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Platinum(II) and Palladium(II) Complexes of Bis(diphenylphosphino)calix[4]arene Tetrabenzyl Ether: Fluxional Behavior Caused by Two Motions

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The synthesis and complexation behavior of a novel bis-phosphine ligand based on a calix[4]arene scaffold, 5,17-bis(diphenylphosphino)-25,26,27,28-tetrabenzyloxycalix[4]arene (**3**), are reported. Reaction of **3** with $PdCl_2$(cod) under dilute conditions results in formation of the trans-coordinated dinuclear complex $[PdCl_2 \cdot \mathbf{3}]_2$ (**4**). The X-ray structure of **4** reveals that the two phosphinocalix[4]arene molecules are linked by the two $PdCl_2$ fragments. On the other hand, reaction of **3** with $PtCl_2$(cod) affords the cis-chelating mononuclear complex $PtCl_2 \cdot \mathbf{3}$ (**5**). The X-ray structure, low-temperature NMR measurements, and geometry optimization of **5** reveal that the structure in solution at −80 °C and in solid-state has a C_1 symmetry where the P−Pt−P plane is inclined and the calix[4]arene moiety is twisted. It was also found that **3** reacts with $[Pd(\eta^3\text{-}C_3H_5)(cod)]BF_4$ to yield the corresponding cationic complex $[Pd(\eta^3\text{-}C_3H_5)\cdot\mathbf{3}]BF_4$ (**6**) quantitatively. Low-temperature NMR measurements suggest that **6** exists as a mixture of two stereoisomers (**6a** and **6b**) possessing a C_1 symmetry. Although both **5** and **6** exhibit C_1 structure at −80 °C, their NMR spectra measured at 20 °C indicate a C_{2v} symmetry for **5** and a C_s symmetry for **6**. These fluxional behaviors of **5** and **6** in solution are caused by two separable motions: rollover motion of the coordination plane (R motion) and twist motion of the calix[4]arene scaffold (T motion).

Introduction

Calix[4]arenes are cyclic tetramers consisting of four phenol units connected by methylene bridges in the ortho positions.[1] Since they are a class of host compounds having a versatile π-electron-rich cavity, many useful applications (e.g. receptors or sensors) in the field of supramolecular chemistry are now known.[2] The combination of calix[4]arene functionality with transition metals may provide novel organometallic materials which realize unique supramolecular catalysis[3] by utilizing a spatially confined environment.

Tertiary phosphines are one of the most useful and widely employed ligands for transition-metal complexes, many of which display excellent activity and selectivity in homogeneous catalytic reactions.[4] Therefore, calix[4]arenes possessing the P(III) functionality are receiving considerable attention as the ligands of transition-metal complexes.[5] To date, a great many calix[4]arenes in which P(III) functionalities are connected to the lower rim via an ether linkage have been prepared, because of the relative ease with which the phenolic fragments can be treated chemically.[6] On the other hand, calix[4]arenes containing P(III) moieties at the upper rim are much more limited.[7−12] Especially, calix[4]arenes pos-

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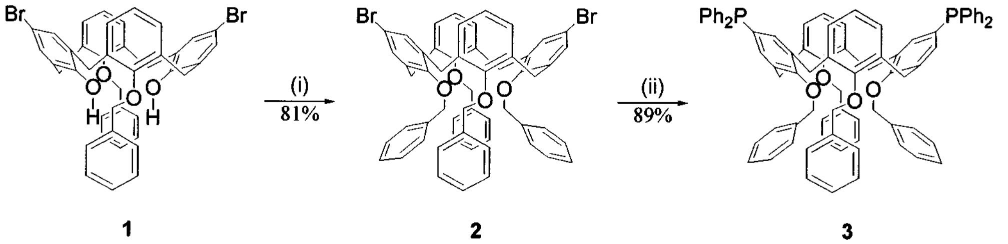
Scheme 1[a]



[a] Legend: (i) NaH/PhCH$_2$Br in THF and DMF (5:1), room temperature, 19 h; (ii) *n*-BuLi/Ph$_2$PCl in THF, −78 °C to room temperature, 12 h.

sessing a P(III) functionality directly connected to the upper rim[9−12] have been surprisingly unexplored, even though specific cavities of calix[4]arenes might be exploited with P(III) coordination sites nearby. Among them, there are only two reports[11,12] on their complexations with late transition metals. Matt and co-workers reported the preparation of calix[4]arene propyl ether having *two* diphenylphosphino groups at distal positions.[11] They studied its complexation with transition metals to obtain the corresponding Ag(I), Pt(II), Pd(II), and Ru(II) complexes with a trans configuration. Recently, Harvey et al. have prepared Rh phosphine complexes in which *one* P(III) functionality is connected directly to the upper rim of calix[4]arene propyl ether.[12] These complexes show highly fluxional behavior in solution due to their conformers.

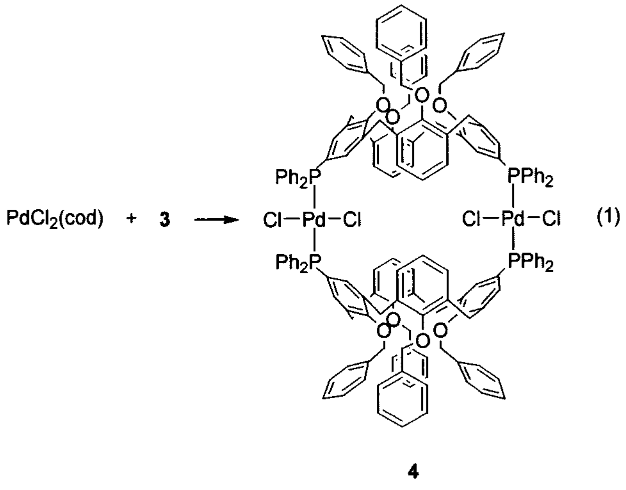
We prepared a new bis(diphenylphosphino)calix[4]arene ligand (**3**) possessing the benzyl ether group[13] at the lower rim, which fixes the cone conformation.[14] In this paper, Pt(II) and Pd(II) complexes bearing **3** as a ligand were prepared and characterized. These complexes involve trans-dinuclear and cis-mononuclear derivatives. Especially, the latter show unique fluxional behavior caused by two simultaneous motions.

Results

The Diphosphinated Calix[4]arene Ligand 3. The novel diphosphinated calix[4]arene **3** can be synthesized from known bromo-substituted calix[4]arenes, **1**[7] and **2**,[7] as shown in Scheme 1. In each step, the reaction proceeds smoothly and the product can be obtained in high yield. Since no solid-state structures of **1** and **2** have been reported, X-ray crystallographic analyses of them were carried out. The X-ray structures of **1** and **2** (Figures S1 and S2 in the Supporting Information) clearly showed a pinched-cone conformation, in which the brominated aryl rings are splayed outward and the nonbrominated aryl rings are pinched together. As for structures in solution, ^{1}H and ^{13}C NMR spectra of **1**−**3** are all indicative of a cone conformation.[1a,b] Particularly, the meta and the para (to the benzyloxy substituent) proton resonances of the nonbrominated aromatic rings of **1** appear at 6.88 and 6.80−6.76 ppm and those of **2** at 6.52 and 6.61−6.57 ppm, respectively. It is well-known that proton resonances of aromatic rings facing parallel to each other in calix[4]arene scaffolds appear at such higher field due to a strong magnetic shielding by the facing aryl ring.[15,16] Accordingly, in solution the nonbrominated aryl rings of **1** and **2** are pinched together as in the X-ray structures.

The ^{31}P NMR spectrum of **3** affords the expected resonance at −6.1 ppm, and the FD-MS spectrum shows the molecular ion peak (*m*/*z* 1152) of **3**. Similarly to **1** and **2**, the meta and the para (to the benzyloxy substituent) protons of the nonphosphinated aryl rings of **3** appear at 6.08 ppm as a doublet (4H, $^3J_{\mathrm{HH}} = 7.6$ Hz) and at 6.33 ppm as a triplet (2H, $^3J_{\mathrm{HH}} = 7.6$ Hz), respectively. This observation indicates that **3** adopts a pinched-cone conformation where the two aryl rings bearing the diphenylphosphino group are splayed outward and the other two aryl rings are almost parallel to each other. Variable-temperature ^{1}H NMR spectra of **3** in the range −50 to +70 °C showed no significant change and indicated that the pinched-cone conformation is stable.

The Dichloro Pd(II) Complex [PdCl$_2$·3]$_2$ (4). First, a dichloropalladium(II) complex was prepared from an equimolar mixture of PdCl$_2$(cod) (cod = 1,5-cyclooctadiene) and **3** in ClCH$_2$CH$_2$Cl. The reactions in their usual concentrations were hampered by the formation of polymeric species and resulted in immediate precipitation of insoluble products. Therefore, complexations were carried out under dilute conditions (ca. 4 mM). The reaction proceeded smoothly to afford the *dinuclear* palladium complex **4** in 60% yield (eq 1). The ESI-MS spectrum displays two peaks for [M + H + H$_2$O]$^+$ (*m*/*z*



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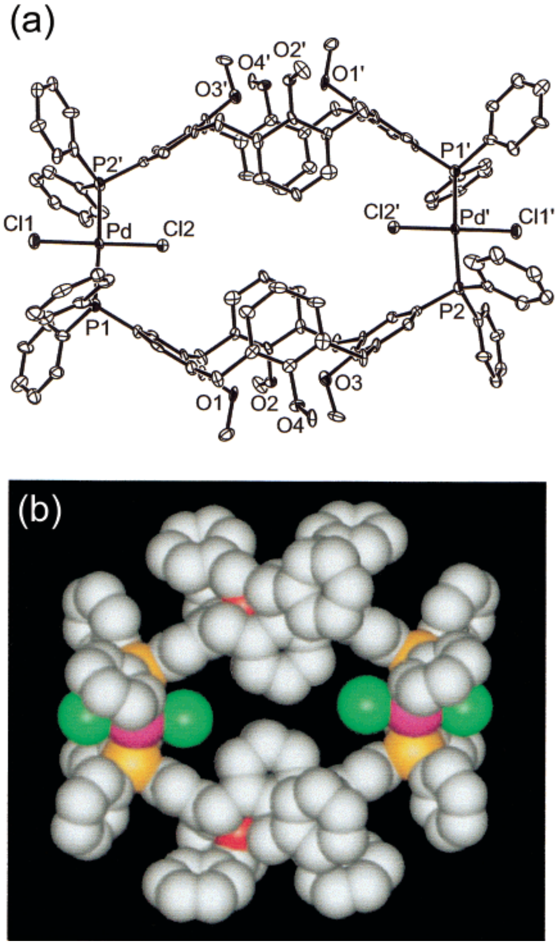

Figure 1. Crystal structure of the dinuclear Pd complex **4**: (a) ORTEP drawing with partial atomic labeling (phenyl rings of the benzyl moieties are omitted for clarity); (b) space-filling drawing.

Table 1. Crystallographic Data for the Dinuclear Palladium Complex 4

formula: $C_{160}H_{132}O_8Cl_4P_4Pd_2 \cdot C_4H_{10}O \cdot 2H_2O$	fw: 2771.46
cryst size: 0.10 × 0.10 × 0.05 mm	$T = -177$ °C
cryst habit: block	$a = 17.6870(1)$ Å
cryst color: yellow	$b = 17.9715(3)$ Å
cryst syst: triclinic	$c = 13.0382(3)$ Å
space group: $P\bar{1}$	$\alpha = 96.711(1)°$
$D_{calcd} = 1.317$ g/cm^3	$\beta = 106.965(1)°$
μ(Mo Kα) = 4.41 cm^{-1}	$\gamma = 114.131(2)°$
$R^a = 0.097$	$V = 3494.7(1)$ Å
$R_w{}^b = 0.133$	$Z = 1$
GOF = 1.76	

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2\}^{1/2}$.

2679) and $[M - Cl]^+$ (m/z 2626), indicating the dinuclear structure.

The X-ray structure of **4** unambiguously shows that the product is the dinuclear complex in which two molecules of **3** are linked by the two $PdCl_2$ units in a trans fashion (Figure 1). The crystallographic data of **4** are summarized in Table 1. Table 2 lists selected atom distances and bond angles of **4**. The calix[4]arene moieties in **4** have a pinched-cone conformation similar to that of the free ligand **3**: the dihedral angles between the mean plane of the bridging methylene carbons and the aryl rings bonded to O1, O2, O3, and O4 (see Figure 1a) are 140.27, 78.85, 152.97, and 84.59°, respectively. There is a crystallographic inversion center midway between the two Pd atoms that are nonbonded with a separation of 13.187(2) Å, leading to a C_i symmetry for the dinuclear complex. This length is remarkably longer than those (5.97−9.09 Å)[17] of similar dinuclear dichloro Pd complexes. The bulky bridging calix[4]arene ligand **3** in **4** is able to cause the long separation. The dinuclear complex **4** has a large hydrophobic cavity surrounded by the eight aromatic rings of the two calix[4]arene ligands (Figure 1b). It is noteworthy that the two of the four Cl atoms of **4** are included in the cavity, while the other two Cl atoms stay outside the cavity. The distance between the Cl atoms in the cavity, i.e., Cl(2)···Cl(2′), is 8.667(8) Å, and that between the Cl atoms outside the cavity, i.e., Cl(1)···Cl(1′), is 17.818(7) Å.

Table 2. Selected Atom Distances and Angles for 4

Distances (Å)			
Pd−P(1)	2.319(5)	Pd−Cl(1)	2.323(4)
Pd−P(2′)	2.313(5)	Pd−Cl(2)	2.289(4)
Pd···Pd′	13.187(2)	Cl(1)···Cl(1′)	17.818(7)
P(1)−P(2)	13.326(6)	Cl(2)···Cl(2′)	8.667(8)
Angles (deg)			
P(1)−Pd−P(2′)	176.1(2)	Cl(1)−Pd−Cl(2)	176.9(2)
P(1)−Pd−Cl(1)	88.1(2)	P(1)−Pd−Cl(2)	91.2(2)
P(2′)−Pd−Cl(1)	88.4(2)	P(2′)−Pd−Cl(2)	92.4(2)

The solution structure of **4** was studied by NMR in CD_2Cl_2 at room temperature. The ^{31}P resonance of **4** (at 23.3 ppm as a singlet) is very close to the chemical shift of *trans*-$PdCl_2(PPh_3)_2$ (23.1 ppm),[18] not *cis*-$PdCl_2(PPh_3)_2$ (28.9 ppm),[18] indicating that **4** maintains the trans configuration in solution.[19] In the ^{13}C NMR spectrum, all the bridging methylene carbons of **4** are equivalent, giving a singlet at 30.9 ppm. In ^{1}H NMR spectrum, the bridging methylene protons of **4** appear at 4.23 ppm (axial) and 2.93 ppm (equatorial), respectively, with a geminal coupling ($^2J_{HH} = 13.7$ Hz). In addition, the meta and the para (to the benzyloxy group) protons of the nonphosphinated aryl rings appeared as a less-resolved peak centered at 6.23 ppm. All these results clearly indicate that **4** has a D_{2h} symmetry in solution, where the calix[4]arene moieties adopt a pinched-cone conformation. This D_{2h} symmetry is retained at −80 °C, judging from the ^{1}H, ^{13}C, and ^{31}P NMR spectra.

The Dichloro Pt(II) Complex $PtCl_2 \cdot 3$ (5). Next, a dichloroplatinum(II) complex was prepared from $PtCl_2$(cod) and **3**. Unlike the corresponding palladium(II) complex (**4**), a *mononuclear* platinum complex (**5**) was isolated in 67% yield under the same reaction conditions

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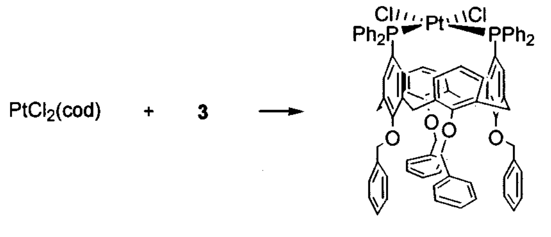
[19] It is reported that by so-called virtual coupling,[20] each ^{13}C resonance of *trans*-$(R_3P)_2PdCl_2$ complexes appears as a 1:2:1 triplet, while the corresponding cis isomers show the ^{13}C resonance as a doublet, a doublet of doublets, a five-line multiplet, or a non-1:2:1 triplet.[21,22] The ^{13}C NMR spectrum of the binuclear complex **4** displays a 1:2:1 triplet for the carbons ipso, ortho, and meta to the phosphorus atom. These observations also support the trans configuration of **4** in solution.

that were used for **4** (eq 2). The FD-MS spectrum of **5**

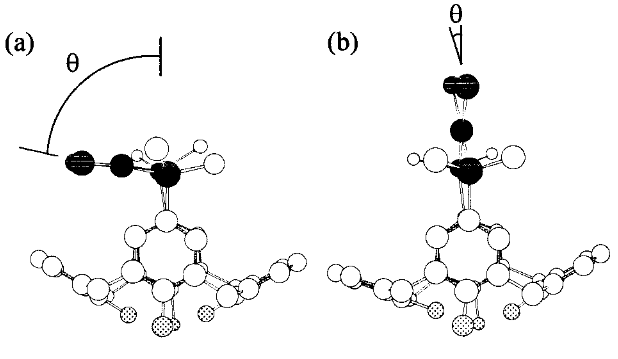


(2)

5

exhibits two intense signals for $[M]^+$ (*m/z* 1418) and $[M - Cl]^+$ (*m/z* 1383), indicating the mononuclear structure.

It is a generally known property of calixarenes that they are often difficult to grow as crystals and, when they are grown, the crystals are often of a poor quality because of solvent molecules and their inherent flexibility.[12,23] We carried out an X-ray crystal structure analysis of **5**. However, even after several trials, disorder of the structure inevitably occurred and prevented a detailed discussion about the structure of **5**. Nevertheless, the structure around the Pt atom is reliable enough to establish the inclination of the P−Pt−P plane toward the mean plane of the bridging methylene carbons of the calix[4]arene moiety and the cis orientation of the phosphine ligand (Figure S3 in the Supporting Information). To confirm this structure of **5**, ab initio MO calculations for the model complex *cis*-$[PtCl_2\{(Ph_2PC_6H_2CH_2OH)(C_6H_3CH_2OH)\}_2]$ (**5m**), in which the benzyl moieties of **5** are replaced with H, were carried out by the Hartree−Fock method[24] employing the LANL2MB[25] basis set (HF/LANL2MB). The ground state structure was optimized as **5m**-GS (Figure 2a), which has the same inclination of the P−Pt−P plane as shown in Figure S3: the dihedral angle (θ in Figure 2) between the P−Pt−P plane and a vertical plane determined by the two P atoms and a midpoint between the two aryl ipso carbons connected to the PPh$_2$ is 77.3° for **5m**-GS and 75.0° for the X-ray structure in Figure S3. Importantly, **5m**-GS has C_1 symmetry and the two P atoms should be inequivalent. On the other hand, the complex **5m**-TS (Figure 2b), whose P−Pt−P plane is almost parallel to the vertical plane (θ = 3.8°), was found to be a transition state: there is one imaginary frequency in the frequency calculations.

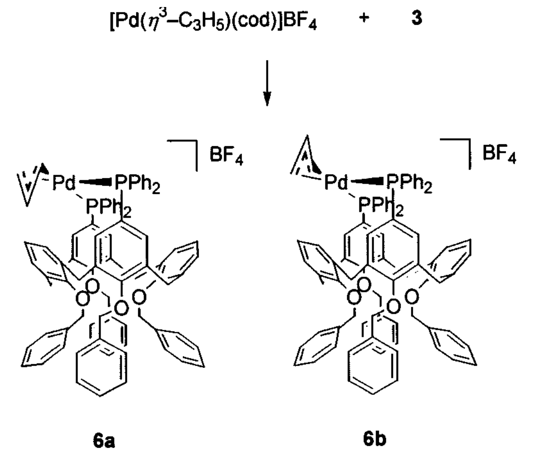


5m-GS **5m**-TS

Figure 2. Optimized structures of the model compound **5m** for Pt complex **5** at the HF/LANL2MB level: (a) ground state (**5m**-GS); (b) transition state (**5m**-TS). For Ph groups on the P atoms, only the ipso-C atoms are presented.

The CPMAS solid-state ^{31}P NMR spectrum of **5** showed two resonances with the same intensity at 14.5 ppm ($^1J_{PPt}$ = 3680 Hz) and 9.8 ppm ($^1J_{PPt}$ = 3540 Hz). These large $^1J_{PPt}$ values indicate the cis coordination of the phosphine ligand of **4**, as shown by the X-ray structure (Figure S3). The solution ^{31}P NMR spectrum measured at −80 °C (see Figure 3a) also showed two resonances of equal intensity at 12.8 ppm ($^1J_{PPt}$ = 3760 Hz) and 6.9 ppm ($^1J_{PPt}$ = 3599 Hz) with a $^2J_{PP}$ coupling of 16.2 Hz. In the ^{13}C NMR spectrum measured at −80 °C in CD$_2$Cl$_2$, the bridging methylene carbons (30.4, 30.1, 29.1, and 28.7 ppm), the methylene carbons of the benzyl groups (76.0, 75.5, 75.1, and 72.4 ppm), and the aryl ipso-C atoms attached to the benzyloxy moiety (156.0, 155.3, 153.8, and 152.8 ppm) are all nonequivalent and appeared as four peaks of same intensity. All these observations clearly indicate the C_1 symmetry of **5** at −80 °C in solution.

η^3-Allyl Pd(II) Complex: $[Pd(\eta^3\text{-Allyl})\cdot 3]BF_4$ (6). As another Pd(II) complex bearing **3** as ligand, the cationic η^3-allyl complex **6** was prepared from $[Pd(\eta^3\text{-}C_3H_5)(cod)]BF_4$ and **3** in quantitative yield (eq 3). The



(3)

6a **6b**

FD-MS spectrum of **6** shows a solitary peak at *m/z* 1299,

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(22) The ^{13}C NMR spectra of *trans*-PdCl$_2$(PPh$_3$)$_2$ were measured in CDCl$_3$: δ 135.1 (virtual t, $|^2J_{CP} + {}^4J_{CP}|$ = 6.1 Hz, *o*-ArC), 130.6 (s, *p*-ArC), 129.6 (virtual t, $|^1J_{CP} + {}^3J_{CP}|$ = 24.8 Hz, *ipso*-ArC), 128.1 (virtual t, $|^3J_{CP} + {}^5J_{CP}|$ = 5.3 Hz, *m*-ArC).

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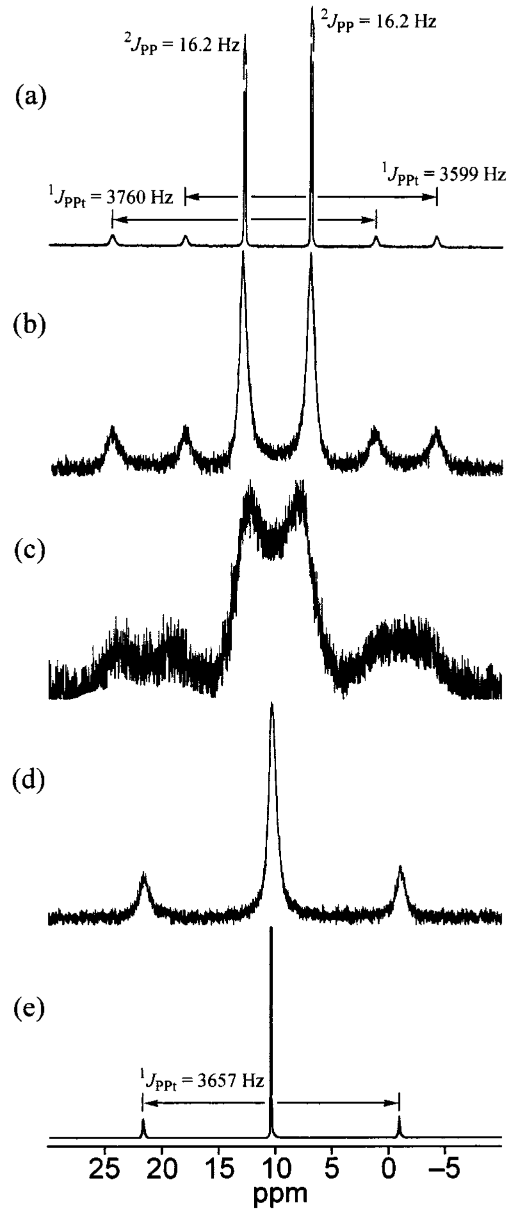


Figure 3. ^{31}P NMR spectra of **5** measured in CD_2Cl_2 at (a) −80 °C, (b) −50 °C, (c) −40 °C, (d) −20 °C, and (e) 20 °C.

possessing the expected isotopic profile of the [M − BF_4]$^+$ cation.

In the ^{31}P NMR spectrum measured at −80 °C in CD_2Cl_2, the phosphorus atoms appear as two pairs of doublets in a 5:2 ratio (Figure 4a): the one pair (major) at 22.6 and 20.9 ppm ($^2J_{PP}$ = 36.1 Hz) and the other (minor) at 22.1 and 21.5 ppm ($^2J_{PP}$ = 38.3 Hz). In the ^{13}C NMR spectrum measured at −80 °C in CD_2Cl_2, the aryl ipso-C atoms attached to the benzyloxy moiety appear as two sets of four equal-intensity peaks: the ratio of the major (at 155.7, 155.2, 153.7, and 153.1 ppm) and the minor sets (at 155.7, 155.2, 154.1, and 152.7 ppm) is also 5:2. From these results, it is concluded that, at −80 °C in solution, **6** exists as a mixture of two stereoisomers of C_1 symmetry, in which the center carbon of the η^3-allyl moiety points inside (**6a**) and outside (**6b**), respectively. The ^{1}H NMR spectrum of **6** was so complicated at −80 °C that an assignment could not be done.

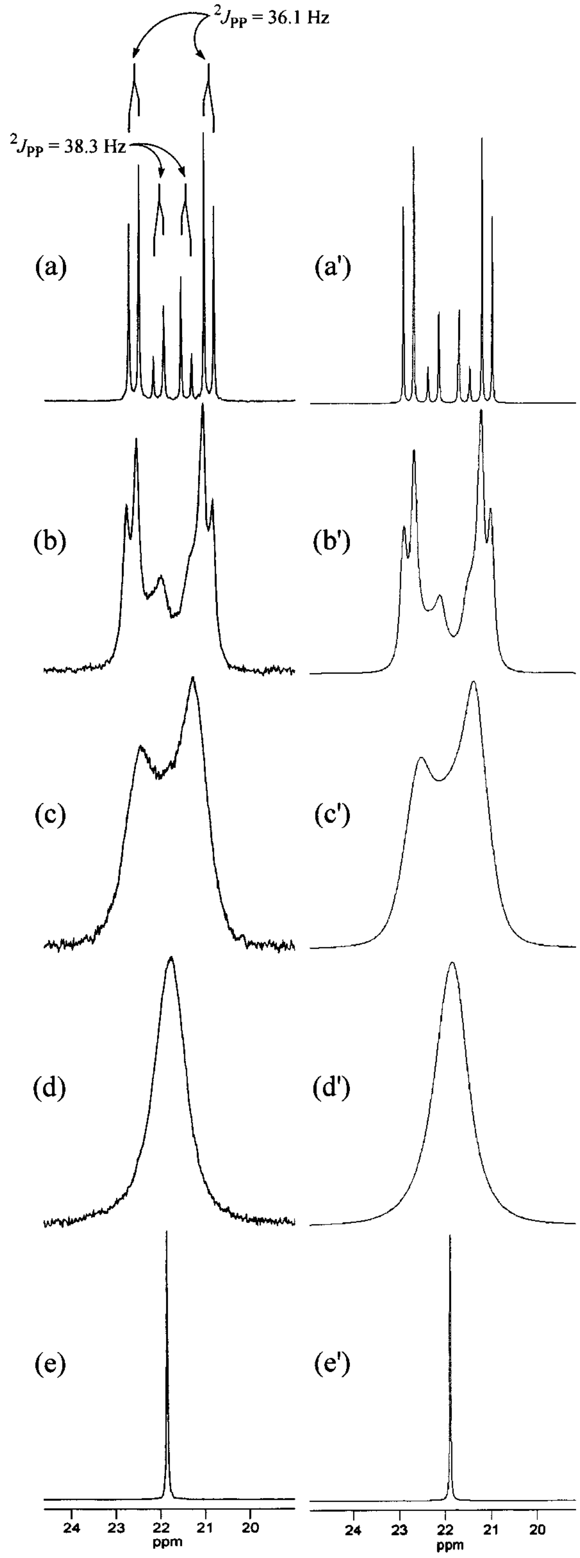
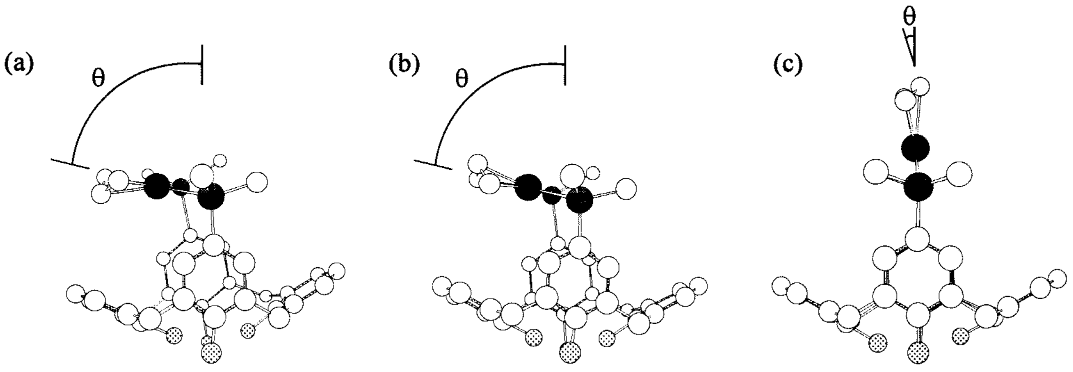


Figure 4. ^{31}P NMR spectra of **6** measured in CD_2Cl_2 at (a) −80 °C, (b) −50 °C, (c) −40 °C, (d) −30 °C, and (e) 20 °C. The spectra in a−e are simulated in a′−e′, respectively.

Ab initio MO calculations were carried out for model complexes of **6a** and **6b**, [Pd(η^3-C_3H_5){($Ph_2PC_6H_2CH_2$-OH)($C_6H_3CH_2OH$)}$_2$]$^+$ (**6am** and **6bm**). Optimized ground states by the HF/LANL2MB method are shown as **6am**-GS and **6bm**-GS in Figure 5a,b: the dihedral angle (θ in Figure 5) between the P−Pd−P plane and the vertical plane is 75.1° for **6am**-GS and 73.0° for **6bm**-GS. Energy



6am-GS **6bm**-GS **6m**-TS

Figure 5. Optimized structures of the model compound **6m** for the η^3-allyl Pd complex **6** at the HF/LANL2MB level: (a) ground state (**6am**-GS); (b) ground state (**6bm**-GS); (c) transition state (**6m**-TS). For Ph groups on the P atoms, only the ipso-C atoms are presented.

calculations by the B3LYP[26] method using the LANL2DZ[25c−e,27] basis set (B3LYP/LANL2DZ//RHF/LANL2MB) showed that **6am**-GS is more stable than **6bm**-GS by 3.1 kJ/mol. Therefore, **6a** would be the major isomer in Figure 4a. Furthermore, **6m**-TS, whose P−Pd−P plane is parallel to the vertical plane of the calix[4]arene moiety ($\theta = 4.6°$), was found to be the transition state (Figure 5c).

Fluxional Behavior of Mononuclear Complexes 5 and 6 in Solution. In solution at −80 °C and in the solid state, the structure of **5** has C_1 symmetry (vide supra). At 20 °C, however, in the ^{13}C NMR spectra of **5** the aryl ipso-carbon atoms attached to the benzyloxy group appear as two signals in a 1:1 ratio (at 157.4 and 155.1 ppm) and the bridging methylene carbons show a single peak at 31.5 ppm (at −80 °C, the four aryl ipso-carbon atoms and the four bridging methylene carbons are all nonequivalent, vide supra). Furthermore, in the ^{1}H NMR spectrum of **5** at 20 °C, only one kind of the axial (4.24 ppm) and one kind of the equatorial protons (2.96 ppm) of the bridging methylene appear with a geminal coupling ($^2J_{HH} = 13.9$ Hz). These observations clearly indicate that the symmetry of **5** changes from C_1 to C_{2v} by raising the temperature from −80 to 20 °C. Variable-temperature ^{31}P NMR spectra of **5** show the fluxional behavior (Figure 3). At −80 °C, **5** shows two nonequivalent ^{31}P resonances due to the C_1 symmetry, as mentioned above (Figure 3a). When the temperature is raised above −50 °C, the resonances become broader (Figure 3b−d). Finally, at 20 °C one sharp singlet with ^{195}Pt satellites ($^1J_{PPt} = 3657$ Hz) is observed at 10.5 ppm (Figure 3e), consistent with the C_{2v} symmetry at this temperature. This fluxional behavior is reversible.

The complex **6** exists as a 5:2 mixture of the two isomers **6a** and **6b** with C_1 symmetry in solution at −80 °C (vide supra). At 20 °C, however, in the ^{13}C NMR spectrum of **6** the aryl ipso-carbon attached to the benzyloxy group appeared as three peaks in a 1:1:2 ratio (at 155.0, 155.1, and 157.0 ppm, respectively) and the bridging methylene carbons showed two peaks in a 1:1 ratio (at 31.0 and 31.1 ppm). Furthermore, in the ^{1}H NMR spectrum of **6** at 20 °C, the bridging methylene protons appeared as four doublets of equal intensity (at 4.23, 4.21, 2.95, and 2.87 ppm) with geminal coupling ($^2J_{HH} = 13.9$ Hz), indicating that **6** has two kinds of axial and two kinds of equatorial protons. These observations elucidate that **6** has C_s symmetry at 20 °C. Variable-temperature ^{31}P NMR spectra of **6** show the fluxional behavior (Figure 4). At −80 °C, **6** gives two pairs of doublets in a 5:2 ratio, as mentioned above (Figure 4a). When the temperature is raised, the resonances become broader (Figure 4b,c) and coalesce into a broad resonance (Figure 4d). Finally, at 20 °C *one* sharp singlet is observed at 21.9 ppm (Figure 4e), due to the C_s symmetry at this temperature. This fluxional behavior is reversible.

Discussion

As shown above, the C_1 symmetry of **5** and **6** at −80 °C is changed to C_{2v} and C_s at 20 °C, respectively. These fluxional behaviors would be explained by the motions shown in Scheme 2. Here, C^1 and C^2 correspond to the ipso-carbon connected to P^1 and P^2 of the PPh_2 moiety. The $P^1{-}C^1$ and $P^2{-}C^2$ bonds must be twisted with respect to each other to realize the C_1 symmetry observed at −80 °C. Actually, the dihedral angles $P^1{-}C^1{\cdots}C^2{-}P^2$ of **5** (Figure S3), **5m**-GS (Figure 2a), **6am**-GS (Figure 5a), and **6bm**-GS (Figure 5b) are 7.1° (by X-ray) and 10.0, 11.2, and 10.3° (by HF/LANL2MB), respectively. Scheme 2 describes the two motions. One is the twist motion (T motion) between **Ia** and **Ia′** and between **Ib** and **Ib′**. The other is the rollover motion (R motion) between **Ia** and **Ib** and between **Ia′** and **Ib′**. The R motion involves rotation of the PPh_2 moieties and stretching of the calix[4]arene moiety: the P···P distance at the transition state elongates by 0.219 Å in Figure 2 and 0.202−0.216 Å in Figure 5. The R motion was first postulated by Matt et al. for lower-rim-modified phosphinocalix[4]arene Pt(II) complexes,[28] but quantitative treatment was not carried out. With respect to **5**, either the T motion or the R motion alone only causes C_s or C_2 symmetry, respectively. Therefore,

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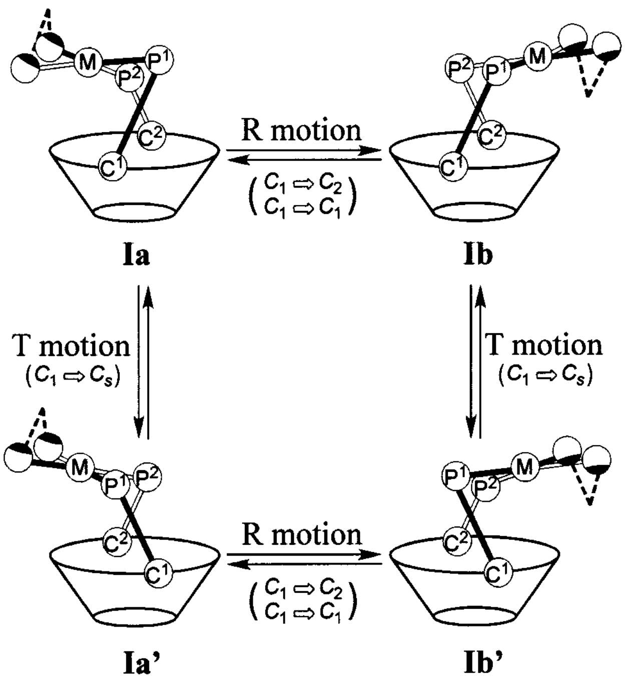
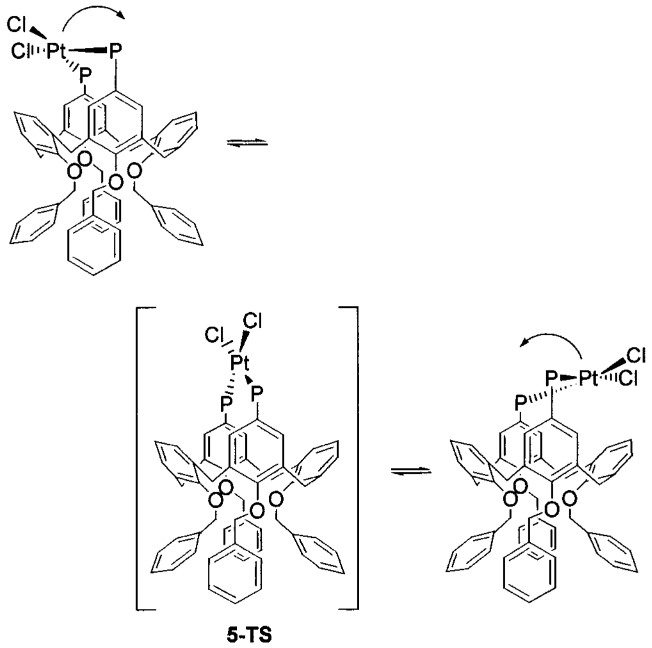
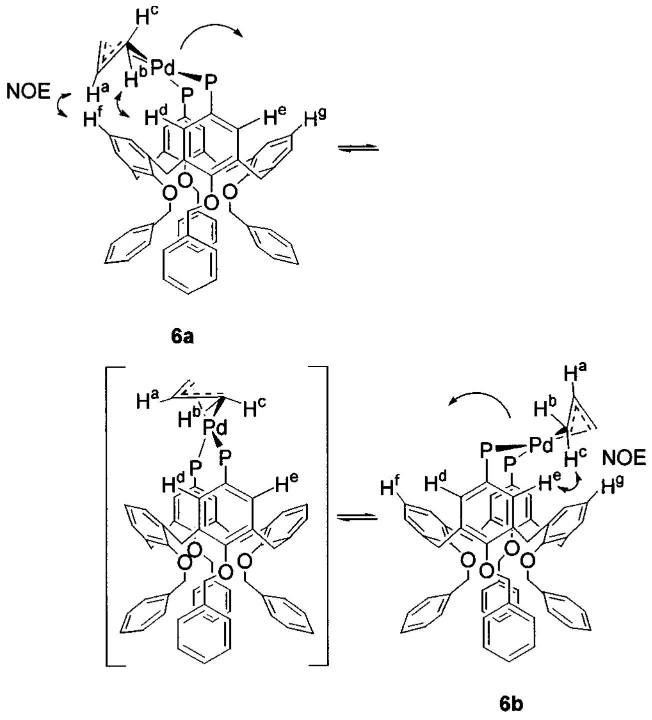
Scheme 2



Scheme 3



Scheme 4



both the T motion and the R motion should occur simultaneously, because C_{2v} symmetry was observed at 20 °C. On the other hand, concerning **6**, only the T motion will afford a mixture of C_s species in a 5:2 ratio. To achieve the *single* ^{31}P resonance as observed in Figure 4e, both the T motion and the R motion must occur at the same time: T motion alone will afford two singlets for each C_s structure in a 5:2 ratio, while R motion alone will cause a single C_1 species which shows an AB spin system in the ^{31}P NMR spectrum.

By assuming that both the T motion and the R motion occur simultaneously, Figure 4a–e can be simulated[29] exactly as shown in Figure 4a′–e′, and the Eyring plot afforded activation enthalpy for the T motion ($\Delta H^{\ddagger}$ = 43 ± 1.5 kJ mol^{-1}) and for the R motion ($\Delta H^{\ddagger}$ = 41 ± 1.4 kJ mol^{-1}). Energy calculation for **6am**-GS, **6bm**-GS, **6m**-TS by B3LYP/LANL2DZ//HF/LANL2MB provided $\Delta H^{\ddagger}$ for the R motion (33 or 36 kJ mol^{-1}), which is in good agreement with the observed value. Similar simulation of Figure 3 afforded the activation enthalpy ($\Delta H^{\ddagger}$ = 41 ± 0.9 kJ mol^{-1}) for the whole fluxional process of **5**. Energy calculations for **5m**-GS and **5m**-TS by B3LYP/LANL2DZ//HF/LANL2MB provided $\Delta H^{\ddagger}$ (23 kJ mol^{-1}) for the R motion of **5** (Scheme 3).

At 20 °C, the η^3-allyl protons of **6** appear at 5.41 ppm (H^a, m), 3.83 ppm (H^b, broad d), and 3.26 ppm (H^c, five-line m) (Scheme 4). Even at 80 °C, the resonances remain intact, indicating that no π–σ–π rearrangement[6a,30] occurs. On the other hand, by the aid of HSQC and HMBC spectra of **6**, two triplet proton resonances at 6.15 ppm ($|^3J_{HP} + {}^5J_{HP}|$ = 4.1 Hz) and 6.39 ppm ($|^3J_{HP} + {}^5J_{HP}|$ = 4.1 Hz) which are virtually coupled[20] with two P atoms are assigned to H^d and H^e, respectively (Scheme 4). The NOESY spectrum of **6** measured at 20 °C indicates that there are NOE's between H^a and H^f, between H^b and H^d, and between H^c and H^e but no NOE's between H^a and H^g, between H^b and H^e, or between H^c and H^d (Scheme 4). Furthermore, the η^3-allyl carbon resonances (the central carbon at 121.3 ppm with $^3J_{CP}$ = 5.4 Hz and the methylene carbons at 76.5 ppm with $|^2J_{CP-cisoido} + {}^2J_{CP-transoido}|$ = 15.1 Hz) of **6** at 20 °C did not change essentially and retained the carbon–phosphorus couplings up to 80 °C. These results reveal that throughout the R motion the η^3-allyl moiety sticks to the palladium with the same side.

Experimental Section

All reactions were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried and

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purified before use by the usual methods.[31] $PdCl_2(cod)$,[32] *trans*-$PdCl_2(PPh_3)_2$,[33] $PtCl_2(cod)$,[34] and $[Pd(\eta^3\text{-}C_3H_5)(cod)]BF_4$[35] were prepared according to procedures in the literature. ^1H NMR (400.13 MHz), $^{13}C\{^1H\}$ NMR (100.61 MHz), and $^{31}P\{^1H\}$ NMR (161.98 MHz) spectra were recorded on a Bruker ARX 400 instrument. The ^1H NMR data are referenced relative to residual protiated solvent: 5.32 and 7.24 ppm in CD_2Cl_2 and $CDCl_3$, respectively. ^{13}C NMR chemical shifts are reported relative to either CD_2Cl_2 (53.1 ppm) or $CDCl_3$ (77.0 ppm). The ^{31}P NMR data are given relative to external 85% H_3PO_4. CPMAS solid-state ^{31}P NMR spectrum (121.00 Hz) was recorded on a Bruker AC 300 instrument using a standard CP pulse sequence. The crystalline powder sample was mixed with glass powder, and the mixture was loaded in a zirconia rotor and spun at ca. 6 kHz at the magic angle. The chemical shifts are reported relative to 85% H_3PO_4 in a capillary without spinning. A ^{31}P NMR simulation was carried out using gNMR 4.1.[29] Medium-pressure column chromatography was performed on silica gel (Wakogel C-400HG; particle size 20∼40 μm) with a UV detector (YAMAZEN UV-10V). Recycling preparative-scale GPC was carried out on a Japan Analytical Industry LC-918 system equipped with Jaigel-1H and Jaigel-2H columns using $CHCl_3$ as an eluent. FD and ESI mass spectra were recorded on a JEOL JMS-SX102A instrument at the GC-MS & NMR Laboratory of Faculty of Agriculture, Hokkaido University. Elemental analysis was performed at the Center for Instrumental Analysis of Hokkaido University. HSQC, HMBC, and NOESY spectra were recorded on a JEOL α-500 instrument at the High-Resolution NMR Laboratory of Faculty of Science, Hokkaido University. DFT (B3LYP[26]/LANL2DZ[25c−e,27]) molecular orbital calculations were performed with the Gaussian 98 program[24a] on an HP Exemplar V2500 instrument at the Computing Center of Hokkaido University.

5,17-Dibromo-26,28-dibenzyloxycalix[4]arene (1).[7] A solution of dibenzyloxycalix[4]arene[36] (1.98 g, 3.27 mmol) and NBS (1.16 g, 6.54 mmol) in methyl ethyl ketone (100 mL) was stirred at room temperature for 22 h. The reaction solution was evaporated to afford a yellow residue, which was redissolved in $CHCl_3$. The organic phase was washed with a 10% $NaHSO_3$ aqueous solution and water, successively. The $CHCl_3$ solution was dried over $MgSO_4$, followed by filtration to remove the drying reagent, and then evaporated to dryness. The resulting yellow solid was recrystallized from a $CHCl_3$−MeOH mixture to give colorless crystals. Yield: 3.24 g, 99%. Mp: 287−288 °C (lit. mp 300−305 °C). FD-MS: *m*/*z* 762 ($[M]^+$). ^1H NMR ($CDCl_3$): δ 7.91 (s, 2H, O*H*), 7.59−7.56 (m, 4H, *m*-Ph), 7.38−7.34 (m, 6H, *o*,*p*-Ph), 7.15 (s, 4H, *m-H* of Ar attached to Br), 6.88 (d, 4H, $^3J_{HH}$ = 7.5 Hz, *m*-Ar*H*), 6.80−6.76 (m, 2H, *p*-Ar*H*), 5.02 (s, 4H, OCH_2Ph), 4.22 (d, 4H, $^2J_{HH}$ = 13.2 Hz, $ArCH_2Ar$), 3.26 (d, 4H, $^2J_{HH}$ = 13.2 Hz, $ArCH_2Ar$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.5 (Ar*C* attached to OCH_2Ph), 151.8 (Ar*C* attached to OH), 136.4, 132.5, 130.8, 129.9, 129.4, 128.9, 128.2, 127.6, 125.7 (Ar*C*), 110.5 (Ar*C* attached to Br), 78.6 (OCH_2Ph), 31.2 ($ArCH_2Ar$).

5,17-Dibromo-25,26,27,28-tetrabenzyloxycalix[4]arene (2).[7] To a solution of **1** (1.00 g, 1.31 mmol) in 20 mL of THF and 4 mL of DMF was added an excess of NaH (0.16 g, 6.6 mmol) and benzyl bromide (0.95 mL, 8.0 mmol). The reaction mixture was stirred at room temperature for 18 h. After removal of the solvents, the residue was partitioned between $CHCl_3$ and water. The organic layer was washed with water and dried over $MgSO_4$. The clear filtrate was evaporated to yield a yellow oil, which was purified by medium-pressure column chromatography on silica gel using *n*-hexane/CH_2Cl_2 (2:1) as an eluent. The product was recrystallized from ether−MeOH to give colorless crystals. Yield: 1.01 g, 81%. Mp: 194−195 °C (lit. mp 190−192 °C). FD-MS: *m*/*z* 942 ($[M]^+$). ^1H NMR ($CDCl_3$): δ 7.32−7.20 (m, 20H, Ph), 6.74 (s, 4H, *m-H* of Ar attached to Br), 6.61−6.57 (m, 2H, *p*-Ar*H*), 6.52 (d, 4H, $^3J_{HH}$ = 7.1 Hz, *m*-Ar*H*), 4.92 (s, 4H, OCH_2Ph), 4.90 (s, 4H, OCH_2Ph), 4.10 (d, 4H, $^2J_{HH}$ = 13.6 Hz, $ArCH_2Ar$), 2.85 (d, 4H, $^2J_{HH}$ = 13.6 Hz, $ArCH_2Ar$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.0, 154.5 (Ar*C* attached to OCH_2Ph), 137.7, 137.4, 137.1, 134.5, 130.9, 129.8, 129.7, 128.4, 128.15, 128.13, 128.11, 128.0, 122.8 (Ar*C*), 115.0 (Ar*C* attached to Br), 76.6, 76.5 (OCH_2Ph), 31.2 ($ArCH_2Ar$).

5,17-Bis(diphenylphosphino)-25,26,27,28-tetrabenzyloxycalix[4]arene (3). To a solution of **2** (0.72 g, 0.76 mmol) in 15 mL of dry THF cooled to −78 °C was added 2.00 mL (3.20 mmol) of *n*-butyllithium (1.60 M solution in *n*-hexane) over 10 min. The solution was maintained at that temperature for an additional 1 h. Chlorodiphenylphosphine (0.76 g, 3.5 mmol) was added dropwise to the cooled solution with a syringe, and then the reaction mixture was warmed to room temperature and stirred for 15 h. After evaporation of the solvent the residue was purified by medium-pressure column chromatography on silica gel using *n*-hexane/CH_2Cl_2 (3:2) as an eluent. The product could not be crystallized due to the high solubility. Thus, the resulting oily material was solidified by freeze-drying using benzene to give white powders. Yield: 0.78 g, 89%. Mp: 83−85 °C. FD-MS: *m*/*z* 1152 ($[M]^+$), 576 ($[M]^{2+}$). Anal. Calcd for $C_{80}H_{66}O_4P_2$: C, 83.31; H, 5.77. Found: C, 83.41; H, 5.90. ^1H NMR ($CDCl_3$): δ 7.41−7.09 (m, 40H), 6.98 (d, 4H, $^3J_{HP}$ = 7.8 Hz, *m*-Ar*H* attached to PPh_2), 6.33 (t, 2H, $^3J_{HH}$ = 7.6 Hz, *p*-Ar*H*), 6.08 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *m*-Ar*H*), 5.19 (s, 4H, OCH_2Ph), 4.67 (s, 4H, OCH_2Ph), 4.22 (d, 4H, $^2J_{HH}$ = 13.6 Hz, $ArCH_2Ar$), 2.90 (d, 4H, $^2J_{HH}$ = 13.6 Hz, $ArCH_2Ar$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.9, 154.8 (Ar*C* attached to OCH_2Ph), 138.2, 138.1, 137.8, 137.7, 137.6, 137.4, 134.6, 134.4, 133.7, 133.5, 133.0, 130.4, 129.3, 129.2, 128.9, 128.5, 128.4, 128.3, 128.1, 127.8, 127.70, 127.66 (Ar*C*), 122.4 (*p*-Ar*C*), 77.4, 75.3 (OCH_2Ph), 31.3 ($ArCH_2Ar$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.2.

$[PdCl_2\cdot 3]_2$ (4). To a solution of $PdCl_2(cod)$ (11.6 mg, 40.6 μmol) in 10 mL of $ClCH_2CH_2Cl$ was added a solution of the ligand **3** (47.1 mg, 40.8 μmol) in 10 mL of $ClCH_2CH_2Cl$ over a period of 15 min. The colorless solution was refluxed for 12 h and then cooled to room temperature. The solvent was removed in vacuo to afford a crude product, which was purified by recycling preparative GPC using $CHCl_3$ as an eluent. Yellow crystals suitable for X-ray structure analysis were obtained by slow diffusion of ether into a solution of **4** in CH_2Cl_2. Yield: 32.4 mg, 60%. Mp: 236−239 °C dec. ESI-MS: *m*/*z* 2679 ($[M + H + H_2O]^+$), 2626 ($[M - Cl]^+$). Anal. Calcd for $C_{160}H_{132}O_8Cl_4P_4Pd_2$: C, 72.21; H, 5.00. Found: C, 72.05; H, 5.15. ^1H NMR (CD_2Cl_2): δ 7.90−7.03 (m, 88H), 6.20 (s, 12H, *m*- and *p*-Ar*H*), 5.17 (s, 8H, OCH_2Ph), 4.67 (s, 8H, OCH_2Ph), 4.23 (d, 8H, $^2J_{HH}$ = 13.7 Hz, $ArCH_2Ar$), 2.93 (d, 8H, $^2J_{HH}$ = 13.7 Hz, $ArCH_2Ar$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 157.6, 154.0 (Ar*C* attached to OCH_2Ph), 137.5, 137.1 (*ipso*-Ar*C* of benzyl group), 137.0 (virtual t, $|^3J_{CP} + {}^5J_{CP}|$ = 5.8 Hz, *o*-Ar*C* attached to PPh_2), 135.1 (virtual t, $|^2J_{CP} + {}^4J_{CP}|$ = 6.3 Hz, *o*-Ar*C* of PPh_2), 134.6 (virtual t, $|^2J_{CP} + {}^4J_{CP}|$ = 6.1 Hz, *m*-Ar*C* attached to PPh_2), 132.0 (*o*-Ar*C*), 130.2 (virtual t, $|^1J_{CP} + {}^3J_{CP}|$ = 24.2 Hz, *ipso*-Ar*C* of PPh_2), 130.2, 129.7, 128.4, 128.0, 127.8 (Ar*C*), 127.7 (virtual t, $|^3J_{CP} + {}^5J_{CP}|$ = 5.2 Hz, *m*-Ar*C* of PPh_2), 127.6, 127.3, 127.2 (Ar*C*), 123.0 (*p*-Ar*C*), 122.2 (virtual t, $|^1J_{CP} + {}^3J_{CP}|$ = 26.5 Hz, *ipso*-Ar*C* attached to PPh_2), 76.9, 74.7 (OCH_2Ph), 30.9 ($ArCH_2Ar$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 23.3.

$PtCl_2\cdot 3$ (5). In a manner similar to the preparation method of **4**, a solution of $PtCl_2(cod)$ (15.2 mg, 40.6 μmol) and the ligand **3** (46.6 mg, 40.4 μmol) in 20 mL of $ClCH_2CH_2Cl$ was refluxed.

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Colorless crystals were obtained after recrystallization from $CHCl_3$/*n*-pentane. Yield: 38.2 mg, 67%. Mp: >300 °C. FD-MS: *m*/*z* 1418 ($[M]^+$), 1383 ($[M - Cl]^+$). Anal. Calcd for $C_{80}H_{66}O_4Cl_2P_2Pt$: C, 67.70; H, 4.69. Found: C, 67.43; H, 4.89. ^1H NMR (CD_2Cl_2): −80 °C, δ 8.23−5.78 (m, 50H, Ar*H*), 5.38−4.69 (m, 8H, OC*H*$_2$Ph), 4.28 (br, 2H, ArC*H*$_2$Ar), 4.05 (br d, 1H, ArC*H*$_2$Ar), 3.93 (br d, 1H, ArC*H*$_2$Ar), 3.26 (br d, 1H, ArC*H*$_2$Ar), 3.07 (br d, 1H, ArC*H*$_2$Ar), 2.68 (br d, 1H, ArC*H*$_2$Ar), 2.60 (br d, 1H, ArC*H*$_2$Ar); 20 °C, δ 7.43−6.87 (m, 50H, Ar*H*), 5.26 (s, 4H, OC*H*$_2$Ph), 4.91 (s, 4H, OC*H*$_2$Ph), 4.29 (d, 4H, $^2J_{HH}$ = 13.9 Hz, ArC*H*$_2$Ar), 2.99 (d, 4H, $^2J_{HH}$ = 13.9 Hz, ArC*H*$_2$Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): −80 °C, δ 156.0, 155.3, 153.8, 152.8 (Ar*C* attached to OCH_2Ph), 137.2−116.2 (Ar*C*), 76.0, 75.5, 75.1, 72.4 (O*C*H$_2$Ph), 30.4, 30.1, 29.1, 28.7 (Ar*C*H$_2$Ar); 20 °C, δ 157.2, 154.9 (Ar*C* attached to OCH_2Ph), 137.1, 136.6, 136.6 (Ar*C*), 134.7 (br m, Ar*C*), 133.5, 132.8 (br, Ar*C*), 130.3 (Ar*C*), 130.2 (br d, $^1J_{PC}$ = 65.1 Hz, Ar*C* attached to P), 129.2, 129.2, 129.0, 128.1, 128.0, 127.6, 127.3 (Ar*C*), 127.2 (br m, Ar*C*), 123.7 (Ar*C*), 119.0 (d, $^1J_{PC}$ = 62.5 Hz, Ar*C* attached to P), 77.4, 75.5 (O*C*H$_2$Ph), 31.5 (Ar*C*H$_2$Ar). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −80 °C, δ 12.8 (d with Pt satellites, $^1J_{PPt}$ = 3760 Hz, $^2J_{PP}$ = 16.2 Hz), 7.0 (d with Pt satellites, $^1J_{PPt}$ = 3599 Hz, $^2J_{PP}$ = 16.2 Hz); 20 °C, δ 10.9 (s with Pt satellites, $^1J_{PPt}$ = 3639 Hz).

[Pd(η^3-C$_3$H$_5$)·3]BF$_4$ (6). The ligand **3** (73.2 mg, 63.5 μmol) and [Pd(η^3-C$_3$H$_5$)(cod)]BF$_4$ (21.9 mg, 63.9 μmol) was dissolved in 10 mL of THF. The reaction mixture was refluxed for 12 h and evaporated to afford a crude product. A pure product was obtained by medium-pressure column chromatography on silica gel using CH_2Cl_2/acetone (15:1) as an eluent, followed by recrystallization from CH_2Cl_2/*n*-pentane to give **8** as a colorless crystal. Yield: 82.7 mg, 94%. Mp: 191−193 °C dec. FD-MS: *m*/*z* 1299 ($[M - BF_4]^+$). Anal. Calcd for $C_{83}H_{71}O_4BF_4P_2Pd$: C, 71.84; H, 5.16. Found: C, 71.51; H, 5.43. ^1H NMR (CD_2Cl_2, 20 °C): δ 7.40−6.75 (m, 46H), 6.39 (virtual t, 2H, $|^3J_{HP} + {}^5J_{HP}|$ = 4.1 Hz, *m-H* of Ar attached to P), 6.15 (virtual t, 2H, $|^3J_{HP} + {}^5J_{HP}|$ = 5.2 Hz, *m-H* of Ar attached to P), 5.41 (m, 1H, C*H* of η^3-C$_3$H$_5$), 5.29 (s, 2H, OC*H*$_2$Ph), 5.28 (s, 2H, OC*H*$_2$Ph), 4.92 (d, 2H, $^2J_{HH}$ = 11.2 Hz, OC*H*$_2$Ph), 4.88 (d, 2H, $^2J_{HH}$ = 11.2 Hz, OC*H*$_2$Ph), 4.23 (d, 2H, $^2J_{HH}$ = 13.9 Hz, axial-ArC*H*$_2$Ar), 4.21 (d, 2H, $^2J_{HH}$ = 13.9 Hz, axial-ArC*H*$_2$Ar), 3.83 (pseudo d, 2H, $^3J_{HH}$ = 6.5 Hz, syn-*H* of η^3-C$_3$H$_5$), 3.26 (m, 2H, anti-*H* of η^3-C$_3$H$_5$), 2.95 (d, 2H, $^2J_{HH}$ = 13.9 Hz, equatorial-ArC*H*$_2$Ar), 2.87 (d, 2H, $^2J_{HH}$ = 13.9 Hz, equatorial-ArC*H*$_2$Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): −80 °C, δ 155.7, 155.2, 154.1, 153.7, 153.1, 152.7 (Ar*C* attached to OCH_2Ph), 137.6−118.0 (Ar*C*), 76.2−72.8 (O*C*H$_2$Ph), 30.7−27.4 (Ar*C*H$_2$Ar); 20 °C, δ 157.0, 155.1, 155.0 (Ar*C* attached to OCH_2Ph), 137.3, 137.1 (*o-C* of Ar with no substituent), 136.5, 136.4, 136.2 (*ipso-C* of benzyl), 135.5 (t, $^3J_{CP}$ = 5.9 Hz, *o-C* of Ar attached to P), 135.1 (t, $^3J_{CP}$ = 5.1 Hz, *o-C* of Ar attached to P), 132.4, 132.2, 131.6, 130.3, 130.2, 129.0, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 127.8, 127.8, 127.4, 127.4, 123.1, 122.7 (Ar*C*), 121.3 (t, $^3J_{CP}$ = 5.4 Hz, *C*H of η^3-C$_3$H$_5$), 119.9, 119.7, 119.5 (Ar*C*), 77.2 (O*C*H$_2$Ph), 76.5 (virtual t, $|^2J_{CP} + {}^4J_{CP}|$ = 15.1 Hz, *C*H$_2$ of η^3-C$_3$H$_5$), 75.4, 75.0 (O*C*H$_2$Ph), 31.1, 31.0 (Ar*C*H$_2$Ar). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −80 °C, δ 22.6 (d, $^2J_{PP}$ = 36.1 Hz), 22.1 (d, $^2J_{PP}$ = 38.3 Hz), 21.5 (d, $^2J_{PP}$ = 38.3 Hz), 20.9 (d, $^2J_{PP}$ = 36.1 Hz); 20 °C, δ 21.8.

X-ray Structure Determination of 4. The data were collected with Mo Kα radiation (λ = 0.71069 Å) at −177 °C on a Rigaku RAXIS RAPID imaging plate area detector to a maximum 2θ value of 55.0°. The structure was solved by direct methods using the program SIR92[37] and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. No hydrogen atoms were included. The final cycle of full-matrix least-squares refinement was based on 8279 observed reflections ($I > 1.20\sigma(I)$) and 787 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber.[38] Anomalous dispersion effects were included in F_c.[39] All calculations were performed using the CrystalStructure[40] crystallographic software package.

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Supporting Information Available: Tables of crystal data and refinement details, atomic coordinates, thermal parameters, bond distances, bond angles, and least-squares planes for **4**, ORTEP figures of **1**, **2**, and **5**, and Cartesian coordinates of optimized structures for **5m**-GS, **5m**-TS, **6am**-GS, **6bm**-GS, and **6m**-TS. This material is available free of charge via the Internet at http://pubs.acs.org.

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