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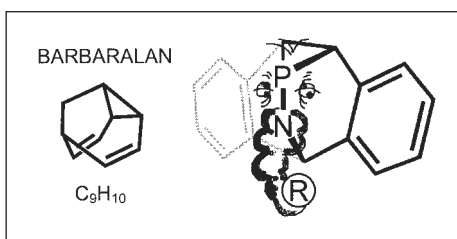


Fig. 2. Structure of barbaralane, C_9H_{10} , and BABAR-Phos the 'elephant'.

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Abstract: The molecular forms of LiF , LiFHF and Na_2SiF_6 have been stabilized using trinuclear metallamacrocyclic complexes of (cymene) Ru^{II} , $(\text{Cp}^*)\text{Rh}^{\text{III}}$ and $(\text{Cp}^*)\text{Ir}^{\text{III}}$ as specific receptors. The host-guest complexes were characterized by NMR spectroscopy and single crystal X-ray diffraction. Based on these results, a highly selective chemosensor for fluoride anions has been developed.

Keywords: Chemosensor · Fluoride · Lithium · Metallamacrocyclic · Sodium · Stabilization

1. Introduction

Recently, we have investigated the self-assembly of (cymene) Ru^{II} , $(\text{Cp}^*)\text{Rh}^{\text{III}}$ and $(\text{Cp}^*)\text{Ir}^{\text{III}}$ complexes using 3-hydroxy-2-pyridone as the bridging ligand [1–3]. Trinuclear metallamacrocyclics were obtained

in all cases. They possess three oxygen donor atoms positioned in close proximity to each other and can thus be considered as organometallic analogues of 12-crown-3 (Scheme). The metallacrown complexes were attested to be powerful ionophores with outstanding affinities toward Na^+

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even under 5 atm. of pure oxygen in the solid state. In accordance with the results from the calorimetry experiments cited above [6], in solution the complexes **12a** are rather labile and the *i*Pr-BABAR^{Ph}-Phos ligands are quantitatively displaced when stronger ligands such as PPh₃ or P(OMe)₃ are added. Interestingly, while we could observe complexes with a heteroleptic coordination sphere when [PtMe₂(*i*Pr-BABAR)₂] was reacted with phosphanes, PR₃, comparable complexes, *i.e.* [RhCl(*i*Pr-BABAR^{Ph})_{3-x}(PR₃)_x], were not observed. Only the homoleptic complexes **12a** beside [RhCl(PR₃)_x] (*x* = 2,3) and free *i*Pr-BABAR^{Ph} were detected. This finding together with the observation that in the syntheses of rhodium(I) BABAR-phos complexes frequently the per-substituted complexes [Rh(BABAR-Phos)₄]⁺ or [RhCl(BABAR-Phos)₃] are formed even when a less than stoichiometric amount of ligand is used, leads us to suspect that additional van-der-Waals interactions within the ligand sphere augment the stability of the products. This aspect as well as catalytic reactions with the BABAR-Phos compounds described here are under current investigation.

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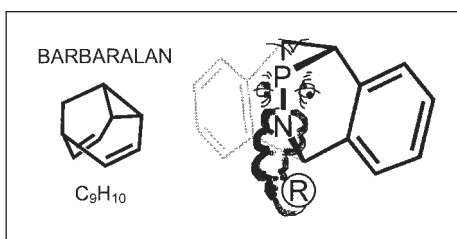


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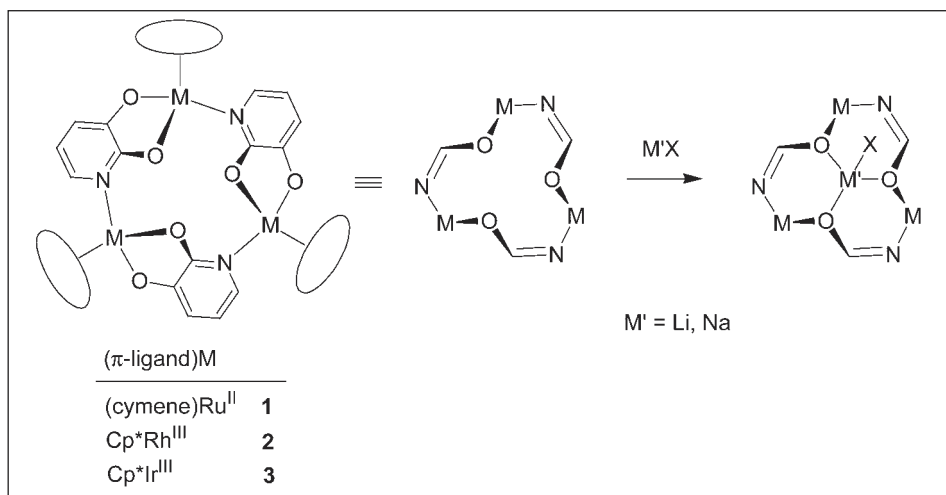
in all cases. They possess three oxygen donor atoms positioned in close proximity to each other and can thus be considered as organometallic analogues of 12-crown-3 (Scheme). The metallacrown complexes were attested to be powerful ionophores with outstanding affinities toward Na⁺

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and/or Li^+ . In terms of binding constants, they are even able to match cryptands. The selectivity of these receptors is controlled by the steric demand of the π -ligand. Whereas the (cymene) Ru^{II} complex **1** binds both Li^+ and Na^+ , the $(\text{Cp}^*)\text{Rh}^{\text{III}}$ and $(\text{Cp}^*)\text{Ir}^{\text{III}}$ complexes **2** and **3** bind exclusively Li^+ . Crystallographic analyses and NMR spectroscopic data suggest that the guest molecule is bound as an ion pair. All these features have led us to explore the utilization of these metallamacrocycles to stabilize the molecular forms of unusual salts such as LiF , LiFHF , and Na_2SiF_6 [4][5]. Prior to our work, complexes of these salts had not been described, which is not surprising bearing in mind their extremely large lattice energy. In extension of this work, we have also investigated the construction of a highly selective chemosensor for fluoride anions [6].

2. Stabilization of Molecular LiF and LiFHF [4]

Due to the very low solubility of LiF and LiFHF , complexes of these salts were prepared *in situ*. For this purpose, the LiBF_4 adducts of **1**, **2**, and **3** were first synthesized. The weakly bound tetrafluoroborate anion was subsequently exchanged either by F^- or FHF^- in a salt metathesis reaction. The successful anion exchange was established by ^7Li and ^{19}F NMR spectroscopy. The ^7Li NMR spectra of the LiF complexes display a doublet due to the coupling to the adjacent ^{19}F atom and the ^{19}F NMR spectra show the corresponding quartet. The observed coupling constants are very large and range from 95 to 101 Hz. For the LiFHF adducts, a more intricate situation was noticed. The ^{19}F NMR spectra of **2** • LiFHF and **3** • LiFHF display two resonances assigned to the proximal and the distal fluorine, respectively (Fig. 1b). It was



Scheme. Self-assembled organometallic metallamacrocycles as specific receptors for alkali metal salts.

shown that the acidic proton is only coupled to the distal fluorine ($^1J_{\text{HFd}} = 317$ and 324 Hz), which points to a highly asymmetric hydrogen bond. The ^{19}F NMR spectrum of **1** • LiFHF , on the other hand, displays a broad resonance at room temperature which only upon cooling splits into two different signals. This indicates an intramolecular exchange between the proximal and distal fluorine, presumably *via* a pentacoordinated lithium ion. A fluxional process of this kind was not noticed for **2** • LiFHF and **3** • LiFHF because of the presence of the more sterically demanding Cp^* ligands. Single crystal X-ray analyses were carried out for **1** • LiF , **2** • LiF , **3** • LiF , **1** • LiFHF and **3** • LiFHF . In all cases, the lithium ion is coordinated to three adjacent oxygen donor atoms and the fourth coordination site is occupied by F^- or FHF^- (Fig. 1a). The $\text{Li}-\text{F}$ bonds are very short ($\text{Li}-\text{F} = 1.77\text{--}1.81$ Å). In crystalline LiF , for example, a $\text{Li}-\text{F}$ distance of 2.009 Å is found. For the LiFHF complexes, the hydrogen difluoride anion is bound in a bent fashion *via* one fluorine atom to the lithium ion.

3. Encapsulation of Molecular Na_2SiF_6 [5]

Because of the low solubility of Na_2SiF_6 , a similar procedure as described above was used. Thus, the NaBF_4 adduct of **1** was first synthesized and the BF_4^- anion was then exchanged to form the Na_2SiF_6 complex **4**. The latter was characterized by NMR spectroscopy and single crystal X-ray analysis. In the ^1H , ^{13}C and ^{19}F NMR spectra of **4**, two sets of signals are observed, the relative ratio of which is 7:3. They are attributed to the two diastereoisomers formed upon complexation of Na_2SiF_6 by two *chiral* metallamacrocycles, which indicates that there is a chiral recognition between the two metallamacrocycles. The molecular structure of complex **4** in the crystal shows a SiF_6^{2-} anion coordinated *via* three fluorine atoms to the two respective sodium ions (Fig. 2). The latter are bound to the three adjacent oxygen atoms of the metallamacrocycles.

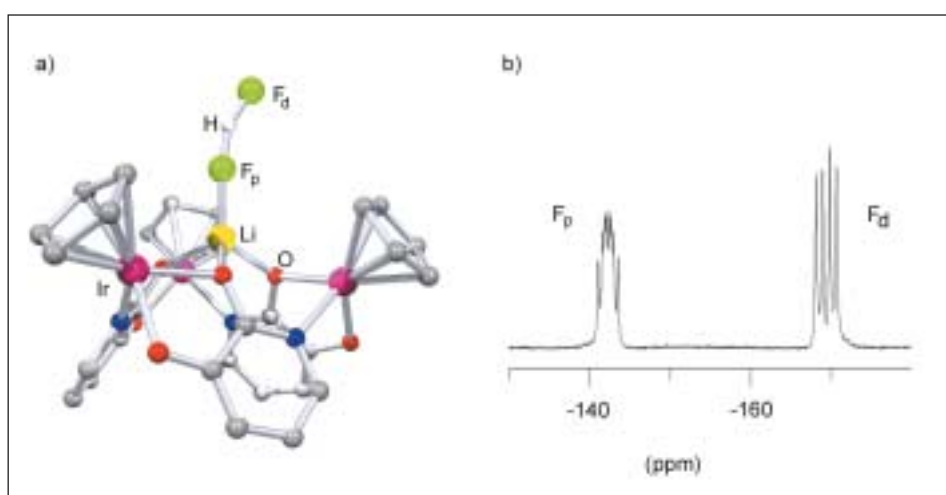


Fig. 1. a) Ball and stick representation of the molecular structure of **3** • LiFHF in the crystal. The hydrogen atoms and the side chains of the aromatic π -ligand are not shown for clarity; b) ^{19}F NMR spectrum of **3** • LiFHF in C_6D_6 . F_p and F_d are assigned to the proximal and the distal fluorine atom, respectively.

4. Fluoride Anions Recognition and Sensing [6]

The ability of the receptors **1–3** to stabilize molecular LiF led us to explore the possibility to construct a highly selective receptor for fluoride anions. For this purpose, receptor **3** seemed to be ideally suited. Its binding site is well shielded by the sterically demanding Cp* ligands. Consequently, only small ions such as the fluoride anion should be able to coordinate to a lithium ion bound inside the receptor (Fig. 3a). In order to test this, the adduct **3** • LiBF₄ was synthesized. This complex shows solvent-separated Li⁺ and BF₄⁻ ions in solution. The ability of this complex to act as a specific receptor for the fluoride anion was tested in a series of competition experiments. When **3** • LiBF₄ was dissolved in CDCl₃/CD₃CN (2:1) containing fluoride anions and a large excess of competing anions X⁻ (X⁻ = Cl⁻, Br⁻, I⁻, NO₃⁻; receptor/F⁻/X⁻ 1:2:100), only the presence of the fluoride adduct **3** • LiF was detected by NMR spectroscopy. This indicates a fluoride/X⁻ selectivity of at least 1.6 × 10³. Based on these promising results, differential pulse voltammetry experiments were carried out to investigate if the binding of the fluoride anion could be detected electrochemically. The peak potential for the first oxidation of the Li⁺ complex in CHCl₃/CH₃CN (2:1) was observed at 890 mV (against Ag/AgCl). Upon addition of F⁻, a difference of 203 mV was recorded, whereas upon addition of other anions (Cl⁻, Br⁻, NO₃⁻, HSO₄⁻ or ClO₄⁻) only small changes were observed (Fig. 3b). Similar results were obtained in solutions containing methanol. This is of special interest since most fluoride receptors do not work in protic solvents because of the high solvation energy of the fluoride anion.

5. Conclusion and Outlook

Complexes of molecular LiF, LiFHF, and Na₂SiF₆ were synthesized using the trimeric metallamacrocycles **1**, **2**, and **3** as receptors. Based on these results, it was possible to build a selective chemosensor, which permits the detection of fluoride anions electrochemically, even in protic solvents. Current efforts are devoted to investigate the ability of these metallamacrocycles to act as stabilizing hosts for other unusual guest molecules such as NaF or NaFHF.

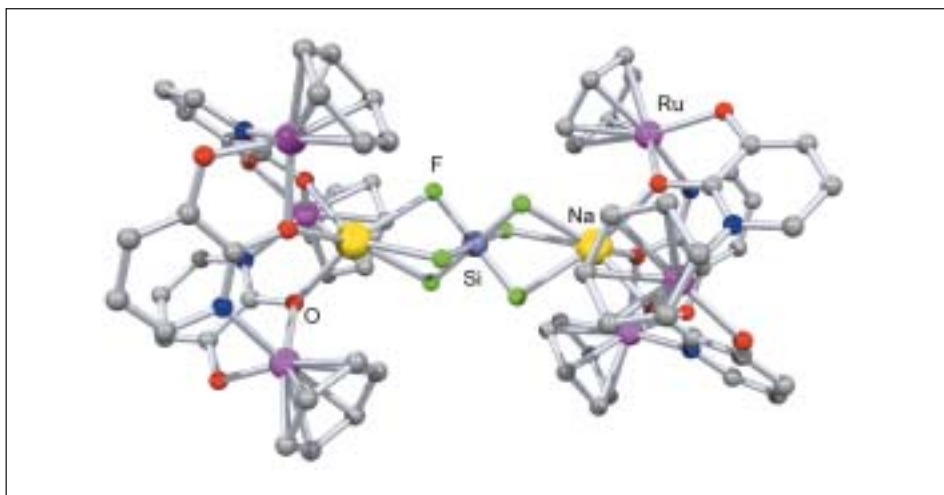


Fig. 2. Ball and stick representation of the molecular structure of **4** in the crystal. The hydrogen atoms and the side chains of the aromatic π -ligand are not shown for clarity.

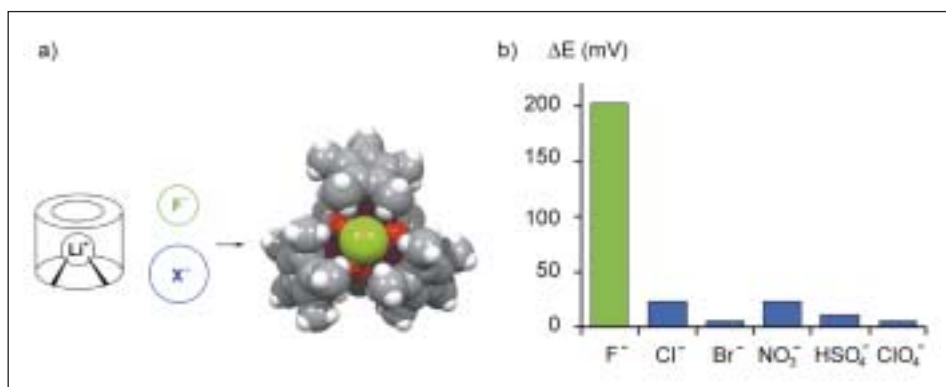


Fig. 3. a) CPK representation of the molecular structure of **3** • LiF highlighting the tight encapsulation of the LiF guest molecule; b) Absolute difference of the peak potential for the first oxidation of **3** • LiBF₄ after addition of various anions X⁻ (CHCl₃/CH₃CN 2:1).

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