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

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Abstract: BABAR-Phos is a very stable polycyclic phosphirane which is easily synthesized in few steps from dibenzosuberenone. BABAR-Phos is remarkably stable and is not oxygenated with O_2 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 PC_2 heterocycle can be introduced and asymmetric BABAR-Phos were prepared. The coordination chemistry of rhodium complexes containing these as ligands was investigated.

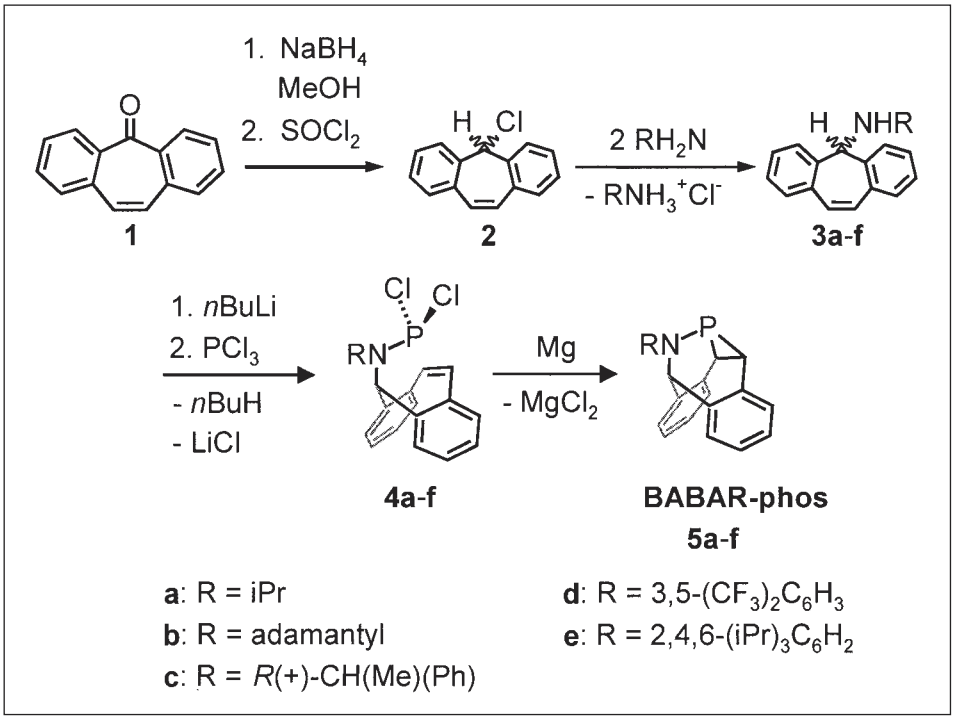
Keywords: Coordination chemistry · Phosphanes · Phosphiranes · Rhodium

Introduction

Phosphiranes are three-membered rings containing a strained PC_2 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 PC_2 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 $MeOSO_2CF_3$. 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 dibenzosuberenone **1** which is converted *via* the chloride **2** and amine **3** to the amino(dichloro)phosphanes **4** (Scheme 1). Dehalogenation of the PCl_2 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 phosphinide and olefinic unit within the rigid boat conformation of the dibenzotropylidene unit, this key-step is favored. The reaction proceeds at room temperature with excellent yields (> 90%).



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

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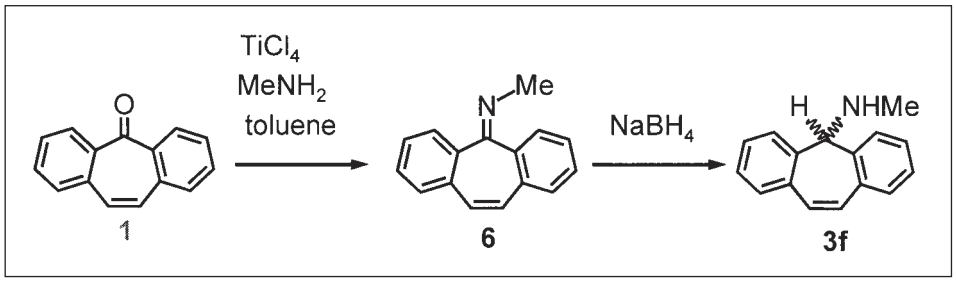
Due to the strong pyramidalization at the phosphorus center [Σ°(P) 240–250°], one might expect that BABAR-Phos behaves as a π-acceptor but also as a rather poor σ-donor because the donor-orbital (HOMO) at the phosphorous has a high s-character and is strongly contracted [5]. In a recent thermochemical study combined with DFT calculations, we could show that BABAR-Phos is the most weakly binding phosphane known to date in the series $[Pt(cod)Me_2] + 2\ PR_3 \rightarrow [PtMe_2(PR_3)_2] + cod$; with PR_3 = BABAR-Phos: ΔH_r = –11.8 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 ⇆ 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].



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

Results and Discussion

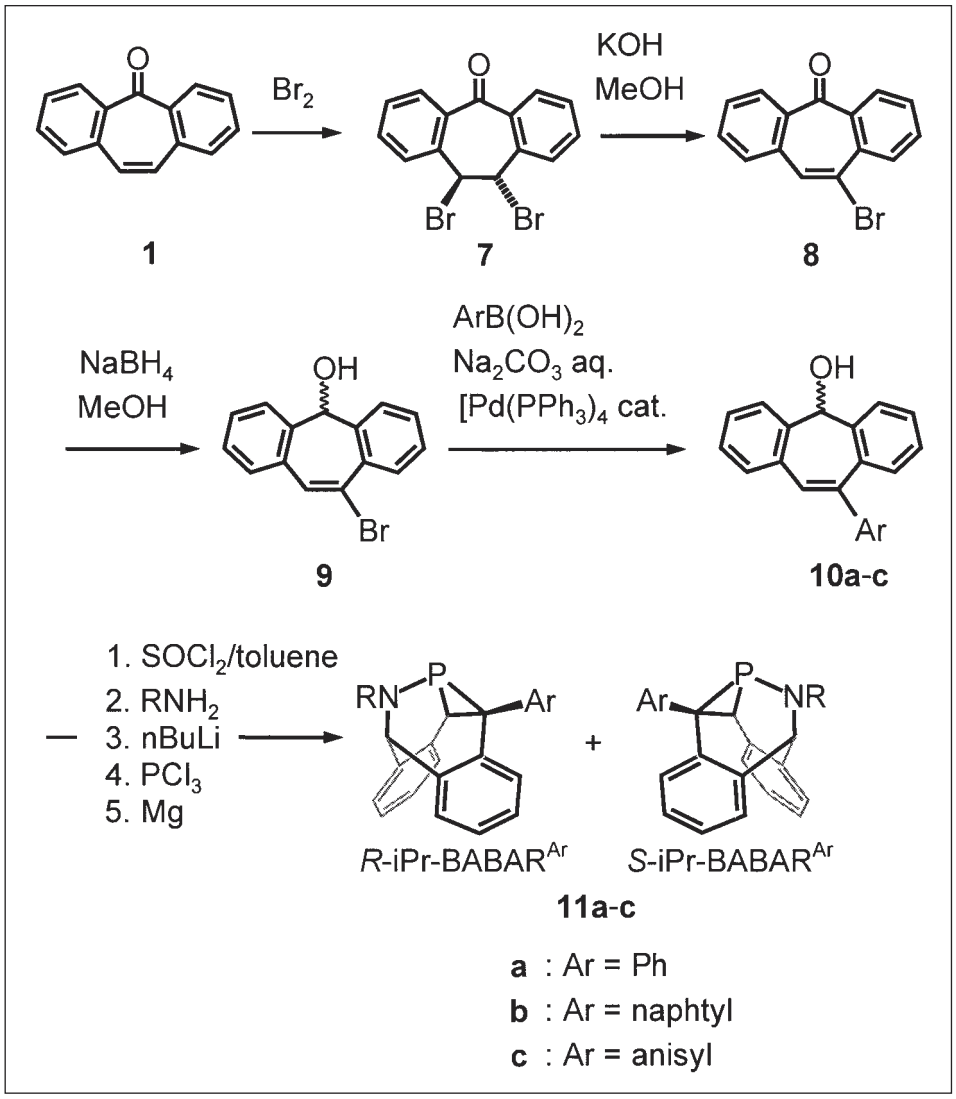
To further investigate the properties of BABAR-Phos as a ligand, we started to introduce various substituents R into the polycyclic framework. Evidently, changing the N-bonded group R is simple and experimentally realized using different sufficiently bulky primary amines in the reaction with the chloride **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 dibenzosuberenone **1** *via* bromination to give **7**, dehydrobromination to give **8**, and reduction of ketone **8** with $NaBH_4$ in almost quantitative yield (Scheme 3).

The alcohol **9** turned out to be a versatile reagent in palladium-catalyzed Suzuki cross coupling reactions [10]. The reaction with arylboronic acids, $ArB(OH)_2$ (Ar = aryl = phenyl, naphtyl, 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 iPr-BABAR^{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 terminus). The phosphirane ring was successfully formed with all aryl substituents. However, with the rather bulky 1-naphtyl substituent side products were observed, presumably polyphosphanes, because the $C{=}C_{trop}$ 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-napthyl 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.



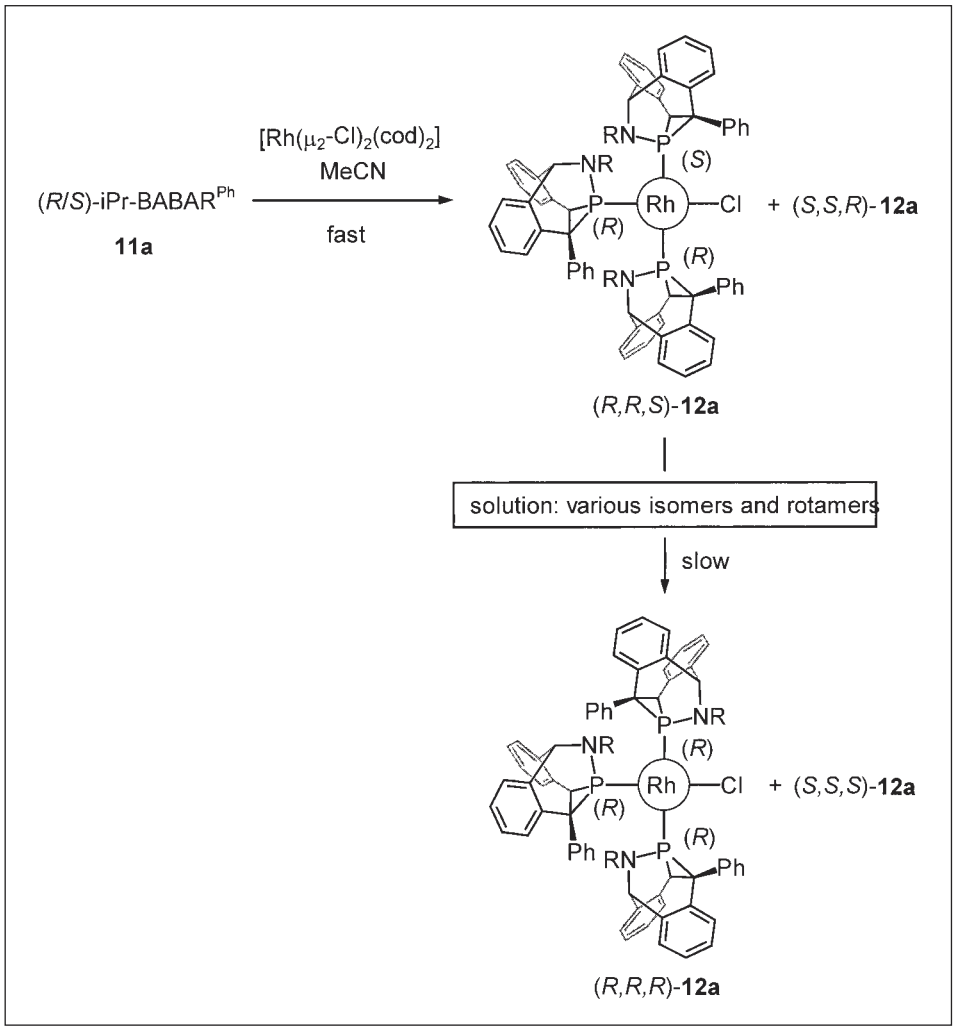
Scheme 3. Synthesis of the iPr-BABAR^{Ar}-Phos **11a–c**

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 $[Rh_2(\mu_2\text{-}Cl)_2(cod)_2]$ 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 ^{31}P 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 ^{31}P resonances and each of them is split into an eight-line pattern (ddd) by coupling with two ^{31}P nuclei and one ^{103}Rh 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 ^{31}P 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*,*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**.

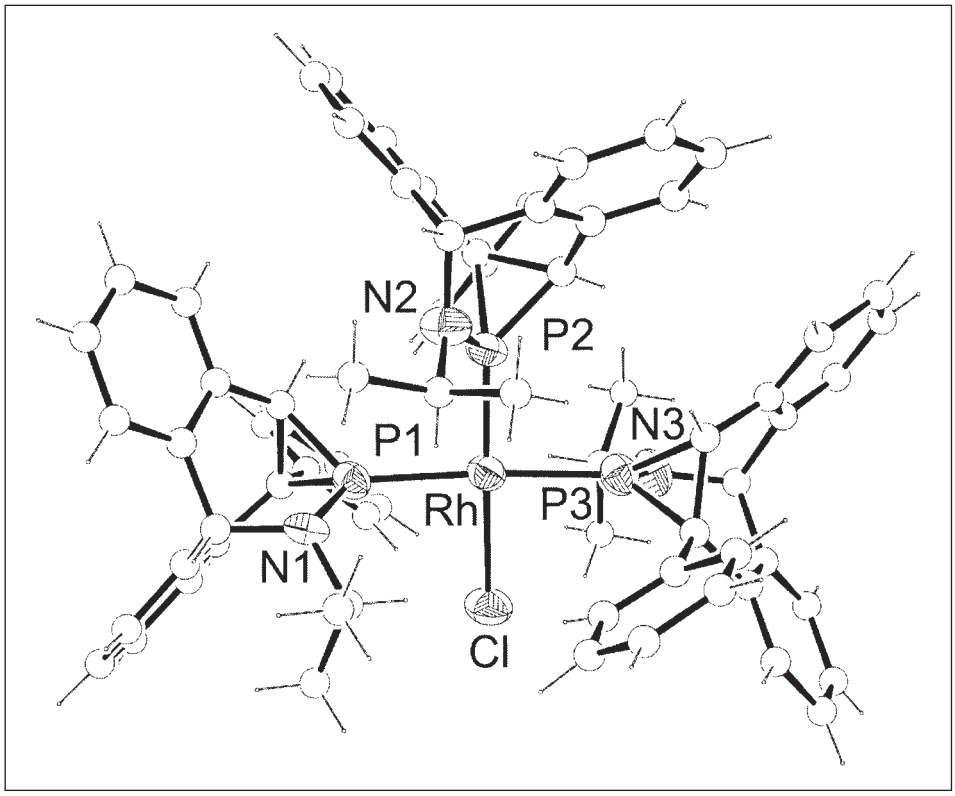


Fig. 1. Structure of the (*R*,*R*,*R*)-isomer of [RhCl(iPr-BABAR^{Ph})$_3$] **12a**.

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 PPh_3 or $P(OMe)_3$ are added. Interestingly, while we could observe complexes with a heteroleptic coordination sphere when [$PtMe_2$(iPr-BABAR)$_2$] was reacted with phosphanes, PR_3, comparable complexes, *i.e.* [RhCl(iPr-BABAR^{Ph})$_{3-x}$(PR_3)$_x$], were not observed. Only the homoleptic complexes **12a** beside [$RhCl(PR_3)_x$] (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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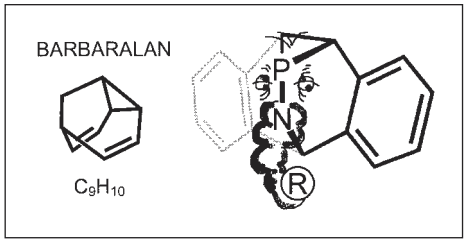

Fig. 2. Structure of barbarlane, C_9H_{10}, and BABAR-Phos the 'elephant'.

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Stabilization of Molecular LiF, LiFHF, and Na_2SiF_6 Using Metallamacrocyclic Hosts

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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}, (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 · Metallamacrocycle · 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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