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Phosphite ligands derived from distally and proximally substituted dipropyloxy calix[4]arenes and their palladium complexes: Solution dynamics, solid-state structures and catalysis

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ABSTRACT

Two bisphosphite ligands, 25,27-bis-(2,2′-biphenyldioxyphosphinoxy)-26,28-dipropyloxy-*p*-*tert*-butyl calix[4]arene (**3**) and 25,26-bis-(2,2′-biphenyldioxyphosphinoxy)-27,28-dipropyloxy-*p*-*tert*-butyl calix[4]arene (**4**) and two monophosphite ligands, 25-hydroxy-27-(2,2′-biphenyldioxyphosphinoxy)-26,28-dipropyloxy-*p*-*tert*-butyl calix[4]arene (**5**) and 25-hydroxy-26-(2,2′-biphenyldioxyphosphinoxy)-27,28-dipropyloxy- *p*-*tert*-butyl calix[4]arene (**6**) have been synthesized. Treatment of (allyl) palladium precursors $[(\eta^3\text{-}1,3\text{-}R,R'\text{-}C_3H_4)Pd(Cl)]_2$ with ligand **3** in the presence of NH_4PF_6 gives a series of cationic allyl palladium complexes (**3a**–**3d**). Neutral allyl complexes (**3e**–**3g**) are obtained by the treatment of the allyl palladium precursors with ligand **3** in the absence of NH_4PF_6. The cationic allyl complexes $[(\eta^3\text{-}C_3H_5)Pd(\mathbf{4})]PF_6$ (**4a**) and $[(\eta^3\text{-}Ph_2C_3H_3)Pd(\mathbf{4})]PF_6$ (**4b**) have been synthesized from the proximally (1,2-) substituted bisphosphite ligand **4**. Treatment of ligand **4** with $[Pd(COD)Cl_2]$ gives the palladium dichloride complex, $[PdCl_2(\mathbf{4})]$ (**4c**). The solid-state structures of $[\{(\eta^3\text{-}1\text{-}CH_3\text{-}C_3H_4)Pd(Cl)\}_2(\mathbf{3})]$ (**3f**) and $[PdCl_2(\mathbf{4})]$ (**4c**) have been determined by X-ray crystallography; the calixarene framework in **3f** adopts the pinched cone conformation whereas in **4c**, the conformation is in between that of cone and pinched cone. Solution dynamics of **3f** has been studied in detail with the help of two-dimensional NMR spectroscopy.

The solid-state structures of the monophosphite ligands **5** and **6** have also been determined; the calix[4]arene framework in both molecules adopts the cone conformation. Reaction of the monophosphite ligands (**5**, **6**) with (allyl) palladium precursors, in the absence of NH_4PF_6, yield a series of neutral allyl palladium complexes (**5a**–**5c**; **6a**–**6d**). Allyl palladium complexes of proximally substituted ligand **6** showed two diastereomers in solution owing to the inherently chiral calix[4]arene framework. Ligands **3**, **6** and the allyl palladium complex **3f** have been tested for catalytic activity in allylic alkylation reactions.

1. Introduction

Interest in synthetic receptors containing pendent phosphorus atoms stems from the perception that such systems will facilitate both molecular recognition and catalysis involving transition metals. In this context, the chemistry of calixarenes incorporating trivalent phosphorus donor atoms [1] has been investigated by several research groups. In recent years, there is a surge of interest on the solution dynamics, solid-state structure and catalytic activity of calixarene phosphites in which the phosphorus atoms are closely appended to the macrocyclic cavity [2]. Most of theses studies are concerned with calix[4]arene bisphosphites. There are only a few examples of calixarene monophosphites known in the literature [3]. Moreover, to the best of our knowledge, proximally substituted bisphosphites (phosphorus atoms attached to the adjacent oxygen atoms of the lower rim of calix[4]arene) have not been reported. In this paper, we report the synthesis of mono and bisphosphites derived from proximally and distally substituted (dipropyloxy)calix[4]arenes and their (allyl) palladium complexes.

While (allyl) palladium complexes of phosphorus containing bidentate ligands have engendered a lot of interest owing to their dynamic behavior in solution and catalytic applications [4], there are only a few reports on the allyl(palladium) complexes of phosphorus functionalized calixarenes [2c,2d,5] and neutral allyl(palladium) complexes of monodentate phosphites [6]. Our aim is to design a series of calix[4]arene phosphite ligands in such a way that the coordination of the ligands to the palladium center can

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be easily tuned. We have chosen sterically bulky propyl groups as lower-rim substituents for two reasons. The presence of two bulky propyl groups in the lower rim of the mono or bisphosphite ligand increases the steric interaction between the adjacent bulky group/s and the *tert*-butyl group/s of the inverted aryl ring. As a result, "cone" conformation of the calixarene framework becomes highly stable. The presence of bulky substituents in the lower rim of the calix-matrix may also affect the mode of binding of a transition metal to the phosphorus donor sites of the ligand. Fig. 1 shows the probable coordination modes and bite angles of the 1,3- and 1,2-dipropyloxy calix[4]arene bisphosphite ligands.

2. Results and discussion

2.1. Synthesis and conformational aspects of ligands 3–6

Reaction of dipropyloxy calix[4]arenes (**1** or **2**) with [1,1′-biphenyl]-2,2′-phosphorochloridite in the presence of sodium hydride yields the phosphite ligands **3**–**6** (Scheme 1). Even when the stoichiometry of the reactants is carefully controlled, both mono- and bis-phosphites along with some minor conformational isomers are formed in each reaction. The ^{31}P–^{31}P NOESY measurements show that the conformers do not exchange among themselves. The ligands **3**, **5** and **6** could be isolated in a pure form by column chromatography followed by fractional crystallization. Efforts to isolate ligand **4** in a pure form were unsuccessful (see Section 4 and supporting information).

The ^{1}H NMR spectrum of ligand **3** shows two singlets at 1.02 and 1.17 ppm for the *tert*-butyl protons in the ratio of 1:1 and two doublets for the methylene bridge protons (Fig. S1, Supporting Information). There is a large difference in the chemical shifts ($\Delta\delta > 0.9$) of the two sets of geminal methylene protons. A single triplet for the terminal methyl groups of the propyl substituents indicates that the two propyl groups are magnetically equivalent. The ^{31}P NMR spectrum displays a singlet indicating that the two phosphorus nuclei are equivalent. From these observations, it can be concluded that the calix[4]arene framework in the ligand (**3**) adopts the cone conformation characterized by the presence of two planes of symmetry in the molecule [7]. These mirror-planes pass through the pair of aryl rings facing each other and perpendicular to the plane passing through the methylene bridge carbon atoms. Because of the complicated nature of the ^{1}H NMR spectrum of the reaction mixture containing ligand **4**, the conformation of the major component in solution could not be determined. A cone conformation would be expected on steric grounds. The observation of a single resonance in the ^{31}P NMR spectrum of **4** is consistent with cone conformation (Fig. S2).

The ^{1}H NMR spectrum of ligand **5** shows three singlets at 0.86, 1.25, and 1.31 ppm for the *tert*-butyl protons (relative intensities 2:1:1, respectively) and four doublets for the methylene protons of the calixarene framework. A single triplet for the terminal methyl groups of the propyl substituents indicates that the two propyl groups are magnetically equivalent (Fig. S3). These data

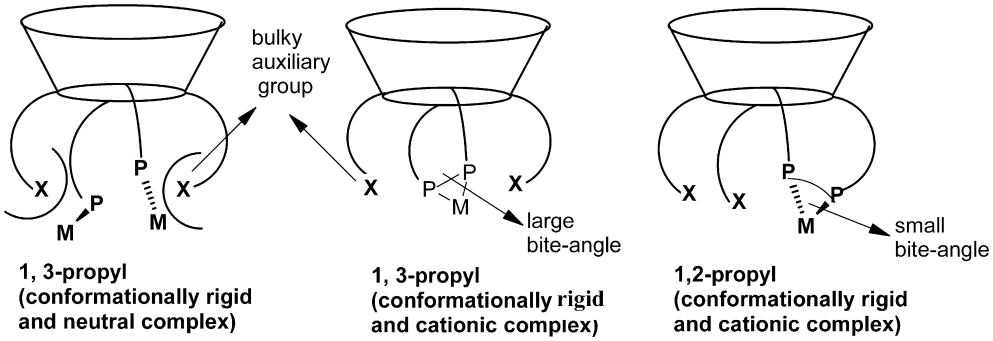
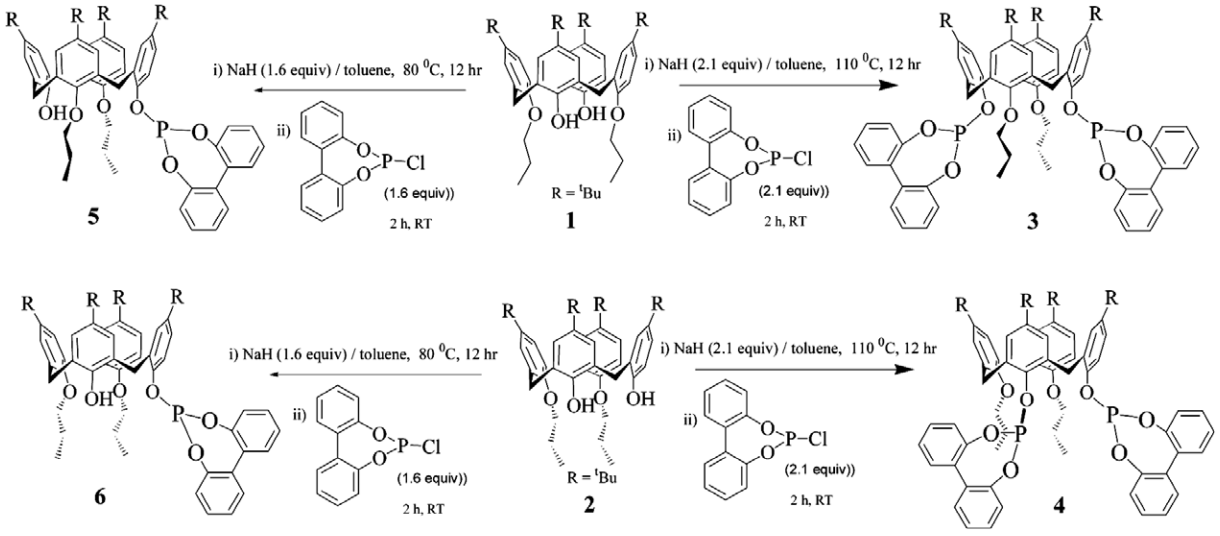


Fig. 1. Effect of propyl group substitution in the lower rim of calix[4]arene bisphosphites on the coordination of pendent phosphorus atoms to a transition metal.



Scheme 1. Synthesis of phosphite ligands **3**, **4**, **5** and **6**.

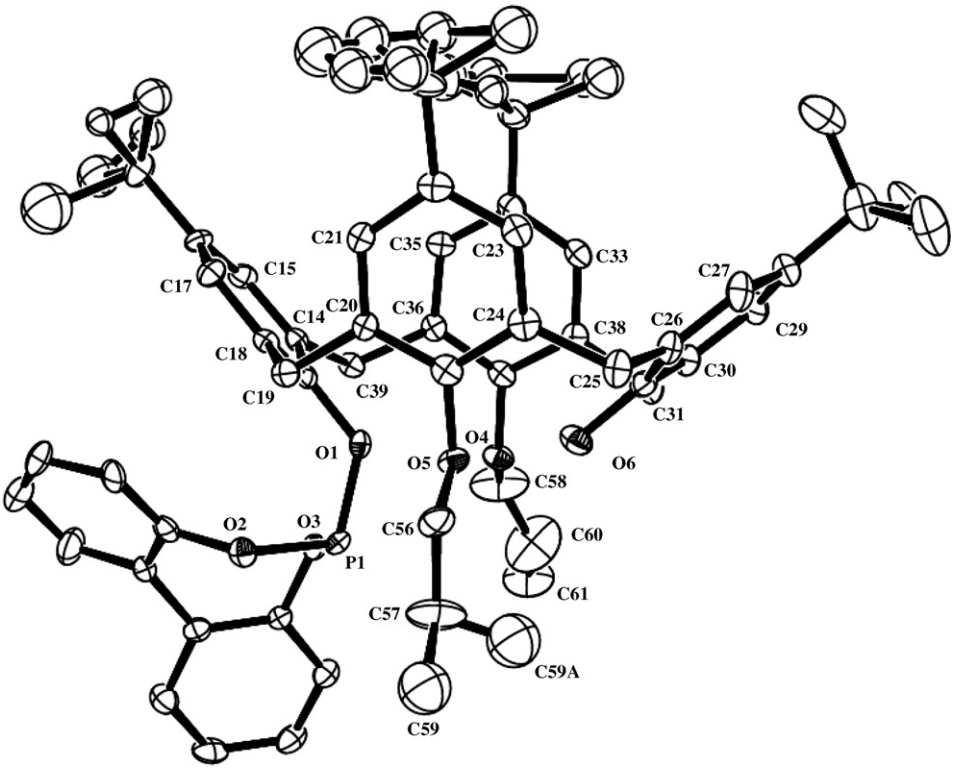


Fig. 2. Molecular structure of **5**.

suggest the presence of a plane of symmetry in the molecule as would be expected for cone or partial cone conformation. Two-dimensional ^1H–^1H COSY measurement shows that the chemical shift difference ($\Delta\delta > 0.9$) for the geminal methylene protons is in the characteristic range for cone conformation of the calix[4]arene framework [7]. The ^{31}P NMR spectrum of **6** shows a singlet indicating the presence of a single conformer (Fig. S4). The ^1H NMR spectrum shows eight doublets for the methylene protons signifying the absence of any symmetry element in the molecule. Hence, ligand **6** can be considered as inherently chiral [8]. The geminal methylene protons of the calix[4]arene framework are identified by carrying out a ^1H–^1H COSY experiment; the characteristic difference in their chemical shifts ($\Delta\delta > 0.9$) supports the cone conformation. The solid-state structures of ligands **5** and **6** (Figs. 2 and 3) show cone conformation of the calixarene framework (see Tables 1 and 2 and SI for details).

A variable temperature NMR study (CD_3COCD_3, 400 MHz), carried out between 190 and 321 K reveals that the ligands **3**, **5** and **6** do not undergo any significant structural changes in solution in this temperature range.

2.2. Allyl palladium complexes of ligand *3*

The complexation reactions were carried out under two different reaction conditions (Scheme 2). A series of cationic allyl palladium complexes (**3a**–**d**) were synthesized by using NH_4PF_6 as the anion scavenger and acetone as the solvent. A series of neutral allyl palladium complexes (**3e**–**3g**) were obtained when the (allyl) palladium chloro dimers were treated with ligand **3** in dichloromethane in the absence of NH_4PF_6. Complexes **3b** and **3f** have been isolated in pure form and characterized by ^1H and ^{31}P NMR spectroscopy and elemental analysis. All other complexes were characterized only in solution by ^{31}P NMR spectra of the reaction mixtures (Fig. S5). The ^{31}P chemical shifts for the neutral complexes (≈150 ppm) lie downfield from those for the cationic complexes (120–130 ppm).

A single resonance in the ^{31}P NMR spectra and two singlets for the *tert*-butyl protons in the ^1H NMR spectra of the neutral allyl complexes (**3e** and **3g**) point to the presence of a single species in solution. The room temperature ^{31}P NMR spectrum of complex **3f** shows two closely spaced singlets at 152.4 and 152.5 ppm; this result is in accord with two different orientations of the allyl ligands (*exo* and *endo*) at the two palladium centers as observed in the solid state (see later). The *exo* isomer is one in which central allyl proton is oriented away from the calixarene core whereas the *endo* isomer is defined as one in which the central allyl proton is oriented towards the calixarene core (see Section 2.6). The difference in the orientation of the two allyl moieties in the solution state could not be confirmed by ^1H NMR measurements because of the overlapping of the resonances of the protons of the two different allyl ligands. (Fig. S6a). The ^1H–^1H NOESY spectrum shows strong exchange cross peaks between the meta aryl protons H_a—$H_{a'}$ and H_b—$H_{b'}$ (Fig. S8). Protons H_a, H_b, $H_{a'}$, $H_{b'}$ were identified by the through space contacts with the nearest *tert*-butyl groups, (see Fig. S7). This observation clearly shows exchange between H_a and H_b as well as $H_{a'}$ and $H_{b'}$ protons. The exchange among these protons is only possible through *exo*–*endo* exchange of the allyl ligands. Three isomers (I, II and III) are possible for complex **3f** as shown in Fig. 4. It may be noted that only for the *exo*–*endo* isomer (I), the allyl moiety would undergo exchange between two indistinguishable forms (I and I′). In all the isomers, the substituted terminal allyl carbon is oriented trans to the phosphorus atom. The ^{31}P NMR spectrum of complex **3f** at −80 °C shows three signals of different intensities. This result suggests that the complex exists as a mixture of three isomers exchanging among themselves in solution. At a higher temperature (>30 °C), fast exchange among the isomers gives rise to a single signal.

2.3. Reactions of *4* with (allyl) palladium dimers $[(\eta^3\text{-}C_3H_3R_2)PdCl]_2$

The reaction of ligand **4** with (allyl) palladium chloro dimers, $[(\eta^3\text{-}C_3H_3R_2)PdCl]_2$(R=H or Ph) in the presence of ammonium

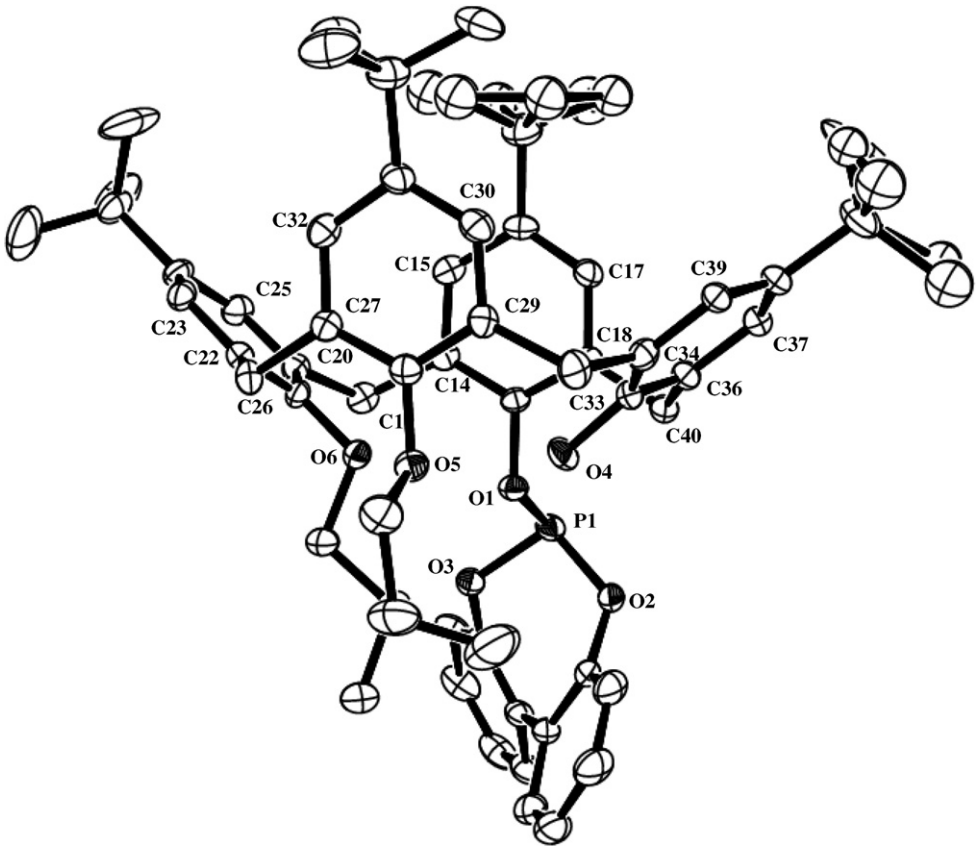


Fig. 3. Molecular structure **6**.

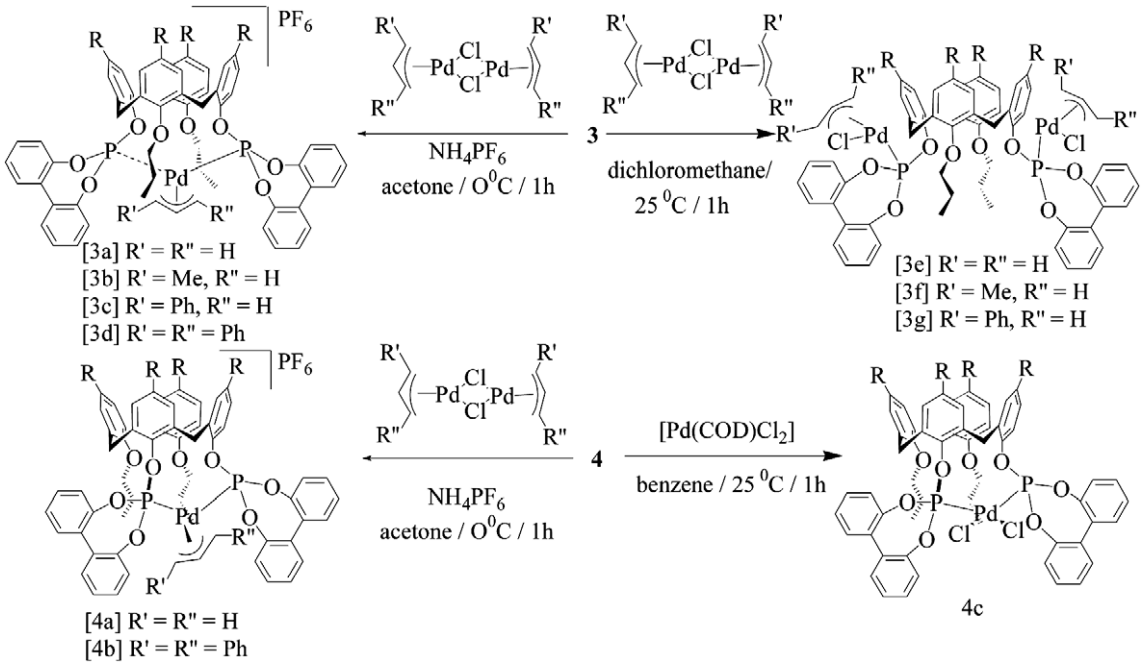
Table 1
Crystallographic data for **5**, **6**, **3f** and **4c**

Identification code	**5**	**6**	**3f**	**4c**
Empirical formula	$C_{66}H_{85}O_6P$	$C_{73}H_{99}O_6P$	$C_{86}H_{100}Cl_{14}O_8P_2Pd_2$	$C_{82.25}H_{102}Cl_2O_8P_2Pd$
Formula weight	1005.31	1103.49	2032.70	1457.88
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
Unit cell dimensions				
a (Å)	10.431(3)	11.162(4)	14.698(4)	39.805(2)
b (Å)	14.643(5)	13.305(5)	15.864(4)	23.308(6)
c (Å)	21.153(7)	23.191(9)	22.708(6)	18.167(5)
α (°)	88.450(5)	86.067(8)	79.789(5)	90
β (°)	82.521(5)	80.510(7)	83.130(4)	98.893(5)
γ (°)	84.826(5)	88.467(8)	70.934(4)	70.934(4)
Volume (Å^3)	3190.2(17)	3389(2)	4914(2)	16653(7)
Z	2	2	2	8
d_{calc} (Mg/m^3)	1.047	1.082	1.374	1.163
Absorption coefficient (mm^{-1})	0.089	0.089	0.828	0.375
$F(000)$	1088	1200	2080	6156
Crystal size (mm^3)	0.78 × 0.47 × 0.02	0.14 × 0.10 × 0.09	0.44 × 0.30 × 0.10	0.42 × 0.30 × 0.10
θ Range for data collection (°)	0.97–24.00	0.89–26.37	0.91–24.96	1.02–26.07
Index ranges	$-11 \leqslant h \leqslant 11$, $-16 \leqslant k \leqslant 15$, $-24 \leqslant l \leqslant 24$	$-13 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 16$, $-28 \leqslant l \leqslant 28$	$-17 \leqslant h \leqslant 17$, $-18 \leqslant k \leqslant 18$, $-26 \leqslant l \leqslant 26$	$-48 \leqslant h \leqslant 48$, $-28 \leqslant k \leqslant 28$, $-22 \leqslant l \leqslant 22$
Reflections collected	20888	35762	35267	63935
Independent reflections [$R_{(int)}$]	9976 [0.0473]	13582 [0.1081]	17046 [0.0675]	16358 [0.1519]
Completeness to θ (%)	99.7	98.2	98.9	99.3
Maximum and minimum transmission	0.9980, 0.9339	0.9925, 0.9872	0.9233, 0.7111	0.9642, 0.8578
Data/restraints/parameters	9976/0/624	13582/0/650	17046/0/1009	16358/0/804
Goodness-of-fit on F^2	1.517	0.942	1.077	1.016
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1619$, $wR_2 = 0.3756$	$R_1 = 0.0995$ $wR_2 = 0.2539$	$R_1 = 0.1116$ $wR_2 = 0.2395$	$R_1 = 0.1156$ $wR_2 = 0.2607$
R indices (all data)	$R_1 = 0.2073$, $wR_2 = 0.3980$	$R_1 = 0.2746$, $wR_2 = 0.3369$	$R_1 = 0.2033$ $wR_2 = 0.2887$	$R_1 = 0.2429$ $wR_2 = 0.3317$
Largest difference in peak and hole (e Å^{-3})	0.932, −0.623	0.651, −0.245	0.983, −0.672	1.064, −1.016

Table 2
Dihedral angles (°) between the planes of the aryl rings of the calixarene framework and the mean plane (X) defined by methylene carbon atoms[a]

Planes	Dihedral angles [ligand (**5**)]	Dihedral angles [ligand (**6**)]	Dihedral angles [complex (**3f**)]	Dihedral angles [complex (**4c**)]
A–X	85.1	80.3	43.7	75.7
B–X	49.2	38.2	89.9	49.1
C–X	75.8	84.3	43.9	84.9
D–X	40.5	42.4	89.3	44.9

[a] A B, C and D are the plane of aromatic rings defined by C26–C32, C34–C39, C13–C18 and C20–C25, respectively for **6**; C33–C38, C13–C18, C20–C24 and C26–C30 for **5**; C40–C45, C33–C38, C54–C59 and C47–C52 for **3f**; C46–C51, C39–C44, C32–C37 and C25–C30 for **4c**.



Scheme 2. Reactions of ligands **3** and **4** with palladium precursors.

hexafluorophosphate gives the expected complexes (**4a** and **4b**) (Scheme 2). Both the complexes have been characterized in solution by ^{1}H and ^{31}P NMR spectroscopy (Figs. S9 and S10). Attempts to synthesize (allyl) palladium complexes in which ligand **4** would bridge two palladium centers were unsuccessful. Complex **4b** could be isolated in a pure form and characterized by elemental analysis. The structures of the allyl complexes **4a** and **4b** in solution, as deduced from NMR data, are shown in Fig. 5. The ^{31}P NMR spectrum of complex **4a** shows two closely spaced singlets at δ 128.3 and 128.8 in the ratio of 1:1.5, indicating the presence of two isomers. The resonances arising from the protons of the methylene bridge as well as allyl carbon atoms were not resolved and as a result, unambiguous assignment of the structures of the two isomers could not be made. However, the cone conformation of the major isomer can be predicted from a pair of singlets (δ 0.95 and 1.25) for the four *tert*-butyl groups. The minor isomer also shows a pair of singlets (δ 0.96 and 1.23) for the four *tert*-butyl groups. This observation signifies the presence of a symmetry plane bisecting the plane formed by methylene bridge carbon atoms and passing through two of these carbon atoms and would be consistent with the presence of the 1,2-alternate conformer. However, the formation of this high-energy conformer can be ruled out on steric grounds. Two isomers can arise because of the *exo* and *endo* configuration of the allyl ligand with respect to the calixarene framework. A similar kind of *exo–endo* isomerism was observed by Matt and coworkers for the palladium methyl allyl complex of a pendent calix[4]arene-1,3-bisphosphinite ligand [2c]. Assignment of the *exo* and *endo* isomers by 2D NMR experiments was not possible because of the overlapping of the resonances arising from the protons of the propyl, methylene and terminal allyl groups. Tentatively the major isomer (**4a**′) is assigned the *exo* configuration and the minor isomer (**4a**) the *endo* configuration. The $^{1}H–^{1}H$ NOESY experiment shows the absence of exchange between the isomers.

The ^{31}P NMR spectrum of the diphenyl allyl complex **4b** shows a single resonance at δ 125.6. The $^{1}H–^{1}H$ NOESY experiment shows the absence of any cross peak between the central allyl proton (δ 6.36) and the protons of the propyl groups (Fig. S11). This observation suggests that the central allyl proton is oriented away from the calixarene core i.e *exo* arrangement of the allyl ligand. The cone conformation of the calix-matrix can be deduced from the presence of only two singlets (δ 0.91 and 1.22) for the four *tert*-butyl groups and also by the characteristic difference $\Delta\delta$ (>0.9) in the chemical shifts of the adjacent methylene protons. All the methylene protons of the calixarene framework have been assigned by $^{1}H–^{1}H$ COSY measurement.

2.4. Reactions of ligand *5* with (allyl) palladium precursors

The reactions of (allyl) palladium precursors with the monophosphite ligand (**5**) in dichloromethane give the neutral allyl complexes **5a–c** as shown in Scheme 3. The ^{31}P NMR spectra of **5a–c** display a singlet in each case (Fig. S13); the chemical shifts ($\delta \approx 150$) lie in the region observed for neutral allyl complexes of phosphite ligands (e.g complex **3f**). The ^{1}H NMR spectra of

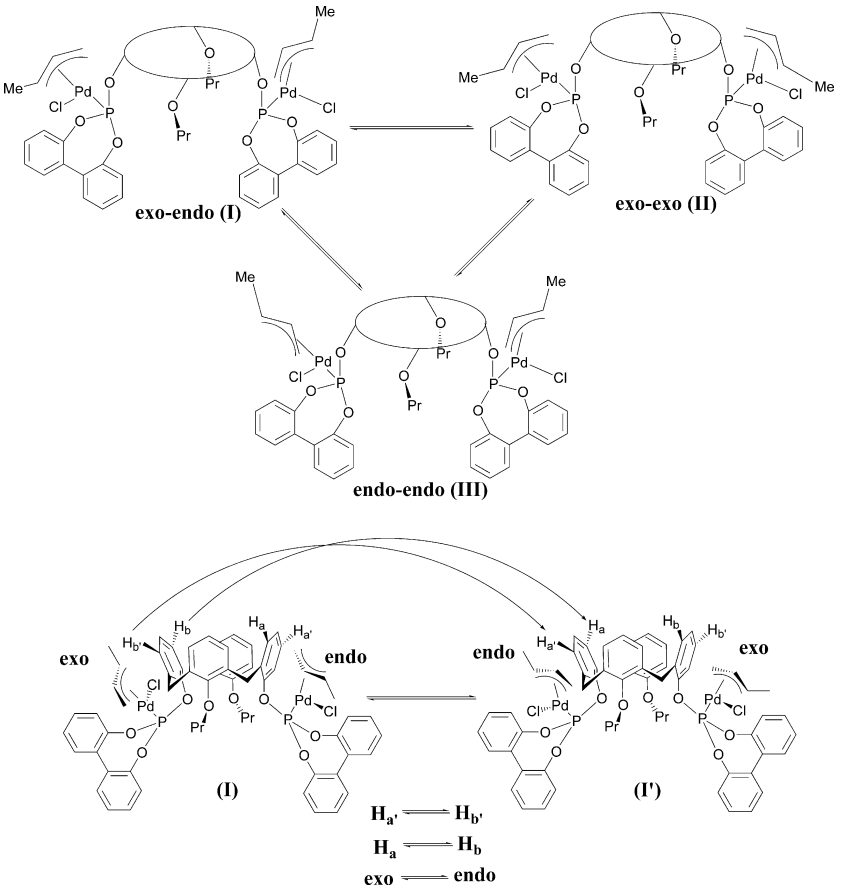


Fig. 4. Schematic representation of exchange among three isomers of complex **3f**. Arrows indicate exchanging protons.

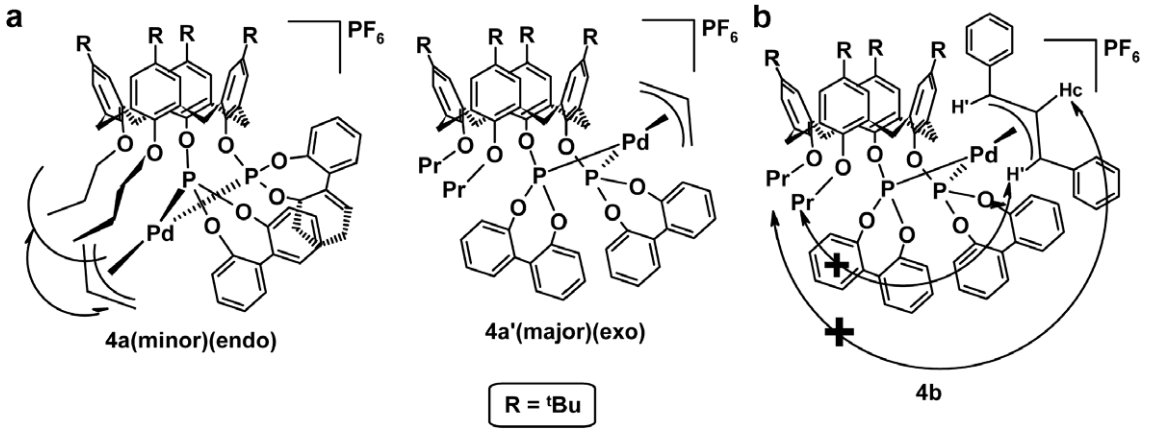
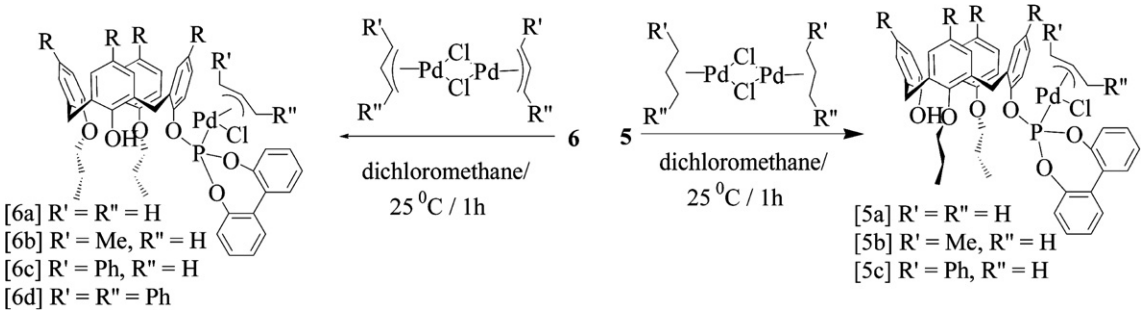


Fig. 5. Probable solution structures of (a) (allyl) palladium (**4a**, **4a**′) and (b) (diphenyl-allyl) palladium (**4b**) complexes.



Scheme 3. Reactions of ligands **5** and **6** with chloro-bridged allyl palladium dimers.

complexes **5b** and **5c** are broad and could not be analyzed. The ^{1}H NMR spectrum of **5a** is more informative (Fig. S14). Three singlets for the *tert*-butyl protons in the ratio of 1:2:1 and one triplet for the six methyl protons of the two propyl groups indicate the retention of the plane of symmetry in the molecule. The only difference observed from the ^{1}H NMR spectrum of the ligand is the further splitting of methylene proton resonances to give rise to six doublets at δ 3.18, 3.35, 3.43, 4.35, 4.69 and 4.77 in the ratio of 2:1:1:2:1:1, respectively. The two 'higher-intensity' doublets are due to the resonances of the protons (H_e, H_f) attached to two methylene bridge carbons located far from the palladium center. Four protons of the methylene bridge carbons near the palladium center are all magnetically nonequivalent and give rise to four doublets. This nonequivalence of methylene bridge protons arises because of the coordination of two different atoms (P and Cl) to palladium.

2.5. Allyl palladium complexes of ligand *6*

The reactions of the monophosphite ligand (**6**) with (allyl) palladium precursors $[(\eta^3\text{-}C_3H_5)PdCl]_2$, $[(\eta^3\text{-}1\text{-}Me\text{-}C_3H_4)PdCl]_2$, $[(\eta^3\text{-}1\text{-}Ph\text{-}C_3H_4)PdCl]_2$ and $[(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)PdCl]_2$ give the expected neutral allyl palladium complexes **6a**–**d** (Scheme 3). The complexes have been characterized in solution by ^{31}P and ^{1}H NMR spectra. Formation of the neutral complexes is confirmed by observing the ^{31}P resonances in the 150 ppm region (Fig. S15), characteristic of neutral allyl complexes such as **3e**–**g** (See Section 2.2). The spectra of the complexes **6a** and **6c** show two resonances with almost equal intensities. These allyl palladium complexes, formed by an inherently chiral calixarene, exist in two diastereomeric forms. The spectra of **6b** and **6d** show two additional singlets due to the presence of two other minor isomers [(III) and (IV)] (Fig. 6). Room temperature ^{31}P–^{31}P NOESY measurements on **6a** and **6d** reveal that the diastereomers undergo exchange in solution. Complex **6d** also undergoes exchange among major and minor isomers. Although two distinct peaks appeared in the ^{31}P NMR spectra of the complexes, the ^{1}H NMR spectra of the complexes were not clearly resolved at room temperature. The NMR data are consistent with cone conformation of the calixarene framework as found in the ligand **6**.

The ^{1}H resonances of the allyl protons of diastereomers I and II were assigned by comparison with literature data [6d] and also from the "through-bond" coupled allyl protons identified from the ^{1}H–^{1}H COSY spectrum (Fig. S16). High field shifts of H_f and $H_{a'}$ points to the close proximity of these protons to aromatic rings of calix[4]arene framework. Fig. S17 shows the phase sensitive ^{1}H–^{1}H NOESY spectrum of complex **6b**. Fig. 6 shows possible isomers (I–IV) of complex **6b** in solution and the observed exchange pattern among the protons of the allyl moiety. Clearly there is exchange between analogous protons of the two diastereomers (I and II) as well as between protons of the same diastereomer. Cross peaks between the *syn* (H_a) and the *anti* (H_f) protons as well as those between $H_{a'}$ and $H_{f'}$ protons indicate the presence of *syn-anti* isomerization. Cross peaks between H_f and $H_{f'}$ as well as between H_b and $H_{b'}$ protons indicate the presence of *syn–syn*/*anti–anti* isomerization processes [4e,4f,9]. *Cis* arrangement of the terminal methyl group with respect to the central allyl proton in both the isomers I and II can be inferred by the presence of NOE cross peaks between the protons of methyl group and that of the central allyl carbon (Fig. S18). Fig. S19 shows the exchange cross peaks between the allyl protons of two major isomers I and II and those of the minor isomers (III and IV).

2.6. Chirality of Pd(allyl) complexes

We have considered the possibility of restricted rotation of phenyl groups of biphenyldioxy units around C_1—C_1' bond in the ligands **2**–**6** and their palladium complexes. There are only a few metal complexes of unsubstituted (biphenyldioxy)phosphorus ligands known for which different ^{31}P and ^{1}H NMR peaks have been observed at low temperatures for isomers arising from the restricted rotation around C_1—C_1' bond. Piarulli and coworkers have observed that biphenolic phosphorus ligands (both phosphite and phosphoramidite types) exhibit tropos behavior even at 190 K. The Rh complexes of biphenolic phosphites show tropos nature of the ligand upto 230 K, the lowest temperature at which measurements could be made[10]. Similarly, Hartwig and coworkers have noted that the iridium complex of a phosphoramidite ligand with a biphenol backbone shows atropoisomerism only below 230 K [11]. In the present investigation, variable temperature ^{31}P and ^{1}H NMR spectra of the ligands **3**, **5**, **6** and complexes **3b**, **4a**, **4b**, **5a**, **6a**, **4c** did not show any significant changes upto 193 K showing the tropos (free-to-rotate) nature of biphenyldioxy units throughout this temperature range. The tropos nature of the biphenyldioxy units has also been supported by high thermal parameters of biphenyldioxy carbon atoms in the solid-state structures of **3f** and **4c**. Moreover, the solid-state structures of these complexes clearly show that the biphenyldioxy units are away from the calixarene backbone. As a result, any steric interaction which might be responsible for atropos nature of biphenyldioxy unit can be ruled out. In the case of complex **3f** and **6b**, broadening of the ^{31}P NMR signals has been observed at 193 K (see Fig. S22 and S23). Although, the origin of three ^{31}P resonances at low temperature for complex **3f** and four ^{31}P resonances (two major and two minor) at room temperature for complex **6b** have been already described in Figs. 4 and 6, respectively (see also Fig. S22), the presence of other isomers due to restricted rotation of biphenyldioxy C_1—C_1' bond at temperatures below 193 K cannot be discounted.

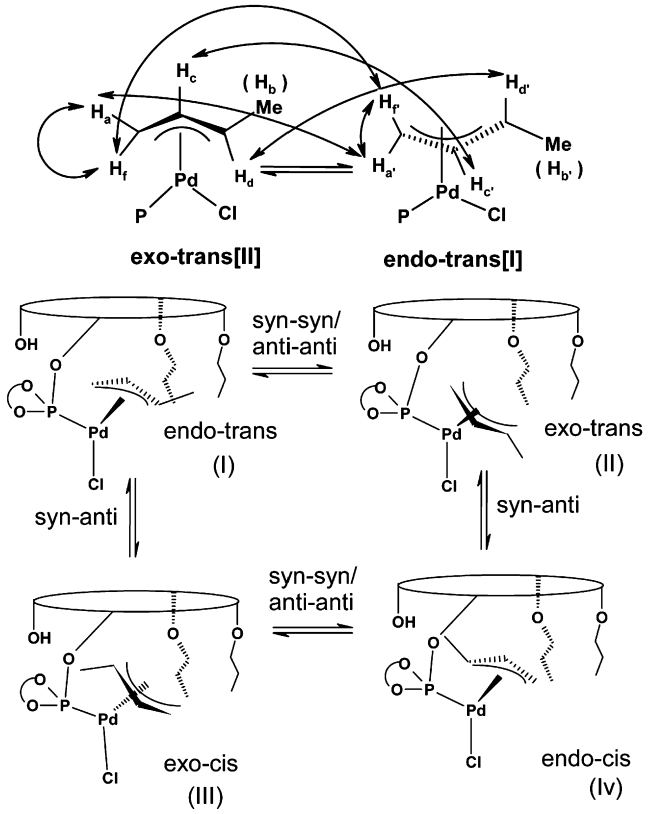


Fig. 6. Probable isomers of complex **6b** in solution. [In the present study '*cis–trans*' configurations are defined by the relative orientation of phosphorus (bonded to calix[4]arene unit) and terminal methyl group of the allyl moiety. When both are on the same side of the palladium square plane, the arrangement is named as '*cis*'].

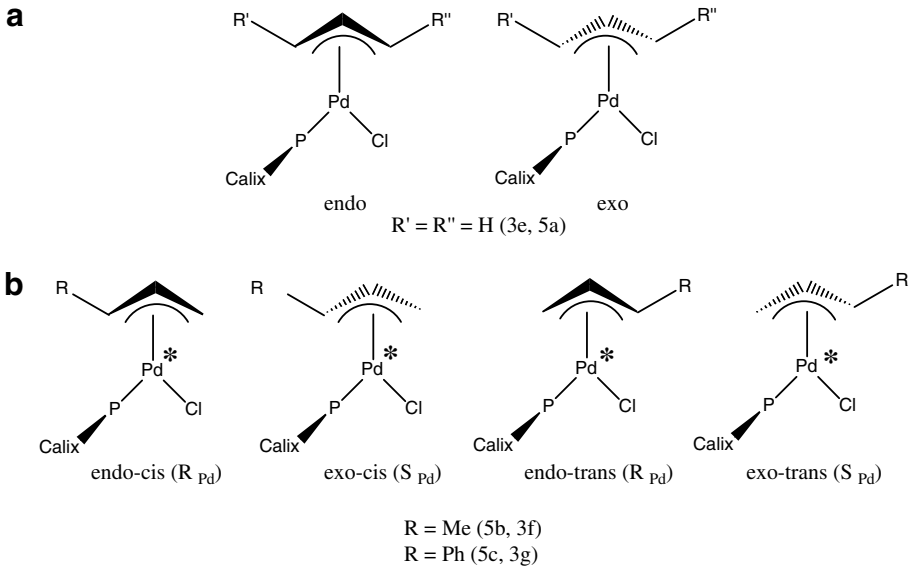


Fig. 7. Different diastereomers produced by the combinations of (a) symmetric allyl or (b) unsymmetrical allyl moiety with calixarene backbone.

Neutral (allyl) palladium complexes with a symmetric allyl moiety can show *exo* or *endo* diastereomers (Fig. 7a) whereas the Pd center itself is chiral for nonsymmetric allyl complexes, for which the possible diastereomers are shown in Fig. 7b. The situation becomes more complicated when a chiral calixarene ligand (**6**) is used to generate neutral allyl complexes. Possible diastereomers with different combinations of allyl and calixarene backbone can be described as follows: (1) symmetric allyl (where R′=R″) Pd complexes can form only *exo* and *endo* isomers; (2) coordination of an unsymmetrical allyl (where R′ # R″) moiety with Pd will generate a chiral Pd center and such a complex can exist as four diastereomers, *viz*. *exo-cis*, *endo-cis*, *exo-trans*, *endo-trans*; (3) symmetric allyl complex with a chiral calixarene backbone can exist as four diastereomers, *viz.* R(calix)-*exo*, R(calix)-*endo*, S(calix)-*exo*, S(calix)-*endo*; (4) unsymmetrical allyl complex with a chiral calixarene backbone can produce eight diastereomers, *viz*. R(calix)-*exo-cis*, R(calix)-*endo-cis*, R(calix)-*exo-trans*, R(calix)-*endo-trans*, S(calix)-*exo-cis*, S(calix)-*endo-cis*, S(calix)-*exo-trans* and S(calix)-*endo-trans*. The spatial arrangement of the substituents at the Pd coordination center attached to an asymmetric calixarene ligand is shown in Fig. 8. The exchange between the diastereomers V and VI is a forbidden process as it involves the breaking of Pd–P bond and the detachment of the Pd(allyl)(Cl) moiety from the calixarene backbone. Diastereomers (I–IV) of complex **6b** shows exchange among each other (see Fig. S17 and S19). Thus, the possibility of generation of these diastereomers from the chiral calixarene backbone can be ruled out. In essence, the relative arrangement of the Pd substituents with respect to the calixarene backbone remains same in all the complexes (either V or VI) and as a result, instead of eight probable diastereomers of complex **6b**, only four have been observed.

2.7. Molecular structure of the allyl(palladium) complex *3f*

The molecular structure of the palladium methyl allyl complex (**3f**) is shown in Fig. 9. The steric interaction of the two bulky bisphenol units with the pendent propyl arms causes the two bisphenol substituted aryl rings to be oriented perpendicular to the plane (X) of the methylene bridge carbon atoms (Table 2). The other two aryl rings are inclined at an angle of ≈45° with respect to the same plane (X) leading to an ideal pinched cone conformation of the calix[4]arene framework with a C_{2v} symmetry axis passing through the center of calixarene cavity [12]. The sequence of signs i.e. + −, + −, + −, + − of the torsional angles (see Table S3)

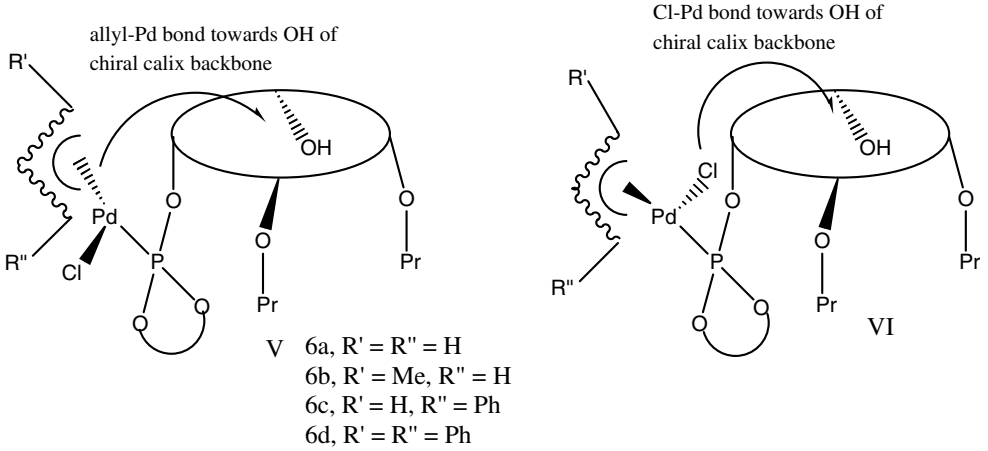


Fig. 8. Diastereomers produced due to the asymmetry of calixarene backbone. One of the forms V or VI has been observed for each complex of ligand **6a**–**6d**.

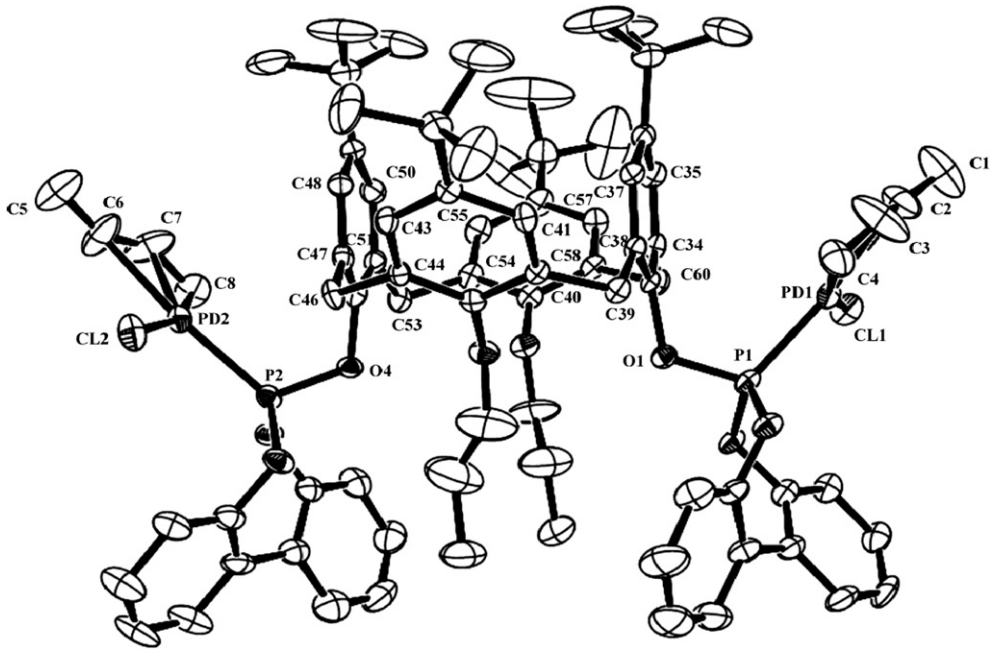


Fig. 9. Molecular structure of **3f**.

confirms the cone conformation of the calix[4]arene framework. Selected bond lengths, bond angles and dihedral angles around palladium coordination plane are listed in Table 3 and Table S4, respectively. The geometry around both the palladium is almost planar as can be seen from the low value of the dihedral angles between the planes of the terminal allyl carbon atoms passing through palladium (C–Pd–C) and that of coordinated phosphorus and chlorine atoms passing through corresponding palladium center (P–Pd–Cl). The angles made by the two terminal allyl carbons to the palladium and also by the chlorine and phosphorus atoms to the palladium deviate considerably from 90°. This observation suggests that the coordination of the ligands to palladium differ to an appreciable extent from the square geometry. A considerable difference in the bending of the terminal methyl groups can be observed for the two allyl ligands coordinated to the two palladium centers. This bending of terminal methyl groups is indicated by the dihedral angles (4° and 16°) between the planes passing through the terminal carbon atom attached to the methyl group, methyl group itself and the palladium atom and the plane passing through two terminal allyl carbon atoms and the palladium center (Table S4). An expanded view of the palladium coordination plane is shown in Fig. S21, which clearly shows that the hydrogen attached to the central allyl carbon C3 is oriented away from calixarene framework whereas the hydrogen attached to the central allyl carbon C7 is directed towards the calixarene framework. The Pd–Cl and Pd–P bond lengths are similar to those observed in other palladium complexes. Greater trans influence of the phosphorus atoms is reflected in the higher (0.16 and 0.09 Å) bond distances of the terminal allyl carbons (C6, C2) bonded trans to the phosphorus atoms with respect to the terminal allyl carbons (C4, C8) bonded trans to the chlorine atoms. Both the biphenol units are in *R*/*S* configuration in the solid-state structure of complex **3f**.

Table 3
Selected bond distances (A°) and bond angles for complex **3f**

Atoms	Distance (A°)	Atoms	Angle (°)
P(1)–PD(1)	2.238(3)	C(2)–PD(1)–C(4)	67.0(6)
CL(1)–PD(1)	2.356(2)	C(6)–PD(2)–C(8)	68.1(6)
C(2)–PD(1)	2.21(2)	C(2)–C(3)–C(4)	149.2(4)
C(3)–PD(1)	2.13(2)	C(6)–C(7)–C(8)	146.4(2)
C(4)–PD(1)	2.12(1)	CL(1)–PD(1)–P(1)	102.4(1)
P(2)–PD(2)	2.237(2)	CL(2)–PD(2)–P(2)	101.9(1)
CL(2)–PD(2)	2.361(3)		
C(6)–PD(2)	2.25(1)		
C(7)–PD(2)	2.11(1)		
C(8)–PD(2)	2.09(1)		

2.8. Molecular structure of $PdCl_2$ complex (**4c**)

The molecular structure of the palladium dichloride complex (**4c**) has been established by the single crystal X-ray diffraction analysis and is shown in Fig. 10. This complex is the first of its kind arising from the chelation of phosphorus atoms, appended to the lower rim of two adjacent aryl rings of the calix-matrix, to a single palladium center. The conformation of the calix[4]arene framework in the complex (**4c**) can be described in terms of torsion angles (Table S5) and dihedral angles (Table 2). Opposite signs of the consecutive torsion angles (− +, − +, − +, − +) showed that the calix[4]arene matrix adopts a cone conformation. However, the dihedral angles between the aryl rings of calix-matrix and the plane of the methylene bridge carbons show a considerable deviation from the values expected for a cone or a pinched cone conformation. Chelation of the phosphorus atoms, attached to the lower rim of two adjacent aryl rings of the calix-matrix to the palladium center is probably responsible for this intermediate conformation. One of the aryl rings, attached to the coordinated phosphorus, makes an angle of 75° with the methylene bridge plane and consequently the dihedral angles of the other aryl rings also show values between 45° and 90°. These values lie in between the dihedral angles for an ideal cone (all 45°) and pinched cone (two 45° and two 90°) conformations [12]. Selected bond lengths, bond angles around palladium coordination center are listed in Table 4. The deviation of P1–Pd1–P2 and Cl1–Pd1–Cl2 angles, from the ideal value (90°) expected for a square geometry, is small. The dihedral angles between the planes passing through the atoms (P1–Pd1–P2) and (CL1–Pd1–CL2) is low (3.1°). The P–Pd–P bite angle is 5–8° lower than any other chelated allyl palladium complexes of calix[4]arene reported in literature [2d]. The Pd–P and Pd–Cl bond lengths are within the range reported for palladium dichloride complexes of calix[4]arene bisphosphite ligands [2a,13]. One of the biphenol

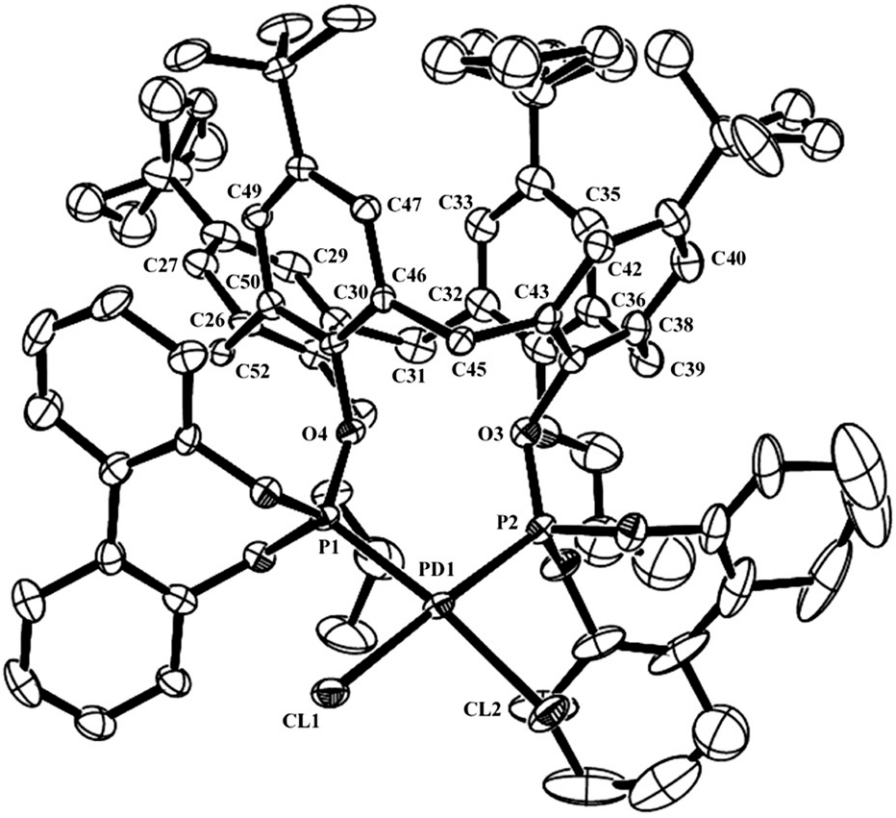


Fig. 10. Molecular structure of **4c**.

Table 4
Selected bond distances (Å) and bond angles (°) at the palladium coordination center for the complex **4c**

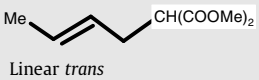
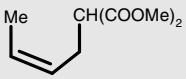
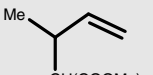
Atoms	Distance and angles
PD1–P1	2.215(2)
PD1–P2	2.242(2)
PD1–CL1	2.316(2)
PD1–CL2	2.331(2)
P(1)–PD(1)–P(2)	98.7
CL(1)–PD(1)–CL(2)	91.4

units adopts *R*/*S* and the other *S*/*R* configuration in the solid-state structure of complex **4c**.

2.9. Catalytic studies

Matt and cowokers have reported that inherently chiral calix[4]arene phosphines gave superior enatioselectivities in Pd-catalyzed allylic alkylations compared to those induced by related diphosphines in which the only sources of chirality are the asymmetric carbon atoms of substituents attached to phosphorus [14]. They have also shown that calixarene bisphosphites bearing chiral binaphthol backbone gave linear products with 98% selectivity [2d]. These results prompted us to study the catalytic activity of conformationally rigid bisphosphite ligand **3** and its palladium methyl allyl complex **3f** in allylic alkylation reactions of crotyl acetate using dimethyl malonate as the nucleophile. The relative amounts of the products were determined by the integrated intensities of the respective signals in the ^{1}H NMR spectrum. The results are shown in Table 5. The relative yield of the branched product is considerably high. This increase is probably due to the involvement of neutral allyl complex in the catalytic cycle as shown in Fig. S24. As can be seen from the solid-state structure of the allyl complex **3f**, the methyl group substituted terminal allyl carbon is oriented trans to the phosphorus atom. The trans directing effect of phosphorus is higher than that of chloride and as a result, the substituted allyl terminus is more susceptible to nucleophilic attack than the unsubstituted allyl terminus, leading to higher yield of the branched isomer [15]. The relative yield of the branched product is higher (51%) with complex **3f** than that observed

Table 5
Relative yields (%) of products in the palladium catalyzed nucleophilic substitution of (E) crotyl acetate using dimethyl malonate (DMM) as nucleophile[a]

Catalyst	Reagents	 Linear *trans*	 Linear *cis*	 Branched	Yield
3 + Pd-precursor	BSA/KOAc/DMM	55	7	38	60
Complex **3f**	Sodium salt of DMM	49	0	51	30
Complex **3f**[b]	Sodium salt of DMM	45	0	55	82

[a] Reaction conditions: 25 °C, 0.05 mol% of catalyst; time taken for the completion of reaction (as monitored by TLC): 24 h.
[b] Stoichiometric.

(38%) with ligand **3**. Presumably, the neutral allyl complex is more active than the chelated cationic complex formed in the latter case (see SI for the ^{31}P NMR evidence of the formation of cationic complex during the reactions of ligand **3** with allyl palladium dimers). The monophosphite ligand **6** is also able to catalyze the reaction but there is no significant amount of branched product formed during the catalytic reaction. Our effort to apply the proximally substituted ligand **4** in catalytic allylic alkylation reaction to verify the effect of smaller bite angle on the relative amount of branched product was not successful because of the difficulty in isolating ligand **4** in a pure form.

3. Conclusions

In conclusion, we have synthesized four conformationally rigid calix[4]arene phosphite ligands and their palladium complexes. Relative positioning of the phosphorus atoms in the lower rim of the calixarene unit plays an important role in determining the nature of coordination to the palladium center: 1,3-Substituted bisphosphites give neutral as well as cationic (allyl) palladium complexes whereas 1,2-substituted bisphosphite forms only cationic (allyl) palladium complexes. The P–Pd–P bite angle shows significant difference between palladium complexes of 1,2-substituted bisphosphite (complex **4c**) and those of the analogous 1,3-substituted bisphosphite [16]. Neutral allyl complex (involving coordination of single phosphorus to palladium) appears to be more effective in forming the branched product during the catalytic allylic alkylation reactions than the chelated cationic complex.

4. Experimental

The general experimental procedures and details of spectroscopic and other physical measurements were as described in our previous publications [17,18]. Phosphorochloridite ($C_{12}H_8O_2$)-PCl [19], 1,3-dipropyloxy calix[4]arene [20], 1,2-dipropyloxy calix[4]arene [21] and the organometallic precursor complexes, $[Pd(COD)Cl_2]$ [22], $[(\eta^3\text{-}C_3H_5)PdCl]_2$ [23], $[(\eta^3\text{-}1\text{-}Me\text{-}C_3H_4)PdCl]_2$ [24], $[(\eta^3\text{-}1\text{-}Ph\text{-}C_3H_4)PdCl]_2$ [24], and $[(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)PdCl]_2$ [25] were prepared by published procedures. Modified literature procedures were followed for catalytic allylic alkylation reactions of crotyl acetate (see Supporting Information) [26]. Isomer distribution was determined from the ^1H NMR intensities [26,27].

4.1. Synthesis of 25,27-bis-(2,2′-biphenyldioxyphosphinoxy)-26,28-dipropyloxy-p-tert-butyl calix[4]arene (3)

A suspension of 25,27-dihydroxy-26,28-dipropyloxy-*p-tert*-butyl calix[4]arene (**1**) (1.61 g, 2.2×10^{-3} mol) and NaH (60% dispersion in oil) (0.185 g, 4.6×10^{-3} mol) in toluene (60 mL) was heated under reflux for 12 h at 110 °C. [1,1′-Biphenyl]-2,2′-phosphorochlororidite (4.6×10^{-3} mol) in toluene (30 mL) was added at 0 °C and the reaction mixture stirred for 2 h at room temperature. The reaction was followed by TLC [R_f = 0.8 (ligand **3**); SiO_2; EtOAc/petrol (1/99-v/v)]. Solvent was evaporated under reduced pressure and the residue was subjected to column chromatography to obtain the title compound as a colorless solid which consisted of the desired bisphosphite ligand as the major product with the corresponding monophosphite as the minor product. The sample was dissolved in minimum volume of petrol and the solution kept over night to give a precipitate of the pure bisphosphite ligand (**3**) (yield = 0.8 g, 31%); m.p = 205–210 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 136.1 (s); ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.52 (t, 6H, $-C_2H_5CH_3$), 1.02 (s, 18H, $-C(CH_3)_3$), 1.17 (s, 18H, $-C(CH_3)_3$); 1.85(m, 4H, $-C_2H_5CH_3$), 3.21 (d, ^2J(H,H) = 12 Hz, 4H, $ArCH_2Ar$), 3.75 (t, 4H, $-OCH_2C_2H_5$), 4.69 (d, ^2J(H,H) = 12 Hz, 4H, $ArCH_2Ar$), 6.69, 6.90 (2s, 8m-ArH, calixarene); 7.1–7.5 (m, 8H, biphenol ArH). MS (MALDI, M = 1161.2): m/z = 1162.2 (MH^+).

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

A suspension of 25,26-dihydroxy-27,28-dipropyloxy-*p-tert*-butyl calix[4]arene (**2**) (1.61 g, 2.2×10^{-3} mol) and NaH (60% dispersion in oil) (0.185 g, 4.6×10^{-3} mol) in toluene (60 mL) was heated under reflux for 12 h at 110 °C. The solution was cooled to 0 °C and [1,1′-biphenyl]-2, 2′-phosphorochlororidite (4.6×10^{-3} mol) in toluene (30 mL) was added. The reaction mixture was stirred for 2 h at room temperature. The reaction was followed by TLC [R_f = 0.8 (ligand **4**); silicagel; EtOAc/petrol (1/99-v/v)]. Solvent was evaporated under reduced pressure and the residue was subjected to column chromatography to obtain a colorless solid which consisted of the desired bisphosphite ligand (**4**) as the major component with the corresponding monophosphite (**6**) as the minor component. The ^{31}P NMR spectrum showed several other resonances of low intensity indicating the presence of other conformational isomers of both mono and bisphosphites. The ligand (**4**) could not be separated in a pure form. This mixture of compounds was used as such for further complexation reactions. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 113.7 (s), 128.1 (s), 129.2 (s, major product, bisphosphite, **4**), 133.1(s), 137.5 (s), 145.1 (s), 147.1 (s, monophosphite **6**). ^1H NMR ($CDCl_3$, 400 MHz): Not resolved.

4.3. Synthesis of 25-hydroxy-27-(2,2′-biphenyldioxyphosphinoxy)-26,28-dipropyloxy-p-tert-butyl calix[4]arene (5)

A suspension of 25,27-dihydroxy-26,28-dipropyloxy-*p-tert*-butyl calix[4]arene (**1**) (1.61 g, 2.2×10^{-3} mol) and NaH (60% dispersion in oil) (0.14 g, 3.5×10^{-3} mol) in toluene (60 mL) was heated for 12 h at 80 °C. [1,1′-Biphenyl]-2,2′-phosphorochlororidite (3.5×10^{-3} mol) in toluene (30 mL) was added at 0 °C and the reaction mixture stirred for 2 h at room temperature. The reaction was followed by TLC [R_f = 0.65 (ligand **5**); SiO2; EtOAc/petrol (1/99-v/v)]. Solvent was evaporated under reduced pressure and the residue was subjected to column chromatography to obtain the title compound as a colorless solid which consisted of the desired monophosphite ligand (**5**) as the major component along with the corresponding bisphosphite (**3**) as the minor component. The product was purified further by subjecting it to column chromatography for a second time to obtain a pure sample of ligand **5** (yield = 0.6 g, 28.8%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 128.1 (s); ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.86 (s, 18H, $-C(CH_3)_3$), 0.94 (t, 3H, $-C_2H_5CH_3$), 1.25 (s, 9H, $-C(CH_3)_3$), 1.31 (s, 9H, $-C(CH_3)_3$); 1.93 (m, 2H, $-C_2H_5CH_3$), 3.24 (2d, 4H, $ArCH_2Ar$), 3.74 and 3.91 (2m, 4H, $-C_2H_5CH_3$), 4.35 (d, ^2J(H,H) = 13.2 Hz, 2H, $ArCH_2Ar$), 4.87 (d, ^2J(H,H) = 12.8 Hz, 2H, $ArCH_2Ar$); 6.59, 6.62, 7.03, 7.05 (4s, 8m-ArH, calixarene). 7.20–7.43 (m, 8H, biphenol ArH). MS (MALDI, M = 947.2): m/z = 985.8 ($M + K^+$, from matrix).

4.4. Synthesis of 25-hydroxy-26-(2,2′-biphenyldioxyphosphinoxy)-27,28-dipropyloxy-p-tert-butyl calix[4]arene (6)

A suspension of 25,26-dihydroxy-27,28-dipropyloxy-*p-tert*-butyl calix[4]arene (**2**) (1.61 g, 2.2×10^{-3} mol) and NaH (60% dispersion in oil) (0.14 g, 3.5×10^{-3} mol) in toluene (60 mL) was heated for 12 h at 80 °C. [1,1′-Biphenyl]-2,2′-phosphorochlororidite (3.5×10^{-3} mol) in toluene (30 mL) was added at 0 °C and the reaction mixture stirred for 2 h at room temperature. The reaction was followed by TLC [R_f = 0.7 (ligand **6**); SiO_2; EtOAc/petrol (1/99-v/v)]. Solvent was evaporated under reduced pressure and the residue subjected to column chromatography to obtain a colorless solid which consisted of the desired monophosphite ligand (**6**) as the

major component and the corresponding bisphosphite (**4**) as the minor component. The mixture was dissolved in petrol and the solution kept overnight to obtain colorless crystals of **6** (yield = 0.75 g, 36%); m.p = 100–105 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 147.1 (s); ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.33 (t, 3H, $-C_2H_5CH_3$), 0.73 (s, 9H, $-C(CH_3)_3$), 0.90 (s, 9H, $-C(CH_3)_3$), 1.09 (t, 3H, $-C_2H_5CH_3$), 1.34 (s, 18H, $-C(CH_3)_3$); 1.83(m, 2H, $-C_2H_5CH_3$), 1.91 (m, 2H, $-C_2H_5CH_3$), 3.129 (d, ^2J(H,H) = 12.4 Hz, 1H, $ArCH_2Ar$), 3.253 (d, ^2J(H,H) = 12.8 Hz, 1 H, $ArCH_2Ar$), 3.321 (d, ^2J(H,H) = 10.0 Hz, 1H, $ArCH_2Ar$), 3.354 (d, ^2J(H,H) = 9.6 Hz, 1H, $ArCH_2Ar$), 3.585 (t, 2H, $-OCH_2C_2H_5$), 3.721 (m, 1H, $-OCH_2C_2H_5$), 3.85 (m, 1H, $-OCH_2C_2H_5$), 4.155 (d, ^2J(H,H) = 13.6 Hz, 1H, $ArCH_2Ar$), 4.268 (d, ^2J(H,H) = 12.4 Hz, 1H, $ArCH_2Ar$), 4.566 (d, ^2J(H,H) = 13.2 Hz, 1H, $ArCH_2Ar$), 4.741 (d, ^2J(H,H) = 12.8 Hz, 1H, $ArCH_2Ar$), 6.43, 6.45, 6.62, 6.65, 7.05, 7.15 (6s, 8m-ArH, calixarene), 7.28–7.6 (m, 8H, biphenol ArH). MS (MALDI, M = 947.2): m/z = 985.8 ($M + K^+$, from matrix).

4.5. Synthesis of [(η^3-C_3H_5)Pd(κ^2-P,P′-**3**)](PF_6) (**3a**)

Calix[4]arene phosphite (**3**) (94 mg, 8×10^{-5} mol) in acetone (30 mL) was added drop-wise to a suspension of [(η^3-C_3H_5)PdCl]$_2$ (14 mg, 4×10^{-5} mol) and NH_4PF_6 (15 mg, 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 colorless precipitate of the title compound (**3a**). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 127.2 (s).

Complexes **3b**–**3d**, **4a**, **4b** were synthesized by a procedure similar to that used for the preparation of complex **3a**.

4.6. Synthesis of [(η^3-1-Me-C_3H_4)Pd(κ^2-P,P′-**3**)](PF_6) (**3b**)

Starting materials: [(η^3-1-Me-C_3H_4)PdCl]$_2$ (15 mg, 4×10^{-5} mol); NH_4PF_6 (15 mg, 8.8×10^{-5} mol) and ligand (**3**) (94 mg, 8×10^{-5} mol). (yield = 0.060 g, 50.5%); m.p. = 215–220 °C (dec.); ^{31}P NMR: (162 MHz, $CDCl_3$): δ 126.0 and 129.5; AB pattern, J_{PP} 128.0 Hz [major isomer] 126.8 and 128.3 (broad) [minor isomer]. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.77 (t, 6H, $-C_2H_5CH_3$), 0.80, 0.83 (2s, 9H each, $-C(CH_3)_3$), 1.09 (m, 3H, CH_3-allyl), 1.29 (s, 18H, $-C(CH_3)_3$); 1.7 (m, 4H, $-C_2H_5CH_3$), 3.30 (2d, 2H, $ArCH_2Ar$), 3.55 (m, 2H, terminal allyl), 3.83 and 4.05 (2m, 4H, $-C_2H_5CH_3$), 4.8–5.0 (4d, 4H, $ArCH_2Ar$), 5.05 (m, H, central allyl), 6.42 and 6.48 (2s, 4H, m-ArH, calixarene); 6.9–7.6 (m, 16H, biphenol ArH, 4H m-ArH-calixarene). Elemental Anal. Calc. for $C_{70}H_{89}O_8P_3PdF_6$: C, 61.3; H, 6.5. Found: C, 62.2; H, 6.3%.

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

Starting materials: [(η^3-1-Ph-C_3H_4)PdCl]$_2$ (20 mg, 4×10^{-5} mol); NH_4PF_6 (15 mg, 8.8×10^{-5} mol) and ligand (**3**) (94 mg, 8×10^{-5} mol). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 122.7 and 129.6; $J_{P,P}$ = 147.4 Hz.

4.8. Synthesis of [(η^3-1,3-Ph_2-C_3H_3)Pd(κ^2-P,P′-**3**)](PF_6) (**3d**)

Starting materials: [(η^3-1,3-Ph_2-C_3H_3)PdCl]$_2$ (26 mg, 4×10^{-5} mol); NH_4PF_6 (15 mg, 8.8×10^{-5} mol) and ligand (**3**) (94 mg, 8×10^{-5} mol). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 122.7 (s).

4.9. Synthesis of [{(η^3-C_3H_5)Pd(Cl)}$_2$(**3**)] (**3e**)

To a solution of [(η^3-C_3H_5)PdCl]$_2$ (14 mg, 4×10^{-5} mol) in CH_2Cl_2 (10 ml) was added a solution of ligand **3** (47 mg, 4×10^{-5} mol) in CH_2Cl_2 (10 ml) at 0 °C. The reaction mixture was stirred for 1 h at 25 °C and the solution was evaporated under vacuum to obtain the title complex **3e** as a colorless solid. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 149.7 (s).

Complexes **3f**, **3g**, **5a**–**5c**, **6a**–**6d** were synthesized by a procedure similar to that used for the preparation of complex **3e**.

4.10. Synthesis of [{(η^3-1-Me-C_3H_4)Pd(Cl)}$_2$(**3**)] (**3f**)

Starting materials: [(η^3-1-Me-C_3H_4)PdCl]$_2$ (15 mg, 4×10^{-5} mol) and ligand (**3**) (47 mg, 4×10^{-5} mol). Yellow micro-crystals of **3f** were grown from chloroform solution by layering with hexane. (yield = 0.020 g, 62.5%); m.p. = 225–230 °C (dec.); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 152.4 (s), 152.5 (s); ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.04(t, 6H, $-C_2H_5CH_3$), 0.03 and 0.12 (2t, $-C_2H_5CH_3$, other isomers), 0.79, 0.80 (2s, 18H, $-C(CH_3)_3$), 1.36 (s, 18H, $-C(CH_3)_3$); 1.54 (m, 4H, $-C_2H_5CH_3$), 1.62 (2d, 6H, $-CH_3$, $CH_3C_3H_4$) 3.30–3.64 (m, 4H, $-OCH_2C_2H_5$, 4H, $ArCH_2Ar$), 3.91 (m, 4H, terminal-$CH_3C_3H_4$), 4.50–4.58 (m, 4H, $ArCH_2Ar$), 4.62 (m, 2H, terminal-$CH_3C_3H_4$), 4.73 (m, 2H, central-$CH_3C_3H_4$), 6.46, 6.52 (2s, 4H, m-ArH, calixarene); 7.21, 7.22 (2s, 4H, m-ArH, calixarene), 7.25–7.80 (m, 16H, biphenol ArH). Elemental Anal. Calc. for $C_{82}H_{96}O_8P_2Pd_2Cl_2$: C, 63.3; H, 6.2. Found: C, 63.6; H, 6.2%.

4.11. Synthesis of [{(η^3-1-Ph-C_3H_4)Pd(Cl)}$_2$(**3**)] (**3g**)

Starting materials: [(η^3-1-Ph-C_3H_4)PdCl]$_2$ (20 mg, 4×10^{-5} mol) and ligand (**3**) (47 mg, 4×10^{-5} mol). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 152.2 (s).

4.12. Synthesis of [(η^3-C_3H_5)Pd(κ^2-P,P′-4)](PF_6) (**4a**)

Starting materials: [(η^3-C_3H_5)PdCl]$_2$ (14 mg, 4×10^{-5} mol); NH_4PF_6 (15 mg, 8.8×10^{-5} mol) and ligand (**4**) (94 mg, 8×10^{-5} mol). (yield = 0.005 g, 30%); m.p. = 210–220 °C (dec.), $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 128.3 (s, minor), 128.8 (s, major) ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.95 and 1.25 (2s, 18H + 18H, $-C(CH_3)_3$, major); 0.96 and 1.23(2s, 18H + 18H, $-C(CH_3)_3$, minor); 1.01(t, 6H, $-C_2H_5CH_3$, major); 1.07 (t, 6H, $-C_2H_5CH_3$, minor); 1.97 and 2.1 (2m, 4H, major and 4H minor $-C_2H_5CH_3$); 2.61, (m, 2H, terminal allyl $-C_3H_5$, major); 2.72 (m, 2H, terminal allyl $-C_3H_5$,minor) 5.26 (m, 1H, central allyl, minor); 5.51 (m, 1H, central allyl, major); other peaks were not resolved.

4.13. Synthesis of [(η^3-1,3-Ph_2-C_3H_3)Pd(κ^2-P,P′-**4**)](PF_6) (**4b**)

Starting materials: [(η^3-1,3-Ph_2-C_3H_3)PdCl]$_2$ (26 mg, 4×10^{-5} mol); NH_4PF_6 (15 mg, 8.8×10^{-5} mol) and ligand (**4**) (94 mg, 8×10^{-5} mol). (yield = 0.052 g, 40%). m.p. = 192–200 °C (dec.); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 125.6(s); ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.81 (t, 6H, $-C_2H_5CH_3$); 0.91 and 1.22 (2s, 18H + 18H, $-C(CH_3)_3$); 1.82 (m, 4H, $-C_2H_5CH_3$); 2.98, 3.84, 4.26, 4.67 (4d, 1H each, ArCH2Ar), 3.97 and 5.47 (2d, 2H each, ArCH2Ar); 3.51 and 3.60 (2m, 4H, $C_2H_5CH_3$); 5.22 (m, 2H, terminal allyl), 6.36 (m, 1H, central allyl); 6.5–8.0 (ArH). Elemental Anal. Calc. for $C_{89}H_{95}O_8P_3PdF_6$: C, 66.6; H, 6.0. Found: C, 66.8; H, 5.5%.

4.14. Synthesis of [{(η^3-C_3H_5)Pd(Cl)}(**5**)] (**5a**)

Starting materials: [(η^3-C_3H_5)PdCl]$_2$ (3.5 mg, 1×10^{-5} mol); ligand **5** (19 mg, 2×10^{-5} mol) (yield = 0.010 g, 44.1%); m.p. = 217–225 °C (dec); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 148.4 (s) (major isomer); 126.9 (s) (minor isomer); ^1H NMR ($CDCl_3$, 400 MHz): 0.65 (t, 6H, $-C_2H_5CH_3$), 0.95 (s, 9H, $-C(CH_3)_3$), 1.12 (s, 18H, $-C(CH_3)_3$); 1.14 (s, 9H, $-C(CH_3)_3$), 1.75 (m, 4H, $-C_2H_5CH_3$), 1.96 (d, 1H, terminal allyl), 3.18 (d, ^2J(H,H) = 13.2 Hz, 2H, $ArCH_2Ar$), 3.35 (d, ^2J(H,H) = 15.6 Hz, 1H, $ArCH_2Ar$), 3.43(d, ^2J(H,H) = 12.7 Hz,

1H, $ArCH_2Ar$), 3.53 (m, 2H, terminal allyl), 3.6 (m, 2H, $-C_2H_5CH_3$), 3.8 (m, 2H, $-C_2H_5CH_3$), 4.35 (d, ^2J(H,H) = 12.8 Hz, 2H, $ArCH_2Ar$), 4.57 (m, 1H, terminal allyl), 4.69 (d, ^2J(H,H) = 13.7 Hz, 1H, $ArCH_2$-Ar), 4.77 (d, ^2J(H,H) = 12.7 Hz, 1H, $ArCH_2Ar$), 4.98 (m, 1H, central allyl), 6.76, 6.80, 6.86, 6.88, 6.97, 6.98 (6s, 8m-ArH, calixarene), 7.35–7.82 (m, 8H, biphenol ArH). Elemental Anal. Calc. for $C_{65}H_{80}O_6PPdCl$: C, 67.2; H, 6.9. Found: C, 68.0; H, 6.7%.

4.15. Synthesis of [{(η^3-1-Me-C_3H_4)Pd(Cl)}(**5**)] (**5b**)

Starting materials: [(η^3-1-Me-C_3H_4)PdCl]$_2$ (4 mg, 1×10^{-5} mol) and ligand (**5**) (19 mg, 2×10^{-5} mol). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 151.3 (s).

4.16. Synthesis of [{(η^3-1-Ph-C_3H_4)Pd(Cl)}(**5**)] (**5c**)

Starting materials: [(η^3-1-Ph-C_3H_4)PdCl]$_2$ (5 mg, 1×10^{-5} mol) and ligand (**5**) (19 mg, 2×10^{-5} mol). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 152.2 (s).

4.17. Synthesis of [{(η^3-C_3H_5)Pd(Cl)}(**6**)] (**6a**)

Starting materials: [(η^3-C_3H_5)PdCl]$_2$ (3.5 mg, 1×10^{-5} mol); ligand **6** (19 mg, 2×10^{-5} mol). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 149.8 (s) and 150.2 (s); ^1H NMR ($CDCl_3$, 400 MHz): ^1H NMR ($CDCl_3$, 400 MHz): 0.20 (t, 3H, $-C_2H_5CH_3$), 0.73 (s, 9H, $-C(CH_3)_3$), 0.88 (s, 9H, $-C(CH_3)_3$), 1.05 (t, 3H, $-C_2H_5CH_3$), 1.33 (s, 9H, $-C(CH_3)_3$), 1.35 (s, 9H, $-C(CH_3)_3$), 1.74 (m, 2H, $-C_2H_5CH_3$), 1.88 (m, 2H, $-C_2H_5CH_3$), 2.15, 2.23 (2d, 2H, terminal allyl), 3.12 (d, 1H, ArCH2Ar), 3.33 (d, 1H, ArCH2Ar), 3.43 (d, 1H, ArCH2Ar), 3.46–3.82 (m, 1H, ArCH2Ar, 4H, $-C_2H_5CH_3$); 4.11 (d, 1H, ArCH2Ar); 4.23 (d, 1H, ArCH2Ar), 4.49 (m, 1H, ArCH2Ar, 1H, terminal allyl); 4.78 (d, 1H, ArCH2Ar, 1H, central allyl); 4.98 (m, 1H, central allyl); 6.4–6.7 (6 br s, 8H, m-ArH); 7.05–7.9 (m, 8H, ArH-calix, 8H, ArH-biphenol).

4.18. Synthesis of [{(η^3-1-Me-C_3H_4)Pd(Cl)}(**6**)] (**6b**)

Starting materials: [(η^3-1-Me-C_3H_4)PdCl]$_2$ (8 mg, 2×10^{-5} mol) and ligand (**6**) (38 mg, 2×10^{-5} mol). (yield = 0.030 g, 66.2%); m.p. = 210–215 °C (dec.); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 153.0 (s) and 152.4 (s) (major isomer); 153.7 (s) (minor isomer). ^1H NMR ($CDCl_3$, 400 MHz): 0.19 (t, 6H, $-C_2H_5CH_3$), 0.74 (br, s, 18H, $-C(CH_3)_3$), 0.88(br, s, 18H, $-C(CH_3)_3$), 1.06 (t, 6H, $-C_2H_5CH_3$), 1.34 (s, 18H, $-C(CH_3)_3$), 1.36(s, 18H, $-C(CH_3)_3$), 1.54-1.64 (m, 6H, allyl-CH_3), 1.73 (m, 4H, $-C_2H_5CH_3$), 1.87 (m, 4H, $-C_2H_5CH_3$), 2.03 (d, 2H, terminal allyl), 3.12 (d, 2H, ArCH2Ar), 3.33 (d, 2H, ArCH2Ar), 3.4–3.7 (m, 4H, ArCH2Ar, 4H, $-C_2H_5CH_3$, 2H, terminal allyl); 3.8 (m, 2H, $-C_2H_5CH_3$,1H, terminal allyl), 4.00 (m, 1H, terminal allyl); 4.13 (d, 2H, ArCH2Ar), 4.22 (d, 2H, ArCH2Ar), 4.46 (2d, 1H, ArCH2-Ar), 4.53 (d, 1H, ArCH2Ar), 4.60 (m, 1H, central allyl); 4.80 (d, 2H, ArCH2Ar); 4.85 (m, 1H, central allyl); 6.4–6.6 (5 br s, 8H, m-ArH); 7.1–7.6 (m, 8H, ArH-calix, 8H, ArH-biphenol). Elemental Anal. Calc. for $C_{66}H_{82}O_6PPdCl$: C, 69.3; H, 7.2. Found: C, 68.9; H, 7.2%.

4.19. Synthesis of [{(η^3-1-Ph-C_3H_4)Pd(Cl)}(**6**)] (**6c**)

Starting materials: [(η^3-1-Ph-C_3H_4)PdCl]$_2$ (5 mg, 1×10^{-5} mol) and ligand (**6**) (19 mg, 2×10^{-5} mol). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 147.1 (s).

4.20. Synthesis of [{(η^3-1,3-Ph_2-C_3H_4)Pd(Cl)}(**6**)] (**6d**)

Starting materials: [(η^3-1,3-Ph_2-C_3H_4)PdCl]$_2$ (5 mg, 1×10^{-5} mol) and ligand (**6**) (19 mg, 2×10^{-5} mol). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 145.5 (s) and 144.4 (s) (major isomer); 144.9 (s) and 143.5 (s) (minor isomer).

4.21. Synthesis of [Cl_2Pd(**4**)] (**4c**)

A mixture of ligand **4** (50 mg, 4.33×10^{-5} mol) and [Pd(COD)Cl_2] 13 mg (4.33×10^{-5} mol) was dissolved in 20 mL of benzene. The solution was stirred for 1 hr at 25 °C. Reaction mixture was washed with hot petrol and the residue was dissolved in chloroform. Addition of petrol to the chloroform solution in 5:1 ratio gave the title compound **4c** as pale green crystals. (yield 10 mg, 17.3%); m.p. = 198–205 °C (dec); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 94.1 (s); ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.91 and 1.20 (2s, 18H + 18H, $-C(CH_3)_3$); 0.97 (t, 6H, $-C_2H_5CH_3$); 1.97 and 2.09 (2m, 4H, $-C_2H_5CH_3$); 3.07, 3.98, 4.34, 4.87 (4d, 4H, $ArCH_2Ar$); 2.38 and 4.23 (2d, 2H each, ArCH2Ar); 5.94, 6.53, 6.65, 6.72 (4s, 2H each, calix m-ArH); 8.84–7.63 (m, ArH).

4.22. X-ray crystallography

X-ray diffraction data were collected 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 [28] and the SAINT software was used for data reduction [29]. An absorbtion correction was made on the intensity data using the SADABS programme [30]. All the structures were solved using SHELXTL [31] and the WinGX graphical user interface [32]. Least-square refinements were performed by the full-matrix method with SHELXL-97 [33]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. The crystal data and details of structure refinement are summarized in Table 1.

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Appendix A. Supplementary material

CCDC 663232, 663233, 663234 and 663235 contain the supplementary crystallographic data for compounds **5**, **6**, **3f** and **4c**. 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.jorganchem.2008.03.008.

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