

Polycyclic Phosphiranes: Synthesis of C-Substituted BABAR-Phos Compounds

Florian B. Läng* and Hansjörg Grützmacher

Abstract: BABAR-Phos is a very stable polycyclic phosphirane which is easily synthesized in few steps from dibenzosuberone. BABAR-Phos is remarkably stable and is not oxygenated with O₂ nor does it react with sulfur in boiling toluene. BABAR-Phos can be used as a ligand in homogenous catalysis. Substituents at the carbon of the PC₂ heterocycle can be introduced and asymmetric BABAR-Phos were prepared. The coordination chemistry of rhodium complexes containing these as ligands was investigated.

Keywords: Coordination chemistry · Phosphanes · Phosphiranes · Rhodium

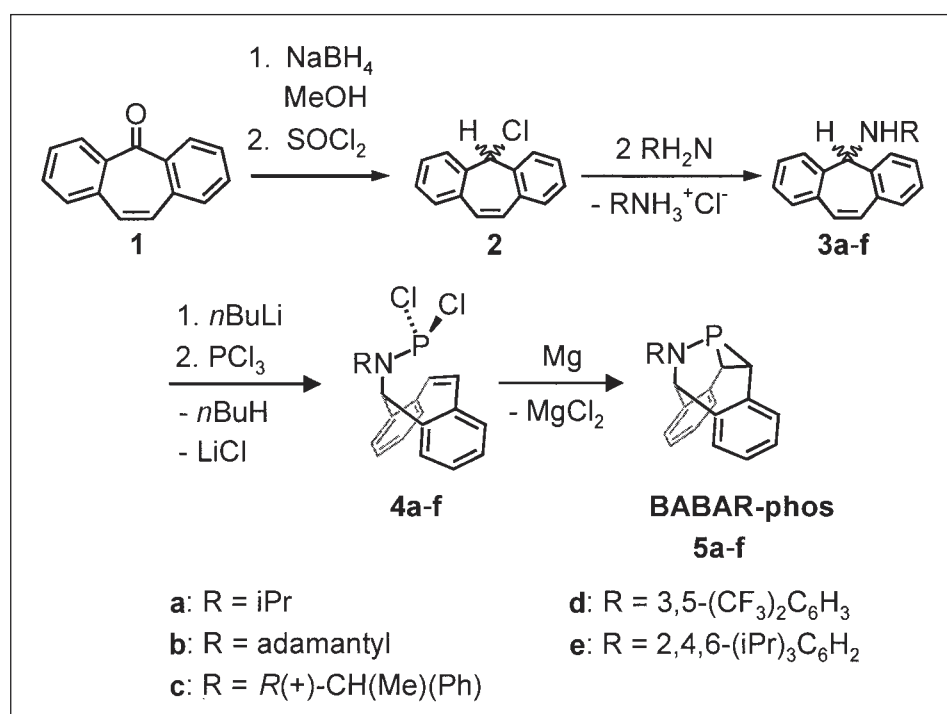
Introduction

Phosphiranes are three-membered rings containing a strained PC₂ heterocycle. Various methods for their synthesis have been developed and their reactivity has been explored [1][2]. A typical property is their tendency to undergo [2+1] cycloreversions which has been used to generate phosphinidenes, R–P:, as reactive intermediates. Frequently, this reaction is even facilitated in phosphirane complexes and phosphinidene complexes, [M(=PR)L_n], are obtained. However, this decomposition impedes the use of phosphiranes as ligands. We therefore embedded the heterocyclic PC₂ unit into a polycyclic framework and obtained very stable phosphiranes **5**, which we named BABAR-Phos [3]. These compounds can be handled and stored in air without decomposition and are not sensitive against sulfurization with elemental sulfur in boiling toluene or strong alkylating agents like MeOSO₂CF₃. They also resist aqueous acids or bases. However, degradation is observed when solutions of BABAR-Phos in halogenated solvents are exposed to light and air for longer periods of time.

Synthesis

The synthesis of BABAR-Phos starts from the commercially available dibenzosuberone **1** which is converted *via* the chloride **2** and amine **3** to the amino-(dichloro)phosphanes **4** (Scheme 1). Dehalogenation of the PCl₂ compounds **4** with magnesium turnings in THF leads to formation of the phosphiranes **5**. This new method most likely proceeds *via* (amino)-

phosphinidene magnesium complexes of the type [R(trop)N–P=Mg] [4] which undergo an intramolecular cycloaddition with the C=C double bond of the seven-membered ring of the trop unit (trop = 5H-dibenzo[a,d]cyclohepten-5-yl). Due to the spatial proximity of the phosphinidene and olefinic unit within the rigid boat conformation of the dibenzotropyliene unit, this key-step is favored. The reaction proceeds at room temperature with excellent yields (> 90%).



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Scheme 1. Syntheses of various BABAR-Phos compounds with sterically demanding substituents at the N-atom.

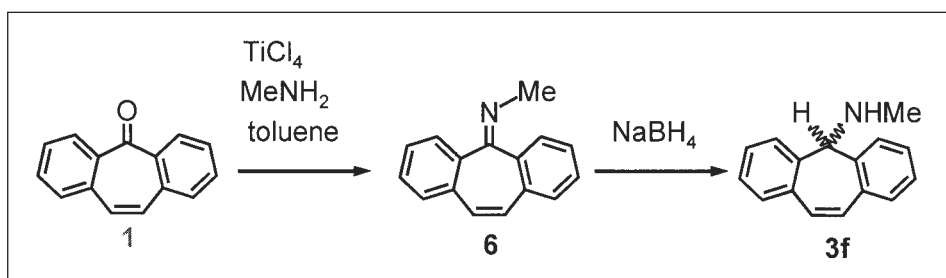
Due to the strong pyramidalization at the phosphorus center [$\Sigma^\circ(\text{P})$ 240–250°], one might expect that BABAR-Phos behaves as a π -acceptor but also as a rather poor σ -donor because the donor-orbital (HOMO) at the phosphorous has a high s-character and is strongly contracted [5]. In a recent thermochemical study combined with DFT calculations, we could show that BABAR-Phos is the most weakly binding phosphane known to date in the series $[\text{Pt}(\text{cod})\text{Me}_2] + 2 \text{PR}_3 \rightarrow [\text{PtMe}_2(\text{PR}_3)_2] + \text{cod}$; with $\text{PR}_3 = \text{BABAR-Phos}$: $\Delta H_f = -11.8 \text{ kcal/mol}$, [6]. We also found that metal centers can be *reversibly* inserted into one of the P–C bonds of the PC_2 cycle [7]. This equilibrium, metal BABAR-Phos complex \rightleftharpoons metallaphosphetane, is very sensitive with respect to the coordinating metal center and the electronic properties of the further co-ligands. With both the complexes containing the intact BABAR-Phos ligand as well as with the metallaphosphetanes, we could perform promising hydroboration and hydrosilylation experiments [6–8].

Results and Discussion

To further investigate the properties of BABAR-Phos as a ligand, we started to introduce various substituents R into the polycyclic framework. Evidently, changing the N-bonded group R is simple and experimentally realized using different sufficiently bulky primary amines in the reaction with the chloride **2** (see Scheme 1 for with R = alkyl or arene). However, the reaction presented in Scheme 1 is not practical with small amines (*i.e.* MeNH_2), as one ends up with the expected mixture of di- and tri(alkylated) amines. In this case, tropolone **1** is converted to the corresponding imine **6** which can be reduced with NaBH_4 to the desired amine **3f** (Scheme 2).

Although the N-bonded substituent has a significant influence on the activity and selectivity of the catalyst in hydroborations [9] a chiral group as in **5c** gave disappointingly no enantioselectivity. We therefore thought to introduce one substituent at the C-atom of the PC_2 heterocycle which also would lead to a break-down of the mirror symmetry of BABAR-Phos.

To functionalize the C-atom of the heterocycle, we prepared the 10-bromo substituted dibenzocycloheptenol **9** which is easily accessible in three steps from dibenzosuberone **1** *via* bromination to give **7**, dehydrobromination to give **8**, and reduction of ketone **8** with NaBH_4 in almost quantitative yield (Scheme 3).

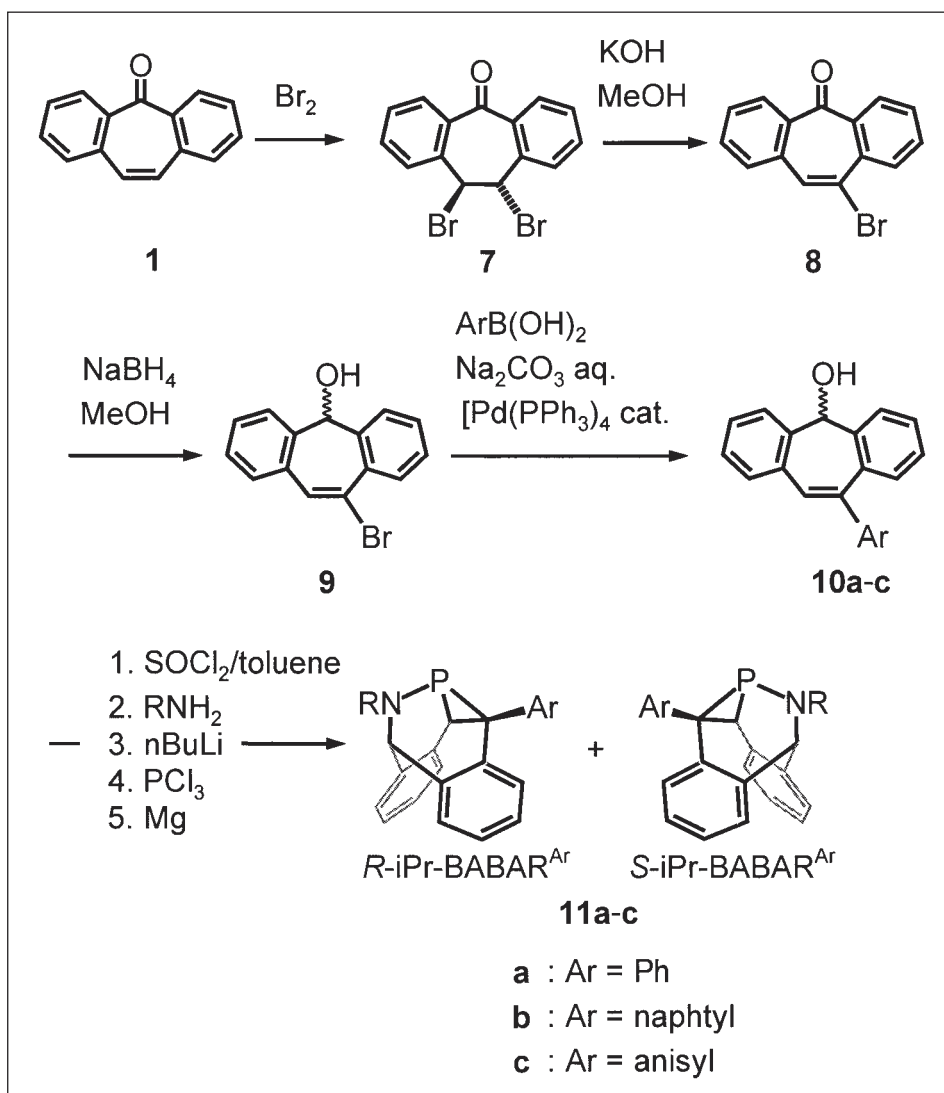


Scheme 2. Synthesis of the sterically less demanding tropamine **3f** as precursor for a N-methyl BABAR-Phos **5f**.

The alcohol **9** turned out to be a versatile reagent in palladium-catalyzed Suzuki cross coupling reactions [10]. The reaction with arylboronic acids, $\text{ArB}(\text{OH})_2$ (Ar = aryl = phenyl, naphthyl, anisyl) provides the C-substituted alcohols **10a–c** in very good yields (> 80 %).

The C-substituted alcohols **10a–c** were subsequently converted to the corresponding chlorides and further transformed into the final $\text{iPr-BABAR}^{\text{Ar-Phos}}$ **11a–c** according to Scheme 1 (in our notation, the N-bonded substituent is given as prefix and the C-bonded one as superscript at the ter-

minus). The phosphirane ring was successfully formed with all aryl substituents. However, with the rather bulky 1-naphthyl substituent side products were observed, presumably polyphosphanes, because the $\text{C}=\text{C}_{\text{trop}}$ double bond is less accessible. The observed ^{31}P chemical shifts of the C-substituted phosphiranes are in the range of –128 to –132 ppm. Note that free rotation of the 1-naphthyl and the 2-anisyl substituents in the phosphiranes **11b,c** is frozen on the NMR time scale and hence two ^{31}P NMR signals are observed, each indicating one rotational isomer.



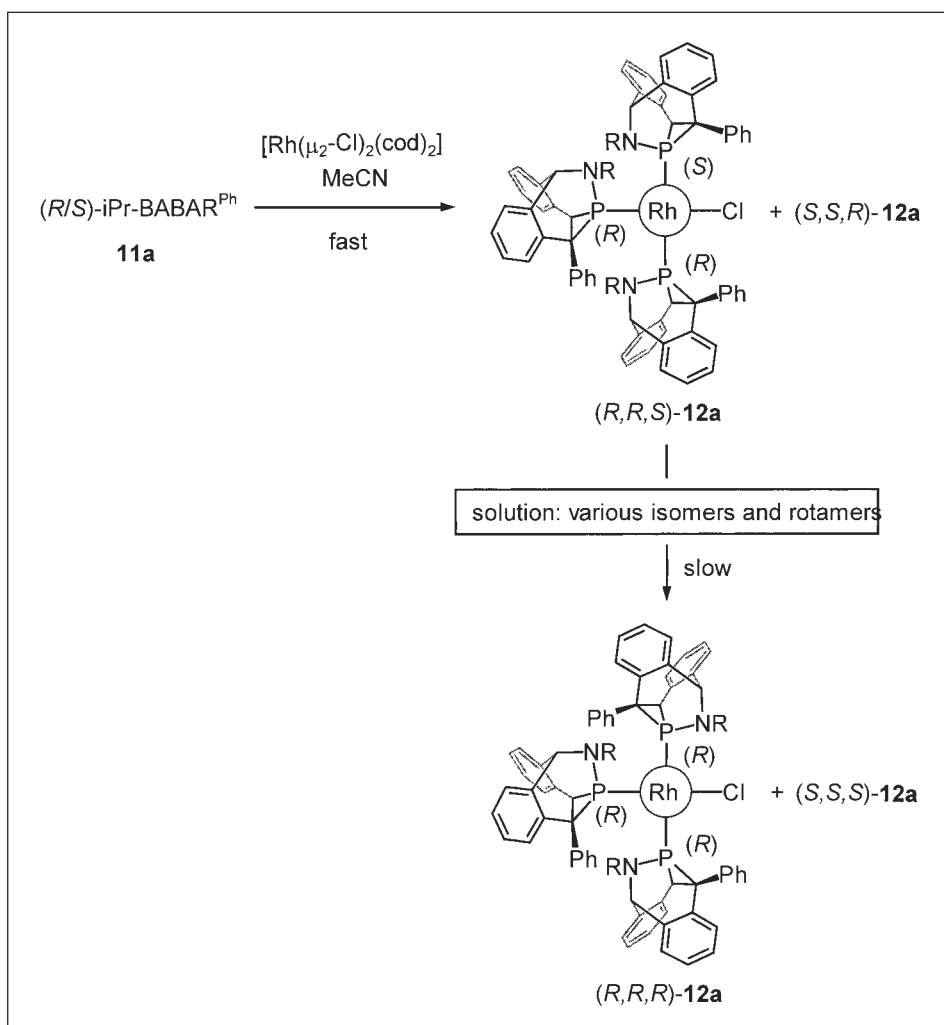
Scheme 3. Synthesis of the $\text{iPr-BABAR}^{\text{Ar-Phos}}$ **11a–c**

In these reactions, the phosphiranes **11a–c** are obtained as a racemic mixture of both enantiomers (see Scheme 4 where we denoted the stereochemistry at each phosphorus center as (*R*) or (*S*), respectively). We introduced an additional stereogenic center at the N-substituent in the hope of being able to eventually separate the diastereomers. This approach was realized by transforming the alcohol **10a** into the corresponding chloride and then reacting this with enantiomeric pure (*R*)-(+)-1-phenylethylamine. Unfortunately, however, we were not able to separate the finally obtained diastereomeric phosphiranes by chromatography.

We started to investigate the coordination chemistry using the C-substituted phosphiranes **11a–c** as ligands for rhodium complexes. When the racemic mixture of (*R/S*)-iPr-BABAR^{Ph} **11a** was reacted with [Rh₂(μ₂-Cl)₂(cod)₂] in acetonitrile as solvent, independently of the molar ratios of the reactants, the Rh(I) complex **12a** was obtained exclusively as a brown powder which rapidly precipitates out of the reaction mixture.

The isolated complex consists of a Rh(I) center which is coordinated by one chloro and three iPr-BABAR^{Ph} ligands **11a**. Using two-dimensional NMR methods, the structure was determined to be the (*R,R,S*)-isomer and the enantiomeric (*S,S,R*)-form, respectively, as is shown in Scheme 4. When this isolated complex is re-dissolved in THF, complicated ³¹P NMR spectra are obtained which slowly evolve with time. We assign these to a number of different conformational and rotational isomers formed slowly in equilibria involving complexes of type **12a**. Each of these species shows three inequivalent ³¹P resonances and each of them is split into an eight-line pattern (ddd) by coupling with two ³¹P nuclei and one ¹⁰³Rh nucleus. Finally, on storing a THF solution of **11a** layered with n-hexane over two weeks at room temperature, single crystals of **12a** were obtained. The result of an X-ray structure analysis is given in Fig. 1, which shows this isomer to have an (*R,R,R*)-conformation (the (*S,S,S*)-enantiomer, which is also included in the crystal lattice, is not shown). Note, however, that also these all-(*R*)-, respectively, all-(*S*)-isomers show three different ³¹P resonances indicating hindered rotation around the P–Rh bonds. The otherwise slow rate of the isomerization of the initially formed kinetic product **12a** with (*R,R,S/S,R*)-conformation can be increased to minutes when AgOTf is added to the THF solution.

As the free phosphiranes, the complexes **12a** show an unusually high robustness against oxidation and are not decomposed



Scheme 4. Synthesis of rhodium(I) complexes **12a** with the racemic mixture of **11a**.

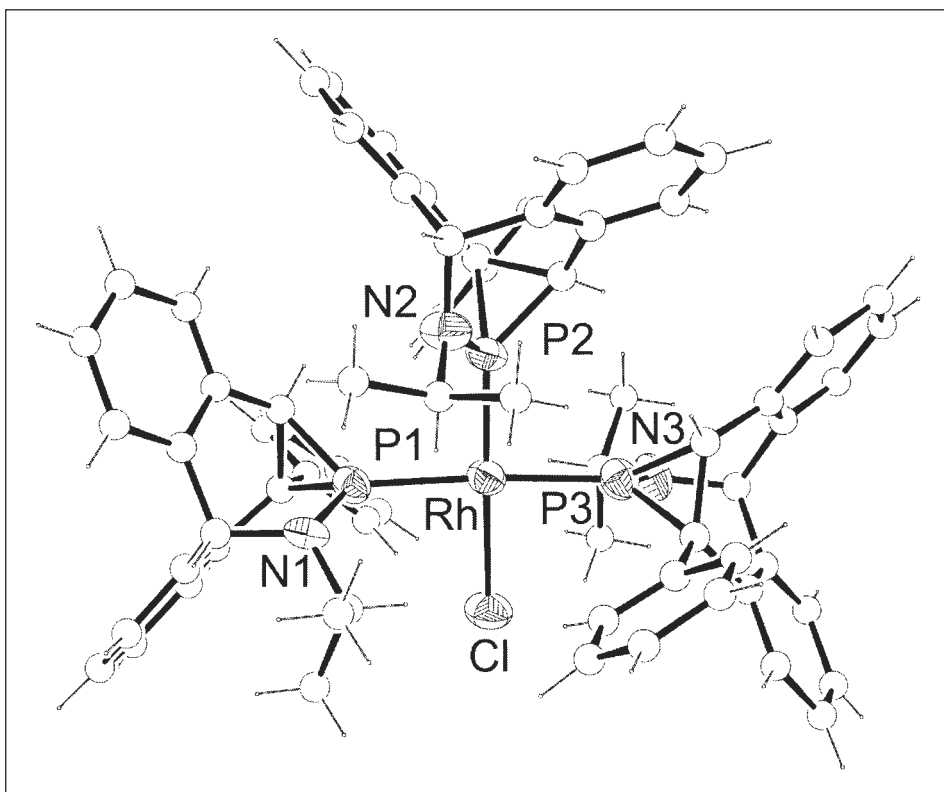


Fig. 1. Structure of the (*R,R,R*)-isomer of [RhCl(iPr-BABAR^{Ph})₃] **12a**.

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 iPr-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(iPr-BABAR)₂] was reacted with phosphanes, PR₃, comparable complexes, *i.e.* [RhCl(iPr-BABAR^{Ph})_{3-x}(PR₃)_x], were not observed. Only the homoleptic complexes **12a** beside [RhCl(PR₃)_x] (*x* = 2,3) and free iPr-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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- [1] F. Mathey, 'Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain', Pergamon Press, Amsterdam, **2001**.
 [2] K.B. Dillon, F. Mathey, J.F. Nixon, 'Phosphorous: The Carbon Copy', Wiley, New York, **1998**.
 [3] J. Liedtke, S. Loss, G. Alcaraz, V. Gramlich, H. Grützmacher, *Angew. Chem.* **1999**, *114*, 1724, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1623. The name BABAR-Phos is a symbiosis out of the related hydrocarbon barbaralane and the obvious resemblance of BABAR-Phos to the famous green elephant from the children's books (see sketch below).

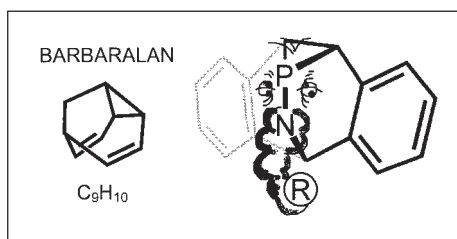


Fig. 2. Structure of barbaralane, C₉H₁₀, and BABAR-Phos the 'elephant'.

- [4] H. Bock, M. Bankmann, *J. Chem. Soc., Chem. Commun.* **1989**, 1130.
 [5] B.J. Dunne, R.B. Morris, A.G. Orpen, *J. Chem. Soc. Dalton Trans.* **1991**, 635.

- [6] C. Laporte, G. Frison, H. Grützmacher, A.C. Hillier, W. Sommer, S.P. Nolan, *Organometallics*, in press.
 [7] J. Liedtke, H. Rüegger, S. Loss, H. Grützmacher, *Angew. Chem.* **2000**, *112*, 2596, *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 2479.
 [8] J. Liedtke, S. Loss, H. Grützmacher, *Tetrahedron* (Symposium in Print) **2000**, *56*, 143.
 [9] H. Grützmacher, J. Liedtke, G. Frasca, F. Läng, N. Pè, *Phosphorous, Sulfur and Silicon* **2002**, *177*, 1771.
 [10] F. Läng, unpublished results of the planned PhD thesis.

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Stabilization of Molecular LiF, LiFHF, and Na₂SiF₆ Using Metallamacrocyclic Hosts

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Abstract: The molecular forms of LiF, LiFHF and Na₂SiF₆ have been stabilized using trinuclear metallamacrocyclic complexes of (cymene)Ru^{II}, (Cp*)Rh^{III} and (Cp*)Ir^{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}, (Cp*)Rh^{III} and (Cp*)Ir^{III} complexes using 3-hydroxy-2-pyridone as the bridging ligand [1–3]. Trinuclear metallamacrocycles 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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