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Calix[4]arene bisphosphite ligands bearing two distal 2,2′-biphenyldioxy or 2,2′-binaphthyldioxy moieties: conformational flexibility and allyl–palladium complexes

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ABSTRACT

Achiral and chiral calix[4]arene bisphosphite ligands (**2** and **3**) bearing two distal 2,2′-biphenyldioxyphosphinoxy and 2,2′-binaphthyldioxyphosphinoxy moieties, respectively, have been synthesized. Each of these ligands exists in two pairs of interconverting conformations in solution. The partial cone conformer (A) of the (bis)biphenyldioxyphosphinoxy ligand **2** has been separated by fractional crystallization and its structure established by X-ray crystallography. The mechanism of interconversion of the pairs of conformers (A/B and C/D) has been probed by two-dimensional NMR spectroscopy. The ^{1}H and ^{31}P NMR evidence strongly supports a similar kind of exchange mechanism for ligand **3**. Freezing of the cone conformer from the interconverting C/D pair of conformers of ligand **2** has been achieved by complexation with (allyl)palladium moieties. The methyl–allyl complex (**2d**) is moderately effective for catalytic regioselective allylic alkylation of crotyl acetate.

1. Introduction

Calixarenes, in particular calix[4]arenes, and allyl–palladium complexes have engendered considerable interest in the field of supramolecular chemistry and organometallic chemistry, respectively. There has been no significant attempt to combine these two chemically and structurally diverse areas of chemistry. Only a few examples of allyl–palladium complexes of conformationally rigid phosphorus functionalized calix[4]arenes are known,[1] but a detailed and combined study of the solution and solid-state structures of phosphorus functionalized calix[4]arenes and their allyl–palladium complexes is lacking.

Calix[4]arenes can exist in four different conformations, viz., cone, partial cone, 1,3-alternate, 1,2-alternate, and this feature provides a convenient handle for modifying the properties of calix[4]arenes.[2] 5,11,17,23-Tetra-(*p*-*tert*-butyl)-25,26,27,28-tetramethoxycalix[4]arene[3a–d] and upper rim calix-crowns[3e] have been used as model systems to study the mechanism of interconversion among the different conformations of calixarenes in solution. Matt and co-workers have reported the isolation of two isomers (cone and 1,2-alternate conformers) of 5,11,17,23-tetra-(*tert*-butyl)-25,27-bis(diphenylphosphinoxy)-26,28-dimethoxycalix[4]arene and their dynamic behavior in solution by variable temperature ^{1}H NMR measurements.[4] More recently, they have reported the synthesis, structure, and catalytic activity of a conformationally rigid calix[4]arene dipropoxy bisphosphite bearing 2,2′-binaphthyldioxyphosphinoxy moieties.[5] Schmutzler, Borner and their co-workers have reported a calix[4]arene bisphosphite and a bisphosphonite bearing the methoxy and *tert*-butyl substituted biphenyldioxy or biphenylmonoxy moieties, respectively, and demonstrated the utility of the Rh(I) complexes of these calixarene phosphorus derivatives as catalysts for hydroformylation of 1-octene.[6] In this paper, we wish to report the synthesis of semi-flexible 26,28-dimethoxycalix[4]arene bisphosphite ligands (**2** and **3**) bearing two distal 2,2′-biphenyldioxyphosphinoxy or 2,2′-binaphthyldioxyphosphinoxy moieties, which exist as two pairs of mutually interconverting conformers. We have probed the mechanism of conformational interconversion with the help of two-dimensional NMR spectroscopy. We have been able to freeze a particular conformer from the mixture of two thermodynamically stable and interconverting conformers by complexation with (allyl)palladium moieties. The conformations of the calix[4]arene framework as well as the regiochemistry of the allyl ligands in these complexes in solution and solid-state have been investigated. Preliminary accounts of our work reported here have been presented in two National Conferences.[7]

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2. Results and discussion

2.1. Synthesis and 2D NMR study of conformational interconversion of ligand 2

When a suspension of 1,3-dimethoxy-*p*-*tert*-butyl-calix[4]arene (**1**),[8] in toluene, is treated with [1,1′-biphenyl]-2,2′-phosphorochloridite in the presence of NaH, the biphenyldioxyphosphinoxy calix[4]arene derivative (**2**) is obtained in 27% yield (Scheme 1). This compound exists as a mixture of four conformers (A, B, C, and D). Fractional crystallization of the mixture from $CHCl_3$–hexane gave single crystals of conformer (A), leaving behind the conformers (C) and (D) in the mother liquor with a trace amount of the mixture of (A) and (B) (Scheme 2). When the solid sample of conformer (A) is dissolved in $CDCl_3$, the solution shows the presence of two interconverting conformers (A) and (B) as revealed by its ^1H and ^{31}P NMR spectra. Two singlets at δ 121.1 and 134.7 are assigned to the partial cone conformer (A) with a C_s point group symmetry; the singlet at δ 139.5 is assigned to 1,2-alternate conformer (B), which has a center of symmetry at the mid point of the plane of the methylene bridge carbon atoms [point group C_i] (Scheme 2). The ^1H NMR spectral data (eight doublets for methylene bridge protons and two singlets for methoxy protons) are also consistent with the presence of two conformers (see Section 4). The structure of the partial cone conformer (A) has been established by X-ray crystallography (see later). For the other pair of conformers (C/D), left behind in the mother liquor after the isolation of A, the ^1H NMR spectrum shows two doublets at δ 4.48 and 3.24 ($\Delta\delta$=1.24) for the methylene bridge protons typical of cone conformation (C). Four doublets for the $-CH_2-$ protons and two singlets (δ 3.12 and 3.47) for the two non-equivalent $-OCH_3$ protons are observed for the partial cone conformer (D). One singlet at δ 37.77 in the ^{13}C NMR spectrum of the mixture of conformers C and D supports the inverted orientation of the adjacent phenyl rings in the partial cone conformation (D).[9,10]

2.1.1. Assignment of the resonances for the $-CH_2-$ and $-OCH_3$ protons

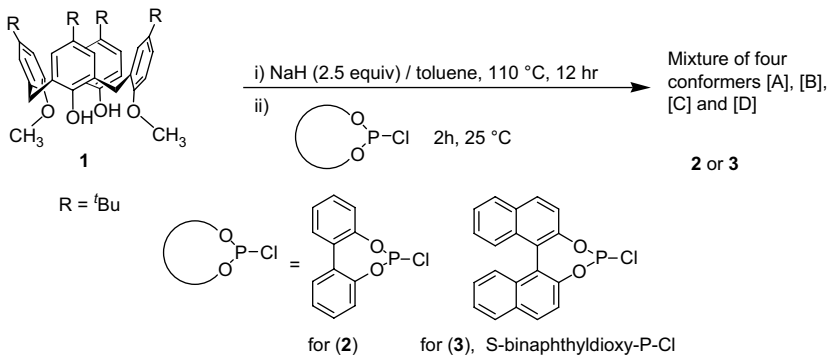
All the $-CH_2-$ and $-OCH_3$ protons for the A/B pair of conformers have been identified on the basis of the variation of shielding effect of the π-electron current of the aryl rings and through-space interaction among the proton signals of $-CH_2-$ and $-OCH_3$ groups. To ascertain the latter, a phase sensitive ^1H–^1H NOESY experiment has been carried out at −30 °C, to suppress the exchange peaks and to obtain clear cross-peaks for through-space contacts (Fig. S2, see Supplementary data). Among the $-CH_2-$ protons of the conformer (A), two equivalent H_a protons flanked by the π-electron cloud of two aryl rings would be expected to resonate at a relatively high field region. Hence the doublet at δ 3.10 is assigned to H_a protons. As expected, the H_a signal shows a cross-peak with H_b, which resonates at relatively low field region at δ 4.69 due to the absence of any shielding effect of the aryl rings. Two additional NOE signals are observed between $-OCH_3(2)$ and H_b, and between $-OCH_3(2)$ and H_d protons. These cross-peaks together with another cross-peak between H_d and H_c establish the partial cone conformation of (A) and confirm the assignment of protons in the methylene region. Similarly the resonances of the protons of the conformer (B) have been assigned.

The resonances arising from the protons of the other pair of conformers (C/D) have been identified by following the same procedure as above except that instead of recording a low temperature NOESY spectrum, we have performed the ^1H–^1H COSY (Fig. S3, see Supplementary data) and room temperature NOESY (Fig. 1) experiments. The through-bond and through-space contacts are listed along with the corresponding spectra.

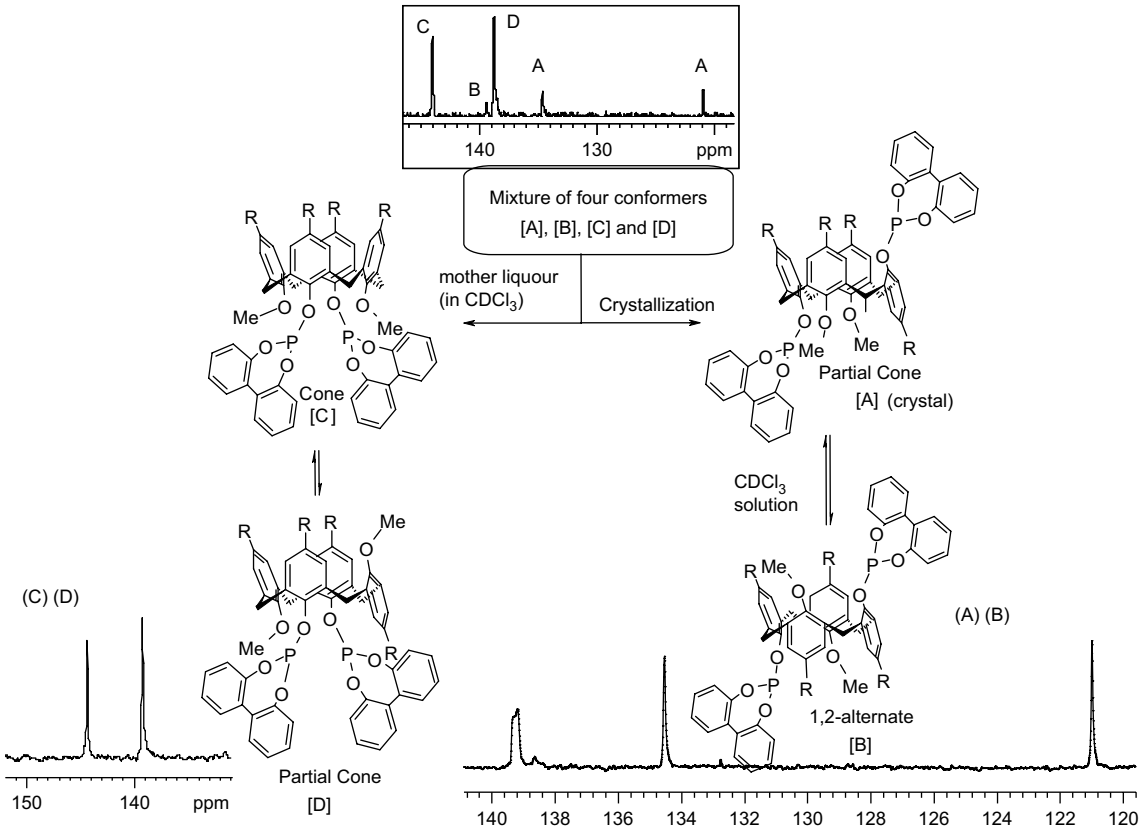
We have measured the rate constant k and ΔG^* for the exchange process between the conformers A and B as well as between C and D by monitoring the overlapping of the doublets at δ 4.91/4.73 and 4.71/4.48, respectively, at the coalescence temperature T_c, which is found to be +70 °C for both the pairs. The rate constant k and ΔG^* for the exchange process are calculated by using a standard method[11] and are 0.40 s^{-1}/87 kJ mol^{-1} and 0.51 s^{-1}/86 kJ mol^{-1}, respectively. The presence of sterically bulky biphenyldioxy units in the lower rim of the calixarene framework may be responsible for the higher magnitude of ΔG^* compared to the values previously reported.[3d]

2.1.2. Mechanism for the exchange process

The assignment of the resonances arising from $-CH_2-$ and $-OCH_3$ protons enabled us to study the mechanism of interconversion of A and B as well as that of C and D conformers. For both the pairs, NOESY spectra at room temperature have been recorded (see Fig. S4 in Supplementary data for A/B and Fig. 1 for C/D). Distinct cross-peaks with same phase with respect to the diagonal peaks signify the presence of exchange processes among the conformers. The exchange peaks for each of the two pairs have been analyzed and the predicted mechanism of interconversion of the conformers of the respective pairs are shown in Figures 2 and 3 along with the list of exchanging $-CH_2-$ and $-OCH_3$ protons. Intense exchange peaks between H_a–H_h, H_a–H_e, H_b–H_g, H_b–H_f, H_c–H_f, H_d–H_e, $OCH_3(1)$–$OCH_3(2)$ for the A/B pair of conformers indicates the flipping of one of the two aryl rings containing $-OCH_3$ as the *para*-substituent. This flipping would result in the conversion of partial cone (B or B′) to 1,2-alternate (A or A′) conformers. The intense cross-peaks between H_g–H_f, H_h–H_e and H_a–H_d, H_b–H_c point to the simultaneous rotation of both the $-OCH_3$ containing aryl rings, which would lead to the exchange of the two indistinguishable partial cone (B–B′) topomers and also of the two indistinguishable



Scheme 1. Synthesis of ligands **2** and **3**.



Scheme 2. Separation of conformers of ligand **2**; ^{31}P NMR spectra of the mixture of conformers before and after separation.

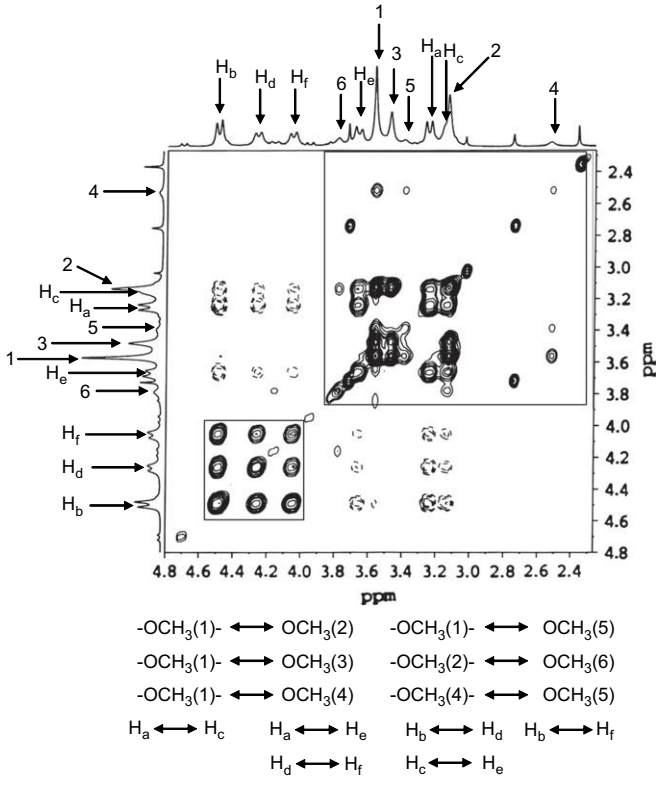


Figure 1. The ^{1}H–^{1}H NOESY spectrum of the conformers C and D of ligand **2**; cross-peaks with continuous circles (inside the square boxes) represent exchange processes. Diagonal peaks and peaks with the same phase as that of diagonal peaks are denoted by continuous lines [numbers inside the circle are used to denote different –OMe groups; symbol '↔'indicates exchange of designated protons].

1,2-alternate (A–A′) topomers, respectively (Fig. 2). Simultaneous rotations of both the aryl rings have been taken into consideration for the exchange mechanism because we find no evidence for the presence of 1,3-alternate intermediate, through which the interchange among the topomers could take place.[3b]

For the pair of conformers C and D, intense exchange cross-peaks between H_a–H_e, H_a–H_c, H_b–H_d, H_b–H_f and also those between H_c–H_e, H_d–H_f (see Fig. 1) provide evidence, respectively, for two exchange processes that involve the rotation of either one or both the aryl rings. Rotation of one aryl ring would result in the interconversion of partial cone (D or D′) and cone (C) conformers, whereas simultaneous rotation of both the rings would lead to the interconversion of the two equivalent partial cone (D and D′) topomers (Fig. 3). The observation of an additional exchange peak between a less intense –OCH_3(6) signal with the –OCH_3(2) signal of partial cone (D) conformer indicates that the exchange of D and D′ topomers also proceeds via a short-lived intermediate having a 1,3-alternate conformation (Fig. 3). The existence of the 1,3-alternate intermediate and other two less stable species E, E′ can only be observed during NOESY experiment by keeping the sample in $CDCl_3$ for 5 h. This intermediate can arise by the flipping of a single aryl ring of the partial cone conformer (D or D′). There are two other signals of low intensity (–OCH_3(4) and –OCH_3(5)), which show exchange cross-peaks with themselves and with –OCH_3(1) of cone conformer (C). This observation indicates the presence of two indistinguishable high-energy topomers (E and E′ in Fig. 3) containing a highly shielded –OCH_3(4) group. Such an intermediate can result from the movement of the –OCH_3 group of the cone conformer (C) toward and away from the calixarene core.

2.1.3. ^{31}P–^{31}P NOESY experiment

As an additional support for the exchange process, we have recorded the ^{31}P–^{31}P NOESY spectrum of the mixture of all the

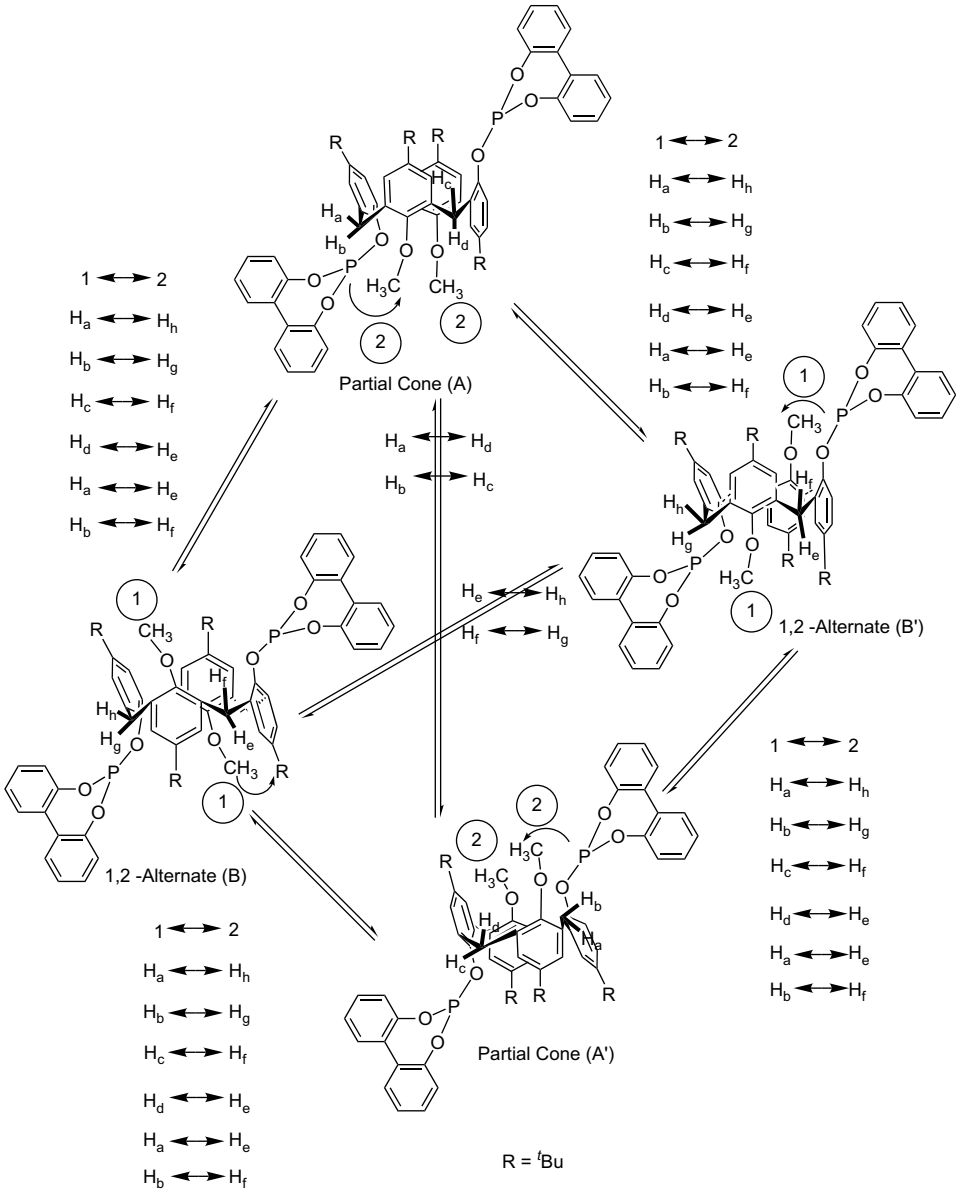


Figure 2. Mechanism of interconversion of conformers A and B [numbers inside the circle are used to denote different –OMe groups; '↔' symbol indicates exchange of designated protons].

conformers (A, B, C, and D) (Fig. S5, see Supplementary data). To the best of our knowledge, there is only one report on the use of ^{31}P NMR spectroscopy to explore the conformational interchange of phosphorous functionalized calix[4]arenes.[12] The exchange cross-peaks between the two magnetically non-equivalent phosphorus nuclei of the partial cone conformer (A) clearly signifies the rotation of both the $-OCH_3$ substituted aryl rings, whereas exchange within the A/B or C/D pair signifies the rotation of only one aryl ring through the cavity of the calix[4]arene framework. These results provide support for the mechanism predicted from ^{1}H–^{1}H NOESY experiments. Absence of cross-peaks between the conformers A and C, A and D, B and C or B and D points to a high-energy barrier for the flipping of aryl rings, substituted by the biphenyl moieties at the *para*-positions.

2.2. Solid-state structure of the conformer A

The solid-state structure of conformer A is shown in Figure 4 and clearly reveals the partial cone conformation in which two methoxy carbon atoms point outward from the calixarene core. Three of the aryl rings are parallel to each other and the remaining one is oriented outward resulting in a flattened partial cone conformation. The relevant torsion angles φ and ψ are shown in Table S1 (see Supplementary data). The dihedral angles between the mean plane of the methylene carbon atoms and the aryl rings bearing C46–C51, C3–C18, C24–C29, and C35–C40 atoms are 85.6°, 89.7°, 84.8°, and 43.1°, respectively (Table S2, see Supplementary data). The distance between the two phosphorus atoms is large (7.3 Å), precluding chelation with transition metals.

2.3. Synthesis of binaphthol based ligand (3) and NMR analysis of their conformational isomers

When a suspension of 1,3-dimethoxy-*p*-*tert*-butyl-calix[4]arene in toluene is treated with optically pure *S*-[1,1′-binaphthyl]-2,2′-phosphorochloridite in the presence of NaH, the binaphthyldioxy-phosphinoxycalix[4]arene derivative **3** is obtained in 30% yield

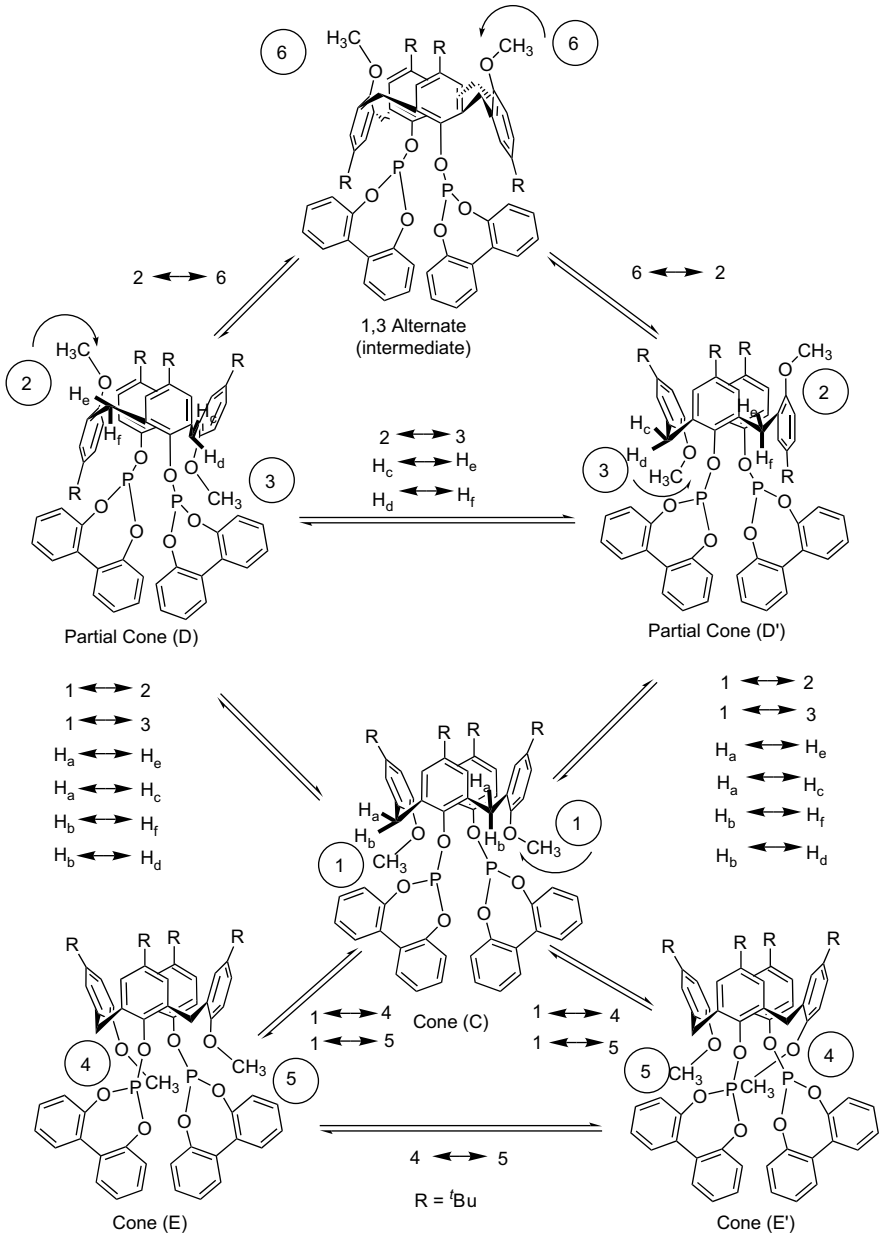


Figure 3. Mechanism of interconversion of conformers C and D [numbers inside the circle are used to denote different –OMe groups; '↔' symbol indicates exchange of designated protons].

(Scheme 1). Seven resonances at δ 121.2, 134.2, 137.2, 139.7, 140.9, 141.4, and 143.1 in the ^{31}P NMR spectrum of optically pure calix[4]arene bisphosphite ligand **3** (Fig. S6, see Supplementary data) supports the presence of several conformational isomers. Four conformers could be identified as observed for ligand **2**, but in this case, partial separation of the conformers could not be realized. Solution structures of the conformers have been predicted by comparing the ^{31}P NMR resonances of the corresponding conformers (A, B, C, and D) of the analogous biphenyl ligand (**2**) (Scheme 2). The dynamic behavior of the mixture of conformers of ligand **3** has been verified by a ^{31}P–^{31}P NOESY NMR spectrum (Fig. S7, see Supplementary data). From NMR studies, it is inferred that the mechanism of the conformational interconversion for **3** is similar to that discussed above for ligand **2**; random rotation of the aryl rings containing –OMe groups is responsible for the exchange process.

2.4. Preparation of Pd–allyl complexes of ligand 2: freezing of conformations

In the second phase of our investigation, we have tried to freeze the rotation of the two mobile aryl rings of the pair of conformers C and D by complexation with a suitable transition metal. Treatment of a mixture of conformers C and D with a series of (allyl)palladium chloro dimers in the presence of ammonium hexafluorophosphate gives the Pd–allyl complexes (**2a**, **2b**, **2c**, and **2d**) (Scheme 3). In all these complexes, the calix[4]arene framework is frozen in the cone conformation (C) with the complete conversion of the other ligand conformer (D) into the cone (C) conformation. This is a rare situation where one of the stable ligand conformers is converted to the other upon complexation with a metal. Freezing of the conformational mobility of a calix[4]arene bis(imidazolyl) derivative by complexation with Cu(I) has been reported by Reinaud and

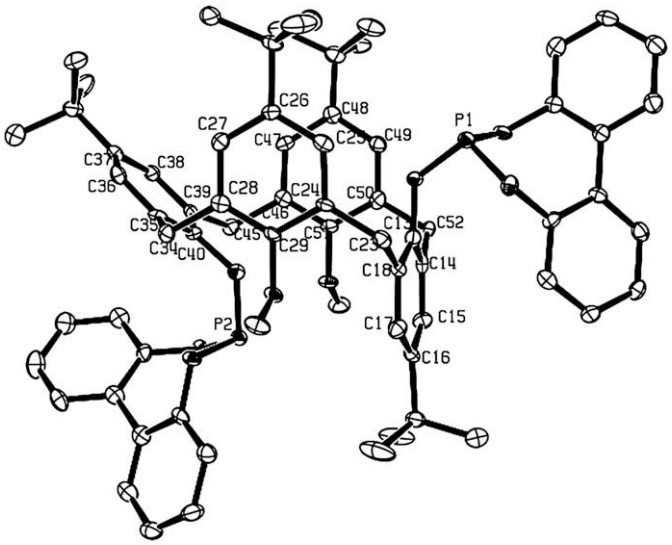
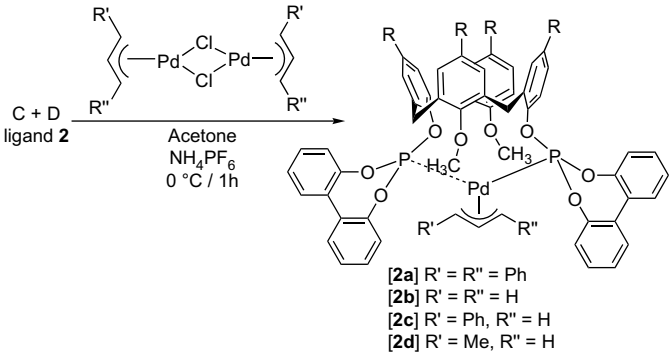


Figure 4. ORTEP drawing of partial cone conformer A of ligand **2**. Thermal ellipsoids are drawn at 30% probability level. Lattice held solvent molecule (chloroform) and the hydrogen atoms are not shown.

co-workers but the nature of the conformers of the ligand had not been established.[13] Our result represents a new approach for freezing the conformational mobility of phosphorus functionalized calix[4]arenes. The pinched cone conformation of calixarene framework has been established by single crystal X-ray analysis of the allyl complexes **2a**, **2b**, and **2d**. The ^{1}H and ^{31}P NMR data for these complexes are also in agreement with cone conformation. Only one singlet in the ^{31}P NMR spectra and four doublets in the methylene region of the ^{1}H NMR spectra for symmetrically substituted allyl complexes **2a** and **2b** point to the presence of a plane of symmetry bisecting the parallel aryl rings containing $-OCH_3$ groups.



Scheme 3. Reaction of the chlorobridged (allyl)palladium dimers with a mixture of conformers C and D of ligand **2**.

The ^{31}P NMR spectrum of complex **2c** displays two doublets (AB pattern) because of the unsymmetrical nature of the allyl moiety in this complex. The ^{1}H NMR spectrum shows eight doublets for the Ar–CH_2–Ar protons. The cone conformation of all the allyl complexes in solution is further supported by the absence of any peak in the region of δ 35–40 ppm (region for the resonance of methylene bridge carbon connecting two inverted adjacent aryl rings) in their ^{13}C NMR spectra.[9] The $^{31}P\{^{1}H\}$ spectrum of complex **2d** in $CDCl_3$ (see Section 4) shows the presence of two isomers in the ratio 3:1. The AB splitting pattern of the ^{31}P NMR spectra indicates the presence of two magnetically non-equivalent phosphorus in each isomer. The assignment of allyl protons of the major isomer in the ^{1}H NMR spectrum was not possible owing to the overlapping of the calixarene-CH_2– resonances with some of the allyl proton resonances. However, the orientation of the terminal $-CH_3$ group has been shown to be '*anti*' with respect to the proton of central allyl carbon in the minor isomer (Figs. S12–S15, see Supplementary data for details). The absence of any exchange peaks between the two species in ^{1}H–^{1}H and ^{31}P–^{31}P NOESY experiments clearly shows that they do not exchange in solution at 298 K. Two types of crystals could be observed in the crystal crop, obtained from chloroform/petrol. Partial separation of the two types of crystals was possible (Fig. S16, see Supplementary data). The solid-state structure of one of the isomers has been determined (Fig. S11, see Supplementary data) by single crystal X-ray diffraction. The structure of the other isomer could not be determined owing to poor quality of the crystals.

Details of the allyl–palladium complexes of ligand **3** and the use of ligand **3** in enantioselective catalysis are given in Supplementary data.

2.5. Solid-state structures of complexes 2a, 2b, and 2d

The molecular structure of complex **2b** is shown in Figure 5 (see Supplementary data for the ORTEP plots and crystallographic parameters of **2a** and **2d**). The calix[4]arene framework adopts the cone conformation in all the three complexes. The calixarene bisphosphite ligand is coordinated to Pd in a chelating mode and the coordination geometry around Pd is nearly square planar. The dihedral angles between the P–Pd–P and C_t–Pd–$C_{t'}$ planes for the complexes **2a**, **2b**, and **2d** are 7.5°/8.5°(for two molecules in the unit cell), 1°, and 4.7°, respectively. Selected bond lengths and bond angles are listed in Tables S9 and S10, respectively. The most noticeable feature of the structures of the complexes is the large P–Pd–P bite angle 102.7°, 107.2°, and 104.3° for the complexes **2a**, **2b**, and **2d**, respectively. There are only a few examples of the solid-state structure of cationic allyl–palladium complexes of chelated homo- or hetero-donor ligands with large bite angles.[14] Apparently an increase in the steric bulk of the substituents at the terminal allyl carbon atoms forces the chelating phosphorus atoms to come closer, and as a result, the P–Pd–P bite angle decreases in the order **2b**>**2d**>**2a**.

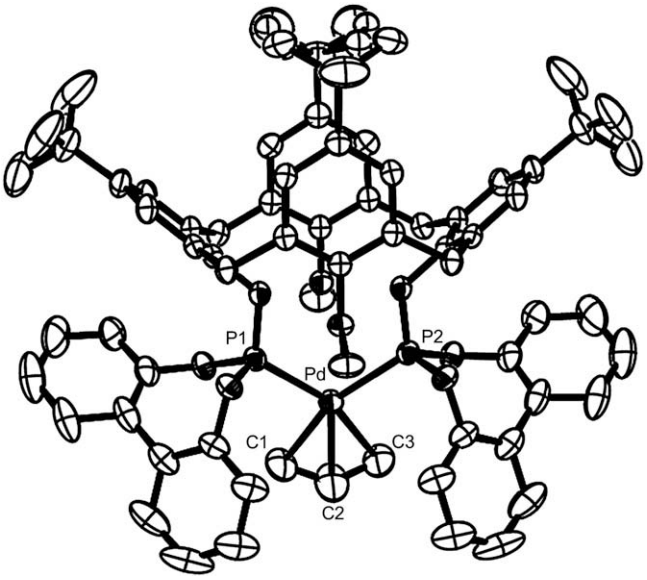


Figure 5. ORTEP drawing of complex **2b**. Thermal ellipsoids are drawn at 30% probability level. Lattice held solvent molecules (chloroform), counter anion (PF_6), and the hydrogen atoms are not shown.

The allyl moiety in **2a** adopts '*exo-syn-syn*' configuration whereas in **2b**, it adopts an '*endo*' configuration (Fig. S10, see Supplementary data) ('*exo*' refers to the relative orientation of the central allylic C–H vector pointing away from the bisphenyldioxy core). Owing to a disorder in the position of the central allyl carbon atom of complex **2d**, the configuration (*syn*/*anti* or *exo*/*endo*) of the allyl ligand in the solid-state could not be determined.

A variable temperature NMR study (CD_3COCD_3, 400 MHz), carried out between −85 °C and 48 °C revealed that the allyl complexes **2a**, **2b**, and **2d** do not undergo any significant structural changes in solution in this temperature range.

2.6. Catalytic study

One of the major problems in developing asymmetric allylic substitution is its undesirable stereochemistry. In most of the cases, the linear product is formed due to the attack of nucleophile at the unsubstituted carbon atom, and the reaction cannot be extended to asymmetric synthesis because the linear isomer lacks the chiral carbon center. A few mono[15] and hetero[16] donor ligands, known in the literature, increase the branched product up to 90% but there is no homo-donor phosphite ligand known to produce moderate to high yields of branched product in the alkylation reaction. The palladium catalyzed allylic alkylation of *E*-2-butenyl acetate (crotyl acetate) and crotyl chloride has been investigated using the sodium salt of diethyl methylmalonate as the nucleophile with 0.01 mol % of complex **2d** as the catalyst. The amount of branched product (>20%) is more than that formed in the usual catalytic reactions (<10%) (Table S12). The relative amount of *Z* product formed in the catalytic reaction is 9–12%, which corresponds to the amount of '*anti*' (minor) isomer present in the mixture of isomers of complex **2d** (see Supplementary data for details).[17] We have to consider two opposing effects. The presence of highly electron withdrawing phosphorus atoms makes the substituted allyl carbon atom more susceptible for nucleophilic attack, leading to the branched product. At the same time, the high P–Pd–P bite angle of the intermediate would be responsible for the formation of the linear product.[18] The relative increase of branched product in our case suggests that the electronic effect is predominant. A similar kind of catalytic reaction involving calix[4]arene bisphosphite with cinnamyl acetate as the substrate gave 98% linear isomer.[5] This result may be due to the presence of the bulky phenyl group at one end of the substrate, which prevents the formation of branched product; in this case, the high P–Pd–P bite angle has a predominant effect on the catalytic reaction.

3. Conclusions

In conclusion, we have synthesized two conformationally semi-flexible calix[4]arene bisphosphite ligands (**2** and **3**) from a conformationally flexible calix[4]arene (**1**). Partial separation of the conformers of the 2,2′-biphenyldioxyphosphinoxy derivative (**2**) has been realized. A notable feature of this ligand (**2**) is that there are appreciable chemical shift differences among all the methylene and $-OCH_3$ protons of its conformers; as a result, distinct signals for the different methylene and $-OCH_3$ protons are observed in the ^{1}H NMR spectrum. Since the conformers are in slow equilibrium on the ^{1}H NMR time scale at room temperature, a detailed study of the conformational interconversion is possible. Freezing of the cone conformer is achieved from a mixture of two interconverting conformers (cone and partial cone) by complexation with (allyl)palladium moieties. The present study constitutes a new approach to control the rotation of the aryl rings of the calix[4]arene and to understand its conformational flexibility. This methodology can be applied to higher-membered calix[*n*]arenes (*n*=5–8) and other supramolecular systems. The new bisphosphite ligands (**2**, **3**) function as efficient catalysts for allylic alkylation reactions. The enantioselectivity obtained with the chiral ligand **3** is negligible; however, a significant amount of branched product is obtained with ligand **2**.

4. Experimental section

4.1. General

The general experimental procedures and details of spectroscopic and other physical measurements are as described in our previous publications.[19] Phosphorochloridites, $(C_{20}H_{12}O_2)PCl$[20a] and $(C_{12}H_8O_2)PCl$,[20b] and the organometallic precursor complexes $[(\eta^3\text{-}C_3H_5)PdCl]_2$,[21] $[(\eta^3\text{-}1\text{-}Me\text{-}C_3H_4)PdCl]_2$,[22] $[(\eta^3\text{-}1\text{-}Ph\text{-}C_3H_4)PdCl]_2$,[22] $[(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)PdCl]_2$[23] were prepared by standard literature procedures. The NMR experiments were carried out using $CDCl_3$ as solvent. For the NOESY measurements, the mixing time was chosen as 300 ms. The variable temperature experiments and the NOESY experiment at −30 °C were recorded using toluene-d_8 as solvent. The relative proportions of the conformational isomers (A) and (B) changed slightly in toluene-d_8 compared to that in $CDCl_3$ but the relative peak positions in the ^{1}H NMR spectra were not affected. Literature procedures were followed for catalytic and stoichiometric allylic alkylation reactions of crotyl acetate and crotyl chloride.[15] Isomer distribution was determined from the ^{1}H NMR intensities.

X-ray diffraction data were measured in frames with increasing ω (width of 0.3°/frame) on a Bruker SMART APEX CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube X-ray source. The SMART software was used for cell refinement and data acquisition[24] and the SAINT software was used for data reduction.[25] An absorbtion correction was made on the intensity data using the SADABS program.[26] All the structures were solved using SHELXTL[27] and the WinGX graphical user interface.[28] Least square refinements were performed by the full-matrix method with SHELXL-97.[29] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. The C, H, N analyses were performed on a Thermo Finnigan FLASH EA 1112 CHNS analyzer. Mass spectra were recorded using an Ultraflex MALDI TOF/TOF (Bruker Daltonics) spectrometer.

4.2. Synthesis of 25,27-bis-(2,2′-biphenyldioxyphosphinoxy)-26,28-dimethoxy-*p*-*tert*-butyl-calix[4]arene (2)

A suspension of 25,27-dihydroxy-26,28-dimethoxy-*p*-*tert*-butyl-calix[4]arene (**1**) (4 g, 0.006 mol) and NaH (60% dispersion in oil) (0.29 g, 0.015 mol) in toluene (100 mL) was heated under reflux for 12 h at 110 °C. [1,1′-Biphenyl]-2,2′-phosphorochlororidite (0.015 mol) in toluene (50 mL) was added at 0 °C and the reaction mixture stirred for 2 h at room temperature. Solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (1% EtOAc/petrol) to obtain a colorless solid **2** (1.8 g, 27%), which consisted of all the four conformers A, B, C, and D.; R_f (1% EtOAc/petrol) 0.8.

4.2.1. Separation of conformers

The mixture of the conformers of **2** (1.8 g) was dissolved in chloroform (4 mL) or dichloromethane (5 mL), and hexane (16 mL) was added slowly. The solution was kept aside at 25 °C for five days. Rectangular crystals appeared and were separated from the mother liquor by filtration. The crystals were shown to be that of conformer A in the solid-state. When the crystals were dissolved in $CDCl_3$, the solution showed the presence of two conformers (A and B) in the ratio A/B=1.36. The mother liquor contained the other two conformers (C and D) in the ratio C/D=1.42 and C+D/A+B=16.

A+B: mp: 240–243 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 121.1 (s), 134.7 (s) [for A]; 139.5 (s) [for B]. ^{1}H NMR ($CDCl_3$, 400 MHz):

δ=1.07–1.57 (5s, 36H for A and 36H for B), 2.74 (s, 6H, –OCH_3(1)), 3.1 (d, J_{Ha-Hb}=12.8 Hz, H_a), 3.31 (d, J_{He-Hf}=13.6 Hz, H_e), 3.64 (br d, H_h, H_d), 3.72 (s, 6H, –OCH_3(2)), 3.94 (d, J_{Hc-Hd}=14 Hz, H_c), 4.15 (d, J_{Hg-Hh}=15.6 Hz, H_g), 4.45 (d, J_{He-Hf}=13.6 Hz, H_f), 4.69 (d, J_{Ha-Hb}=12.8 Hz, H_b), 6.62–7.15 (m, 8*m*-H for A, 8*m*-H for B, 16ArH for A and 16ArH for B). Anal. Calcd for $C_{70}H_{74}O_8P_2$: C, 76.1; H, 6.7. Found: C, 76.4; H, 6.6. MS (MALDI): *m*/*z* found 1105.5 (MH^+), $C_{70}H_{74}O_8P_2$ requires 1104.5.

C+D: mp: 246–249 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ=138.8 (s, for D), 144.0 (s, for C). ^1H NMR ($CDCl_3$, 400 MHz): 0.85–1.35 (5s, 36H, –$C(CH_3)_3$ for C, 36H, –C $(CH_3)_3$ for D), 3.11 (br s, 3H, –OCH_3(2)), 3.12 (br d, Hc), 3.23 (d, J_{Ha-Hb}=12 Hz, H_a), 3.47 (s, 3H, –OCH_3(3)), 3.55 (s, 6H, –OCH_3(1)), 3.66 (d, J_{He-Hf}=12.4 Hz, H_e), 4.04 (d, J_{He-Hf}=12.4 Hz, H_f), 4.25 (d, J_{Hc-Hd}=12.4 Hz, H_d), 4.48 (d, J_{Ha-Hb}=12 Hz, H_b), 6.47–7.49 (m, 8*m*-H for C, 8*m*-H for D, 16ArH for C, 16ArH for D). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 31.07, 31.37, 31.76, 33.72, 34.22 (5s, $(CH_3)_3C$–), 32.32, 32.81, 33.91, 37.77 (4s, $ArCH_2Ar$), 57.99, 60.09 and 60.75 (3s, –OCH_3), 122.16–156.11 (aromatic carbons of calixarene and biphenyl moieties). Anal. Calcd for $C_{70}H_{74}O_8P_2$: C, 76.1; H, 6.7. Found: C, 75.8; H, 6.8. MS (MALDI): *m*/*z* found 1104.5, $C_{70}H_{74}O_8P_2$ requires 1104.5.

4.2.1.1. X-ray crystallographic data for A. $C_{70}H_{74}O_8P_2\cdot CHCl_3$, *M*=1224.60, triclinic, space group *P*-1, *a*=12.672(5), *b*=15.169(6), *c*=19.808(8) Å, α=68.092(7), β=71.971(7), γ=65.455(7)°, *V*=3159(2) Å^3, *Z*=2, D_{calcd}=1.287 g cm^{-3}, *T*=110(2) K, *F*(000)=1292, colorless rectangular 0.30×0.12×0.08 mm^3, reflections collected 36,175, independent reflections 14,561, [*R*(int)=0.0683]. Final refinement: data/restraints/parameters 14,561/0/757, goodness-of-fit on F^2=1.127, R_1=0.1363[$I>2\sigma(I)$], *R* indices (all data), wR_2=0.3856 (all data).

*4.2.2. [(η^3-1,3-Ph_2-C_3H_3)Pd(κ^2-P,P′-2)](PF_6) (**2a**)*

The mixture of the conformers (C and D) of ligand **2** (0.09 g, 8×10^{-5} mol) in acetone (30 mL) was added drop-wise to a suspension of [(η^3-1,3-$Ph_2C_3H_3$)PdCl]$_2$ (0.026 g, 4×10^{-5} mol) and NH_4PF_6 (0.015 g, 8.8×10^{-5} mol) in acetone (30 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and filtered through Celite. Solvent was evaporated from the filtrate. The residue was dissolved in chloroform (3 mL) and hexane was added slowly until the solution became hazy. The solution was kept aside for 12 h to obtain orange crystals (0.076 g, 56%). Mp: 200–204 °C (dec). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ=124 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ=0.75 and 0.80 (2s, 9H+9H, –$C(CH_3)_3$), 1.23 (s, 18H, –$C(CH_3)_3$), 3.04, 3.4, 4.59, 4.77 (4d, J_{H-H}=12.8 Hz, 8H, $ArCH_2Ar$), 3.15 (m, 2H, terminal allyl), 3.94 and 4.02 (2s, 3H+3H, –OCH_3), 4.56 (m, 1H, central allyl), 6.33–7.81 (m, 8*m*-H and 10ArH-allyl, 12ArH calixarene). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 30.92–34.14 (6s, $(CH_3)_3C$–), 33.63, 33.73 (2s, $ArCH_2Ar$), 63.00 and 64.22 (2s, –OCH_3), 93.98 (t, terminal allyl C), 113.42 (t, central allyl C), 120.93–152.31 (aromatic carbons of calixarene and biphenyl moieties). MS (MALDI): *m*/*z* found 1403.5 (M−PF_6)$^+$, $C_{85}H_{87}O_8P_3F_6Pd$ requires 1548.5.

The following complexes were synthesized by the same procedure as that described above for the preparation of complex **2a**.

*4.2.3. [(η^3-C_3H_5)Pd(κ^2-P,P′-2)](PF_6) (**2b**)*

Starting materials, ligand (**2**) (0.09 g, 8×10^{-5} mol), [(η^3-C_3H_5)PdCl]$_2$ (0.014 g, 4×10^{-5} mol), and NH_4PF_6 (0.015 g, 8.8×10^{-5} mol) were used to produce **2b** (0.076 g, 62%). Mp: 215–220 °C (dec). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ=127 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ=0.80 and 0.85 (2s, 9H+9H, –$C(CH_3)_3$), 1.30 (s, 18H, –$C(CH_3)_3$), 2.66 and 3.69 (2m, 4H, terminal allyl –C_3H_5), 3.25, 3.46, 4.85, 4.98 (4d, J_{H-H}=13.2 Hz, 8H, $ArCH_2Ar$), 3.87 and 3.88 (2s, 6H, –OCH_3), 4.87 (m, 1H, central allyl), 6.46 and 6.56 (2s, 4H each, *m*-ArH), 7.07–7.55 (m, 16H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 30.96–34.30 (6s, –$C(CH_3)_3$), 33.71, 33.76 (2s, $ArCH_2Ar$), 63.34, 63.50 (s, –OCH_3), 74.12 (t, terminal allyl C), 123.71 (central allyl C), 121.34–149.49 (aromatic carbons of calixarene and biphenyl moieties). MS (MALDI): *m*/*z* found 1251.4 (M−PF_6)$^+$, $C_{73}H_{79}O_8P_3F_6Pd$ requires 1396.4.

4.2.3.1. X-ray crystallographic data. $C_{73}H_{79}O_8F_6P_3Pd\cdot 3CHCl_3$, *M*=1755.78, monoclinic, space group $P2_1$, *a*=10.683(7), *b*=21.774(14), *c*=18.742(12) Å, α=90, β=100.452(11), γ=90°, *V*=4287(5) Å^3, *Z*=2, D_{calcd}=1.360 g cm^{-3}, *T*=293(2) K, *F*(000)=1800, colorless rectangular 0.41×0.13×0.13 mm^3, reflections collected 33,468, independent reflections 8827, [*R*(int)=0.0223]. Final refinement: data/restraints/parameters 8827/0/496, goodness-of-fit on F^2=1.261, R_1=0.0878[$I>2\sigma(I)$], *R* indices (all data), wR_2=0.2942 (all data).

*4.2.3.2. Refinement of the structure of **2b**.* The asymmetric unit contains only half of the molecule. The other half of the molecule can be generated by a plane of symmetry passing through the atoms C37, C35, C30, C38, C24, C27, O4, C41, C25, O5, C42, Pd1, C2, F1, P2, F4, C44. Methyl groups of one of the four *tert*-butyl groups were disordered and hence were refined isotropically with shared occupancy factors. Hydrogen atoms of the chloroform molecules were not fixed and the disordered chlorine atoms were refined isotropically with shared occupancy.

*4.2.4. [(η^3-1-Ph-C_3H_4)Pd(κ^2-P,P′-2)](PF_6) (**2c**)*

Starting materials, ligand (**2**) (0.090 g, 8×10^{-5} mol), [(η^3-1-Ph-C_3H_4)PdCl]$_2$ (0.02 g, 4×10^{-5} mol), and NH_4PF_6 (0.015 g, 8.8×10^{-5} mol) were used to produce **2c** (0.077 g, 60%). Mp: 215–220 °C (dec). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ=122.5 and 129.7 (AB pattern, J_{AB}(P,P)=145.8 Hz). ^1H NMR ($CDCl_3$, 400 MHz): δ=0.79, 0.83, 1.23, 1.31 (s, 9H each, –$C(CH_3)_3$), 3.13–3.19, 3.24, 3.32, 3.46, 4.58, 4.80, 4.89, 4.92 (8d, 8H, $ArCH_2Ar$), 3.85 and 3.99 (2s, 3H each, –OCH_3), 3.39 and 4.65 (2m, 1H+2H, terminal allyl –PhC_3H_4), 5.91 (m, Hc, central allyl), 6.40, 6.43, 6.48, 6.53 (4s, 2H each, *m*-ArH), 6.82–7.54 (16H, –OPh–PhO–, 5H, Ph–C_3H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 30.9–32.6 (4s, –$C(CH_3)_3$), 33.7–34.3 (4s, $ArCH_2Ar$), 63.3, 63.7 (2s, –OCH_3), 68.45 (dd, terminal allyl C), 100.25 (dd, terminal allyl), 116.2 (t, central allyl C), 116.2–145.9 (aromatic carbons of calixarene and biphenol moieties). MS (MALDI): *m*/*z* found 1327.5 (M−PF_6)$^+$, $C_{79}H_{83}O_8P_3F_6Pd$ requires 1472.4. Anal. Calcd for $C_{79}H_{83}O_8P_3F_6Pd$: C, 64.38; H, 5.68. Found: C, 64.1; H, 5.9.

*4.2.5. [(η^3-1-Me-C_3H_4)Pd(κ^2-P,P′-2)](PF_6) (**2d**)*

Starting materials, ligand (**2**) (0.09 g, 8×10^{-5} mol), [(η^3-1-Me-C_3H_4)PdCl]$_2$ (0.015 g, 4×10^{-5} mol), and NH_4PF_6 (0.015 g, 8.8×10^{-5} mol) were used to produce **2d** (0.086 g, 70%). Mp: 205–210 °C (dec). ^{31}P NMR: (162 MHz, $CDCl_3$): 126.8 and 128.5 (AB pattern, J_{PA-PB}=121.7 Hz) [for minor isomer], 126.6 and 129.7 (AB pattern, J_{PA-PB}=128.0 Hz) [for major isomer]. ^1H NMR: (400 MHz, $CDCl_3$) (major isomer): 3.792 and 3.902 (2s, 3H+3H, –OCH_3), 0.821 and 0.831 (2s, 9H+9H, –$C(CH_3)_3$), 1.305 (s, –$C(CH_3)_3$), 1.12 (m, 3H, –CH_3, $CH_3C_3H_4$), 4.29 (m, 1H, H_a, $CH_3H_aCCH_cCH_bH_{b'}$), 4.51 (m, 1H, Hc), 3.04 (m) and 3.25 (not clear) (Hb and Hb′), 3.1–3.6 (m, $ArCH_2Ar$) and 4.8–5.1 (m, $ARCH_2Ar$), 6.4–6.6 (m, ArH), 6.9–7.8 (m, ArH, –OPh–PhO–); (minor isomer): 3.809 and 3.962 (s, 3H+3H, –OCH_3) other peaks are not distinguishable for the minor isomer. MS (MALDI): *m*/*z* found 1265.4 (M−PF_6)$^+$, $C_{74}H_{81}O_8P_3F_6Pd$ requires 1410.4.

4.3. Synthesis of 25,27-bis-(2,2′-*S*-binaphthyldioxyphosphinoxy)-26,28-dimethoxy-*p*-*tert*-butyl-calix[4]arene (3)

A suspension of 25,27-dihydroxy-26,28-dimethoxy-*p*-*tert*-butyl-calix[4]arene (4 g, 0.006 mol) and NaH (60% dispersion in oil) (0.29 g, 0.015 mol) in toluene (100 mL) was heated under reflux for 12 h at 110 °C. *S*-[1,1′-Binaphthyl]-2,2′-phosphorochlororidite

(0.015 mol) in toluene (50 mL) was added at 0 °C and the reaction mixture stirred for 2 h at room temperature. Solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (1% EtOAc/petrol) to obtain a colorless solid **3**, which consisted of all the four conformers A, B, C, and D (2.3 g, 30%). R_f (1% EtOAc/petrol) 0.8; mp: 190–195 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ=121.2, 134.2, 137.2, 139.7, 140.9, 141.4, and 143.1 (all singlets). Anal. Calcd for $C_{86}H_{82}O_8P_2$: C, 79.1; H, 6.3. Found C, 78.9; H, 6.4.

Satisfactory elemental analysis (C and H) data could not be obtained for the palladium complexes **2a**, **2b**, **2d** and hence are not given in experimental section. The marked deviations between the observed and calculated values probably arise because of the presence of varying amounts of occluded solvents in the samples (see Sections 4.2.1.1 and 4.2.3.1).

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Supplementary data

Computational study of ligand **2**, mechanism of interconversion of ligand **3** and its allyl–palladium complexes, solution characterization of minor isomer of complex **2d**, details of the catalytic studies, tables of relevant bond angles, torsion angles, dihedral angles, and X-ray diffraction data collection parameters are provided. CCDC nos. 261937, 261938, 261939, and 639464 contain the supplementary crystallographic data for compounds **2**, **2a**, **2b**, and **2d**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.10.031.

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