5
2·LiCl	2.14	2.11	2.05	79.44	8.4	8.1	2.98	5.38	44.1
3	2.14	2.12	2.05	78.61	15.1	9.8	3.21	5.46	49.5
5	2.13	2.09	2.06	80.12	11.2	5.8	3.10	5.35	43.6
5·LiCl	2.12	2.14	2.06	79.2	10.8	9.1	3.07	5.47	51.2
8	2.14	2.08	2.10	77.81	14.1	11.1	3.11	5.27	37.1

[a] Averaged values are given; M = Ru, Rh. [b] Values from ref. [6]. [c] For a definition of Θ see Figure 11.

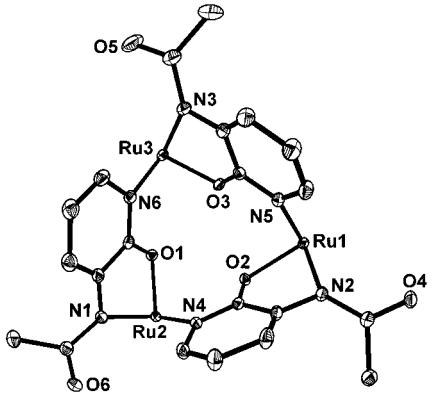


Figure 7. Molecular structure of receptor **8** in the crystal. The hydrogen atoms and the cymene ligands are omitted for clarity.

In all alkali metal halide complexes which have been structurally characterized (**1**·LiCl,[6] **1**·NaCl,[6] **1**·NaI, **2**·LiCl, **2**·NaBr, **5**·LiCl) the alkali metal ion is coordinated to the three adjacent O-atoms of the metallacrown ether (Figure 8). The fourth coordination site is occupied by the halide anion. For **2**·LiCl, we were able to grow a second type of single crystal, the crystallographic investigation of which revealed a lithium ion coordinated to a water molecule instead of the chloride ion. Unfortunately, we were unable to obtain crystallographic data of satisfactory quality and therefore a more detailed analysis of this second type of structure is not presented.

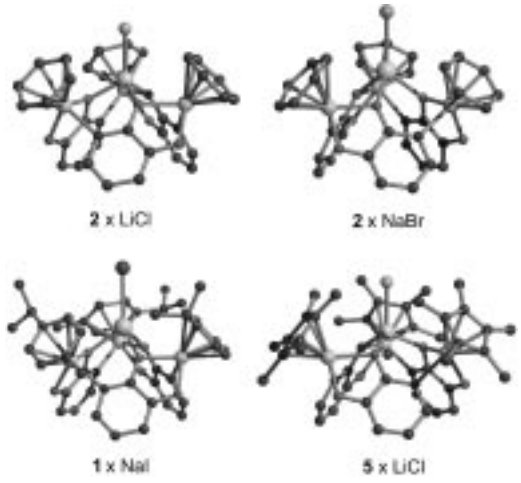


Figure 8. Molecular structures of alkali metal halide complexes in the crystal (ball and stick representation).

For the Li^+ complexes, Li–O distances between 1.94 and 1.97 Å were observed. This is comparable to the values found for organic [12]crown-3 type Li^+ complexes (1.83–1.99 Å).[28] The Li–Cl distances of 2.36, 2.38, and 2.42 Å are in between of what is found for monomeric LiCl (2.02 Å)[29] and crystalline LiCl (2.57 Å)[30] but longer than the Li–Cl bond length observed for [12]crown-**4**·LiCl in the crystal (2.29 Å).[31]

The Na–X distances (X = Cl, Br, I) are remarkably short. Searching the Cambridge Structural Database, we found that NaCl complexes with a Na–Cl bond length between 2.64 and 3.05 Å can be found (for crystalline NaCl the value is 2.82 Å).[32] For **1**·NaCl, a bond length of only 2.53 Å is observed. A similar situation is encountered for **1**·NaI (Na–I = 2.97 Å) and **2**·NaBr (Na–Br = 2.73 Å). Comparable complexes such as [15]crown-5·NaI (Na–I = 3.05 Å)[33] and C-pivot lariat [16]crown-5·NaBr (Na–Br = 2.88 Å)[34] have significantly longer M–X bonds. The unusually short Na–X distances found for **1**·NaCl, **1**·NaI, and **2**·NaBr are most likely the result of the special geometry, with Na^+ having the atypical coordination number four.[35] This was confirmed by a computational study, performed to compare the structural parameters of our metallacrowns with the optimized structures of the corresponding [12]crown-3 alkali metal halide complexes.[36] Energy-minimized geometries were calculated in C_3 symmetry for the LiCl complex and for three NaX adducts (X = Cl, Br, I) at the density functional theory level by using the hybrid method B3LYP. The relevant bond lengths and angles are listed in Table 3. It is important to note that the calculated O–O′ distances for the Na^+ complexes (3.09 Å) closely match the experimentally determined values of 3.11–3.14 Å found for **1**·NaCl, **1**·NaI, and **2**·NaBr which are also similar to the values found for the free receptors. Thus, the three donor atoms of the rigid metallamacrocycles have

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Table 3. Selected bond lengths [Å] and angles [°] for the alkali metal complexes of **1** and **2** (X = Cl, Br, I) in comparison with calculated and experimental values for [12]crown-3 complexes (see Figure 9).[a]

	data	M–X	M–O	X–M–O	O–M–O	O–O′
1 · LiCl[b]	X-ray	2.42	1.95	118.4	99.3	2.97
2 · LiCl	X-ray	2.38	1.96	118.25	99.4	2.98
5 · LiCl	X-ray	2.36	1.97	115.7	102.6	3.07
1 · NaCl[b]	X-ray	2.53	2.23	126.3	88.4	3.11
2 · NaBr	X-ray	2.73	2.23	126.2	88.6	3.11
1 · NaI	X-ray	2.97	2.24	126.1	88.8	3.14
[12]C-3 · LiNCS[c]	X-ray	–	1.93	–	97.2	2.90
[12]C-3 · LiCl	calcd	2.20	1.89	119.4	97.9	2.85
[12]C-3 · NaCl	calcd	2.47	2.36	130.9	81.7	3.09
[12]C-3 · NaBr	calcd	2.62	2.36	130.8	81.9	3.09
[12]C-3 · NaI	calcd	2.84	2.35	130.7	82.1	3.09

[a] Averaged values are given; M = Li, Na. [b] Values from ref. [6]. [c] Values from ref. [28a].

almost the ideal geometry to bind sodium ions in a tetrahedral coordination environment. Given the very high degree of preorganization, this may contribute significantly to the high binding affinity of **1** and **2** towards Na^+. As expected, for [12]crown-3 · LiCl the calculated O–O′ distance of 2.85 Å is shorter than what was found for the Na^+ complexes. This value is in agreement with the 2.90 Å found for [12]crown-3 · LiNCS.[28a] A similar trend is observed for the complexes **1** · LiCl and **2** · LiCl, which show shorter O–O′ distances of only 2.97 and 2.98 Å. The bond angles at the alkali metal ion are also different for the Li^+ and the Na^+ complexes: whereas the X–Na–O ($126.2 \pm 0.1°$) angles are larger than the X–Li–O angles ($118.3 \pm 0.1°$), the opposite is true for the O–M–O angles. Here, the O–Na–O angles ($88.6 \pm 0.2°$) are smaller than the O–Li–O angles ($99.4 \pm 0.1°$). These trends are nicely reflected by the results of the theoretical investigations. The calculated Na–X distances (X = Cl, Br, I) are also remarkably short. This indicates that the tetrahedral coordination geometry for Na^+ in combination with a terminal halogeno ligand is indeed responsible for the short Na–X bonds and not the special stereoelectronic effects of the receptor.

Amongst the various factors which contribute to the thermodynamic stability of ionophore metal complexes, the desolvation of the free receptor has to be considered. The structures of **1** and **2** in the crystal show one molecule of water in the cavity of the receptor fixed by a hydrogen bond to the adjacent O-atom. For **2**, the adduct **2** · H_2O can also be detected by mass spectroscopy. For **3** and **5**, on the other hand, neither the crystal structure nor mass spectroscopy point to solvent molecules within the cavity. Complex **8** co-crystallizes with three molecules of water, none of which is found in the cavity. This data supports the conclusion that the energy requirements for desolvation are rather low and thus do not contribute significantly to the free energy of complexation since a maximum of one molecule of water can occupy the small binding cavity.

The crystallographic data also provide an explanation for the fact that both the nature of the alkali metal ion as well as the nature of the halide ion affect the chemical shifts of the arene protons since they are located in close proximity to each other. In the case of **1** · LiCl, for example, a minimal H_{arom}–Cl distance of only 2.62 Å is observed. For NaCl, this value is

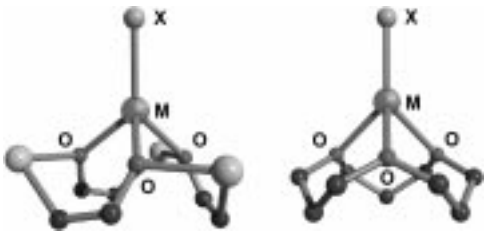

Figure 9. Geometry of the metallacrowns coordinated to an alkali metal halide ion pair (left, only selected atoms are shown) in comparison with the optimized structure of a [12]crown-3 complex (right). For bond lengths and angles see Table 3.

increased to 2.99 Å due to the longer Na–O and Na–Cl bond lengths and smaller O–Na–O angles.

In Figure 10, CPK models (based on crystallographic data) of the receptors **1**, **2**, **3**, and **5** together with the corresponding Li^+ and Na^+ complexes are depicted. The view along the pseudo C_3 axis shows that the arene and Cp* ligands form the

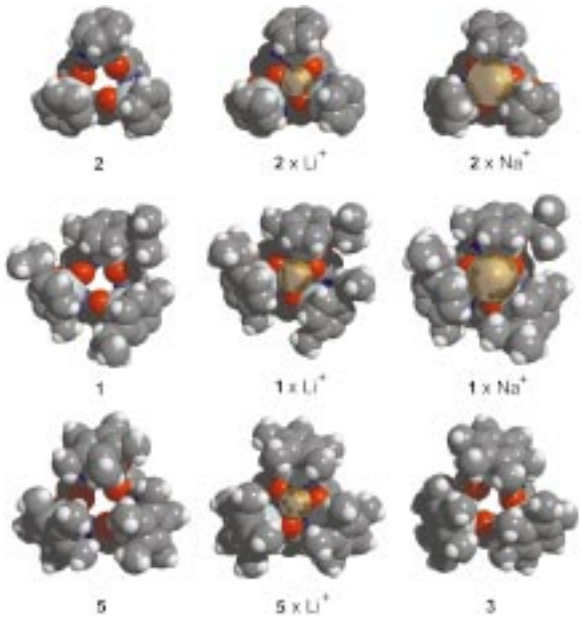

Figure 10. View along the pseudo C_3 axis of the receptors **1**, **2**, **3**, and **5** (CPK model) together with the corresponding Li^+ and Na^+ complexes. The halide atoms are not shown for clarity.

walls of a cavity, on the bottom of which the three oxygen donor atoms are positioned. In the case of **1** and **2**, this cavity is large enough to accommodate lithium and sodium ions. For the hexamethylbenzene complex **3** and the Cp*Rh complex **5**, on the other hand, this cavity is too small for Na^+. Consequently, only lithium salts can be bound. The perfect selectivity of **1** and **2** for Na^+ over K^+ and that of **3** and **5** for Li^+ over Na^+ is a direct consequence of this rigid cavity.

A comparison of the structure of **5** with that of **5** · LiCl highlights the conformational changes, which occur upon binding of LiCl. In **5**, three of the Cp* methyl groups point towards the center of the complex. In **5** · LiCl, the Cp* ligands are rotated by approximately 36° in order to reduce the steric interaction with the guest. But more importantly, the rhodium atoms move apart, and simultaneously the Cp* ligands slightly

flip back. Both changes make the cavity more accessible. Interestingly, there is a direct correlation between the M–M′ distance and the (averaged) angle between the plane defined by the π-ligand (arene or Cp*) and the plane defined by the three O-atoms for all complexes, which were investigated by X-ray diffraction (Figure 11 and Table 2).

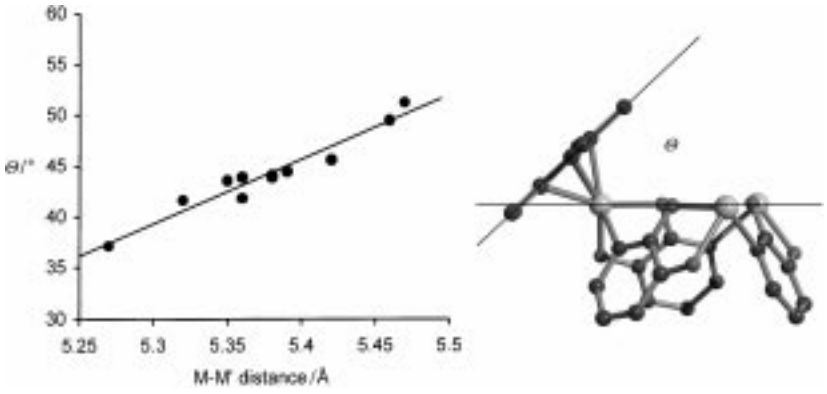

Figure 11. The crystallographic analysis reveals a linear correlation between the M–M′ distance and the angle Θ (for the data see Table 2). The ball and stick representation shows the molecular structure of **5**. Two of the three Cp* ligands as well as the hydrogen atoms are omitted for clarity.

Conclusion

Organometallic analogues of [12]crown-3 have been synthesized in a single-step self-assembly process by using half-sandwich complexes of ruthenium or rhodium in combination with 3-oxy-2-pyridonate ligands. The metallacrown ethers display a very high affinity for Na^+ and/or Li^+ with binding constants comparable to those of cryptands. The selectivity of the receptors was shown to depend on the nature of the organometallic fragment. By using sterically demanding π-ligands, we were able to obtain Li^+ selective ionophores. The molecular structures of the metallacrowns provide an explanation for both the exceptional affinity and selectivity. The receptors are highly preorganized with three oxygen atoms ideally positioned to bind small alkali metal ions. Surrounded by three π-ligands, the donor atoms are hardly solvated, and larger cations are efficiently blocked. The binding of alkali metal halides can be detected electrochemically: in the presence of guest molecules the first oxidation potential is shifted by more than 300 mV toward anodic potential. This behavior was utilized to develop a simple colorimetric test for Li^+ and Na^+. Given the fact that the synthetic access to this class of compounds is very easy, the aforementioned characteristics make them potentially well suited for applications in analytical chemistry.

Experimental Section

General: The synthesis of all complexes was performed under an atmosphere of dry dinitrogen with the use of standard Schlenk techniques. Compounds 3-acetamido-2-pyridone,[37] $[Cp^*RhCl_2]_2$,[38] $[(cymene)RuCl_2]_2$,[39] $[(C_6H_6)RuCl_2]_2$,[40] $[(C_6H_3Et_3)RuCl_2]_2$,[41] and $[(C_6Me_6)RuCl_2]_2$[39] were prepared according to literature procedures. Compounds 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (cryptand-2,1,1), 3-hydroxy-2-pyridone, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were purchased from Aldrich. Cs_2CO_3 (99%) was purchased from Fluka. The ^1H, ^{13}C, and ^7Li spectra were recorded on a JEOL EX400 or a GSX270 spectrometer with the use of the residual protonated solvents as internal standard (^1H, ^{13}C NMR) or LiCl in D_2O as the external standard. All spectra were recorded at room temperature. The molecular weights were determined with a JEOL MStation JMS700 mass spectrometer in the FAB mode (fast atom bombardment) with the use of *m*-nitrobenzyl alcohol (NBA) as the matrix or in the FD mode (field desorption).

$[(C_6H_6)Ru(C_5H_3NO_2)]_3$ (2): The compound $[(C_6H_6)RuCl_2]_2$ (500 mg, 1.00 mmol) was added to a solution of 3-hydroxy-2-pyridone (222 mg, 2.00 mmol) and Cs_2CO_3 (1.63 g, 5.00 mmol) in degassed water (5 mL). The mixture was stirred for 30 min at room temperature. The resulting orange precipitate was isolated by filtration and washed with water. Drying at 65 °C gave an orange powder (yield: 197 mg, 31%). Crystals were obtained by slow diffusion of pentane into a solution of **2** in chloroform.

IR (KBr): $\tilde{\nu} = 1631$ (br, m), 1597 (m), 1541 (s), 1452 cm^{-1} (br, s); ^1H NMR (270 MHz, $CDCl_3$): $\delta = 5.55$ (s, 18H; C_6H_6), 5.72 (dd, $^3J = 7$ Hz, $^3J = 6$ Hz, 3H; CH, pyridone), 6.20 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H; CH, pyridone), 6.70 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3H; CH, pyridone); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 81.85$ (C_6H_6), 110.74, 115.76, 132.97, 156.07, 170.80 (pyridone); $M_{calcd} = 865$; MS (FAB+): (*m*/*z*): 866 $[M+H]^+$; elemental analysis calcd (%) for $C_{33}H_{27}N_3O_6Ru_3 \cdot 5H_2O$: C 41.51, H 3.91, N 4.40; found C 41.57, H 4.24, N 4.32.

$[(C_6Me_6)Ru(C_5H_3NO_2)]_3$ (3): A suspension of $[(C_6Me_6)RuCl_2]_2$ (201 mg, 0.30 mmol), 3-hydroxy-2-pyridone (67 mg, 0.60 mmol), and Cs_2CO_3 (489 mg, 1.50 mmol) in degassed methanol (15 mL) was stirred for 2 h at room temperature. During that time a clear orange solution was obtained. After evaporation of 2/3 of the solvent in vacuo, the flask was placed in a freezer (−20 °C). After 24 h, orange crystals formed, which were washed with water and dried. Crystals were obtained by slow diffusion of pentane into a solution of **3** in dichloromethane (yield: 173 mg, 72%).

IR (KBr): $\tilde{\nu} = 1630$ (br, m), 1596 (m), 1539 (s), 1443 cm^{-1} (br, s); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.12$ (s, 45H; CH_3), 5.56 (dd, $^3J = 7$ Hz, $^3J = 7$ Hz, 3H; CH, pyridone), 5.97 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H; CH, pyridone), 6.33 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H; CH, pyridone); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 16.22$ (CH_3), 88.92 (C_6Me_6), 109.65, 112.70, 131.84, 158.36, 172.39 (pyridone); $M_{calcd} = 1117$; MS (FAB+): (*m*/*z*): 1118 $[M+H]^+$; elemental analysis calcd (%) for $C_{51}H_{63}N_3O_6Ru_3 \cdot CH_2Cl_2$: C 51.95, H 5.45, N 3.50; found C 52.04, H 5.35, N 3.49.

$[(C_6H_3Et_3)Ru(C_5H_3NO_2)]_3$ (4): A suspension of $[(C_6H_3Et_3)RuCl_2]_2$ (334 mg, 0.50 mmol), 3-hydroxy-2-pyridone (111 mg, 1.00 mmol), and Cs_2CO_3 (815 mg, 2.50 mmol) in degassed methanol (20 mL) was stirred for 1 h at room temperature. During that time, a clear orange solution was obtained. After evaporation of the solvent under reduced pressure the product was extracted with diethyl ether (2 × 40 mL). Evaporation of the solvent gave an orange powder which was crystallized from hot hexane (yield: 310 mg, 82%).

IR (KBr): $\tilde{\nu} = 1617$ (br, m), 1594 (m), 1538 (s), 1453 cm^{-1} (br, s); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.30$ (t, $^3J = 8$ Hz, 27H; CH_3), 2.46–2.58 (m, 18H; CH_2), 4.75 (s, 9H; $C_6H_3Et_3$), 5.61 (t, $^3J = 7$ Hz, 3H; CH, pyridone), 6.02 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H; CH, pyridone), 6.57 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H; CH, pyridone); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 14.52$ (CH_3), 26.49 (CH_2), 71.68 (CH, $C_6H_3Et_3$), 105.84 (C, $C_6H_3Et_3$), 109.72, 113.51, 132.48, 157.63, 171.41 (pyridone); $M_{calcd} = 1117$; MS (FAB+): (*m*/*z*): 1118 $[M+H]^+$; elemental analysis calcd (%) for $C_{51}H_{63}N_3O_6Ru_3 \cdot H_2O$: C 53.96, H 5.77, N 3.70; found C 54.07, H 5.98, N 3.58.

$[Cp^*Rh(C_5H_3NO_2)]_3$ (5): A suspension of $[Cp^*RhCl_2]_2$ (309 mg, 0.50 mmol), 3-hydroxy-2-pyridone (111 mg, 1.00 mmol), and Cs_2CO_3 (815 mg, 2.50 mmol) in degassed methanol (25 mL) was stirred for 1.5 h

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at room temperature. During that time a clear orange solution was obtained. After evaporation of the solvent under reduced pressure, the product was extracted with dichloromethane (40 mL). Addition of hexane (20 mL) and evaporation of the solvent gave an orange-brown powder (yield: 312 mg, 90 %). Crystals were obtained by vapor diffusion of pentane into a solution of **5** in toluene.

IR (KBr): $\tilde{\nu} = 1620$ (br, m), 1591 (m), 1535 (s), 1460 cm^{-1} (br, s); ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.72$ (s, 45 H; Cp*), 5.70 (dd, $^3J = 6$ Hz, $^3J = 7$ Hz, 3 H; CH, pyridine), 6.12 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone), 6.69 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 9.33$ (Cp*), 90.03 (d, $^1J_{RhC} = 9$ Hz, $C_5(CH_3)_5$), 109.90, 113.48, 131.39, 158.52, 170.84 (pyridone); $M_{calcd} = 1042$; MS (FD+): (*m*/*z*): 1042 $[M]^+$; elemental analysis calcd (%) for $C_{45}H_{54}N_3O_6Rh_3 \cdot CH_2Cl_2 \cdot H_2O$: C 48.27, H 5.11, N 3.67; found C 47.89, H 5.39, N 3.38.

[(cymene)Ru($C_5H_4NO_2$)Cl] (6): CsOH in methanol (0.40 mmol, 2 M) was added to a solution of $[(cymene)RuCl_2]_2$ (122 mg, 0.20 mmol) and 3-hydroxy-2-pyridone (44 mg, 0.40 mmol) in degassed methanol (10 mL). After stirring for 30 min at room temperature, the solvent was evaporated under reduced pressure. The product was extracted with dichloromethane (3×5 mL). Upon addition of hexane (25 mL) and evaporation of the solvent, an orange powder was obtained (yield: 140 mg, 80 %).

IR (KBr): $\tilde{\nu} = 1589$ (s, br), 1538 cm^{-1} (vs); ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 1.30 (d, $^3J = 7$ Hz, 6 H; $CH(CH_3)_2$), 2.26 (s, 3 H; CH_3, cymene), 2.88 (sept, $^3J = 7$ Hz, 1 H; $CH(CH_3)_2$), 5.27–5.31 (m, 2 H; CH, cymene), 5.49–5.52 (m, 2 H; CH, cymene), 6.15 (t, $^3J = 7$ Hz, 1 H; CH, pyridone), 6.53 (br s, 1 H; CH, pyridone), 6.68 (d, $^3J = 8$ Hz, 1 H; CH, pyridone), 11.35 (br s, 1 H; NH); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 18.63$, 22.43, 22.58 (CH_3), 31.19 ($CH(CH_3)_2$), 77.53, 78.72, 79.99 (CH, cymene), 95.19, 99.52 (C, cymene), 112.33, 117.86, 118.99, 160.31, 165.71 (pyridone); $M_{calcd} = 381$; MS (FAB+): (*m*/*z*): 382 $[M+H]^+$; elemental analysis calcd (%) for $C_{15}H_{18}ClNO_2Ru \cdot 0.5\,CHCl_3$: C 42.26, H 4.23, N 3.18; found C 42.74, H 3.48, N 3.15.

[(C_6Me_6)Ru($C_5H_4NO_2$)Cl] (7): CsOH in methanol (0.20 mmol, 2 M) was added to a suspension of $[(C_6Me_6)RuCl_2]_2$ (67 mg, 0.10 mmol) and 3-hydroxy-2-pyridone (22 mg, 0.20 mmol) in degassed methanol. The mixture was stirred for 1 h at room temperature. Subsequently, the suspension was warmed to 60 °C, and methanol was added until a clear solution was obtained. The solution was placed in a freezer (−20 °C). After 24 h, orange crystals formed, which were isolated and dried in vacuo (yield: 69 mg, 75 %).

IR (KBr): $\tilde{\nu} = 1597$ (br, s), 1537 cm^{-1} (vs); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.15$ (s, 15 H; CH_3), 6.14 (ddd, $^3J = 6$ Hz, $^3J = 8$ Hz, $^4J = 2$ Hz, 1 H; CH, pyridone), 6.64 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 1 H; CH, pyridone), 6.68 (dd, $^3J =$ 8 Hz, $^4J = 2$ Hz, 1 H; CH, pyridone), 10.98 (br s, 1 H; NH); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 15.66$ (CH_3), 88.64 (C_6Me_6), 112.33, 117.64, 118.74, 160.70, 165.88 (pyridone); $M_{calcd} = 409$; MS (FAB+): (*m*/*z*): 410 $[M+H]^+$; elemental analysis calcd (%) for $C_{17}H_{22}ClNO_2Ru \cdot 1.5\,CH_3OH$: C 48.63, H 6.18, N 3.07; found C 48.31, H 5.78, N 3.12.

[(cymene)Ru($C_7H_6N_2O_2$)]$_3$ (8): A suspension of $[(cymene)RuCl_2]_2$ (306 mg, 0.50 mmol), 3-acetamido-2-pyridone (152 mg, 1.00 mmol), and Cs_2CO_3 (815 mg, 2.50 mmol) in degassed methanol (25 mL) was stirred for 1 h at room temperature. During that time, a clear orange solution was obtained. After evaporation of the solvent under reduced pressure, the product was extracted with benzene (2×50 mL). Evaporation of the solvent gave an orange-brown powder (yield: 173 mg, 45 %). Crystals were obtained by vapor diffusion of pentane into a solution of **8** in benzene.

IR (KBr): $\tilde{\nu} = 1589$ (s), 1540 (m), 1457 (vs), 1439 cm^{-1} (s, sh); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.28$ (d, $^3J = 7$ Hz, 9 H; $CH(CH_3)_2$), 1.30 (d, $^3J =$ 7 Hz, 9 H; $CH(CH_3)_2$), 1.85 (s, 9 H; CH_3, cymene), 2.25 (s, 9 H; CH_3, pyridone), 2.71 (sept, $^3J = 7$ Hz, 3 H; $CH(CH_3)_2$), 5.41 (d, $^3J = 5$ Hz, 3 H; CH, cymene), 5.52 (d, $^3J = 6$ Hz, 3 H; CH, cymene), 5.59 (dd, $^3J = 6$ Hz, $^3J =$ 7 Hz, 3 H; CH, pyridone), 5.87 (dd, $^3J = 6$ Hz, $^4J = 1$ Hz, 3 H; CH, pyridone), 5.98 (d, $^3J = 5$ Hz, 3 H; CH, cymene), 6.28 (d, $^3J = 6$ Hz, 3 H; CH, cymene), 6.78 (dd, $^3J = 7$ Hz, $^4J = 1$ Hz, 3 H; CH, pyridone); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 18.04$, 20.92, 23.71, 25.08 (CH_3), 31.86 ($CH(CH_3)_2$), 82.69, 83.13, 87,98 (br) (CH, cymene), 97.43, 98.46 (C, cymene), 108.78, 125.26, 128.41, 139.52, 141.16, 172.96, 178.52 (pyridone); $M_{calcd} = 1156$; MS (FAB+): (*m*/*z*): 1157 $[M+H]^+$; elemental analysis calcd (%) for $C_{51}H_{60}N_6O_6Ru_3 \cdot 3H_2O \cdot 2C_6H_6$: C 55.37, H 5.75, N 6.15; found C 54.70, H 5.80, N 6.21.

General method for the synthesis of alkali metal halide adducts: The receptor and an excess of the respective alkali metal halide were dissolved in methanol (for **2**: $CHCl_3$/MeOH; 1:1). After evaporation of the solvent under reduced pressure, the MX (M = Li, Na; X = Cl, Br, I) complexes were extracted with $CDCl_3$ and examined by ^1H and ^7Li NMR spectroscopy. Evaporation of the solvent gave the products as orange powders.

1·NaI: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.29$ (d, $^3J = 7$ Hz, 9 H; $CH(CH_3)_2$), 1.32 (d, $^3J = 7$ Hz, 9 H; $CH(CH_3)_2$), 1.75 (s, 9 H; CH_3, cymene), 2.85 (sept, $^3J = 7$ Hz, 3 H; $CH(CH_3)_2$), 5.06 (d, $^3J = 6$ Hz, 3 H; CH, cymene), 5.78 (d, $^3J = 6$ Hz, 3 H; CH, cymene), 5.79 (d, $^3J = 6$ Hz, 3 H; CH, cymene), 5.84 (dd, $^3J = 7$ Hz, $^3J = 6$ Hz, 3 H; CH, pyridone), 6.30 (dd, $^3J = 7$ Hz, $^4J =$ 2 Hz, 3 H; CH, pyridone), 6.70 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone). Crystals were obtained by vapor diffusion of pentane into a solution of **1**·NaI in benzene.

2·LiCl: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.91$ (s, 18 H; C_6H_6), 5.91 (pt, $^3J =$ 7 Hz, 3 H; CH, pyridone), 6.39 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone), 6.77 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone); ^7Li NMR (155 MHz, $CDCl_3$): $\delta = -1.47$. Crystals were obtained by slow diffusion of pentane into a solution of **2**·LiCl in chloroform.

2·NaCl: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.81$ (s, 18 H; C_6H_6), 5.85 (dd, $^3J = 7$ Hz, $^3J = 6$ Hz, 3 H; CH, pyridone), 6.33 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone), 6.73 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone).

2·NaBr: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.82$ (s, 18 H; C_6H_6), 5.85 (dd, $^3J = 7$ Hz, $^3J = 6$ Hz, 3 H; CH, pyridone), 6.33 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone), 6.73 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone). Crystals were obtained by slow diffusion of pentane into a solution of **2**·NaBr in chloroform.

3·LiCl: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.15$ (s, 45 H; CH_3), 5.89 (dd, $^3J =$ 7 Hz, $^3J = 6$ Hz, 3 H; CH, pyridone), 6.31 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone), 6.36 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone); ^7Li NMR (155 MHz, $CDCl_3$): $\delta = -1.98$.

4·LiCl: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.25$ (t, $^3J = 5$ Hz, 27 H; CH_3), 2.50–2.55 (m, 9 H; CH_2), 2.88–2.91 (m, 9 H; CH_2), 5.29 (br s, 9 H; $C_6H_3Et_3$), 5.78 (dd, $^3J = 7$ Hz, $^3J = 6$ Hz, 3 H; CH, pyridone), 6.24 (dd, $^3J = 7$ Hz, $^4J =$ 2 Hz, 3 H; CH, pyridone), 6.64 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone); ^7Li NMR (155 MHz, $CDCl_3$): $\delta = -1.59$.

5·LiCl: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.73$ (s, 45 H; Cp*), 6.01 (dd, $^3J =$ 6 Hz, $^3J = 7$ Hz, 3 H; CH, pyridone), 6.39 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone), 6.73 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3 H; CH, pyridone); ^7Li NMR (155 MHz, $CDCl_3$): $\delta = -1.40$. Crystals were obtained by vapor diffusion of pentane into a solution of **5**·LiCl in toluene.

Competition experiments: An equimolar mixture of receptor A, receptor B, and LiCl (6 μmol each) in methanol (5 mL) was allowed to equilibrate for 1 h at 50 °C. After evaporation of the solvent, the resulting mixture was examined by ^1H NMR spectroscopy in $CDCl_3$. The amount of the free receptors and the corresponding LiCl adducts was determined by integration of suitable signals. In competition experiments between complex **3** and complex **5**, the solution in methanol was stirred at room temperature for 3 h. At elevated temperatures, mixing between the two receptors was observed, that is heterometallic trimers were formed. This was confirmed by mass spectrometry. For LiCl, stock solutions were employed.

In competition experiments between receptor **4** and cryptand-2,1,1, equimolar amounts were stirred in methanol with one equivalent of LiCl for 1.5 h at 50 °C. After evaporation of the solvent, half of the mixture was dissolved in CD_3OD, the other half in $CDCl_3$, and transferred into NMR tubes. The tubes were subsequently tempered for several hours (4–7 h) at 55 °C, and ^1H NMR spectra were recorded. This procedure was repeated until the relative amount of free and complexed receptor was constant.

Extraction experiments: A degassed mixture of LiCl dissolved in H_2O (2 M) and complex **4** dissolved in $CDCl_3$ (10 mM) was thoroughly stirred for 24 h. The relative amount of **4**·LiCl was then determined by ^1H NMR spectroscopy.

CV measurements: The voltammetric investigations were carried out on a BAS-100 B/W Electrochemical Analyzer, Bioanalytical Systems (West Lafayette, Indiana). Potentials were measured against the Ag/AgCl "Leek

Free" reference electrode, Cypress Systems, Inc. (Lawrence, Kansas), by using a glassy carbon working electrode (3 mm diameter) at a scan rate of 4015 mV sec^{-1}. The complexes **1**–**5** or the respective alkali metal halide adducts were dissolved in dry CH_3CN/CH_2Cl_2 (1:1) (ca. 5 mM) containing tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte (0.1 m) under a dinitrogen atmosphere.

X-ray structure analyses: The structures of complex **1**·NaI, **2**, **2**·LiCl, **2**·NaBr, **5**, **5**·LiCl, and **8** were determined with a Stoe IPDS instrument (Tables 4 and 5). The structure of complex **3** was determined with an Enraf-Nonius diffractometer. Structure solution was performed by direct methods by using SIR97,[42] SHELXS 97, or SHELXS 86.[43] Refinement: full-matrix least squares on F^2 (SHELXL 97, SHELXL 93).[43] For the hydrogen atoms,

Table 4. Crystallographic data for the receptors **2**, **3**, **5**, and **8**.

	2·H_2O·1.5 $CHCl_3$	**3**·CH_2Cl_2	**5**·2 $C_6H_5CH_3$	**8**·3 H_2O·2 C_6H_6
empirical formula	$C_{34.5}H_{30.5}Cl_{4.5}N_3O_7Ru_3$	$C_{52}H_{65}Cl_2N_3O_6Ru_3$	$C_{59}H_{70}N_3O_6Rh_3$	$C_{63}H_{78}N_6O_9Ru_3$
M_r [g mol^{-1}]	1061.87	1202.18	1225.92	1366.52
crystal size	0.35 × 0.20 × 0.03	0.13 × 0.33 × 0.43	0.30 × 0.13 × 0.07	0.25 × 0.20 × 0.18
crystal system	orthorhombic	triclinic	monoclinic	monoclinic
space group	*Pbca*	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a [Å]	17.5969(9)	10.026(3)	19.674(2)	10.9649(15)
b [Å]	14.2050(8)	12.9999(12)	9.3325(8)	22.518(2)
c [Å]	29.0465(19)	19.724(3)	29.419(3)	25.026(4)
α [°]	90	90.031(10)	90	90
β [°]	90	103.57(2)	95.816(13)	91.770(17)
γ [°]	90	91.757(15)	90	90
V [Å^3]	7260.5(7)	2497.8(8)	5373.9(9)	6176.1(14)
Z	8	2	4	4
ρ [g cm^{-3}]	1.943	1.598	1.515	1.470
T [K]	200(3)	295(2)	200(3)	200(3)
absorption coefficient [mm^{-1}]	1.617	1.054	0.964	0.784
Θ range [°]	1.82 to 24.05	2.56 to 23.97	1.65 to 24.06	1.63 to 24.09
index ranges	$-18 \rightarrow 20$, $-10 \rightarrow 16$, $-33 \rightarrow 33$	$-11 \rightarrow 0$, $-14 \rightarrow 14$, $-21 \rightarrow 22$	$-22 \rightarrow 22$, $-10 \rightarrow 10$, $-33 \rightarrow 33$	$-12 \rightarrow 12$, $-24 \rightarrow 25$, $-28 \rightarrow 28$
reflections collected	24504	8320	30263	35523
independent reflections	5592 ($R_{int} = 0.0536$)	7816 ($R_{int} = 0.0139$)	8445 ($R_{int} = 0.0420$)	9743 ($R_{int} = 0.0478$)
absorption correction	numerical	semiempirical	numerical	numerical
max. and min. transmission	0.9560 and 0.7378	0.9992 and 0.8249	0.9558 and 0.8443	0.9169 and 0.8658
data/restraints/parameters	5592/0/493	7816/42/642	6410/0/652	9743/15/712
goodness-of-fit on F^2	0.896	1.084	0.911	0.987
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0314$, $wR2 = 0.0618$	$R1 = 0.0305$, $wR2 = 0.0754$	$R1 = 0.0287$, $wR2 = 0.0615$	$R1 = 0.0317$, $wR2 = 0.0823$
R indices (all data)	$R1 = 0.0488$, $wR2 = 0.0651$	$R1 = 0.0367$, $wR2 = 0.0798$	$R1 = 0.0434$, $wR2 = 0.0646$	$R1 = 0.0432$, $wR2 = 0.0917$
largest diff. peak/hole [e Å^{-3}]	0.612/ − 0.603	0.378/ − 0.611	0.860/ − 0.509	0.899/ − 0.795

Table 5. Crystallographic data for the complexes **1**·NaI, **2**·NaBr, **2**·LiCl, and **5**·LiCl.

	1·NaI·C_6H_6	**2**·NaBr·$CHCl_3$	**2**·LiCl·$CHCl_3$	**5**·LiCl·H_2O·$C_6H_5CH_3$
empirical formula	$C_{51}H_{57}IN_3NaO_6Ru_3$	$C_{34}H_{28}BrCl_3N_3NaO_6Ru_3$	$C_{34}H_{28}Cl_4LiN_3O_6Ru_3$	$C_{52}H_{64}ClLiN_3O_7Ru_3$
M_r [g mol^{-1}]	1261.12	1087.06	1026.56	1188.68
crystal size	0.23 × 0.16 × 0.08	0.08 × 0.06 × 0.04	0.2 × 0.18 × 0.08	0.23 × 0.13 × 0.10
crystal system	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	11.9783(1)	10.0673(6)	10.0390(1)	10.9512(1)
b [Å]	12.4667(1)	14.4035(7)	14.0522(1)	12.7927(2)
c [Å]	17.3347(1)	25.4963(15)	25.4835(2)	20.4809(2)
α [°]	86.4679(4)	90	90	107.3951(7)
β [°]	78.3356(4)	100.807(7)	100.3306(4)	101.6208(7)
γ [°]	88.0359(3)	90	90	90.2617(4)
V [Å^3]	2529.69(3)	3631.5(4)	3536.68(5)	2675.48(6)
Z	2	4	4	2
ρ [g cm^{-3}]	1.656	1.988	1.928	1.475
T [K]	200(3)	200(3)	200(3)	200(3)
absorption coefficient [mm^{-1}]	1.553	2.614	1.617	0.936
Θ range [°]	1.20 to 21.97	2.06 to 26.01	1.62 to 27.51	1.07 to 23.00
index ranges	$-12 \rightarrow 12$, $-13 \rightarrow 13$, $-18 \rightarrow 18$	$-12 \rightarrow 12$, $-17 \rightarrow 17$, $-31 \rightarrow 31$	$-13 \rightarrow 13$, $-17 \rightarrow 18$, $-33 \rightarrow 33$	$-12 \rightarrow 12$, $-14 \rightarrow 14$, $-22 \rightarrow 22$
reflections collected	34753	25439	57347	24825
independent reflections	6178 ($R_{int} = 0.0366$)	7089 ($R_{int} = 0.1468$)	8111 ($R_{int} = 0.0772$)	7068 ($R_{int} = 0.0334$)
absorption correction	numerical	numerical	numerical	numerical
max. and min. transmission	0.8877 and 0.7244	0.9375 and 0.8562	0.8868 and 0.7499	0.9352 and 0.8742
data/restraints/parameters	6178/0/553	7089/0/443	8111/0/445	7068/3/566
goodness-of-fit on F^2	1.203	0.760	1.172	1.143
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0297$, $wR2 = 0.0945$	$R1 = 0.0518$, $wR2 = 0.0853$	$R1 = 0.0399$, $wR2 = 0.1009$	$R1 = 0.0416$, $wR2 = 0.1416$
R indices (all data)	$R1 = 0.0381$, $wR2 = 0.1276$	$R1 = 0.1369$, $wR2 = 0.1033$	$R1 = 0.0652$, $wR2 = 0.1291$	$R1 = 0.0559$, $wR2 = 0.1736$
largest diff. peak/hole [e Å^{-3}]	1.227/ − 1.127	1.521/ − 1.163	1.291/ − 1.479	1.955/ − 1.218

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a riding model was employed. Complex **3** co-crystallized with one disordered molecule of dichloromethane, for which a split position and restraints were employed. Complex **5** co-crystallized with two molecules of toluene, one of which was disordered and for which a split position was used. Complex **8** co-crystallized with two molecules of benzene and three molecules of water. Restraints were employed for one benzene molecule. Complex **1** · NaI co-crystallized with one molecule of benzene. Complex **2** · NaBr co-crystallized with one molecule of chloroform. The benzene ligands as well as the chloroform molecule were disordered, and split positions were used for the refinement. Complex **2** · LiCl co-crystallized with one molecule of chloroform. The benzene ligands were disordered, and split positions were used. Complex **5** · LiCl co-crystallized with one molecule of toluene and one molecule of water. Restraints were employed for the water molecule.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-157106 (**8**), CCDC-157107 (**5**), CCDC-157108 (**2** · NaBr), CCDC-157109 (**2**), CCDC-157110 (**1** · NaI), CCDC-157111 (**2** · LiCl), CCDC-157112 (**5** · LiCl), and CCDC-157113 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Computational details: The structures of all considered complexes were fully optimized in C_3 symmetry by using the hybrid density functional theory with the program package Gaussian 98.[44] For H, C, O, Li, and Na, a standard 6-31G(d,p) basis set was used, and quasirelativistic pseudopotentials (I: ECP46MWB, Br: ECP28MWB, Cl: ECP10MWB)[45] and (5s5p1d)/[3s3p1d]-DZ + P basis sets were utilized for the halogen atoms.[46] The computations were carried out at the DFT level by using the hybrid method B3LYP, which included a mixture of Hartree–Fock exchange with DFT exchange correlation. Becke's three parameter functional, in which the nonlocal correlation was provided by the LYP expression (Lee, Yang, Parr correlation functional), was used and was implemented in Gaussian 98. For a concise definition of the B3LYP functional see ref. [47]. Atomic charges, natural bond orbitals, and the intramolecular donor–acceptor energies were determined by using the NBO analysis.[48, 49] This data can be obtained from the authors on request.

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