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Self-assembled organometallic receptors for small ions

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Contents

Abstract

Trinuclear metallamacrocycles can be obtained by reactions of (arene)Ru, Cp*Rh and Cp*Ir complexes with pyridonate ligands. Using 3-oxy-pyridonate as the bridging ligand, organometallic analogues of 12-crown-3 are formed, which display an extremely high affinity and selectivity for lithium and sodium ions. In the presence of guest molecules, the redox-potential of the metallamacrocyclic hosts is shifted by more than 300 mV towards positive potential suggesting potential applications as chemosensors. The affinity of the metallacrown complexes is sufficient to allow the stabilization of molecular LiFHF and LiF. The fact that complexes of LiF can be isolated was used to construct a specific receptor for fluoride ions.

Keywords: Receptors; Halfsandwich complexes; LiFHF; LiF; Self-assembly

1. Introduction

In the field of transition metal based self-assembly, organometallic complexes are increasingly being used as building blocks. Carbonyl complexes of Re(I), for example, have successfully been employed for the construction of tri- and tetranuclear metallamacrocycles [1]. Halfsandwich complexes of Ru(II), Rh(III) and Ir(III) with arene or Cp* π-ligands have also received considerable attention. As starting materials, the commercially available—or easily accessible—chloro-bridged complexes $[(arene)RuCl_2]_2$ and $[Cp^*MCl_2]_2$ (M = Rh, Ir) are well suited. After abstraction of the halide ligands, three facial coordination sites are available for the coordination of neutral or anionic ligands. Over the last 10 years, macrocyclic structures containing halfsandwich complexes have been synthesized using bidentate ligands such as cyanide [2], cyanamide [3], diisocyano-compounds [4], and diamino-compounds [5], or tridentate ligands such as nucleobase derivatives [6] and amino acids [7]. In many cases, poly-cationic assemblies were obtained. We have introduced rigid dianionic ligands, in particular oxy-pyridonate ligands, which allow the formation of neutral, trinuclear assemblies (Scheme 1). This article gives an overview about the syntheses, the structures and the host guest chemistry of these metallamacrocycles.

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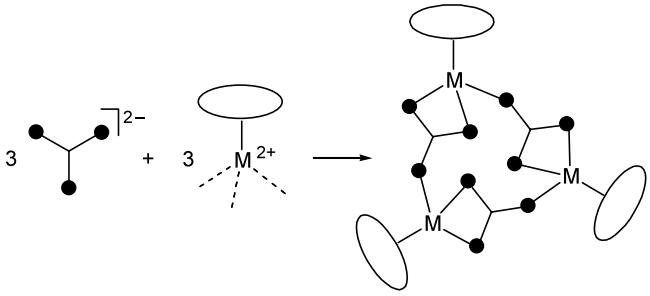


Scheme 1. Synthesis of trinuclear metallamacrocycles using dianionic, tridentate ligands in combination with halfsandwich complexes (M = Ru, Rh, Ir).

2. Syntheses and structures

2.1. Synthesis of trinuclear metallamacrocycles by self-assembly

The reaction depicted in Scheme 1 is very versatile since both the bridging ligand as well as the metal fragment can be varied. To start the self-assembly process, the chloro-bridged complexes $[(\pi\text{-ligand})MCl_2]_2$ (M = Ru, Rh, Ir) react with the protonated ligand in the presence of base. Using the 3-oxo-pyridonate ligand L1, macrocyclic complexes of the general formula $[(\pi\text{-ligand})M(L1)]_3$ have been obtained with various arene ligands (C_6H_6, C_6Me_6, 1,3,5-$C_6H_3Et_3$, cymene, $C_6H_5CO_2Et$) [8,9] and with Cp* ligands [8b,9,10] (Fig. 1). Trinuclear complexes are likewise formed with the bridging ligands L2 and L3 in combination with (cymene)Ru^{2+} (L2, L3) [8b,9–11] and Cp*Ir^{2+} fragments (L2) [11].

With few exceptions (e.g. π-ligand = C_6H_6), the macrocyclic complexes are well soluble in organic solvents such as benzene, chloroform and methanol. The ^{1}H-NMR spectra are quite characteristic. Due to the high symmetry of the complexes, only one set of signals is observed for the

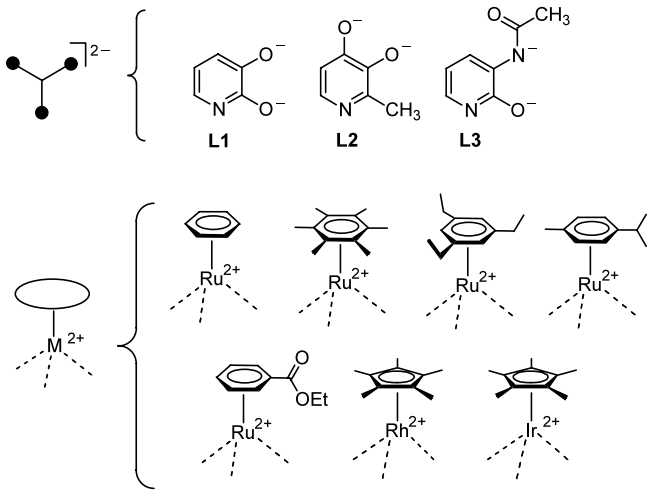


Fig. 1. Ligands and metal fragments, which allow the formation of trinuclear metallamacrocycles according to Scheme 1.

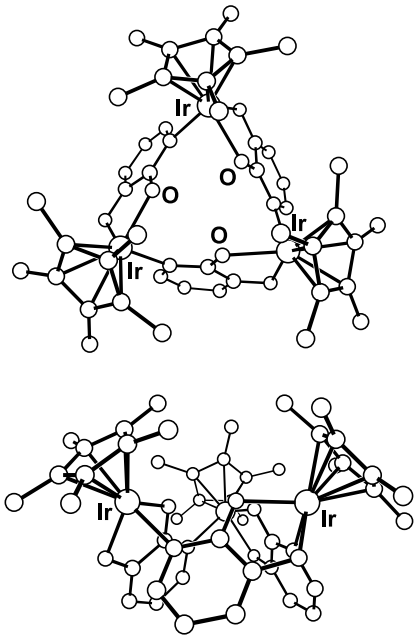


Fig. 2. Molecular structure of $[Cp^*Ir(L1)]_3$ in the crystal. Top: view along the pseudo C_3 axis; bottom: view from the side. The hydrogen atoms are not depicted.

bridging pyridonate ligands as well as for the π-ligands. For all (cymene)Ru complexes, two signals are observed for the methyl protons of the isopropyl side chain. This indicates that the methyl groups are diasterotopic. The metal centers are thus chiral and epimerization is slow compared to the NMR time scale. Since only one set of signals is observed, the self-assembly process is completely diastereoselective.

2.2. Structural characterization

The macrocyclic complexes were comprehensively studied by single crystal X-ray analysis [8–11]. The overall geometry of the assembly is dictated by the 'coordinate vectors' [12] of the bridging ligand L. With L1, slightly concave complexes are obtained (Fig. 2).

The metal centers in these complexes have the same absolute configuration and are between 5.27 and 5.46 Å apart from each other. L1 acts as a tridentate ligand, which bridges the metals by coordination via the oxo groups and the pyridine nitrogen atom. The 12-membered metallamacrocycles contain three oxygen atoms positioned in close proximity to each other. The complexes can thus be regarded as organometallic analogues of 12-crown-3.

Similar to what was found for L1, complexes with L2 show a (pseudo) C_3 symmetric geometry with three tetrahedral (cymene)Ru or Cp*Ir corners (Fig. 3). Again, the ligand is coordinated via the oxygen atoms and the ring nitrogen atom to the metal atoms. The planes defined by the heterocyclic ligand, however, are almost perpendicular to the plane defined by the metal atoms resulting in an expanded macrocycle with M···M distances of 7.24 Å.

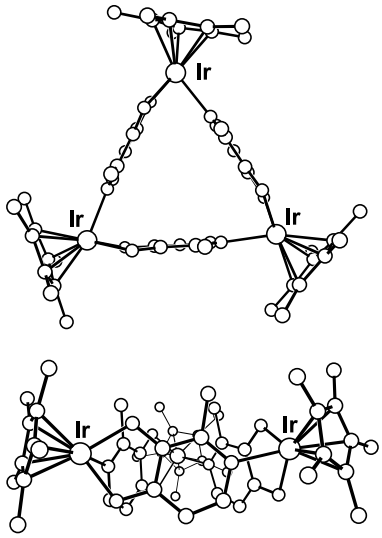


Fig. 3. Molecular structure of $[Cp^*Ir(L2)]_3$ in the crystal. Top: view along the C_3 axis; bottom: view from the side. The hydrogen atoms are not depicted.

Tetranuclear assemblies are not observed, neither in solution nor in the solid state, although the geometry around the metal atoms is favorable for the formation of rectangular complexes (e.g. Cl–Ir–(μ-Cl)=88.49° in $[Cp^*IrCl_2]_2$) [13]. To accommodate the entropically favored trinuclear geometry, the O,O′-chelates are coordinated in a slightly bent fashion. This is in contrast to that found for mononuclear complexes with oxy-pyridonate ligands [14].

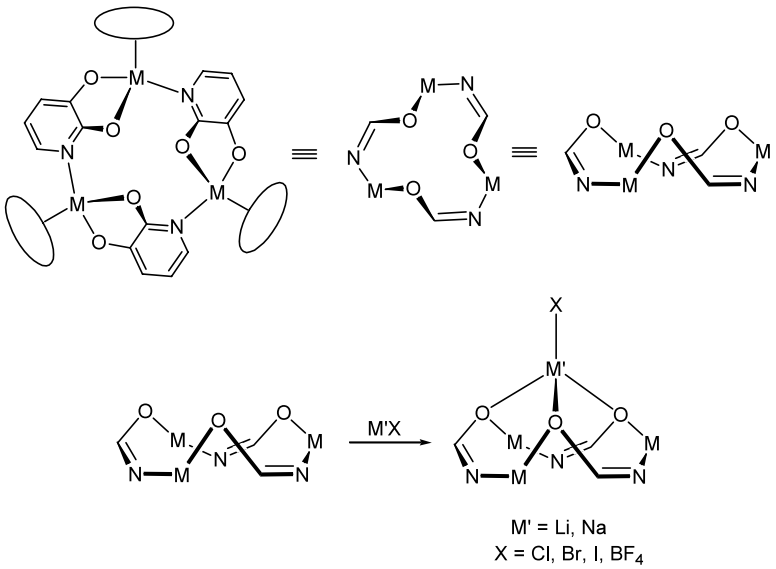
3. Host–guest chemistry

3.1. Selective receptors for lithium and sodium ions

As stated above, complexes of the general formula $[(\pi\text{-ligand})M(L1)]_3$ represent analogues of 12-crown-3. Metallacrown complexes were first reported in 1989 by Pecoraro and co-workers [15]. Today, structurally very diverse metallacrown complexes with ring sizes between 9 and 30 atoms are known [16,17]. Generally, they are obtained in self-assembly reactions using transition metal salts and suited multidentate ligands. The compounds $[(\pi\text{-ligand})M(L1)]_3$ represent the first *organometallic* crown complexes. Similar to their organic counterparts, metallacrown complexes are able to bind cationic guests such as alkali metal ions. So far, we have been able to isolate and structurally characterize adducts of $[(\pi\text{-ligand})M(L1)]_3$ with LiCl, $LiBF_4$, LiF and LiFHF (see Section 3.3), NaCl, NaBr and NaI [8–10]. In all cases, the metal ion M′ is bound to the three adjacent oxygen atoms of the receptor. The fourth coordination site is generally occupied by the anion X (Scheme 2, Fig. 5).

The coordination to guest molecules can easily be detected by ^{1}H-NMR spectroscopy: upon binding to lithium or sodium salts, the signals of the pyridonate ligands and the signals of the π-ligand are shifted towards lower field (Fig. 4). If the guest M′X is added in substoichiometric amounts, two sets of signals are observed indicating that the exchange of M′X is slow compared to the NMR time scale. This makes the quantification of adduct formation under different conditions very easy.

The stabilities of the host–guest complexes are remarkably high. If the adduct $[(\pi\text{-ligand})M(L1)]_3 \times M'X$ is dissolved in $CDCl_3$ ($c = 10$ mM), only the host–guest complex can be observed by ^{1}H-NMR spectroscopy. The association constant must therefore be higher than 10^5 l mol^{-1}. To quantify the stability we have performed competition experiments with various crown ethers and cryptands. These experiments have revealed that the association constants of the metallamacrocyclic receptors $[(\pi\text{-ligand})M(L1)]_3$ are significantly higher than those of crown ethers and similar to those of macrobicyclic ionophores such as 2,2,1-cryptand (for



Scheme 2. Organometallic complexes of the general formula $[(\pi\text{-ligand})M(L1)]_3$ as receptors for lithium and sodium salts.

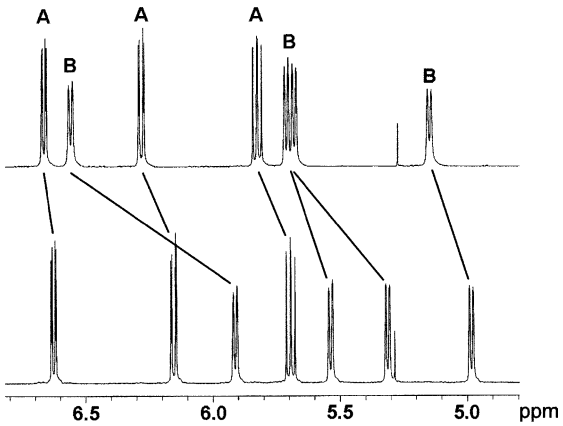


Fig. 4. Part of the ^{1}H-NMR spectrum ($CDCl_3$) of the receptor [(cymene)Ru(L1)]$_3$ (bottom) and the corresponding NaCl adduct (top). The signals of the cymene π-ligand are denoted with 'B', the signals of the bridging pyridonate ligand L1 with 'A'.

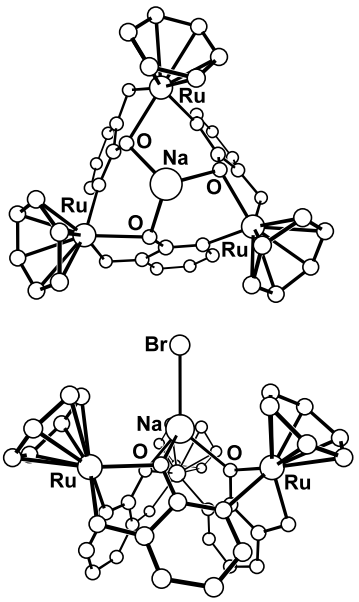


Fig. 5. Molecular structure of the receptor [(C_6H_6)Ru(L1)]$_3$ with a NaBr guest molecule in the crystal. Top: view along the pseudo C_3 axis, the bromine atom is not shown; bottom: view from the side. The hydrogen atoms are not depicted.

NaCl adducts) [8a] and 2,1,1-cryptand (for LiCl adducts) [8b].

As usual, lower values are found in more polar solvents. When the NaX adducts are dissolved in CD_3OD, signals for the free and the complexed receptors [(π-ligand)M(L1)]$_3$ can be observed by ^{1}H-NMR spectroscopy. Thus, a direct calculation of K_a is possible. For the halide salts, values between $K_a = 1.1\pm0.5\ 10^2$ l mol^{-1} (X = Cl, (π-ligand)M = (C_6H_6)Ru) and $K_a = 3.5\pm0.5\ 10^3$ l mol^{-1} (X = Cl, (π-ligand)M = (cymene)Ru) are obtained [8b]. The stability of the Na^+ complexes depends on the nature of the anion: NaI adducts show lower K_a values than NaCl adducts. The Li^+ adducts of the receptors [(π-ligand)M(L1)]$_3$ generally display a higher stability than the corresponding Na^+ adducts: even in polar solvents such as methanol, only the host–guest complex can be detected by NMR for [(π-ligand)M(L1)]$_3$ × LiCl complexes indicating a K_a value of $> 10^5$ l mol^{-1}.

The surprisingly high stability of the LiX and NaX complexes can be attributed to several facts: (a) the receptors are very rigid and ideally preorganized to bind lithium or sodium ions. Upon binding of guest molecules, the bond length and angles change only slightly. (b) The salts are bound as an ion pair which is energetically very favorable in organic solvents such as chloroform. (c) The energetic costs for the desolvation of the receptors is very low because a maximum of one water molecule can fit inside the binding cavity.

The receptors [(π-ligand)M(L1)]$_3$ not only show a very high affinity, they are also very selective. Li^+ adducts are formed with all receptors. Na^+ adducts, however, only for (π-ligand)M = (C_6H_6)Ru, (cymene)Ru and $(C_6H_5CO_2Et)$Ru and K^+ adducts have not been observed at all. The pronounced selectivity can be explained by the geometry of the metallacrown complexes: the π-ligands form the walls of a rather rigid binding cavity. For small π-ligands such as benzene, sodium ions are able to enter. Larger π-ligands such as hexamethyl-benzene, on the other hand, efficiently block the binding site (Fig. 6) and Li^+ specific receptors are obtained.

The host–guest chemistry of the ruthenium complex [$(C_6H_5CO_2Et)$Ru(L1)]$_3$ proved to be of special interest. Although this receptor is principally able to bind Na^+ ions, it shows an outstanding affinity and selectivity for Li^+ salts

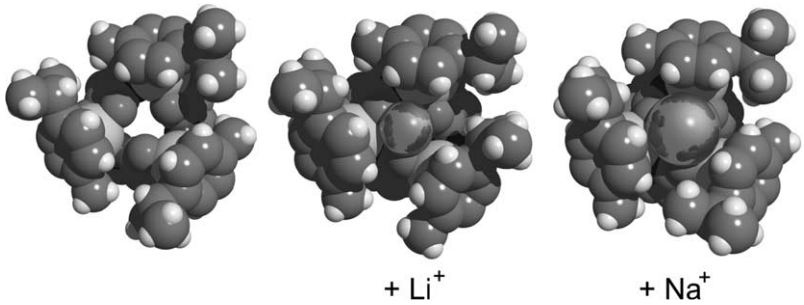
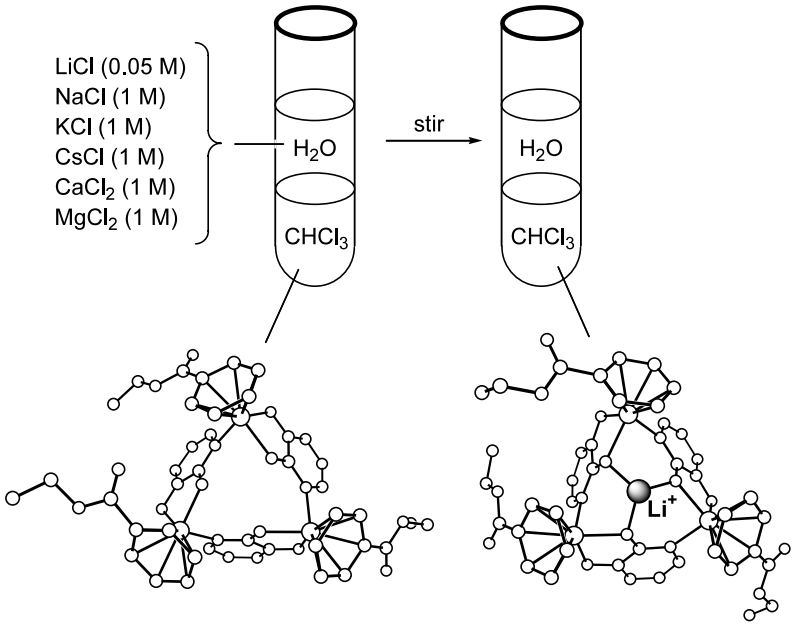


Fig. 6. Space filling representation of the molecular structure of [(cymene)Ru(L1)]$_3$ (left) and the corresponding LiCl (middle) and NaCl adduct (right) in the crystal. The cymene π-ligands enclose the binding site and efficiently block the formation of K^+ complexes. The chlorine atoms are not depicted.



Scheme 3. Selective extraction of LiCl from an aqueous solution containing a large excess of alkali and earth alkaline metal salts using the receptor $[(C_6H_5CO_2Et)Ru(L1)]_3$.

[9]. This is indicated by the following experiment: if an aqueous solution containing LiCl (50 mM) together with a large excess of NaCl, KCl, CsCl, $MgCl_2$ and $CaCl_2$ (1 M each) is shaken with a chloroform solution of this receptor, the exclusive and quantitative extraction of LiCl is observed (Scheme 3). This is remarkable because of two things. First, the extraction of LiCl from water is in principle a very difficult thing to accomplish due to the high enthalpy of hydration of Li^+ (-521 kJ mol^{-1}) and Cl^- (-363 kJ mol^{-1}) [18]. Second, the enthalpy of hydration of the other alkali metal ions is much smaller. The exclusive formation of the LiCl adduct is therefore indicative of an extremely high selectivity.

In this context, it should be mentioned that lithium salts such as Li_2CO_3 are among the most frequently used drugs for the treatment of manic depression [19]. Due to its narrow therapeutic range, the Li^+ concentration in the blood of the patients needs to be controlled on a regular basis. Since blood has a relative high concentration of Na^+ as compared to Li^+, the utilization of chemosensors has so far shown only very limited success. The receptor $[(C_6H_5CO_2Et)Ru(L1)]_3$ with its high affinity and selectivity for Li^+ is therefore of interest and attempts to construct a functional chemosensor are currently being perused in our laboratory.

3.2. Electrochemical behavior

For potential analytical applications, the possibility to transduce the binding of guest molecules into some kind of signal output is of central importance. We have investigated the electrochemical behavior of our receptors by cyclic voltammetry. For the free host compounds, three irreversible oxidations are observed. In the presence of guest molecules M′X, the peak potential for the first oxidation is shifted by more than 300 mV towards positive potential (Fig. 7). A shift of this magnitude is large compared to that found for other redox-responsive ionophores [20]. The metallamacrocyclic receptors $[(\pi\text{-ligand})M(L1)]_3$ can therefore be used to detect Li^+ and Na^+ ions electrochemically, a prerequisite for an amperometric molecular sensor device.

The fact that the host–guest complex is more difficult to oxidize was used to develop a simple test for Li^+ and Na^+ ions [8b]. The basic idea was that an oxidation reagent with a suitable redox potential should be able to selectively oxidize the uncomplexed receptor. 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 proved to be ideally suited. If a yellow solution of $[(cymene)Ru(L1)]_3$ in chloroform is treated with DDQ a

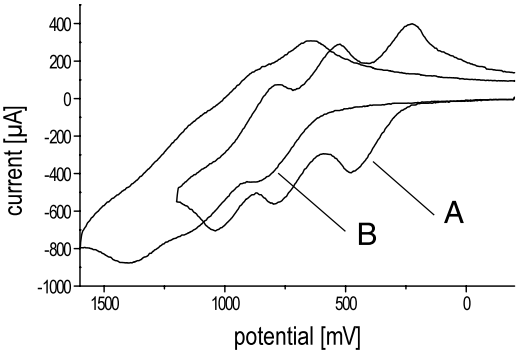


Fig. 7. Cyclic voltammograms of the receptor $[(C_6H_3Et_3)Ru(L1)]_3$ ('A') and the corresponding LiCl complex ('B') in CH_2Cl_2/CH_3CN (1:1) measured against a Ag/AgCl reference electrode. Upon complexation of LiCl, a pronounced shift of the first peak potential towards anodic potential is observed.

dark brown solution is immediately obtained. The respective Li^+ and Na^+ complexes show only slight color changes under otherwise identical conditions. If the same reaction is carried out in a mixture of methanol and chloroform, even the Na^+ and Li^+ complexes can be distinguished.

3.3. Stabilization of LiF and LiFHF

The high affinity of the receptors for Li^+ prompted us to investigate whether complexes of molecular LiF can be obtained. The stabilization of molecular LiF represents a challenging task due to the very high lattice energy of this salt [21]. In fact, complexes of molecular LiF are virtually unknown. Some compounds with Li···F contacts have been described [22], but here the fluoride atom is either coordinatively bound to very strong Lewis acids (e.g. to Ti^{4+}) [23] or covalently bound to other atoms (e.g. in PF_6^- salts). A similar situation is found for the less common but theoretically interesting salt LiFHF. Again, a very high lattice energy has been determined [24].

We have been able to stabilize and structurally characterize complexes of molecular LiF and LiFHF using the metallacrowns [(π-ligand)M(L1)]$_3$ ((π-ligand)M = (cymene)Ru, Cp*Rh and Cp*Ir) [25]. Due to the low solubility of LiF and LiFHF, the molecules have to be prepared in situ. Therefore, we have first synthesized the lithium tetrafluoroborate adducts [(π-ligand)M(L1)]$_3$ × $LiBF_4$ which were subsequently treated with KF, KFHF or Et_4NFHF. After extraction with benzene, the LiF and LiFHF complexes were obtained in pure form.

Evidence for successful anion exchange is provided by the ^{7}Li- and ^{19}F-NMR spectra. The ^{7}Li-NMR spectra of the LiF complexes show doublets with $^1J_{LiF}$ coupling constants between 95 and 101 Hz. These values are large compared to what is found for other compounds with Li···F contacts [22]. The ^{19}F-NMR spectra show the corresponding quartets. A more complicated behavior is observed for the LiFHF complexes. For [Cp*Ir(L1)]$_3$ × LiFHF, two signals are observed in the ^{19}F-NMR spectrum (Fig. 8). The splitting indicates that the acidic difluoride proton is only coupled to the distal fluorine atom ($^1J_{HF}$ = 324 Hz). This points to a highly asymmetric hydrogen bond, contrary to what is observed for the free hydrogen difluoride anion [26]. The ^{19}F-NMR spectrum of [(cymene)Ru(L1)]$_3$ × LiFHF, on the other hand, shows a broad singlet at room temperature. At −60 °C, a spectrum comparable to that of [Cp*Ir(L1)]$_3$ × LiFHF with two chemically distinct fluoride atoms is observed. The underlying dynamic process is most likely an intramolecular exchange between the distal and the proximal fluorine, presumably via a penta-coordinated lithium ion. The fact that this exchange is only observed for the LiFHF complex of the receptor [(cymene)Ru(L1)]$_3$ can be explained by the reduced steric bulk of the cymene ligands as compared to the Cp* ligands.

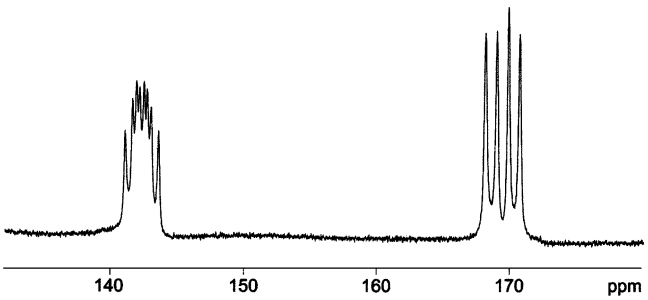


Fig. 8. ^{19}F-NMR spectrum of [Cp*Ir(L1)]$_3$ × LiFHF in C_6D_6.

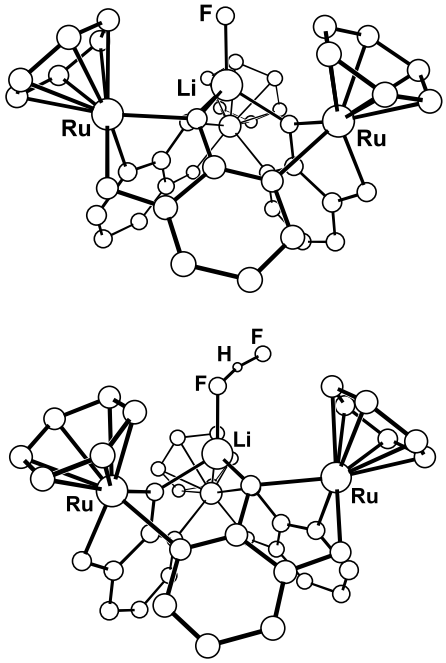
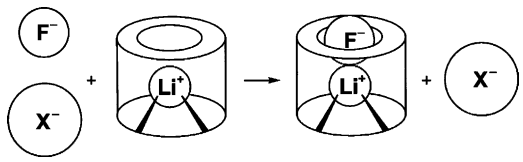


Fig. 9. Molecular structure of the LiF (top) and the LiFHF (bottom) complex of receptor [(cymene)Ru(L1)]$_3$ in the crystal. The cymene side chains and all hydrogen atoms but the difluoride proton are omitted for clarity.

Several LiF and LiFHF complexes were characterized by single crystal X-ray analysis (Fig. 9). As expected, the lithium cation is coordinated to the three oxygen atoms of the receptors. The fourth coordination site is occupied either by the fluoride or the hydrogen difluoride anion. For the LiF complexes, Li–F bond length between 1.77 and 1.81 Å are observed. These values are among the smallest Li···F distances reported so far [22] highlighting the unique situation of monomolecular LiF inside these macrocyclic hosts. In crystalline LiF, for comparison, a Li···F distance of 2.009 Å is observed [27]. The difluoride anions are coordinated in a bent fashion to the lithium ion (Li–F–F = 123–159°) (Fig. 9). The F···F distances observed (2.25–2.30 Å) are similar to those found for simple hydrogen difluoride salts in the crystal (2.24–2.28 Å).

3.4. A selective receptor for fluoride

Since the coordination of ion pairs to [(π-ligand)M(L1)]$_3$ receptors is energetically very favored, the possibility to use



Scheme 4. Schematic representation of a specific fluoride receptor based on a Li^+ containing metallamacrocycle.

complexes of this kind as specific fluoride receptors was investigated [10]. The basic idea is schematically shown in Scheme 4. A lithium ion, which serves as a binding site, is coordinated inside a [(π-ligand)M(L1)]$_3$ receptor. The accessibility of the Li^+ center is controlled by the steric requirements of the π-ligand. If large ligands are employed, only the small fluoride anion is able to enter the cavity whereas larger anions are efficiently blocked. Since the radius of the fluoride ion is significantly shorter than that of most other anions [28], a highly specific receptor is obtained.

To realize this concept, the complex [Cp*Ir(L1)]$_3$ × $LiBF_4$ appeared to be ideally suited. NMR data shows that in solution ($CDCl_3$/CD_3CN, 2:1) the weakly bound BF_4^- ion is not coordinated to the lithium ion. If Bu_4NF is added to this solution, signals of the ion-paired complex [Cp*Ir(L1)]$_3$ × LiF are immediately observed by ^{19}F- and ^{7}Li-NMR spectroscopy. The LiF complex is even formed in the presence of a large excess of other anions X ($X^- = Cl^-$, Br^-, I^-, NO_3^-) indicating a fluoride–X^- selectivity of higher than 10^3.

The structure of [Cp*Ir(L1)]$_3$ × LiF in the crystal gives an explanation for this selectivity (Fig. 10). The fluoride ion is positioned at the opening of the cavity, closely surrounded by the three Cp* ligands. As a result four very short CH···F contacts between the Cp* ligands and F^- can be observed (CH···F = 2.15–2.28 Å). This very tight encapsulation of the fluoride ion is expected to contribute to the overall stability of the host–guest complex and prevents the coordination of larger anions.

When a solution of the complex [Cp*Ir(L1)]$_3$ × $LiBF_4$ in $CHCl_3$/CH_3CN (2:1) is investigated by differential pulse voltammetry, the peak potential for the first oxidation can be observed at 890 (±3) mV (against Ag/AgCl). Upon addition of five equivalents of F^- the complex is significantly easier to oxidize ($\Delta E = -203$ mV). A possible explanation for this shift is the reduced electron withdrawing character of the ion-paired LiF guest compared to that of the solvated lithium ion. In agreement with the NMR studies described above, only small changes are observed upon addition of Cl^-, Br^-, NO_3^-, HSO_4^- or ClO_4^- salts ($\Delta E < 24$ mV). Similar results are obtained in solutions containing methanol. The complex [Cp*Ir(L1)]$_3$ × $LiBF_4$ is therefore a highly selective chemosensor which allows the detection of fluoride anion by electrochemical means, even in protic solvents.

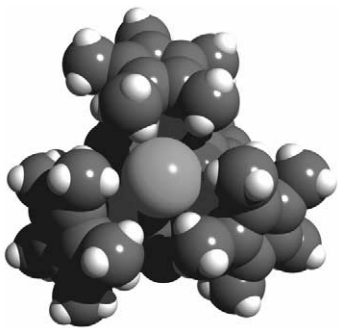


Fig. 10. Space filling representation of the molecular structure of [Cp*Ir(L1)]$_3$ × LiF in the crystal (view along the pseudo C_3 axis). The fluoride anion is tightly encapsulated by the Cp* ligands.

4. Conclusions

There is considerable interest in synthetic receptors with high affinity and selectivity. Current approaches towards this goal are often accompanied with substantial synthetic efforts. We have synthesized new receptors for small cations and anions by self-assembly of organometallic complexes. Compared to other synthetic ionophores, our approach offers major advantages: (a) the synthesis can be accomplished in one step using simple starting materials; (b) the presence of guest molecules can be detected electrochemically; (c) due to a very high degree of preorganization excellent affinities and selectivities are observed.

The modular nature of our assemblies makes it easy to incorporate structural variations. Preliminary results in our group have shown that many other ligands and metal fragments can be used to construct receptors with related geometries. We are thus able to modulate the affinity, selectivity and redox-properties in a controlled fashion. For the optimization of the receptor properties, it should also be possible to employ combinatorial methods. Given the exceptional performance of these types of receptors when compared to classical ionophores such as crown ethers and cryptands, various applications can be envisioned.

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