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Dedicated to Professor Alexandru T. BALABAN
on the occasion of his 90th anniversary

ETHOXY-TETHERED CALIX[4]ARENES CONTAINING P(III) SUBSTITUENTS AND TRIMETHYLSILOXY GROUPS AS BUILDING BLOCKS IN SUPRAMOLECULAR CHEMISTRY; *CIS/TRANS* INTRA- AND INTERMOLECULAR COMPLEXATION OF DICHLOROPLATINUM(II) FRAGMENTS

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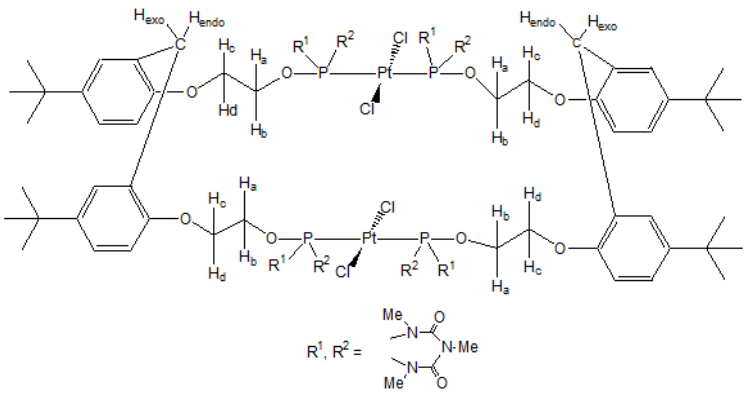
p-*tert*-Butylcalix[4]arene **1** reacts with bromoethyl acetate and $LiAlH_4$ to form the p-*tert*-butyl-tetrakis(2-hydroxyethoxy)calix[4]arene **8** bearing four ethyl-spacers at the lower rim of the calixarene. Reaction of **8** with Et_2NSiMe_3 leads to the tetrakis-substituted derivative **9**. Treatment of **9** with PF_2Cl gives the stable tetrakis-fluorophosphite **10**, while the reaction with 2-chloro-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione furnishes the tetrakis-substituted molecule **11**. When **11** was allowed to react with SO_2Cl_2, formation of the tetrakis(2-chloro)ethyl substituted calix[4]arene **13** was observed. All examined calixarene derivatives are exclusively obtained in the cone conformer.



Reaction of **11** with dichloro(cyclooctadiene) platinum(II) leads to the symmetrically four-times bridged dimmer **15**, which exhibits a trans orientation of the atoms surrounding the platinum(II) atom and involves all eight phosphorus atoms in the bridges. When **10** was treated with $(COD)PtCl_2$, the cis intermolecular complex **16** was obtained.

INTRODUCTION

The design of highly selective synthetic receptors based on calixarenes is of increasing importance in supramolecular chemistry.[1-21] The great interest, that is shown in calixarenes, is due to their ability to bind guest molecules in recognition processes as sufficiently preorganized macrocycles.[9]

Their different sizes and shapes, as well as the intramolecular bridging mode and functionalization at the molecules periphery influence the recognition

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properties of the macrocycle.[1-27] A hydrophobic and a hydrophilic site, defined cavities and ordered surfaces, endow these macrocycles with special properties: selective binding of metal ions as aggregates,[28,29] building blocks in supramolecular chemistry (chemo-and stereoselective recognition of carbohydrates),[30,31] design of supramolecular architectures by self organisation processes,[32] liquid crystals,[33] sensor technology[34] or visual distinction between enantiomers of biologically relevant substrates.[35] Chiral calixarenes are "host" molecules capable of enantio- or diastereoselective recognition.[36]

Functionalization of calix[4]arene derivatives with phosphorus containing groups in more than one coordination and/or oxidation state of the phosphorus atom bonded to the lower rim of the molecules (*e.g.* derivatives **A**, **B**, **C**, **D** in Fig. 1) has attracted the attention of several research groups.[2,4,5,37–39,40,41]

Phosphorus(III)-containing calix[4]arenes are extensively investigated, because of their ability to act as multidentate ligands in transition metal chemistry.[10-17, 37-42] Complexation of transition metal ions by p-*tert*-butylcalix[4]arene-tetrakis(diphenylphosphinite) and p- *tert*-butylcalix [4]arenetetrakis-(dimethylphosphinite) with formation of the mono-, homodi- and heterodimetallic complexes[42] was reported. The chemistry of compounds containing PF-groups received increasing attention because, for example, fluorophosphates can be incorporated into oligodesoxyribonucleosides in such a way that they can control the growth of viruses and cells.[43]

It is obvious that the use of chlorodifluorophosphines as reactants can provide new fluorine-containing groups as **synthon** for the synthesis of physiologic active compounds. The discovery of the cytostatic activity of the so-called "cis-platinum"[44] is important to this problem. An increased cytostatic effect (synergetic effect) of the cis- and trans-platinum(II) complexes described in this paper could be expected. Particular attention was given to the investigation of the cis/trans-complexation *via* NMR spectroscopy, by monitoring the bridging methylene, which can be used as spectroscopic proof to examine the cis or trans stereoisomery of the $PtCl_2$-units attached to the P4 system.

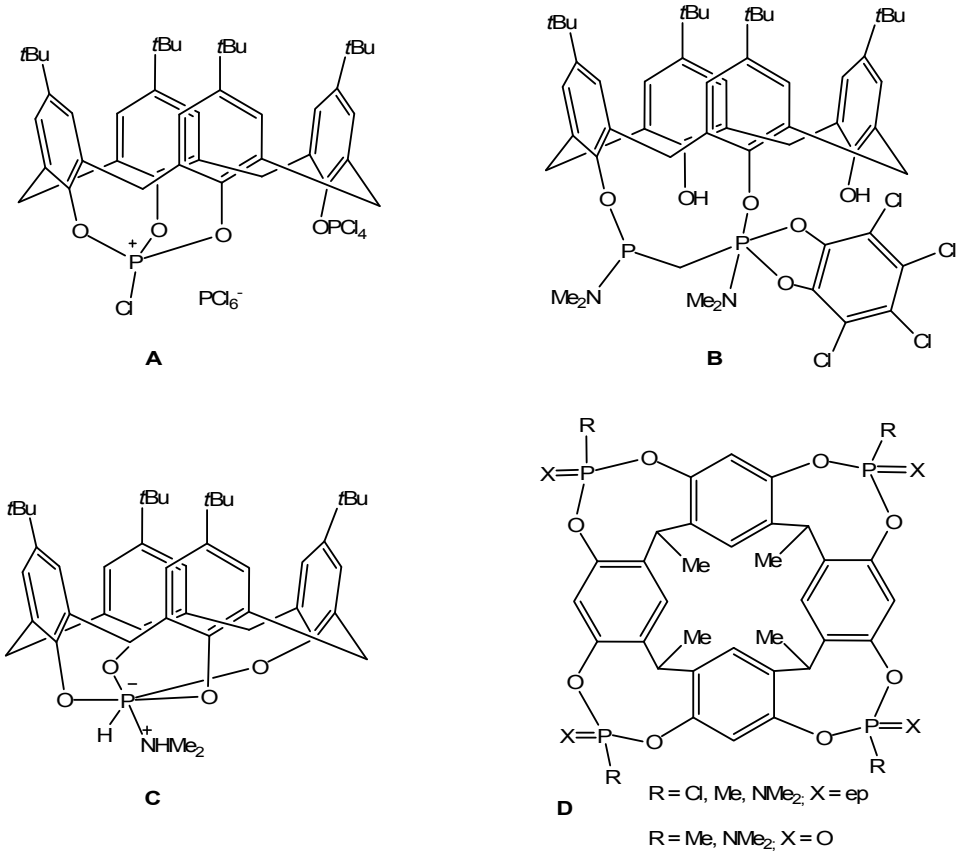
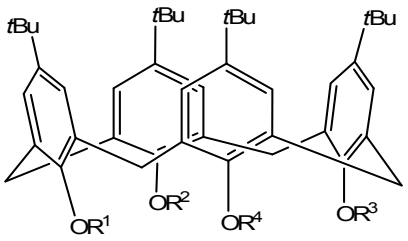


Fig. 1 – Calix[4]arene derivatives containing phosphorus(III) and phosphorus(V) atoms at the lower rim of the molecule.



1: R^1 - R^4 = H

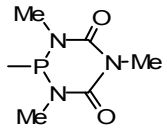
2: R^1 - R^4 = $SiMe_3$

3: R^1, R^3 = $SiMe_3$; R^2, R^4 = H

4: R^1 - R^4 = Li

5: R^1, R^2 = H; R^3 = $SiMe_3$, R^4 = PF_2

6: R^1, R^2 = H; R^3, R^4 = PF_2

7: R^1 - R^4 = 

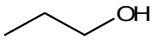
8: R^1 - R^4 = 

Fig. 2 – Calix[4]arene precursors used in this report.

One of the problems in calix[4]arene chemistry is the fact that they can exist in four different conformers: cone, partial cone, 1,2- and 1,3-alternate.[45,46] Furthermore, equilibrium reactions of these different conformers occur in solution[46]. Separation of the conformers is experimentally difficult or even impossible,[10] but all conformers can be distinguished by their characteristic splitting patterns of the Ar*C*H_2Ar signals in the ^{1}H- and ^{13}C-NMR spectra.[45,47,48] It is known that an unmodified p-*tert*-butylcalix[4]arene adopts a cone conformation because of the strong hydrogen-bonding interaction among the OH-groups.[18-20] Shinkai *et al.* described that O-substituents larger than ethyl can inhibit the rotation of the phenol unit, whereas the OH-groups can still rotate even in tetra-*tert*-butyl-tris(propy-loxy)calix[4]arene derivatives.[45] In a previous paper, we described the partial silylation of the OH-groups of p-*tert*-butylcalix[4]arene with Et_2NSiMe_3, affording dihydroxy-bis(trimethylsilyl)calix[4]-arene **3.**[10] Compounds obtained by reacting the calix[4]arene **1** (depicted in Fig. 2) with Et_2NSiMe_3 are of special interest as building blocks in the phosphorus functionalization of the lower rims of the calix[4]arene skeleton. Until now, it was not possible to substitute all four hydrogen atoms of the OH-groups in **1** by trimethylsilyl groups, generating the calix[4]arene **2** as possible precursor to phosphor-rus containing calix[4]arenes. Only the dihydroxy-bis(trimethylsiloxy)calix[4]arene **3** has been reported.[10]

The non-existence of **2** is presumably due to steric reasons and to the strong hydrogen-bonding in **1,**[3,9-17] preventing the substitution of all four hydrogen atoms at the lower rim by $SiMe_3$ groups. Reaction of compound **3** with phosphorus(III) halides such as chlorodifluorophosphine led to only partially substituted compounds.[10,22,23] Although reaction of **1** with *n*-butyl lithium furnishes the fully lithiated compound **4**, only a mixture of the four conformers[1,10,42] was formed, because the formation of hydrogen bonds, which stabilize only one conformer, is not possible any longer. Thus, reaction of **4** with various 2-chloro-5,6-benzo-1,3-diaza-2$\sigma^3\lambda^3$-phosphorin-4-ones and 2-chloro-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione led to mixtures of cone, partial cone and 1,2- and 1,3-alternate conformers, which were difficult to separate.[10]

We reported that the reaction of **7** with (COD)$PtCl_2$ afforded an intramolecular bridged complex and that only two phosphorus atoms are trans-coordinated to the platinum atom.[10] Only in case of compound **7** (see Fig. 2), the cone conformer could be separated by crystallization from acetonitrile/hexane (volume ratio 3:1).

RESULTS AND DISCUSSION

The interest in the design of artificial, supramolecular conductors by metal induced self-organization processes has increased considerably.[37-39, 54-56]

This manuscript focuses on the investigation of the analogous reactions, employing conformationally frozen calix[4]arenes bearing hydroxyl groups bonded via a spacer to the lower rim of the molecule, assuring an appropriate distance of these groups from the calixarene ring system. Thus, steric effects should be minimized and substitution reactions generating completely substituted products should be facilitated. Hence, compound **8**

was silylated with Et_2NSiMe_3 and reactions of the silylated product **9** with PF_2Cl and with 2-chloro-1,3,5-trimethyl-1,3,5-triaza-$\sigma^3\lambda^3$-phosphorin-4,6-dione to gain compounds **10** and respectively **11** were studied. Reaction of **11** with SO_2Cl_2 afforded the p-*tert*-butyl-tetrakis(2-chloroethyl)calix[4]arene **13**. Conformationally fixed derivatives **10**, **11** and **13** represent new and significant building blocks in supramolecular chemistry. For example, the reaction of **8** with **10** led to the macrocycle **14**. Reactivities of **10** and **11**, as representative examples, are compared with those of the corresponding calix[4]arene derivatives **5**–**7** without spacers.[10-17] Tetrakis phosphorus(III)-substituted products **10** and **11** frozen in the cone conformation can be employed as unusual tetradentate ligands in transition metal complex chemistry. They were reacted with $(COD)PtCl_2$ in order to study their complexation behaviour.

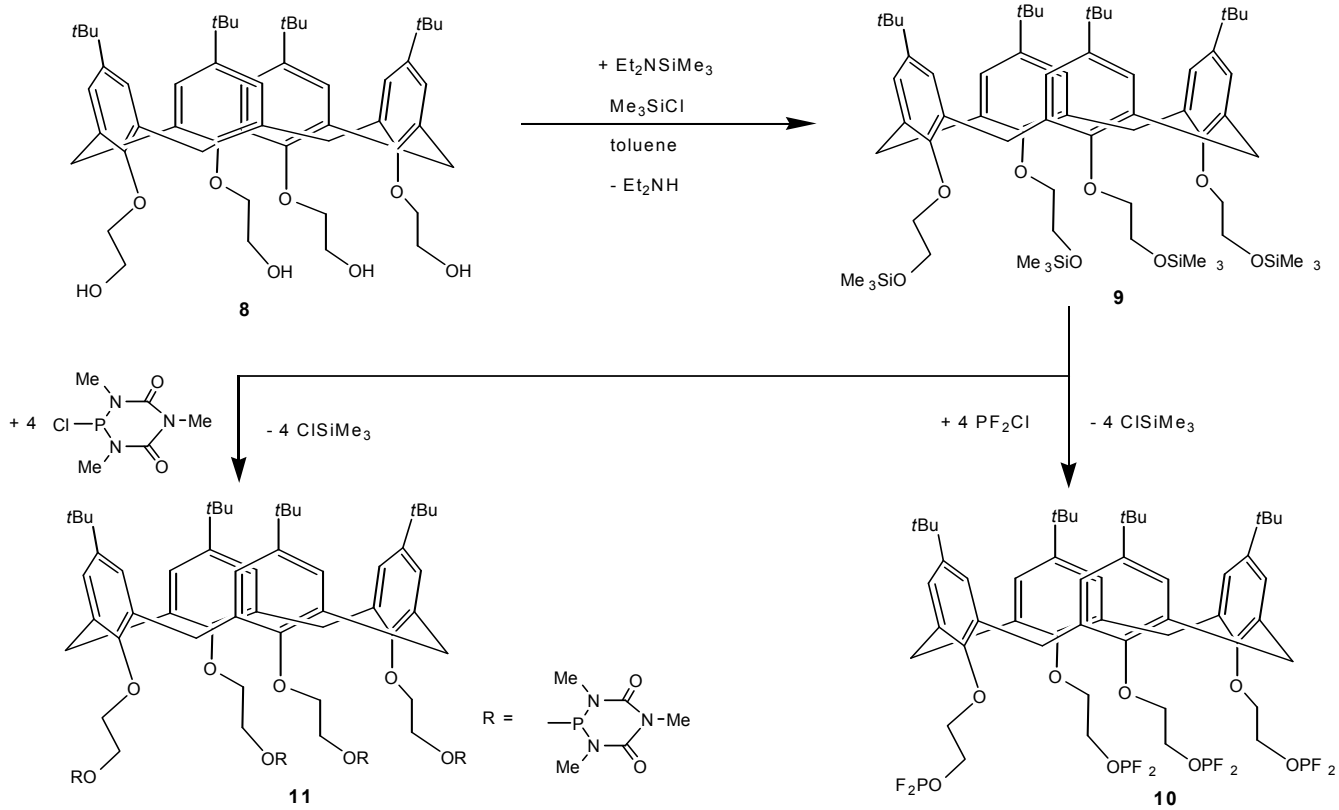
Synthesis of 9-11

A calix[4]arene with four 2-hydroxyethyl groups bonded to its lower rim (derivative **8**)[49] was allowed to react with Et_2NSiMe_3 according to Scheme 1, furnishing in good yield compound **9**, as a white solid, with a very good solubility in most common organic solvents.

All four hydrogen atoms of the terminal hydroxyl groups in **8** could be substituted by trimethylsilyl groups. In contrast to the corresponding compound **1** (illustrated in Fig. 2), steric effects do not influence the silylation reaction. The insertion of the spacer group CH_2CH_2O enabled the formation of the tetrakis(trimethylsiloxy) derivative **9**, which exists at room temperature exclusively in the cone conformation. ^{1}H- and ^{13}C-NMR spectroscopy, mass spectrometry and elemental analysis confirmed the formation of this product.

We are now able to present a facile functionalization of the lower rim of the tetra-*tert*-butylcalix-[4]arene derivative **9** with PF_2 and $P(N(Me)C(=O))_2NMe$ units *via* ethoxy-tethered trimethylsiloxy groups.

The object of our investigation was to utilize the fully PF_2 and $P(N(Me)C(=O))_2NMe$ functionalized tetra-p-*tert*-butyl-tetrakis(ethoxy)calix[4]arene derivatives **10** and **11** in their cone conformation for fitting $PtCl_2$-units in the homodimetallic complex **16** (cis-intramolecular complexation) or the homotetrametallic complex **15** (trans-intermolecular complexation).



Scheme 1 – Synthesis of calix[4]arene derivatives **9**, **10** and **11**.

Reaction of **9** with chlorodifluorophosphine gave only the cone conformer of the fully PF_2-functionalized calix[4]arene **10** (see Scheme 1). On the contrary, the reaction of PF_2Cl with O,O'-bis(trimethylsilyl)catechole led to 1-O-(difluorophosphite)-2-O-(trimethylsilyl)catechole. The insertion of a second PF_2-group *via* reaction with another PF_2Cl molecule failed, because the substitution of the silyl group in monosubstituted O-(trimethylsilyl)catechole is slower than the formation of the cyclic product 2-fluoro-1,3,2-benzodiazaphosphole.[50,51] This behaviour is probably caused by the different reactivity of the phenolic and alcoholic $OSiMe_3$-groups, and by steric reasons (distant $OSiMe_3$-groups in **3** and **9**, compared to **10**). The structure of **10** was established by NMR and IR spectroscopy, mass spectrometry and elemental analysis.

Previously, we reported that mono- and disubstituted difluorophosphite derivatives **5** and **6** (illustrated in Fig. 2) led, by heating at 50°C, to the formation of derivative **E** (shown in Fig. 3) and additional fluorotrimethylsilane or PF_3.[10-17]

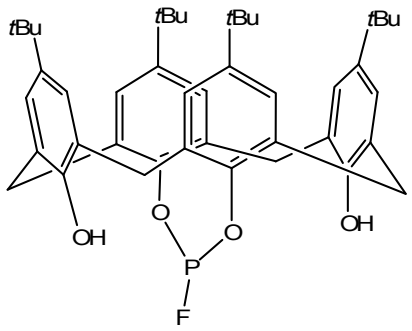


Fig. 3 – Compound **E**, obtained from **5** or **6** after heating.

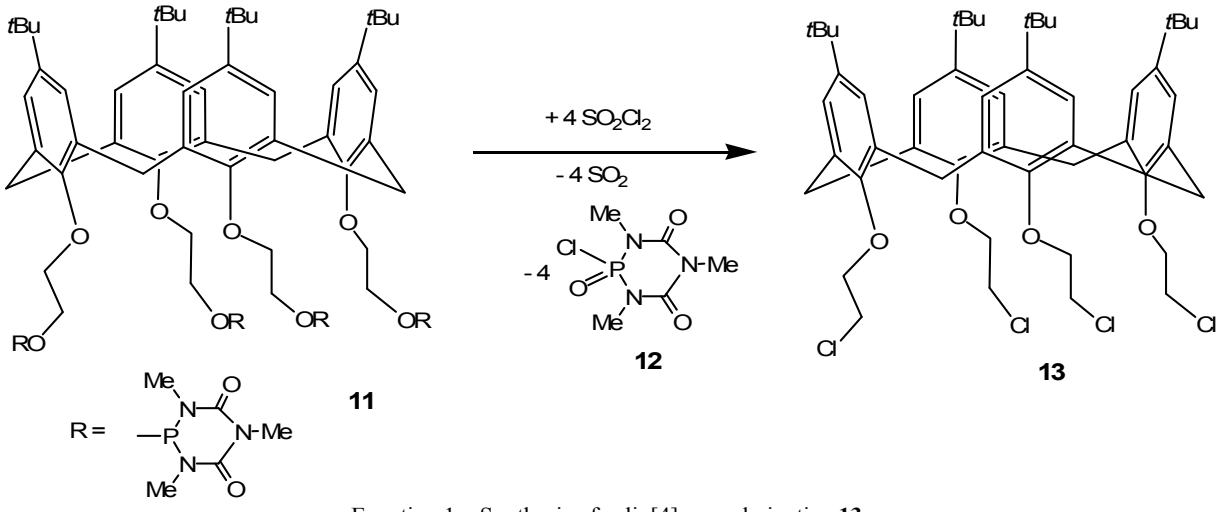
On the contrary, derivative **10** is stable in solution at 115°C. Comparing the behaviour at heating of compound **10** to that of compounds **5** and **6**,[10-17] no intramolecular reaction with elimination of phosphorus trifluoride was observed. The unusual stability of **10** towards **5** and **6** is due to the sufficient distance to each other exhibited by all the PF_2-groups. The driving force of the scrambling process can be explained satisfactorily by the thermodynamically irreversible processes theory, because formation of phosphorus trifluoride means an increase of entropy in closed systems.[52]

In order to determine its stability in solution, 100 mg of **10** were dissolved in 1 ml of C_7D_8 and heated to 115°C for 48 hours. Derivative **10** was recovered unchanged, ^{1}H-, ^{19}F- and ^{31}P-NMR spectra recorded after heating were identical to those recorded before heating.

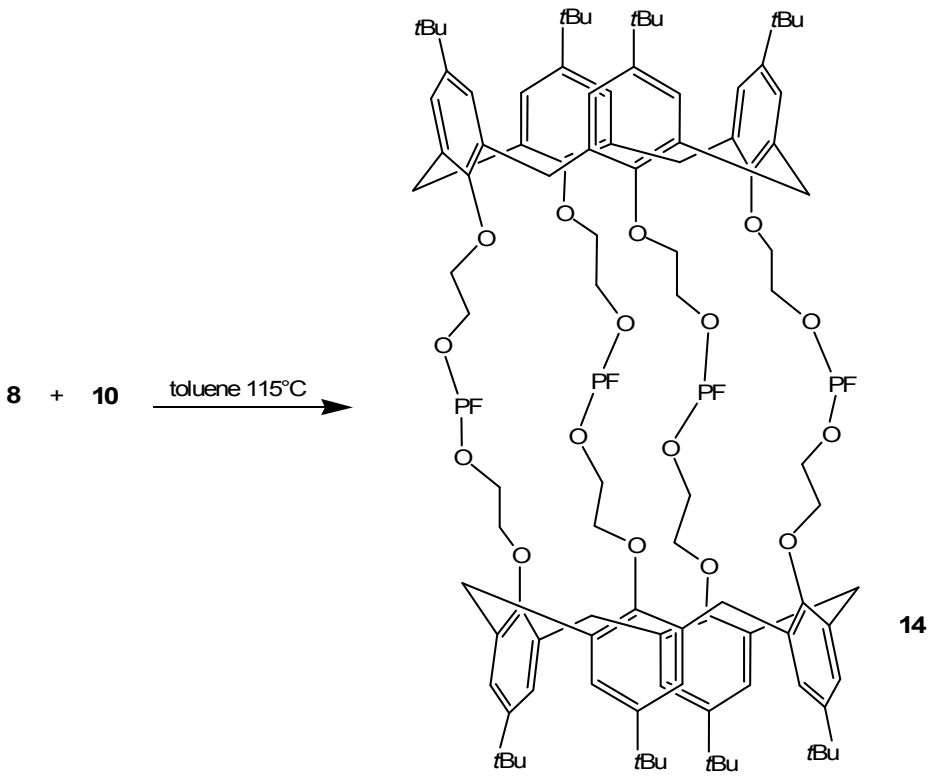
Reaction of **9** with 2-chloro-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione[50] led, with elimination of chlorotrimethylsilane, exclusively to the cone conformer of **11**, confirmed by the ^{31}P-NMR spectrum (shows only one singlet at $\delta(^{31}P)$ = 92.24 ppm).

Reaction of 11 with SO_2Cl_2 affording 13

When compound **11** was allowed to react with sulfuryl chloride, formation of **13** accompanied by the already known 2-chloro-2-oxo-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^4$-phosphorin-4,6-dione **12** was observed[53]. The reaction scheme is illustrated in Equation 1.



Equation 1 – Synthesis of calix[4]arene derivative **13**.



Equation 2 – Synthesis of calix[4]arene derivative **14**.

Compound **13** was unambiguously characterized by NMR and IR spectroscopy and by elemental analysis. Calix[4]arene **13**, bearing a chlorine atom directly bonded to the spacer, was found to be a stable product, existing at room temperature only in the cone conformation.

Reaction of 8 with 10 affording 14

Reaction of **8** with **10** in a molar ratio of 1:1 in toluene at 115°C furnished the macrocycle **14**, according to Equation 2.

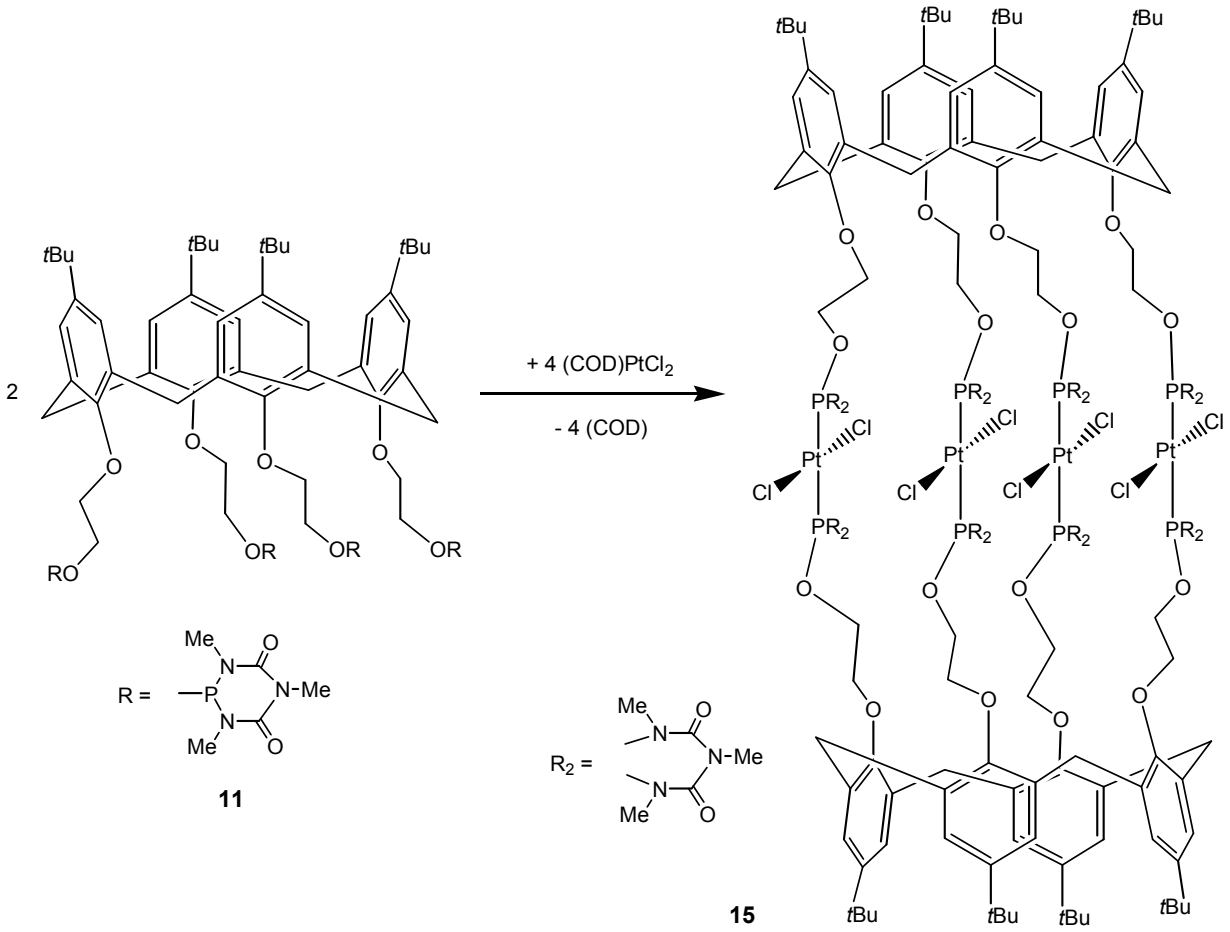
The structure of **14** was assigned on the basis of the ^{1}H-, ^{19}F-, ^{31}P-NMR and IR spectra and on FAB mass spectrometry investigation. According to NMR evidence, compound **14** exists in (C_4) symmetrical structure. No dynamic character was observed in toluene after heating for 12 h to 115°C. The high symmetry of the molecule is illustrated particularly by plain ^{1}H-NMR spectrum, where a pair of doublets is found for the methylene protons (Ar-C$\underline{H}_2$-Ar). The presence of an only single υ(PF) absorption band in the FT-IR-spectrum at 850 cm^{-1} indicates only one P-F bond. Under similar experimental conditions, the FT-IR spectrum of the starting material **10** exhibits two υ(PF) bands, indicating the existence of two P-F bonds in the molecule. The formation of **14** was supported also by FAB mass spectrometry, which indicated the molecular ion. The chemical shift at $\delta(^{31}P)$ = 109 ppm (doublet, $^{1}J(PF)$ = 1213.75 Hz) and the resonance at $\delta(^{19}F)$ = - 41.65 ppm (doublet, $^{1}J(FP)$ = 1212.18 Hz) were attributed to the compound **14.**

The Assembly of Two Molecules of 11 by Trans-Complexation with (COD)$PtCl_2$ affording Compound 15

The connection of two or more phosphorus(III)-containing calix[4]arene units, by complexation of the phosphorus(III) donors to transition metal acceptors, can lead to a receptor having new properties, unknown in simple transition metal phosphine complexes.

In this paper, we present the highly symmetrical structure of the intermolecular tetrakis-bridged trans dichloroplatinum(II) complex **15** containing phosphorus(III) groups.

When **11** was allowed to react in a solution of dichlorormethane with (COD)$PtCl_2$ in a molar ratio of 1:2, the *trans*-dichloroplatinum(II) dimmer **15**, intramoleculary bridged by functionalized calix[4]arene units, involving all four $\sigma^4\lambda^3$-phosphorus atoms of each calix[4]arene unit in the bridges (as depicted by Equation 3), was observed.



Equation 3 – Synthesis of the trans intermolecular dimeric tetranuclear complex **15 .**

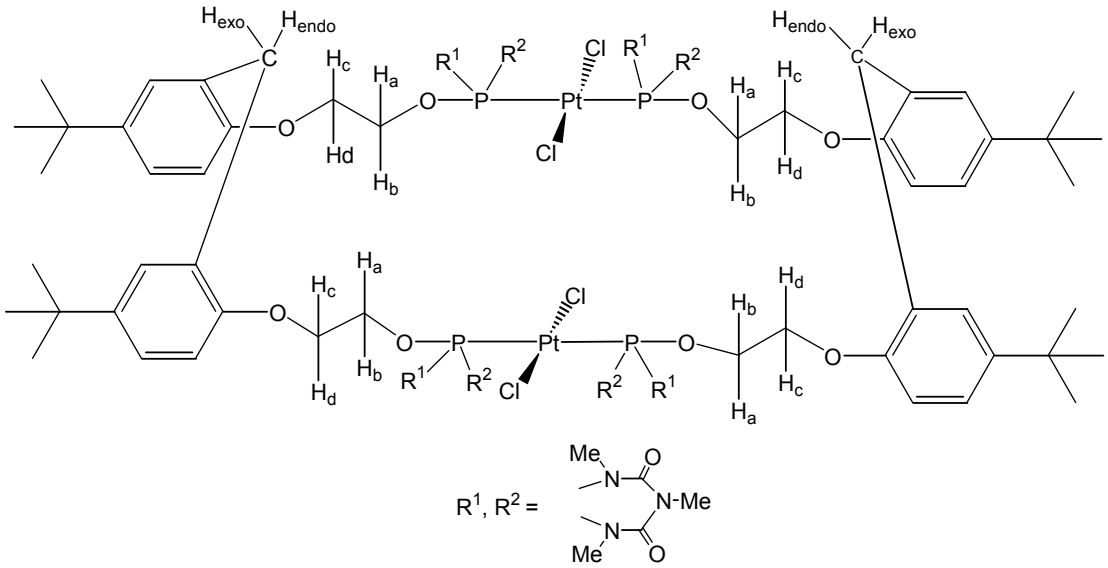


Fig. 4 – Illustration of the *exo* and *endo* protons in **15**.

The formation of the dimmer **15** does not depend on its concentration in dichloromethane. In diluted solution (100 mg in 100 ml dichloromethane) and in concentrated solution (200 mg in 5 mL of dichloromethane), only the formation of the trans-dimeric complex was noticed.

According to ^{1}H-, ^{13}C-, ^{31}P-NMR evidence, **15** exists exclusively in the cone conformation and (C_4) symmetrical structure. No dynamic character was observed at room temperature in solution. The ^{31}P-NMR spectrum of **15**, recorded at 20°C and 50°C , exhibited one triplet at $\delta(^{31}P)$ = 60.4 ppm. In contrast to the results found for some *bis*-functionalized tetrakis-*tert*-butylcalix[4]arene phosphinite derivatives,[37-39,42] the intramolecular *cis*-dichloroplatinum(II) bridged complex was not formed.

The high symmetry of the molecule (C_4) is highlighted particularly by plain ^{1}H-, ^{13}C-, ^{31}P-NMR spectra. The ^{1}H-NMR spectrum of **15** reveals a pair of doublets for the Ar-C$\underline{H_{exo}}(\underline{H_{endo}})$-Ar protons. The diastereotopicity is due to the fact that one proton is oriented out of the calixarene macrocycle (the *exo* proton) and the other oriented inward (the *endo* proton), as depicted in Fig. 4.

The *endo* proton is influenced by the dipolar moments of the neighbouring oxygen atoms (phenyl groups are bonded in "*syn*-position" in calix[4]arenes).[42,45,47,48] A proton-decoupled ^{13}C-NMR spectrum exhibits only one $\delta(^{13}C)$-value for the carbon atom of the methylene group. The difference between the $\delta(^{13}C)$-values for *syn*- and *anti*-conformation is due to steric reasons rather than electronic reasons,[47,48] this is clear evidence for the cone conformation.[47]

The propensity of 1,3-diphosphinooxy-calix[4]arenes to behave as bridging ligands capable of forming oligomeric complexes was also verified with unsymmetrically substituted di-phosphinites.[37] Homodimetallic [{calix[4]-$(PR_2)_4$}$(MCl_2)_2$] (R= Me, Ph; M= Pt, Pd, Rh) and heterodimetallic [{calix[4]-$(PPh_2)_4$}$NiCl_2${$Mo(CO)_4$}] were reported by Floriani.[42] The *cis* stereochemis-try around the metal atoms was described for calix[4]arenes bearing bidentate phosphorus(III) ligands with methy-lene as spacer.[38]

The trans arrangement around the platinum(II) atoms was deduced from ^{31}P-NMR and FT-IR spectra. The presence of a single υ(PtCl) adsorption band in the FT-IR spectrum of **15** indicated a trans orientation of the chlorine atoms. This arrangement is supported by the fact that under similar experimental conditions two υ(PtCl) bands in the range 330 – 280 cm^{-1} were observed for the cis-dichloroplatinum(II) complex.[38]

It is well known that cis- and trans-coordination geometry can be distinguished by the $^{1}J(^{31}P^{195}Pt)$ coupling constant.[57] In case of compound **15**, the $^{1}J(^{31}P^{195}Pt)$ coupling constant of 2755.62 Hz confirms the trans coordination at the platinum atoms.

The dimeric structure of **15** was established by FAB mass spectrometry, the base peak appears at m/z 4063.5 [M^+-Cl] and the parent ion at m/z 4098 [M^+].

Compound **15** is stable in the solid state and in solution. In order to determine its stability in solution, 100 mg of **15** were dissolved in 1 mL of $ClCH_2CH_2Cl$ and heated to 80°C for 4h. **15** was recovered unchanged, fact supported by ^{1}H- and ^{31}P-NMR spectroscopy. Only inclusion of COD and CH_2Cl_2 molecules were observed by ^{1}H-NMR spectroscopy and mass spectrometry.

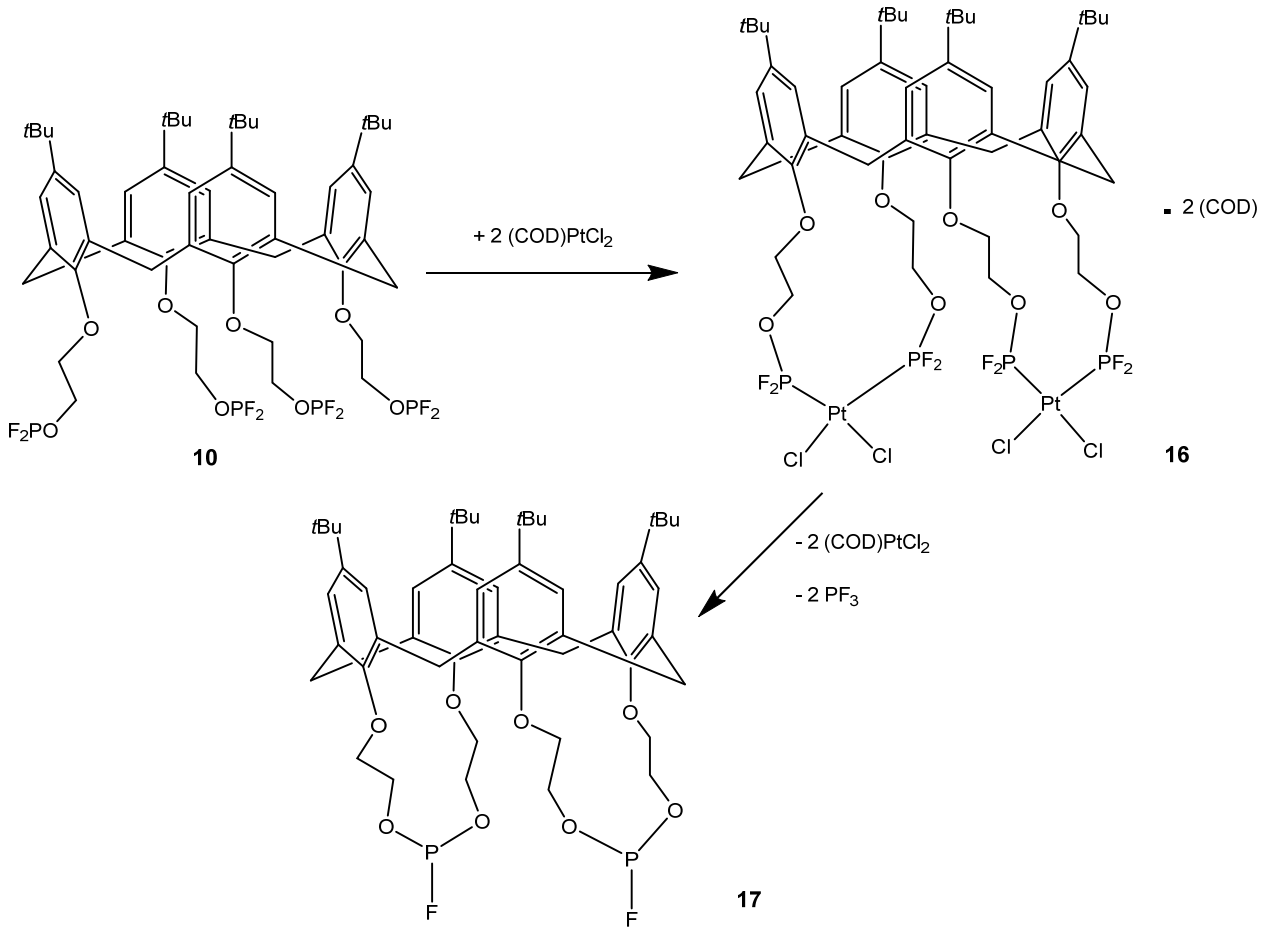
Cis-Intramolecular Complexation of 10 with (COD)$PtCl_2$

The reaction of **10** with (COD)$PtCl_2$ in a molar ratio of 1:2 afforded the cis-complex **16**, according to Scheme 2, in good yield.

Contrary to the observations made when **11** was treated with (COD)$PtCl_2$ (see Scheme 1), this time the cis complex was obtained. We attribute the formation of the cis-intramolecular complex **16** to the decreased basicity (reactivity) and steric demand of **10** in comparison to **11**. Compound **16** was obtained as a crystalline solid in yields > 80%.

The cis-structure of **16** was assigned based on the ^{1}H-, ^{19}F-, ^{31}P-NMR and IR spectra. In contrast to the observations made for **15**, the room temperature ^{1}H-NMR spectrum indicates a (C_2) symmetrical structure for this complex. The signals corresponding to the methylene protons were split into two pairs of doublets with coupling constants of $^{2}J(HH)$ = 13.00 and 13.14 Hz. The doublets at δ = 3.24 and 3.36 ppm were assigned to the *exo* protons of the bridging methylene (Fig. 6), and at δ = 4.08 and 4.47 to the *endo* protons.

The two multiplets at δ = 4.82 and 4.89 ppm were attributed to protons H_a and H_b of the $C\underline{H_aH_b}OPF_2$ groups. The two pairs of multiplets at δ = 4.11, 4.16, 4.56 and 4.59 ppm were assigned to H_c and H_d protons of the Ar-O-C$\underline{H_cH_d}$ groups. This nonequivalency is due to the fact that the four protons are inside the 16-membered metallocycle (H_b,H_d) and two are pointing outside the metallocycle (H_a, H_c, see Fig. 6).



Scheme 2 – Synthesis of complex **16**.

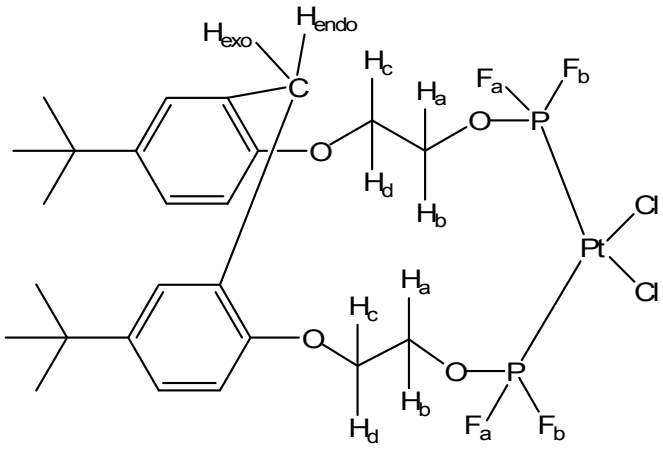


Fig. 6 – Illustration of the different protons in **16**.

The ^{31}P-NMR spectrum of **16** exhibits a ddtt at δ = 73.07 ppm and platinum satellites with coupling constants of $^{1}J(^{31}P^{19}F)$ = 3074.91 Hz, $^{1}J(^{31}P^{195}Pt)$ = 2504.30 Hz, $^{2}J(PP)$ = 25.00 Hz and $^{3}J(PF)$ = 17.70 Hz. The pronounced high-field shift, compared to the value of the free ligand **10** ($\delta(^{31}P)$ = 120 ppm), suggests the presence of a σ/π-synergism.[58] The ^{31}P- and ^{19}F-NMR evidence, (δ (ppm) = - 41.35 (dddt, $^{1}J(FP)$ = 1246.50 Hz, $^{2}J(^{19}F^{195}Pt)$ = 616.20 Hz, $^{3}J(FP)$ = 25,97 Hz, $^{4}J(FF)$ = 15.38 Hz) and the typical value of the $^{1}J(^{31}P^{195}Pt)$ coupling constants, indicates a cis orientation of the ligand at platinum in the square planar coordination geometry of the platinum(II) complex. The presence of two υ(PtCl) absorption bands in the FT-IR spectrum of **16** in the range

350–280 cm^{-1} indicated a cis orientation of the chlorine atoms. These results are similar to those described in the literature.[37-39]

Compound **16** is neither stable in the solid state nor in solution. In order to determine its stability in solution, 100 mg of **16** were dissolved in CD_2Cl_2 at room temperature. ^{1}H- and ^{31}P-NMR spectra recorded after 12 h were not identical with those recorded after 1 h. In contrast to **10**, **15** was found to undergo a transformation in CD_2Cl_2 after 12 h at 25° and respectively 40°C with formation of dimmer **17**, $(COD)PtCl_2$,[59] PF_3[60] and an unidentified product. The disproportionation reaction was monitored by ^{31}P-NMR spectroscopy. According to the ^{31}P-NMR spectrum, a mixture of two different compounds and PF_3.[60] (quartet at $\delta(^{31}P) = 140$ ppm) was formed. The chemical shift at $\delta(^{31}P) = 120$ ppm (doublet, $^1J(PF) = 1212.18$ Hz) can be attributed to compound **17**. The resonance at $\delta(^{31}P) = 95$ ppm (singlet) cannot be attached to a defined molecule, because only **17**, PF_3[60] and $(COD)PtCl_2$[59] could be isolated in pure form from the reaction mixture. The formation mechanism of **17** by an unusual transformation of **16** in solution at room temperature cannot be explained. A scrambling process is assumed in this case, caused by an approach of the PF_2-groups by intermolecular rearrangement of the $(PF_2)_2PtCl_2$ groups (theory of thermodynamically irreversible processes[52]). This effect can be explained by weaker PF_2-Pt bonds.

The FAB mass spectrometry investigation proves the instability of **16**. The parent ion of **16** could not be detected, whereas that of **17** was observed.

EXPERIMENTAL

Experimental conditions, including NMR conditions and instruments, were as described in previous publications, *e.g.* [61-69]

NMR spectra were recorded on a Bruker AC 400 spectrometer and on a Bruker DMX 600 spectrometer with inverse probe head.

Chemical shifts (d) are given in ppm downfield from TMS. Coupling constants are given in Hz. Many assignments were made with support of DEPT, $^1H^1H$-COSY, $^1H^{13}C$-COSY, HMQC, HMBC and TOCSY experiments. Mass spectra (ESI) were recorded using a Finnigan MAT TSQ 700 triple quadrupole mass spectrometer equipped with a NanoES ion source. Elemental analyses were conducted at the Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig. TLC was performed on silica gel 60 F254 coated foil (Merck). Preparative column chromatography was performed with silica gel 60 (63–200 mm, Merck).

"In *vacuo*" refers to a pressure of *ca* 0.1 mm Hg at 25°C. Precursors: Tetrakis-(*tert*-butyl)-tetrakis(2-hydroxy)ethyl-calix[4]arene **8**;[49] 2-chloro-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione;[61-65] chlorodifluorophosphine;[32] dichloro(cycloocta-1,5-dien)platinum(II) $(COD)PtCl_2$.[59,65]

Compound 9

A mixture of 3.0 g (20.7 mmole) of diethylaminotrimethylsilane and a catalytic amount of chlorotrimethylsilane (0.05 mL) was added, at room temperature, dropwise to a solution of 3.0 g (3.6 mmole) of **8** in 50 mL toluene. The reaction mixture was stirred for 16 h at 60-80°C. Solvent and volatile components were removed in *vacuo*. The remaining colourless solid showed no impurities in the ^{1}H- and ^{13}C-NMR spectra. Yield: 3.2 g (80%), m.p. 188°C.

^{1}H-NMR (CD_2Cl_2): δ (ppm) = 0.13 (s, 36H, $Si(C\underline{H}_3)_3$), 1.07 (s, 36H, $(C\underline{H}_3)_3C$), 3.09 (d, 4H, $^2J(HH) = 12.56$ Hz, Ar-$C\underline{H}^1H^2$-Ar), 4.03 (m, 16H, $OC\underline{H}_2C\underline{H}_2O$), 4.41 (d, 4H, ($^2J(HH) = 12.54$ Hz, Ar-$CH^1\underline{H}^2$-Ar), 6.75 (s, 8H, aromatic H). ^{13}C-NMR (CD_2Cl_2): δ (ppm) = – 0.23 (s, $Si(\underline{C}H_3)_3$), 31.55 (s, Ar-$\underline{C}H_2$-Ar), 31.63 (s, $C(\underline{C}H_3)_3$), 34.12 (s, $\underline{C}(CH_3)_3$), 61.94 and 75.91 (2s, $O\underline{C}H_2\underline{C}H_2O$), 125.39 – 153.95 (m $\underline{C}_6H_2$). EI-MS: m/z (%): 1114 (46) [M^+], 1041 (10) [M^+-$SiMe_3$], 997 (18) [M^+-$OCH_2CH_2OSiMe_3$], 117 (75) [$OCH_2CH_2OSiMe_3^+$], 73 (100) [$SiMe_3^+$]. $C_{64}H_{104}O_8Si_4$ (1113.87): calcd. C 69.01, H 9.41; found C 69.02, H 9.44.

Compound 10

In a heavy-walled glass tube, fitted with a Teflon®-stepcock, a solution of 1.0 g (0.9 mmole) of **9** in 25 ml dichloromethane was cooled at -196°C. Subsequently, 1.0 g (9.6 mmole) of chlorodifuoro-phosphine was condensed onto the solution. The reaction mixture was allowed to warm up to room temperature over 1 h and was stirred overnight at this temperature. Solvent and all volatile compounds were removed in *vacuo* and the remaining colourless solid was dried in *vacuo*. Yield: 0.78 g (79%); m.p. 134 – 136°C.

^{1}H-NMR (CD_2Cl_2): δ (ppm) = 1.09 (s, 36H, $(C\underline{H}_3)_3C$), 3.21 (d, 4H, $^2J(HH) = 12.7$ Hz, Ar-$C\underline{H}^1H^2$-Ar), 4.15 (t, 8H, $^3J(HH) = 5.6$ Hz, $OC\underline{H}_2CH_2OPF_2$), 4.37 (d, 4H, ($^2J(HH) = 12.7$ Hz, Ar-$CH^1\underline{H}^2$-Ar), 4.50 – 4.59 (m, 8H, $OCH_2C\underline{H}_2OPF_2$), 6.84 (s, 8H, aromatic H). ^{13}C-NMR (CD_2Cl_2): δ (ppm) = 31.11 (s, Ar-$\underline{C}H_2$-Ar), 31.50 (s, $C(\underline{C}H_3)_3$), 34.16 (s, $\underline{C}(CH_3)_3$), 62.58 (m, $OCH_2\underline{C}H_2OPF_2$), 73.61 (d, $^3J(PC) = 3.10$ Hz, $O\underline{C}H_2CH_2OPF_2$), 125.72 – 152.94 (m, $\underline{C}_6H_2$). ^{19}F-NMR (CD_2Cl_2): δ (ppm) = – 48.9 (d, $^1J(FP) = 1290.7$ Hz). ^{31}P-NMR (CD_2Cl_2): δ (ppm) = 114.8 (t, $^1J(PF) = 1290.7$ Hz). IR (KBr): $\upsilon_{(as)} = 790$ cm^{-1}, $\upsilon_{(s)} = 810$ cm^{-1} (PF_2). EI-MS: m/z (%): 1096 (100) [M^+], 1011 (2) [M^+-OPF_2], 983 (2) [M^+-$CH_2CH_2OPF_2$], 113 (10) [CH_2CH_2 OPF_2^+], 57 (62) [$C(CH_3)^+$]. $C_{52}H_{68}F_8O_8P_4$ (1096.99): calcd. C 56.94, H 6.25; found C 56.87, H 6.54.

Compound 11

To a solution of 1.0 g (0.90 mmole) of **9** in 15 ml dichloromethane was added dropwise (room temperature, 30 min) a solution of 0.57 g (3.60 mmole) of 2-chloro-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione in 5 mL dichloromethane. The solution was stirred for 1 day at room tempera-ture. Solvent and all volatile products were removed in *vacuo* and the residue was washed three times with 10 mL diethyl ether. The remaining colourless solid was dried in *vacuo*. Yield: 1.16 g (86%); m.p. 228 – 230°C.

^{1}H-NMR (CD_2Cl_2): δ (ppm) = 1.06 (s, 36H, ($C\underline{H}_3)_3C$), 3.06 (d, 24H, ^{3}J(HH) = 11.81 Hz, ($C\underline{H}_3$)NP), 3.19 (s, 12H, $C\underline{H}_3N(C(=O))_2$), 4.23 (d, 4H, ^{2}J(HH) = 12.75 Hz, Ar-$C\underline{H}^1H^2$-Ar), 3.90 – 4.15 (m, br, 20H, $OC\underline{H}_2CH_2O$ and Ar-$CH^1\underline{H}^2$-Ar), 6.77 (s, 8H, aromatic H). ^{13}C-NMR (CD_2Cl_2): δ (ppm) = 30.34 (s, ($\underline{C}H_3)N(C(=O))_2$), 31.34 (s, Ar-$\underline{C}H_2$-Ar), 31.48 (s, $C(\underline{C}H_3)_3$), 31.50 (d, ^{2}J(PC) = 28.87 Hz, $(\underline{C}H_3N)_2P$), 34.12 (s, $\underline{C}(CH_3)_3$), 63.59 (s, Ar-$O\underline{C}H_2CH_2$), 73.73 (d, ^{2}J(PC) = 3.32 Hz, $OCH_2\underline{C}H_2OP$), 125.32 – 152.84 (m, $\underline{C}_6H_2$), 153.53 (d, ^{2}J(PC) = 9.89 Hz, $\underline{C}$(=O)). ^{31}P-NMR (CD_2Cl_2): δ (ppm) = 94.98 (s). IR (KBr): υ = 1620 – 1670 cm^{-1} (C(=O)). EI-MS: m/z (%): 1518 (60) [M$^+$], 1344 (40) [M$^+$-MeN(CONMe)$_2$P], 1316 (100) [M$^+$- MeN(CONMe)$_2$PCH$_2$CH$_2$O], 1170 (20) [M$^+$-2MeN(CONMe)$_2$P], 996 (90) [M$^+$-3MeN(CONMe)$_2$P], 174 (90) [MeN(CONMe)$_2$P$^+$]. $C_{72}H_{104}N_{12}O_{16}P_4$ (1517.57): calcd. C 56.98, H 6.90, N 11.07; found C 57.25, H 7.00, N 10.55.

Compound 13

Equimolar amounts of **11** (1.0 g, 0.66 mmole) and SO_2Cl_2 (0.09 g, 0.66 mmole) in 20 mL dichloromethane were stirred for 2 days at room temperature. Subsequently, the solvent and all volatile compounds were removed in *vacuo*. The remaining colourless solid was washed three times with 20 ml portions of diethyl ether and then dried in *vacuo*. The combined etheric solutions were concentrated in *vacuo* to a volume of ca. 20 ml and kept at – 20°C for 1 day, Yield: 78%; dec. 216 – 218°C.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.07 (s, 36H, ($C\underline{H}_3)_3C$), 3.18 (d, 4H, ^{2}J(HH) = 12.08 Hz, Ar-$C\underline{H}^1H^2$-Ar), 4.02 – 4.07 (m, 16H, $OC\underline{H}_2C\underline{H}_2Cl$), 4.38 (d, 4H, ^{2}J(HH) = 12.84 Hz, Ar-$CH^1\underline{H}^2$-Ar), 7.24 (s, 8H, aromatic H). ^{13}C-NMR ($CDCl_3$): δ (ppm) = 30.95 (s, Ar-$\underline{C}H_2$-Ar), 31.38 (s, $C(\underline{C}H_3)_3$), 33.91 (s, $\underline{C}(CH_3)_3$), 42.48 (s, $OCH_2\underline{C}H_2Cl$), 74.70 (s, 4C, $O\underline{C}H_2CH_2Cl$), 125.35 – 152.31 (m, $\underline{C}_6H_2$). IR (KBr): υ = 759.36 cm^{-1} (CH_2-Cl). $C_{52}H_{68}Cl_4O_4$ (898.39): calcd. C 69.48, H 7.57; found C 68.68, H 7.59.

Compound 14

Reaction of **8** with **10** in a molar ratio of 1:1 in toluene at 115°C furnished the macrocycle **14**.

^{1}H-NMR (CD_2Cl_2): δ (ppm) = 1.05 (s, 72H, ($C\underline{H}_3)_3C$), 3.21 (d, 8H, ^{2}J(HH) = 12.6 Hz, Ar-$C\underline{H}^1H^2$-Ar),
4.35 (d, 8H, (^{2}J(HH) = 12.7 Hz, Ar-$CH^1\underline{H}^2$-Ar), 4.18 (t, 16H, ^{3}J(HH) = 5.8 Hz, $OC\underline{H}_2CH_2OPF$), 4.30 – 4.50 (m, 16H, $OCH_2C\underline{H}_2OPF$), ^{13}C-NMR (CD_2Cl_2): δ (ppm) = 31.11 (s, Ar-$\underline{C}H_2$-Ar), 31.50 (s, $C(\underline{C}H_3)_3$), 34.16 (s, $\underline{C}(CH_3)_3$), 60.28 (m, $OCH_2\underline{C}H_2OPF$), 70.30 (d, ^{3}J(PC) = 3.10 Hz, $O\underline{C}H_2CH_2OPF$), 126.72 – 151.94 (m, $\underline{C}_6H_2$), ^{19}F-NMR (CD_2Cl_2): δ (ppm) = – 41.65 (d, ^{1}J(FP) = 1212.18 Hz). ^{31}P-NMR (CD_2Cl_2): δ (ppm) = 109 ppm (d, ^{1}J(PF) = 1213.75 Hz). IR (KBr): $\upsilon_{(s)}$ = 850 cm^{-1} (PF); EI-MS: m/z (%): 1842 (100) [M$^+$], 1748 (2) [M$^+$-CH_2CH_2OPF], 94 (10) [CH_2CH_2 OPF$^+$], 84 (62) [$C(CH_3)_3^+$]. $C_{104}H_{136}F_4O_{16}P_4$ (1842.08): calcd. C 66.80, H 7.44; found C 65.87, H 6.95.

Compound 15

A solution of 200 mg (0.53 mmole) (COD)$PtCl_2$ in 5 ml CH_2Cl_2 was added dropwise at 0°C to a solution of **11** 1.6 g (0.26 mmole) in dichloromethane. The reaction mixture was stirred for 16 h at room temperature. The solvent was removed in *vacuo* and the residue was washed three times with small amounts of ice cold diethyl ether and hexane. The remaining colourless solid was recrystallized from dichloromethane/hexane. Yield: 1.61 g (75%); dec. 260–265°C.

^{1}H-NMR (CD_2Cl_2): δ (ppm) = 1.00 (s, 72H, ($C\underline{H}_3)_3C$), 2.36 (m, 32H, $C\underline{H}_2C\underline{H}_2$ of COD), 2.95 (d, 12H, ^{3}J(PH) = 10.23 Hz, ($C^1\underline{H}_3$)NP), 3.01 (d, 8H, ^{2}J(HH) = 11.69, Ar-$C\underline{H}_{exo}H_{endo}$-Ar), 3.20 (s, 12H, $C\underline{H}_3N(C(=O))_2$), 3.27 (d, 12H, ^{3}J(PH) = 9.78 Hz, ($C^2\underline{H}_3$)NP), 3.77 – 4.11 (m, 32H, $OC\underline{H}_a\underline{H}_bC\underline{H}_c\underline{H}_dO$), 4.73 (d, 8H, ^{2}J(HH) = 11.57 Hz, Ar-$CH_{exo}\underline{H}_{endo}$-Ar), 5.34 (s, 4H, $C\underline{H}_2Cl_2$), 5.58 (t, 16H, $\underline{H}C$=C$\underline{H}$ of COD), 6.75 (s, 16H, aromatic H). ^{13}C-NMR (CD_2Cl_2): δ (ppm) = 28.34 (s, $\underline{C}H_2$ of COD), 31.28 (s, $\underline{C}H_3N(C(=O))_2$), 31.40 (s, $C(\underline{C}H_3)_3$), 31.80 (d, $PN(\underline{C}H_3)_2$), 32.13 (s, Ar-$\underline{C}H_2$-Ar), 34.20 (s, $\underline{C}(CH_3)_3$), 66.85 (s, $\underline{C}H_2Cl_2$), 72.70 (s, Ar$O\underline{C}H_2$), 74.40 (d, ^{2}J(PC) = 3.8 Hz, $OCH_2\underline{C}H_2OP$), 124.27 – 146.77 (m, $\underline{C}_6H_2$), 150.11 and 151.63 (2s, 16C, $\underline{C}$(=O)). ^{31}P-NMR ($CDCl_3$): δ (ppm) = 60.40 (t, ^{1}J(PPt) = 2755.62 Hz). IR (KBr): υ ($PtCl_2$)= 305.7 cm^{-1}, υ (C=O) = 1722 and 1680 cm^{-1}. FAB-MS: m/z (%): 4098 (8) [M$^+$], 4063 (100) [M$^+$-Cl], 2049 (100) [M$^+$/2-C], 2013 (75) [M$^+$/2-Cl]. $C_{144}H_{208}Cl_8N_{24}O_{32}P_8Pt_4$ x4 C_8H_{12} x 2 CH_2Cl_2 (4701.76): calcd. C 45.47, H 5.57; found C 45.39, H 5.60.

Compound 16

A solution of 200 mg (0.53 mmole) (COD)$PtCl_2$ in 500 ml CH_2Cl_2 was added dropwise to a solution of **10** (0.290 g, 0.26 mmole) in dichloromethane. The reaction mixture was stirred for 16 h at room temperature. The solvent was removed in *vacuo* and the residue was washed three times with small amounts of ice cold diethyl ether and hexane to give a crystalline solid. Yield: 0.345 g (80%); dec. 148 – 150°C.

^{1}H-NMR (CD_2Cl_2): δ (ppm) = 1.09 (s, 36H, $C(C\underline{H}_3)_3$), 2.35 (m, 16H, $C\underline{H}_2C\underline{H}_2$ of COD), 3.24 and 3.36 (2d, 4H, $\underline{H}_{exo}$, ^{2}J(HH) = 12.52 and 13.14 Hz), 4.08 and 4.47 (2d, 4H, $\underline{H}_{endo}$, ^{2}J(HH) = 13.42 and 13.00 Hz), 4.11, 4.16, 4.56 and 4.59 (4m, 8H, $OCH_cH_dC\underline{H}_a\underline{H}_bO$), 4.82 and 4.89 (2m, 8H, $C\underline{H}_a\underline{H}_bOPF_2$), 5.33 (s, 6H, $C\underline{H}_2Cl_2$), 5.55 (t, 8H, $\underline{H}C$=C$\underline{H}$ of COD, ^{3}J(HH) = 2.16 Hz), 6.86 (s, 8H, $C_6\underline{H}_2$). ^{19}F-NMR (CD_2Cl_2): δ (ppm) = - 41.35 (dddt, ^{1}J(FP) = 1246.50 Hz, ^{2}J(^{19}F^{195}Pt) = 616.20 Hz, ^{3}J(FP) = 25.97 Hz, ^{4}J(FF) = 15.38 Hz). ^{31}P-NMR (CD_2Cl_2): δ (ppm) = 73.07 (ddtt, ^{1}J(PF) = 3074.91 Hz, ^{1}J(^{31}P^{195}Pt) = 2504.30 Hz, ^{2}J(PP) = 25.00 Hz, ^{3}J(PF) = 17.70 Hz. IR (KBr): υ ($PtCl_2$)= 280 and 319 cm^{-1}, $\upsilon_{(as)}$(PF)= 790 cm^{-1}, $\upsilon_{(s)}$(PF)= 899 cm^{-1}. $C_{52}H_{68}Cl_4F_8O_8P_4Pt_2$ x2 C_8H_{12} x 3 CH_2Cl_2 (1629.04): calcd. C 40.60, H 4.70; found C 40.69, H 4.65.

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