Regioselective upper-rim functionalizations of calix[4]arene by diphenylphosphino groups

Jonathan Gagnon, Martin Vézina, Marc Drouin, and Pierre D. Harvey

Abstract: The regioselective upper-rim functionalization of calix[4]arene have been performed to prepare all the multisubstituted diphenylphosphine derivatives. In addition, the X-ray structures of 5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetra-*n*-propoxycalix[4]arene and 5,11,17,23-tetrakis(diphenylphosphino)-25,26,27,28-tetra-*i*-propoxy-calix[4]arene have been determined. Regioselective functionalizations have been achieved using methods that involve appropriate choices of bases, alkyllithium–solvent systems, stoichiometry, and reaction times. A new and convenient method for selectively preparing derivitized calix[4]arenes at proximal positions in relative large scale quantity has been developed and involves a transesterification of the distal diester derivative into the proximal isomer.

Key words: calix[4]arenes, phosphine, upper-rim, X-ray structure, transesterification.

Résumé : On a réalisé la fonctionnalisation régiosélective de la anneau supérieure du calix[4]arène dans le but de préparer tous les dérivés multisubstitués de la diphénylphosphine. De plus, on a fait appel à la diffraction des rayons X pour déterminer les structures du 5,17-dibromo-11,23-bis(diphénylphosphino)-25,26,27,28-tétra-*n*-propoxycarix[4]arène et du 5,11,17,23-tétrakis(diphénylphosphino)-25,26,27,28-tétra-*i*-propoxycalix[4]arène. La fonctionnalisation régiosélective a été réalisée à l'aide de méthodes impliquant des choix appropriés de bases, des systèmes alkyllithium–solvant, de stoechiométrie et de temps de réaction. On a mis au point une nouvelle méthode pratique de préparer sélectivement et sur une échelle relativement grande des calix[4]arènes dérivatisés dans des positions proximales; elle implique une transestérification du diester distal en isomère proximal.

Mots clés : calix[4]arènes, phosphine, anneau supérieure, structure par diffraction des rayons X, transestérification.

[Traduit par la Rédaction]

Introduction

Calix[4]arenes are versatile molecules that are easy to synthesize (1) and are well-known for the host–guest chemical applications that they provide (1, and for an example also see ref. 2). Indeed with their ability to interact with cationic species in the ionophoric section of the cavity located at the lower rim, a great deal of important research in the area of ion transport, novel sensors, and selective receptors have been performed (3). On the other hand, the supramolecular chemistry offered with their cone conformation, also allows neutral organic guests to interact with the hydrophobic upper-rim cavity. Although multiple examples of neutral guests are already reported for molecules such as toluene (4), acetone (5), alkanes, and other substrates (6), applications have not been fully developed. The chemistry in the area of complexation of transition metals onto calix[4]arene has been mainly focused in the lower rim (7), and it is only recently that some examples of upper-rim derivatized calix[4]arene with transition metal-containing fragments, have appeared (8–10). In fact, such complexes are attractive because of potential applications in regioselective reactivity. When a metal catalyst fragment is anchored at the upper-rim, it is placed near the proximity of a cavity where a guest organic molecule may reversibly bind. Hence, the interactions between the metal fragment and the organic substrate will be molecularly localized. In addition, for multiphosphinated ligands, coordination of more than one metal is conceivable. In this way the multidentate calix[4]arene device can also act as a platform molecule for the construction of polymetallic architectures.

Recently we reported the preparation and the characterization of the monophosphinated calix[4]arene using both the diphenyl- and di-(*i*-propyl)-phosphine groups (9), along with their corresponding oxides, and some rhodium(I) and rhodium(III) complexes (9, 10). We now wish to report the preparation of the complete series of upper-rim diphenylphosphine functionalized calix[4]arenes, which are potential multidentate ligands capable of coordinating soft transition metals. During the course of this work, regioselective derivatizations were necessary. Indeed regioselective lithiation at positions 5 and 17 of a tetrabrominated calix[4]arene, and the *n*-propylation, 3,5-dinitrobenzoylation, and benzoylation at positions 25 and 27 of the tetrahydroxycalix[4]arene will be discussed. A novel and convenient method for converting the 25,27-diester- into the 25,26-diester-27,28-dihydroxycalix-[4]arene has been developed using sodium hydride.

Received April 24, 2001. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on October 9, 2001.

J. Gagnon, M. Véniza, M. Drouin, and P.D. Harvey.[1]
Département de chimie, Université de Sherbrooke, Sherbrooke, QC J1K 2R1, Canada.

[1]Corresponding author (telephone: (819) 821-8000 ext 2005; fax: (819) 821-8017; e-mail: pharvey@courrier.usherb.ca).

 DOI: 10.1139/cjc-79-10-1439

Results and discussion

Tetraphosphines

To secure the cone conformation, calix[4]arene (**1**) is derivatized along the lower rim with propyl residues. It is now well-established that a three-carbon chain is the smallest group, when placed in the lower-rim, required to avoid rotations of the phenyl fragments around the bridging methylenes (11). Reinhoudt and co-workers (12) have developed an efficient propylation procedure of calix[4]arene using sodium hydride in DMF. In this work, this propylation method has been successfully applied for both *n*- and *i*-propyl leading to compounds **2a** and **2b**, respectively (Scheme 1). The cone conformation for all propylated derivatives has been confirmed by ^{1}H NMR, where the typical pattern for methylene protons is observed. Since propylation of *p*-bromocalix[4]arene is much slower than that of the parent calix[4]arene **1**, the propylation was carried out prior to bromination, which affords **3a** and **3b**, respectively.

The synthesis of 5,11,17,23-tetrakis(diphenylphosphino)-25,26,27,28-tetramethoxycalix[4]arene has been reported by Atwood and co-workers (13) with aims to design a molecular device for metal-cation extractions. Based on their procedure of using *n*-BuLi in THF at –78°C, the lithiation reaction was attempted on **3a** to synthesize the corresponding tetraphosphine derivative. However, the disubstituted 5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**5**) is selectively and reproducibly obtained, even with an excess of *n*-BuLi. Performing a subsequent lithiation and phosphination on compound **5** does not lead to the desired tetraphosphine compound **4a**. Examination of literature X-ray structures of the *n*-butyl- and *tert*-butyllithium species crystallized, in general, from ether or alkane solvents, reveals a strong tendency for aggregation (14). In ethers, tetrameric (distorted cubic) and quasi-planar dimeric structures are observed for the *n*-butyl- and *tert*-butyllithium derivatives, respectively, and one ether molecule per lithium is attached to the metal. In alkanes, octahedral and tetrahedral geometries are depicted for the *n*-butyl- and *tert*-butyllithium derivatives, respectively, with evidence for short metal–metal contacts, and no crystallization of solvent molecules. The cases where no solvent molecule is bonded to the lithium atoms offer more favorable geometries, with respect to steric interactions, for lithium–bromide exchange. Similarly, the planar dimeric structure found in [(*t*-BuLi)$_2$·(diethylether)$_2$] exhibits relatively unobscured metal atoms. In contrast, the tetrameric [(*n*-BuLi)$_4$·(1,2-dimethoxyethane)$_4$] cluster shows tetracoordinated lithium atoms that are relatively encumbered. It is anticipated that the first and second lithium–bromide exchange at the 5- and 17-positions of the tetrabromocalix[4]arene in **3a** and **3b** proceeds without any major steric restrictions. However, since the lithium atom has a strong tendency to bind ether molecules (15), the intermediate 5,17-dibromo-11,23-dilithium-25,26,27,28-tetrapropoxycalix[4]arene·2THF (speculative) appears to be severely sterically demanding for an efficient interaction with the already encumbered tetrameric [(*n*-BuLi)$_4$·(THF)$_4$]. While this speculative explanation seems reasonable, an X-ray structure of the 5,17-dibromo-11,23-dilithium derivative with THF or another ether molecule must definitely be obtained to confirm this hypothesis. As stated above, the bromide–lithium exchange followed by phosphination with chlorodiphenylphosphine affords the 5,17-diphosphine-11,23-dibromo derivative (**5**) as the sole product (discussed below).

However, we succeeded in achieving the perphosphination of **3a**. The phosphination proceeds via a bromide–lithium exchange followed by a substitution reaction with chlorodiphenylphosphine. The tetralithiated intermediate is predictably generated either with *n*-BuLi in benzene, or with *t*-BuLi in benzene or THF. Subsequently, reactions with chlorodiphenylphosphine leads to **4a** and **4b** (Scheme 1). The purification of these compounds is performed from multiple precipitations via the additions of acetone to a dichloromethane solution. This procedure leads to pure products, but the yields are modest. Among the impurities, some partially substituted calix[4]arenes, due to incomplete phosphination reactions, are found. The expected $^3J_{\mathrm{P,H\ calixarene}}$ of ~ 8 Hz is measured for **4a** and **4b**: this coupling constant is observed for all the phosphinated derivatives in this work. Both tetraphosphines **4a** and **4b** afforded single crystals of suitable quality for X-ray crystallography, but only the better quality data are reported for **4b**. The structure reveals the predicted cone conformation (Fig. 1). Three of the diphenylphosphine residues form a helical geometry, while the fourth one points in the other direction. The angles between the face-to-face phenyl groups are 88.18(0.11) and 1.19(0.20)°. The flattened bowl structure is typical in the solid state.

The success of the procedure reported by Atwood and coworkers (13) is consistent with the presence of various conformers in equilibrium (cone, partial cone, and 1,2- and 1,3-alternate) as revealed by the ^{1}H NMR data. Since the cone conformation is not retained, the bromide atoms may acquire nonsterically demanding environments in some specific geometries. This equilibrium may explain why, in this case, the tetrasubstitution can be achieved with alkyllithium in THF, which forms aggregates in this medium.

5,17-Diphosphine

Compound **5** conveniently exhibits two bromides at the remaining positions (positions 11 and 23) for further derivatizations. Single crystals of suitable quality for X-ray crystallography were obtained from slow THF–pentane vapor diffusion (Fig. 2). The structure confirms the diphenylphosphino disubstitution at positions 5 and 17 and the cone conformation. The molecule adopts a geometry belonging to the C_2 point group where the diphenylphosphine fragments are oriented in a helical fashion. In contrast with the tetraphosphine **4b**, the cone angles are very different, where the bromophenyl units are rotated inward (–16.72(0.26)°) and the diphenylphosphinophenyl groups are still rotated outward (85.2(0.12)°). Steric hindrance is likely responsible for this difference.

The 5,17-diphosphine compound (**9**) can be prepared via two alternative routes (Scheme 2). The first one is a four-step procedure from **1** and involves dipropylations, brominations, and phosphinations. Indeed, selective propylations at the distal positions (positions 25 and 27) are easily obtained using one equivalent of the weak base K_2CO_3 (16). Literature shows that these protons are the most acidic, as the resonance-stabilized dianionic species is stabilized by

Scheme 1. Syntheses of compounds **4a**, **4b**, and **5**.

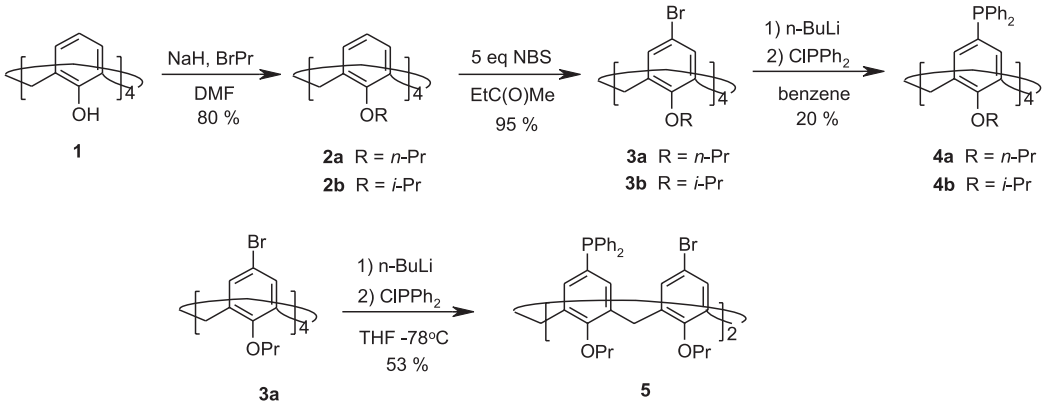


Fig. 1. ORTEP drawing for **4b**. The ellipsoids are shown with a probability of 30%. The H-atoms are not shown for clarity.

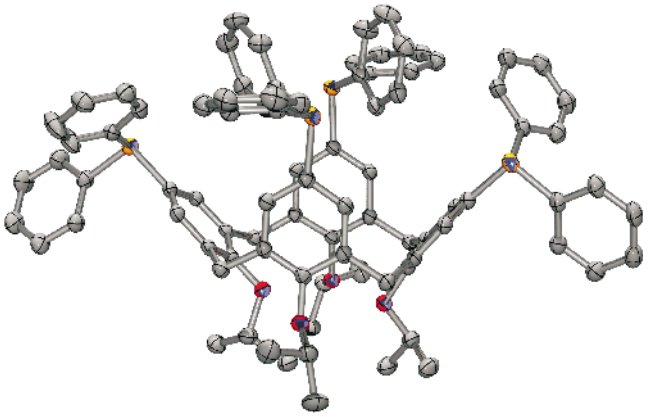
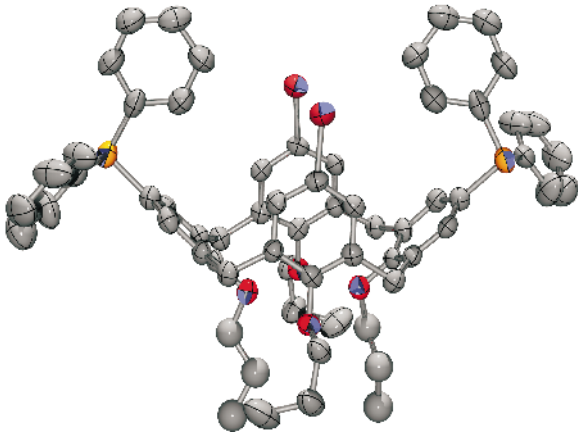


Fig. 2. ORTEP drawing for **5**. The ellipsoids are shown with a probability of 30%. The H-atoms are not shown for clarity.



intramolecular hydrogen bonds with the remaining protons. Thus, propylation of the two first hydroxy groups occurs selectively at these positions, to afford compound **6** (16) in good yields. To subsequently obtain compounds **7** and **8**, bromination followed by a second propylation is performed.

Shinkai and co-workers (17) proposed a bromination step involving the use of 2 equiv of Br_2 in $CHCl_3$ at 0°C for 1 h, to afford the desired product in 87% yield. Later Larsen and Jorgensen (18) claimed that this procedure led to a mixture of products involving several impurities, which could not be separated using recrystallization or column chromatography. Our attempts to reproduce this reaction show that in fact these impurities result from incomplete brominations. To overcome this problem, Larsen and Jorgensen (18) reported an alternative method using 8 equiv of *n*-BuLi in THF at –78°C for 30 min in the presence of **3a**, followed by quenching with water, in 88% yield. In this work, an excess of Br_2 and a shorter reaction time (5 min), allows selective and complete monobromination resulting in compound **7**, which is purified by recrystallization. This selectivity is explained by the greater reactivity of the *para*-position of the phenol group in comparison with the propoxylbenzene. This bromination procedure is a key step for the synthesis of compound **26** (triphosphine, discussed below). The propylation reaction is subsequently performed using *n*-iodopropane in DMF for 48 h to afford **8** as a sole product. The last steps consist of lithiation and phosphination reactions with *n*-BuLi and $ClPPh_2$ in THF to obtain the diphosphine **9**, which is purified by column chromatography.

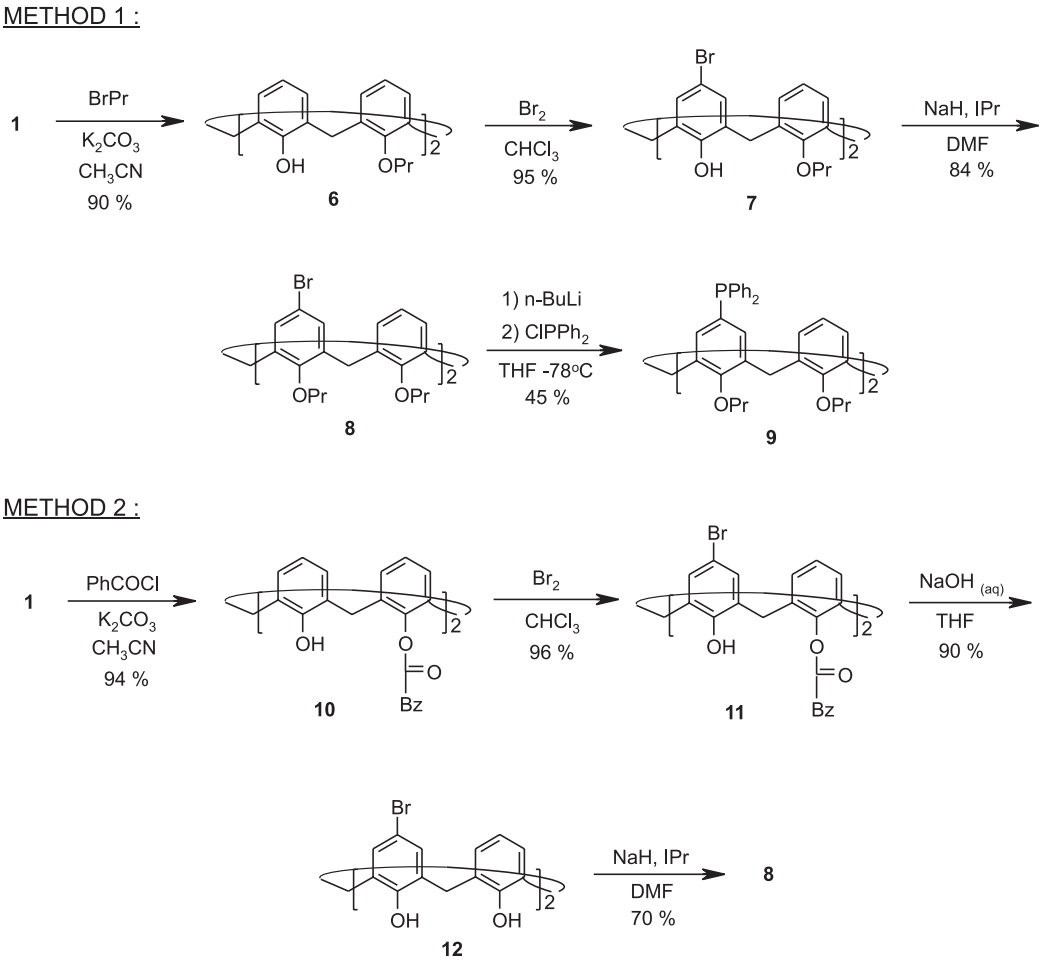
Matt and co-workers (19) reported another convenient way to prepare **9** from **8** in two steps using a procedure of diphosphorylation with Ph_2POEt–$NiBr_2$ (20), which results in a bis(phosphine oxide). The next step involves the reduction of this phosphine oxide with phenylsilane to afford compound **9**. We have indeed been able to reproduce these results.

The second investigated route involves the diesterification of **1** to produce **10**, where the ester groups are anchored at the 25- and 27-positions. This reaction proceeds via a double proton abstraction of the two most acidic protons, followed by a substitution reaction with benzoyl chloride. This derivatization induces a greater difference in electron density between the phenol and phenylbenzoyl residues. In this way, the subsequent brominations can be performed selectively at the highly electron-rich phenol sites without considering reaction time. The ester groups are then easily hydrolyzed, and the cone conformation is still maintained via H-bonding as confirmed by ^1H NMR. The standard propylation of this compound provides compounds **8**, which is the precursor of the final product **9**.

5,11-Diphosphine

This desired and challenging diphosphine **17** is prepared from three alternative routes as summarized in Scheme 3.

Scheme 2. Two different synthesis pathways for compound **9**.

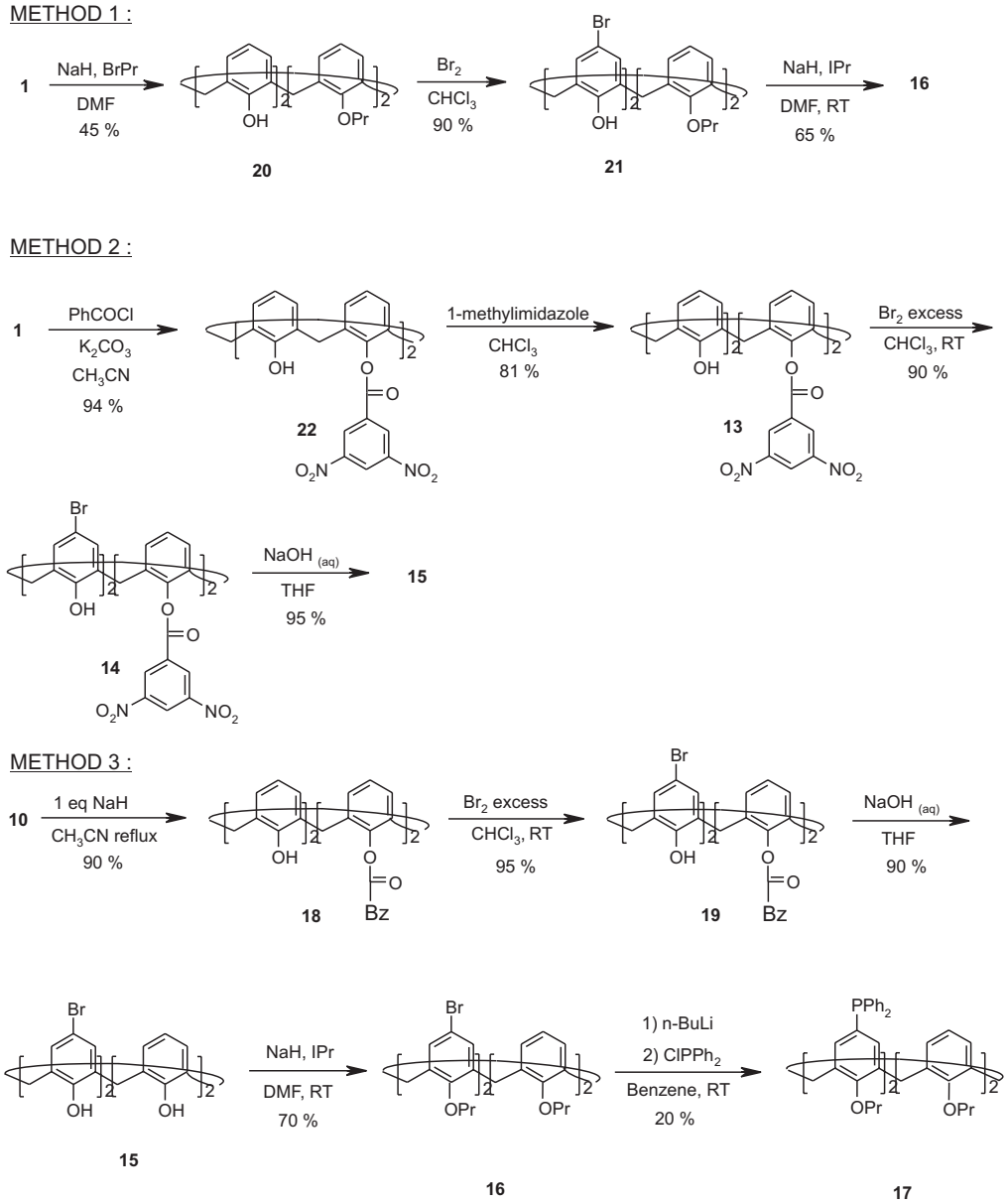


Reinhoudt et al. (21) demonstrated that propylation of **1** using NaH in DMF produce the intermediate compound 25,26-dipropoxycalix[4]arene in the cone conformation. For short reaction times, the 25,26-dipropoxycalix[4]arene compound **20** is observed as one of the intermediates. Unfortunately, the yield for this specific 1,2-disubstitution is low (45% in our work) making this route less attractive. We find that the reaction mixture also contains unreacted **1** and tetrapropylated **2a**. The relative amount of the desired product **20** is best acheived after a 2 h reaction time. Nonetheless, this compound has been prepared and used as precursor. The subsequent bromination and alkylation reactions can be performed with expected results (i.e., formation of compound **16**).

The second strategy is based on the work of Gutsche and co-workers (22), which reports the preparation of 25,26-di(3,5-dinitrobenzoyl)-27,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene from 25,26,27,28-tetrahydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene in the presence of 3,5-dinitrobenzoyl chloride using 1-methylimidazole in acetonitrile. Indeed diester **13** can be synthesized from this methodology, but in very low yield (15–40%). Several impurities were found in the mixture, including the monoester derivative, the starting material, and the corresponding 25,27-diester. The presence of this 25,27-diester compound the is the key to understanding this mechanism and will be discussed below. Compound **13** is poorly soluble, which on one hand has the potential to allow the selective preparation of the desired product, but on the other hand, does not permit preparation on a large scale. The major drawback is that the product must be purified by column chromatography. In an attempt to avoid this important solubility problem, 3,5-dinitrobenzoyl chloride was replaced by benzoyl chloride. Surprisingly, the reaction between **1** and benzoyl chloride in presence of 1-methylimidazole in acetonitrile did not lead to the disubstituted calix[4]arene as the major product, but produced the corresponding triester as major product. Stubbornly, some of this triester compound is still formed even when only one equivalent of benzoyl chloride is used in this reaction. Nonetheless, bromination affords **14** in good yields, as anticipated. Then compound **15**, which is necessary to synthesize **17**, is convieniently obtained by ester cleavage of **14** in basic solution.

The third method involves an intramolecular transesterification of **10** to **18**. Recently, Markovsky et al. (23) reported an elegant intramolecular phosphotropic rearrangement at the lower rim of the calix[4]arene from the 25,27- to the 25,26-positions, hence providing a important clue about the mechanism. Compound **10** is prepared from **1** using K_2CO_3. Again, the two most acidic protons are readily abstracted, allowing the 25,27-diesterification of **1**. The subsequent transesterification of **10** to **18** proceeds with one equivalent of sodium hydride in good yield. This strong base in

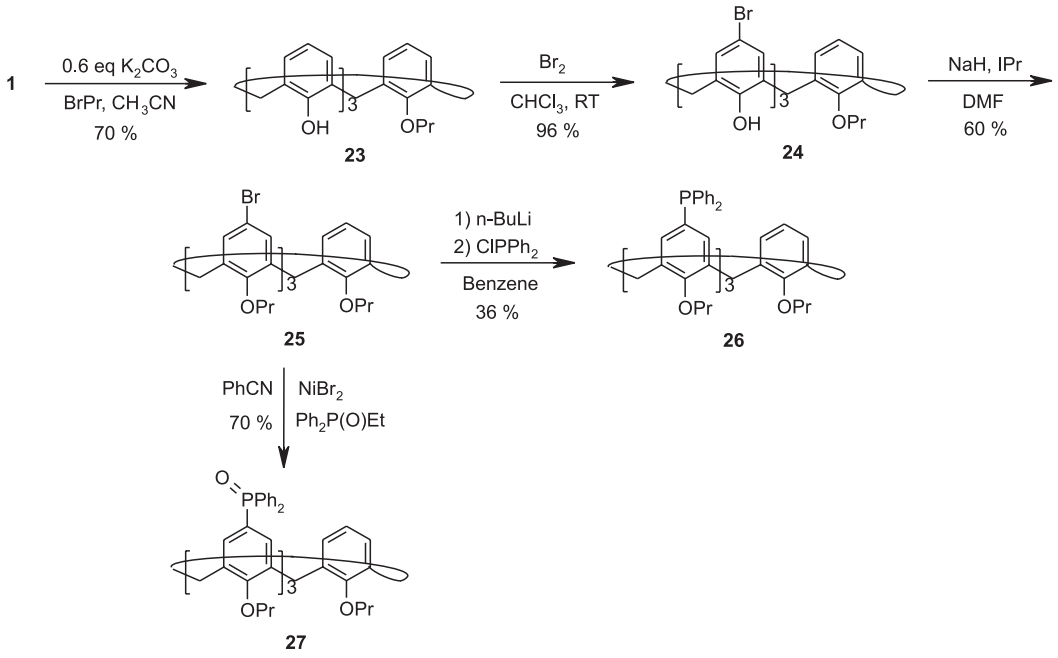
Scheme 3. Different synthesis pathways for compound **17**.



acetonitrile abstracts one of the two remaining protons, generating a phenolate intermediate over a period of 20 h, during which the transesterification occurs. This intramolecular reaction allows for equilibrium between the two disubstituted compounds. The generated 5,11-diester monoanion is stabilized by an intramolecular H-bond between the hydroxy and phenolate groups, which drives the equilibrium to the right. Acidification of the solution leads to the targeted diester **18**, which is obtained in a pure state after column chromatography to eliminate some traces of the reactant. Diester **18** exists in a partial cone conformation with both OH groups pointing in the same direction according to its ^{1}H NMR spectra. This reaction is almost complete in refluxing acetonitrile (82°C), but is not complete even after one week in refluxing THF (66°C). In addition, no transesterification is observed when two or more equivalents of sodium hydride are used. In this case, the dianionic species are generated and electrostatic repulsions between the negatively charged phenolates (doubly deprotonated calix[4]arene) may be at the origin of this selective structure. Interestingly, the 25,26-species can be converted back to the 25,27-compounds by using an excess of bases (two equivalents or more). The following steps include the well-established selective bromination, ester cleavage, propylation, and phosphination to achieve the synthesis of the desired 5,11-diphosphine compound (**17**).

Based upon these experiments, the preparation of the 25,27-di(3,5-dinitrobenzoyl)-26,28-dihydroxycalix[4]arene (**22**) in its pure state has been performed to shed some light on the mechanism for the conversion of **1** into **13**. The preparation of **22** is achieved using **1** in the presence of 3,5-dinitrobenzoyl chloride and potassium carbonate in acetonitrile. Subsequently, **22** is placed in the presence of 1-methylimidazole to produce **13**. This procedure affords better yields. In conclusion, one equivalent of potassium carbonate allows for the preparation of the corresponding

Scheme 4. Synthesis of compound **27**.



25,27-diesters. The transesterification proceeds using an additional equivalent of base to generate a monophenolated calix[4]arene anion. In this work sodium hydride and 1-methylimidazole were used for the conversion of **10** to **18** and **22** to **13**, respectively. The fact that Gutsche and co-workers (22) did not observe the 25,27-di(3,5-dinitrobenzoyl)-26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene may be related to the electron-donor inductive effect of the *tert*-butyl group rendering the corresponding monophenolate anion more basic. Hence in this case, only the monophenolated calix[4]arene is generated, which readily promotes the transesterification. When a large excess of 1-methylimidazole was used (up to 20 equivalents) to see whether the transesterification would be precluded (as seen in the reaction of **10** to **18** with an excess of sodium hydride), the transesterification was still observed.

Gutsche and co-workers (22) also reported the hydrolysis of 25,26,27-tri(3,5-dinitrobenzoyl)-28-hydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene to 25,26-di(3,5-dinitrobenzoyl)-27,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene in the presence of 4-methylimidazole. However, the tribenzoyl ester **28** mentioned above could not be converted to **18** by this method.

From the three described methods, the last one, which utilizes benzoyl chloride and intramolecular transesterification with NaH, was found to be the most convenient. The low solubility of **13**, and also the low yield for the selective propylation of **1** into **20**, make the other described methods much less appealing.

Triphosphine

The strategy for preparing the triphosphine derivative involves the preparation of the monopropoxycalix[4]arene (**23**) (Scheme 4). This can be achieved by abstracting a proton with one equivalent of base. However, when the monophenolated calix[4]arene intermediate is generated an equilibrium sets in, to form the 25,27-diphenolate-26,28-dihydroxycalix[4]arene intermediate and **1**, as evidenced by the appearance of the dipropoxy compound **6** either with the increase or decrease in the amount of base used. By using 0.5 equivalent of K_2CO_3, the monopropoxy derivative **23** is the major product, mixed with **6** and **1**. Compound **6** is easily removed by recrystallization, and subsequently, **23** is purified by column chromatography. The yield is unavoidably low, but the preparation of the desired compound is attained. The subsequent bromination reaction is selective to the phenol residues. The following propylation reaction is preferably performed with 1-iodopropane instead of 1-bromopropane, since the propylation of the *para*-bromophenol fragments is much slower with the latter reactant. The tribromotetrapropoxy derivative **25** is then obtained. The phosphine oxide derivatization of **25** with Ph_2POEt–$NiBr_2$ was performed successfully, but the subsequent reduction of **27** using the procedure of Matt and co-workers (19), with phenylsilane to form **26**, proved very difficult either using phenylsilane-containing solutions or neat. This reaction leads to a mixture of products, which could not be separated. The desired ligand **26** is generated with *n*-BuLi in benzene, followed by a reaction with chlorodiphenylphosphine, in a modest yield. It is anticipated that the use of *n*-BuLi in THF could lead to 5,17-diphosphine-11-bromo-25,26,27,28-tetrapropoxycalix-[4]arene, similar to that describe for compound **5**. This proposed synthesis may lead to further functionalizations as suggested for **5**.

The syntheses presented can also be applied to the upper-rim multifunctionalization of calix[4]arene by dialkylphosphines. Their preparation and characterization, as well as their complexation with low-valent transition metals, will be reported in due course.

Experimental

General

All solvents were freshly distilled before use. All reac-

tions involving air- or moisture-sensitive reagents were conducted under nitrogen atmosphere. Column chromatography was performed on 230–400 mesh silica gel (60 Å). All NMR spectra were acquired (^{1}H 300 MHz, ^{13}C 75 MHz, ^{31}P 121 MHz) using the solvent as chemical shift standard, except in ^{31}P NMR, where the chemical shift are relative to D_3PO_4 (85% in D_2O). All the chemical shifts and the coupling constants are given in ppm and Hz, respectively. The lower number of signals in ^{13}C NMR spectra is due to isochronism. Mass spectra were determined at an ionizing voltage of 70 eV. Compounds **1** (23), **2a** (12), **3a** (24), **6** (16), and **23** (25) were prepared according to literature procedures. The syntheses of all new calix[4]arene compouds are reported in the Supporting Information.[2]

Crystal data for calix[4]arene 4b and 5

Crystallographic measurements were made on an Enraf-Nonius CAD-4 automatic diffractometer with graphite-monchromated Cu Kα radiation. Data were collected at 173 K for **4b** and 293 K for **5** using the θ–2θ scan technique to a maximum 2θ value of 120.0° for both compounds; no reflections above the giving angle were observed. The data collection ranges were $\pm h$, $+k$, $+l$; whereby for **4b**: $-20 \le h \le 19$, $0 \le l \le 15$, $0 \le k \le 32$; **5**: $-20 \le h \le 20$, $0 \le l \le 18$, $0 \le k \le 21$. Scans were made with a constant speed of 2.7° min^{-1} and a background time:scan time ratio of 0.25. Space group determination was based upon systematic absences, packing considerations, statistical analysis of intensity distribution, and successful solution and refinement of the structure. The NRCCAD program (26) was used for centering, indexing, and data collection. The NRCVAX programs (27) were used for crystal structure solution by application of direct methods, and the SHELX-97 program (28) was used for refinement by full-matrix least-squares on F^2.

Compound **4b** (5,11,17,23-tetrakis(diphenylphosphino)-25,26,27,28-tetra-*i*-propoxycalix[4]-arene) gives crystals belonging to the monoclinic space group $P2_1/n$ and at 173 K: a = 18.360(2), b = 13.998(2), c = 29.663(2) Å, β = 101.67(8)°, V = 7466.1(15) Å^3, Z = 4, $R(F)$ = 0.0777, and $wR(F^2)$ = 0.2218. One disordered $CHCl_3$ molecule was located on a center of symmetry, the former atoms were refined as isotropic with 0.25 occupancy factor. Compound **5** (5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetra-*n*-propoxycalix[4]arene) gives crystals belonging to the monoclinic space group $I2/a$ and at 293(2) K: a = 17.957(2), b = 16.681(2), c = 19.336(3) Å, V = 5753.0(11) Å^3, Z = 4, $R(F)$ = 0.0694, and $wR(F^2)$ = 0.1829. The molecule is located on a glide plane, and one of the *n*-propyl ligands is disordered. The disordered atoms were refined as isotropic atoms with 0.5 occupancy factor.

Acknowledgments

This research was supported by Natural Sciences and Engineering Research Council of Canada (NSERC) and Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) for fundings. J.G. thanks NSERC for a graduate scholarship.

References

1. (*a*) C.D. Gutsche. Calixarenes. Royal Society of Chemistry, Cambridge. 1989; (*b*) Calixarenes: a versatile class of macrocyclic compounds. *Edited by* J. Vicens and V. Böhmer. Kluwer Academic Publishers, Dordrecht. 1991; (*c*) Calixarenes 50th anniversary: commemorative issue. *Edited by* J. Vicens; Z. Asfari, and J.M. Harrowfield. Kluwer Academic Publishers, Dordrecht. 1994; (*d*) C.D. Gutsche. Calixarenes revisited. Royal Society of Chemistry, Cambridge. 1998.
2. D. Diamond and M.A. McKervey. Chem. Soc. Rev. **25**, 15 (1996).
3. (*a*) V. Böhmer. Angew. Chem. Int. Ed. Engl. **34**, 713 (1995); (*b*) J. Scheerder, M. Fochi, J.F.J. Engbersen, and D.N. Reinhoudt. J. Org. Chem. **59**, 7815 (1994).
4. (*a*) T. Hascall, A.L. Rheingold, I. Guzei, and G. Parkin. Chem. Commun. 101 (1998); (*b*) L. Giannini, A. Caselli, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, and A. Sgamellotti. J. Am. Chem. Soc. **119**, 9198 (1997); (*c*) L. Giannini, A. Caselli, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, and A. Sgamellotti. J. Am. Chem. Soc. **119**, 9709 (1997); (*d*) M.G. Gardiner, G.A. Koutsantonis, S.M. Lawrence, P.J. Nichols, and C.L. Raston. Chem. Commun. 2035 (1996).
5. S.E. Biali, V. Bohmer, S. Cohen, G. Ferguson, C. Gruttner, F. Grynszzpan, E.F. Paulus, I. Thondorf, and W. Vogt. J. Am. Chem. Soc. **118**, 12938 (1996).
6. (*a*) E.B. Brouwer, K.A. Udachin, G.D. Enright, C.I. Ratcliffe and J.A. Ripmeester. Chem. Commun. 587 (1998); (*b*) E.B. Brouwer, G.D. Enright, and J.A. Ripmeester. J. Am. Chem. Soc. **119**, 5404 (1997); (*c*) G.D. Andreetti, O. Ori, F. Ugozzoli, C. Alfieri, A. Pochini, and R. Ungaro. J. Inclusion Phenom. **6**, 523 (1988); (*d*) M.H. Chrisholm, K. Folting, W.E. Streib, and W. De-Dong. Chem. Commun. 379 (1998); (*e*) B. Castelleno, A. Zanotti-Gerosa, E. Solari, C. Floriani, A. Chiesi-Villa, and C. Rizzoli. Organometallics, **15**, 4894 (1996); (*f*) F. Hajek, E. Graf, M.W. Hosseini, X. Delaigue, A. De Cian, and J. Fischer. Tetrahedron Lett. **37**, 1401 (1996).
7. C. Wieser, C.B. Dieleman, and D. Matt. Coord. Chem. Rev. **165**, 93 (1997).
8. (*a*) I.A. Bagatin, D. Matt, H. Thönnessen, and P.G. Jones. Inorg. Chem. **38**, 1585 (1999); (*b*) B.R. Cameron, and S.J. Loeb. Chem. Commun. 2003 (1996).
9. M. Vézina, J. Gagnon, K. Villeneuve, M. Drouin, and P.D. Harvey. Organometallics, **20**, 273 (2001).
10. M. Vézina, J. Gagnon, K. Villeneuve, M. Drouin, and P.D. Harvey. Chem. Comm. 1073 (2000).
11. (*a*) V. Bocchi, D. Foina, A. Pochini, R. Ungaro, and G.D. Andretti. Tetrahedron, **38**, 373 (1982); (*b*) C.D. Gutsche, B. Dhawan, J.A. Levine, K.H. No, and L.J. Bauer. Tetrahedron, **39**, 409 (1983).
12. E. Kelderman, L. Derhaeg, G.J.T. Heesink, W. Verboom, J.F.J. Engbersen, N.F. Van Hulst, A. Persoons, and D.N. Reinhoudt. Angew. Chem. Int. Ed. Engl. **31**, 1075 (1992).

[2] Supplementary material, including syntheses of all compounds and crystallographic data for compounds **4b** and **5**, may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. For information on obtaining material electronically go to http://www.nrc.ca/cisti/irm/unpub_e.shtml. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 168 292 and 169 293). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

13. F. Hamada, T. Fukugaki, K. Murai, G.W. Orr, and J.L. Atwood. J. Inclusion Phenom. **10**, 57 (1991).
14. (*a*) T. Kottke, R.J. Lagow, D. Hoffmann, and R.D. Thomas. Organometallics, **16**, 789 (1997); (*b*) T. Kottke and D. Stalke. Angew. Chem. Int. Ed. Engl. **32**, 580 (1993); (*c*) M.A. Nichols and P.G. Willard. J. Am. Chem. Soc. **115**, 1568 (1993).
15. (*a*) T. Kottke, K. Sung, and R.J. Lagow. Angew. Chem. Int. Ed. Engl. **34**, 1517 (1995); (*b*) M.M. Olmstead and P.P. Power. J. Organomet. Chem. **408**, 1 (1991); (*c*) W. Zarges, M. Marsch, K. Harms, W. Koch, G. Frenking, and G. Boche. Chem. Ber. **124**, 543 (1991); (*d*) M.A. Beno, H. Hope, M.M. Olmstead, and P.P. Power. Organometallics, **4**, 2117 (1985).
16. J.D. Van Loon, A. Arduini, L. Coppi, W. Verboom, A. Pochini, R. Ungaro, S. Harkema, and D.N. Reinhoudt. J. Org. Chem. **55**, 5639 (1990).
17. P. Linnane, T.D. James, and S. Shinkai. Chem. Commun. 1997 (1995).
18. M. Larsen and M. Jørgensen. J. Org. Chem. **61**, 6651 (1996).
19. C. Wieser-Jeunesse, D. Matt, and A. De Cian. Angew. Chem. Int. Ed. Engl. **37**, 2861 (1998).
20. S. Ozegowski, B. Costisella, and J. Gloede. Phosphorus Sulfur, **1**, 209 (1996).
21. L.C. Groenen, B.H.M. Ruël, A. Casnati, P. Timmerman, W. Verboom, S. Harkema, A. Pochini, R. Ungaro, and D.N. Reinhoudt. Tetrahedron Lett. **32**, 2675 (1991).
22. K.A. See, F.R. Fronczek, W.H. Watson, R.P. Kashyap, and C.D. Gutsche. J. Org. Chem. **56**, 7256 (1991).
23. L.N. Markovsky, M.A. Visotsky, V.V. Pirozhenko, V.I. Kalchenko, J. Lipkowski, and Y.A. Simonov. Chem. Comm. 69 (1996).
24. (*a*) C.D. Gutsche and L.G. Lin. Tetrahedron, **42**, 1633 (1986); (*b*) C.D. Gutsche and M. Iqbal. Org. Synth. **68**, 234 (1989).
25. L.C. Groenen, B.H.M. Ruël, A.C. Casnati, W. Verboom, A. Pochini, R. Ungaro, S. Harkeman, and D.N. Reinhoudt. Tetrahedron, **47**, 8379 (1991).
26. Y. Le Page, P.S. White, and E.J. Gabe. Proc. Am. Crystallogr. Hamilton Meet. 1986. Abstract PA23.
27. E.J. Gabe, Y. LePage, J.-P. Charland, F.L. Lee, and P.S. White. J. Appl. Crystallogr. **22**, 384 (1989).
28. G.M. Sheldrick. SHELXL-97. University of Göttingen, Göttingen, Germany. 1997.