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PREPARATION OF PHOSPHORUS- AND FLUORINE-CONTAINING CALIX[4]ARENE DERIVATIVES, THEIR DICHLOROPLATINUM (II) AND CHLOROGOLD(I) COMPLEXES, CONFORMATIONAL ANALYSIS, SEPARATION OF THE CONFORMERS AND X-RAY CRYSTAL STRUCTURE ANALYSIS OF A CONE CONFORMER.

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Abstract: The reaction of the *p*-tert-butylcalix[4]arene **1** with $\text{Et}_2\text{NSiMe}_3$ was found to lead to the bis(trimethylsilyl) derivative **2**. Treatment of **2** with PF_2Cl gives the mono- and bis-difluorophosphite derivatives **3** and **4**, which undergo spontaneous elimination of Me_3SiF or PF_3 to yield the monofluorophosphite derivative **5**. **6** was allowed to react with *P*-chlorophosphorinone derivatives with formation of a mixture of the four possible conformers **11a** - **11d**, and **12a** - **12d**. In the case of **12a** - **12d** the cone conformer **12a** was isolated. **12a** was allowed to react with $(\text{COD})\text{PtCl}_2$ and $\text{Au}(\text{C}_4\text{H}_8\text{S})\text{Cl}$ to form **13** and **14**.

Key Words: Calix[4]arenes; Supramolecular chemistry

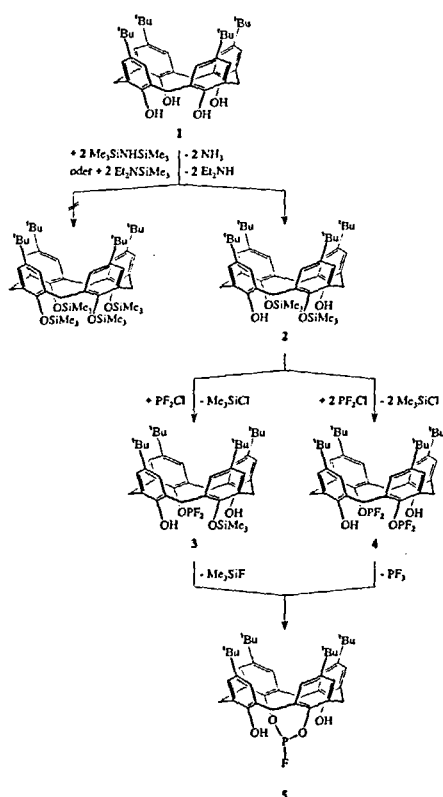
INTRODUCTION

The study of the chemistry of calixarenes including, especially, the calix[4]arenes^[1], is attracting constantly increasing interest. Calixarenes are distinguished by some special features, e.g. a hydrophobic and a hydrophilic region, and a receptor space, and there is a possibility of functionalizing the donor atoms^[2-7]. Phosphorus-containing calix[4]arenes, for example, are of special interest, as a result of the ability of phosphorus to exist in a variety of different oxidation states and/or coordination numbers^[8-18].

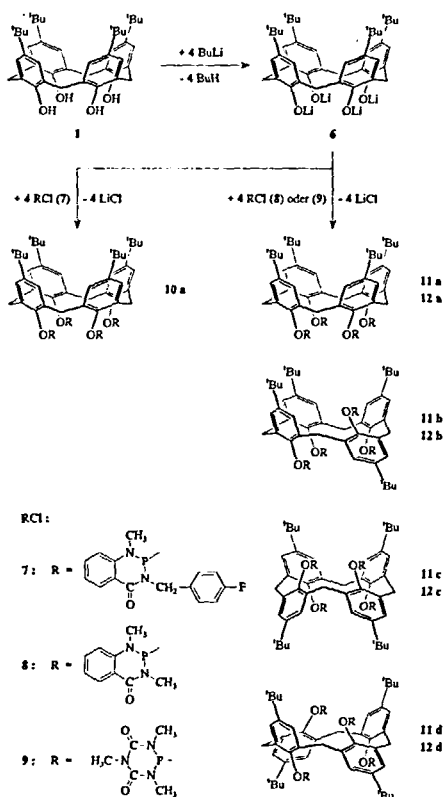
RESULTS AND DISCUSSION

In the reaction of **1** with $\text{Et}_2\text{NSiMe}_3$, **2** is formed (Scheme 1). The reaction of **2** with PF_2Cl in a 1:1 ratio led to the trimethylsiloxy-difluorophosphite derivative, **3** while excess PF_2Cl formed the bis(difluorophosphite) derivative, **4**. Both **3** and **4** are converted to the stable monofluorophosphite derivative **5**; while **4** loses PF_3 spontaneously upon standing in solution in hexane at room temperature over 6 h, the transformation of **3** into **5** requires 8 h heating in toluene solution at 50°C. Compound **5** is obtained from **3** with loss of Me_3SiF ^[19], as from **4**. The higher thermal stability of **3**, compared to that of **4**, is suggested to be due to the thermodynamically more favourable loss of PF_3 , as against the formation of Me_3SiF .

Scheme 1



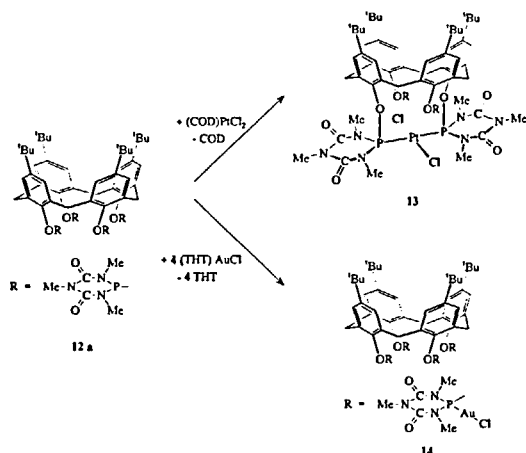
Scheme 2



The fourfold lithiation of **1**^[6], followed by the action of **7** furnished the stable cone conformer **10a** (Scheme 2). Contrary to previous observations^[20] no conformational changes occurred when **10a** was heated in refluxing toluene over 10 h. This must be due to the cone conformation being "frozen" through the bulky substituents at oxygen. The reaction of **1**, after fourfold lithiation^[6], with **8** and **9**, lead to a mixture of all the four conformers **11a** - **11d**, and **12a** - **12d** (Scheme 2). The cone conformer **12a** was separated from the mixture through crystallization from acetonitrile/*n*-hexane (3:1) or from a concentrated solution in THF. Because of the bulky groups at the oxygen atoms no spontaneous conversion of conformers at room temperature was observed. The conformers, **12b** and **12c**, could be separated by column chromatography at kieselgel^[18]. The 1,3-alternating conformer **12d** could not be obtained in a pure state.

Preliminary attempts were undertaken at the study of the coordinating ability of calix[4]arenes, involving P(III) substituents. The formation of the trans-platinum(II) complex **13**, and of the tetrakis-gold(I) complex **14** is typical (Scheme 3).

Scheme 3



STRUCTURAL CONSIDERATIONS

Conformers **12a** - **12d** could easily be distinguished by their characteristic ^1H - and ^{13}C -n.m.r. pattern. Depending upon the symmetry of each conformer the ^1H -n.m.r. spectra were found to exhibit for the ArCH_2Ar resonances either a pair of doublets (**12a**), two pairs of doublets (**12b**), a singlet and a pair of doublets (**12c**), or a singlet (**12d**). In the ^1H -decoupled ^{13}C -n.m.r. spectra the $\delta(^{13}\text{C})$ values were observed in the range, 31 to 37 ppm. The appearance of the ^{13}C -n.m.r. spectra of the carbon atoms of the methylene group was found to be affected by the orientation of the neighbouring aryl groups, i.e. one $\delta(^{13}\text{C})$ value for **12a** and **12d** and two ^{13}C -n.m.r. signals (**12c** and **12c**). A single crystal X-ray structure determination was conducted for the cone conformer **12a**.

It is apparent from the ^{31}P -n.m.r. spectrum of **13** that only two of the four P(III) atoms coordinate to Pt(II). The value of $^1J(^{31}\text{P}^{195}\text{Pt})$ (2728 Hz) suggests a trans-configuration. The identity of **14** was established by n.m.r. spectroscopy (^1H , ^{13}C , ^{31}P) and IR spectroscopy, mass spectrometry, and elemental analysis.

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