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Monophosphanylcalix[6]arene Ligands: Synthesis Characterization, Complexation, and Their Use in Catalysis

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Novel phosphanylcalix[6]arenes having mono-*O*-diphenylphosphanylmethyl (**3**) and mono-*O*-(4-diphenylphosphanylphenyl)methyl substituents (**5**) have been synthesized. The structures of these monophosphanylcalix[6]arenes were determined by NMR spectroscopy, mass spectrometry, and X-ray crystal structure analysis. The X-ray structure reveals that **3** adopts a flattened 1,2,3-alternate conformation in the crystalline state, while the NMR spectra show that **3** and **5** have a cone conformation in solution. Structure optimization and energy calculations for **3** and **5** at the B3LYP/LANL2DZ-CONFLEX5/MMFF94s level of theory show that the cone conformation is slightly more stable than the 1,2,3-alternate conformation by 0.36 kcal mol^{-1} for **3** and 0.96 kcal mol^{-1} for **5**. Complexation of **3** with $[PtCl_2(COD)]$ and $[Rh(COD)_2]BF_4$ gives *cis*-coordinated $[PtCl_2(\mathbf{3})_2]$ and $[Rh(COD)(\mathbf{3})_2]BF_4$, respectively. The X-ray analysis of $[PtCl_2(\mathbf{3})_2]$ shows that **3** adopts a cone conformation upon complexation. Combination of **3** and **5** with $[Rh(COD)_2]BF_4$ provides an active catalyst for the hydroformylation of a variety of terminal alkenes.

Introduction

Calixarenes are macrocyclic compounds having well-defined cavities, and a number of synthetic procedures for their selective functionalization have been developed.[1] In particular, phosphanylcalixarenes,[2] namely phosphanes bearing calixarene moieties, have received considerable attention. Phosphane ligands in general play an important role in transition-metal-catalyzed reactions, and a wide variety of phosphanes have been prepared to realize high catalytic activity and selectivity.[3,4] The phosphanylcalixarenes are attractive ligands since they integrate the strong coordination ability of phosphanes and the unique cavity of the calixarenes to create a spatially confined environment upon complexation with transitional metals.[2]

As far as the size of the cavity is concerned, major attention has been paid to phosphanylcalix[4]arenes[5] due to their rigid conformations. As for the phosphanylcalix[4]arenes, we have reported Pt^{II} and Pd^{II} complexes of a bis(diphenylphosphanyl)calix[4]arene,[6a] solid-state and solution structures of a tetrakis(diphenylphosphanyl)calix[4]arene,[6b] and an Ru^{II} complex of a tetrakis(diphenylphosphanylmethyl)calix[4]arene.[6c] Calix[6]arenes having larger cavities generally display more flexible and variable conformations[7] than calix[4]arenes. Therefore, the chemistry of phosphanylcalix[6]arenes[8] is essentially unexplored owing to their intricacy. We recently synthesized 1,3,5-triphosphanylcalix[6]arene, which functions as a tripodal phosphane ligand to afford novel, capsule-shaped Ir^{I} and Rh^{I} complexes.[9]

In the present study, we describe the synthesis and characterization of novel phosphanylcalix[6]arenes having mono-*O*-diphenylphosphanylmethyl (**3**) and mono-*O*-(4-diphenylphosphanylphenyl)methyl substituents (**5**) as the first examples of a calix[6]arene moiety bearing monodentate phosphane ligands.[10] The monodentate phosphanes are an important class of ligands in transition-metal-catalyzed reactions.[3,11] Furthermore, we have synthesized Pt^{II} and Rh^{I} complexes of **3**, and found that the Rh^{I} complexes of **3** and **5** are active catalysts in the hydroformylation of terminal alkenes.

Results and Discussion

The monophosphanylcalix[6]arene ligands **3** and **5** were prepared as shown in Scheme 1. According to the reported synthetic procedure for phosphanylcalix[4]arenes[5n,12] and triphosphanylcalix[6]arenes,[9] **3** was prepared as follows. Reaction of **1**[13] with $Ph_2P(O)CH_2OTs$[14] with NaH as a base, in toluene at 90 °C for 2 d, gave the phosphane oxide **2** in 95% yield. Reduction of **2** was carried out with $PhSiH_3$

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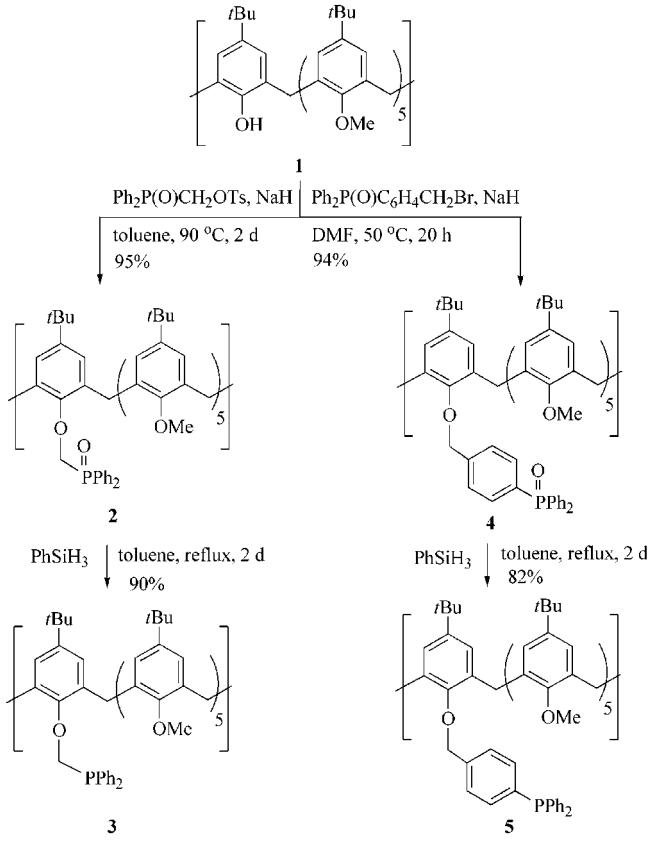
in toluene under reflux to afford **3** in 90% yield. With regard to the synthesis of **5**, the corresponding phosphane oxide (**4**) was prepared from **1**, $Ph_2P(O)C_6H_4CH_2Br$,[15] and NaH in DMF at 50 °C for 20 h by modifying the reported procedure for mono-*O*-benzylation of calix[6]arenes.[16] The desired phosphane (**5**) was obtained in 82% yield after reduction of **4** with $PhSiH_3$.



Scheme 1.

These phosphane compounds (**3** and **5**) were characterized by means of NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystal structure analysis. The $^{31}P\{^1H\}$ NMR spectra (in $CDCl_3$) of **3** and **5** at 25 °C display single resonances at δ = –16.5 and –5.6 ppm assignable to alkyldiaryl- and triarylphosphanes, respectively. The ESI or FD mass spectra of **3** and **5** show peaks at *m*/*z* = 1264 $[M + Na]^+$ (for **3**) and 1318 $[M^+]$ (for **5**). The X-ray structure of **3** is shown in Figure 1. The crystallographic data are listed in the Experimental Section and selected atom distances and bond angles of **3** in Table 1. The X-ray structure shows that **3** adopts a 1,2,3-alternate conformation in which three pairs of diametrically opposite phenyl rings (**A** vs. **D**, **B** vs. **E**, and **C** vs. **F**) orient *anti* to each other.[17] Four of these aromatic rings (**A**, **C**, **D**, and **F**) almost stand up in pinched positions whereas the other two aromatic rings (**B** and **E**) splay outwards in flattened positions. Thus, the dihedral angles between the aromatic rings (**A**–**F**) and the calixarene reference plane (the average plane defined by the six bridging methylene carbon atoms; the maximum deviation is 0.2162 Å) are 84.3(1)°, 137.2(1)°, 66.9(1)°, 73.4(1)°, 136.2(1)°, and 68.7(1)°, respectively. This structure can also be designated as a (u,uo,u,d,do,d) conformation, as suggested by Gutsche.[18] Similar 1,2,3-alternate conformations in the crystalline state have also been reported for several hexasubstituted calix[6]arene derivatives.[19]

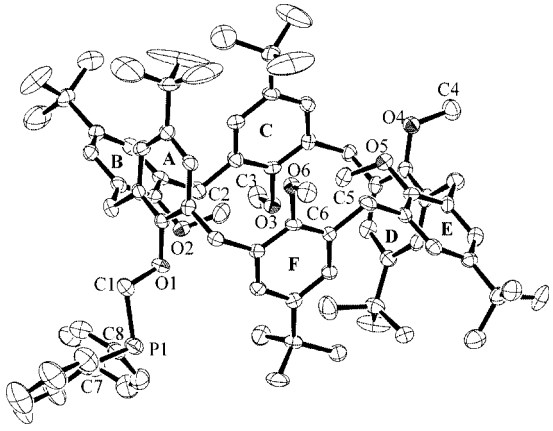


Figure 1. ORTEP drawing of the molecular structure of **3** with thermal ellipsoids at 50% probability levels. Hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for **3**.

P(1)–C(1)	1.863(6)	P(1)–C(7)	1.825(6)
O(1)–C(1)	1.420(6)	O(2)–C(2)	1.431(7)
O(3)–C(3)	1.436(6)	O(4)–C(4)	1.440(6)
O(5)–C(5)	1.413(7)	O(6)–C(6)	1.433(7)
C(7)–P(1)–C(8)	102.2(2)	P(1)–C(1)–O(1)	105.8(3)

To elucidate the structures of **3** and **5** in solution, ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** and **5** were measured in $CDCl_3$ at 25 °C. All the ^1H and ^{13}C resonances were completely assigned by means of HMBC[20] 2D NMR spectroscopy. In solution, both compounds **3** and **5** show quite similar NMR spectra in terms of the conformation of calix[6]arene moieties. The ^1H NMR spectrum of **3** exhibits axial bridging methylene proton resonances as three doublets at δ = 4.03, 4.19, and 4.35 ppm in a 1:1:1 ratio, and the corresponding equatorial proton resonances as three doublets at δ = 3.85, 3.70, and 3.48 ppm in a 1:1:1 ratio, with geminal couplings (J = 14–15 Hz). Similarly, the ^1H NMR spectrum of **5** displays signals of three axial bridging methylene protons at δ = 4.04, 4.16, and 4.43 ppm and of three equatorial protons at δ = 3.81, 3.68, and 3.51 ppm as doublets. With regard to the bridging methylene resonances in the ^1H NMR spectra, the difference of the chemical shift ($\Delta\delta$) between the axial and the equatorial pairs is dependent on the orientation of the two adjacent aromatic rings.[21] The $\Delta\delta$ values (0.87, 0.49, and 0.18 ppm for **3** and 0.92, 0.48, and 0.23 ppm for **5**) are quite similar to the values reported for mono-*O*-benzyl-substituted calix[6]arene (0.94, 0.50, and 0.21 ppm), which was assigned a cone conformation in solution.[22] Furthermore, the *tert*-butyl protons appear as four singlet peaks in a 1:1:2:2 ratio (δ = 0.92, 1.27, 1.06, and 1.30 ppm for **3** and δ = 0.97, 1.23, 1.02, and 1.24 ppm for **5**), and the methoxy

protons as three singlet peaks in a 1:2:2 ratio (δ = 2.81, 2.50, and 3.26 ppm for **3** and δ = 2.76, 2.49, and 3.22 ppm for **5**) in the ^{1}H NMR spectra. It is well known that a signal arising from the bridging methylene carbon atoms (Ar-CH_2-Ar) appears at $\delta \approx 31$ ppm in the $^{13}C\{^1H\}$ NMR spectrum when two adjacent aryl rings are in the *syn* orientation, and close to δ = 37 ppm for the *anti* orientation.[22,23] Here, the bridging methylene carbon resonances appear at δ = 30.38, 30.48, and 30.64 ppm for **3** and δ = 30.42, 30.76, and 30.80 ppm for **5** in 1:1:1 ratios, with no methylene resonances at δ = 36–38 ppm. The ROESY spectrum of **3** at 25 °C shows that all the equatorial protons have ROE correlations with one of the aromatic protons of the calixarene moiety; no ROE correlation was observed between the axial protons and the aromatic protons (see Figure S2 in the Supporting Information). Variable-temperature $^{13}C\{^1H\}$NMR spectra of **3** in the range from –50 to 25 °C showed that the bridging methylene carbon signals (δ = 29–31 ppm) remained virtually unchanged, whereas the ^{1}H NMR spectra showed that two pairs of bridging methylene doublets (δ = 4.19/3.70 and 4.03/3.85 ppm) became slightly broadened, while the remaining pair (δ = 4.35/3.48 ppm) remained as a sharp peak on lowering the temperature to –50 °C. All these NMR spectroscopic data clearly indicate that **3** and **5** adopt a cone conformation[22–24] in solution.[25]

The CPMAS solid-state $^{13}C\{^1H\}$ NMR spectra of **3** (Figure 2) and **5** (as a powder, not a single crystal) show comparable chemical shifts to the solution spectra, although the resonances in the solid state are considerably broader ($\Delta\nu_{1/2}$ = 50–180 Hz). The diagnostic bridging methylene carbon resonances appear at $\delta \approx 30.5$ ppm ($\Delta\nu_{1/2}$ = 172 Hz) for **3** and $\delta \approx 31.1$ ppm (for **5**), rather than at δ = 36–38 ppm, thus indicating that **3** and **5** have the same cone structure in the solid state as in solution.

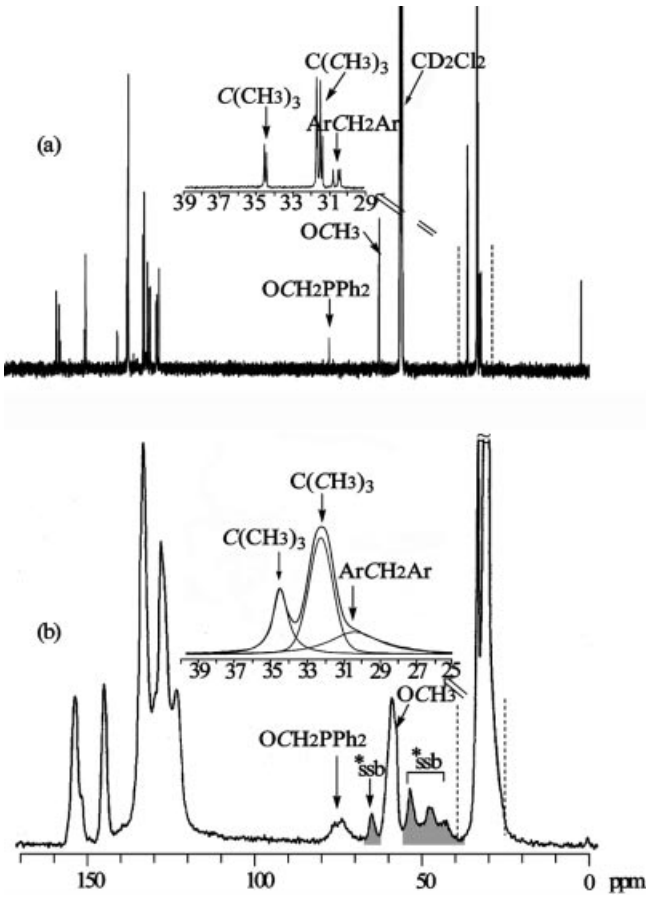


Figure 2. $^{13}C\{^1H\}$ NMR spectra of **3** at 25 °C: (a) measured in CD_2Cl_2; (b) measured in the solid state (CPMAS). *ssb: spinning side-band.

The structural differences between the solution (cone), powder (cone), and the single crystal (1,2,3-alternate) suggest that the energy difference between these conformations is very small. Thus, an MO calculation was carried out for the 1,2,3-alternate (Figure 3a for **3**; Figure 3d for **5**) and the cone conformations (Figure 3b for **3**; Figure 3e for **5**) as well as a common 1,3,5-alternate[18] conformation (Figure 3c for **3**; Figure 3f for **5**). In each conformation, conformational analysis of **3** and **5** was carried out by CONFLEX5[26]/MMFF94s[27] to find the lowest-energy structure. The structures were then further optimized by DFT calculations at the B3LYP[28]/LANL2DZ[29] level. The optimized structures are shown in Figure 3a–f, which reproduce the characteristic structural features: (u,uo,u,d,do,d) for the 1,2,3-alternate (Figure 3a and d), (u,u,u,u,u,u) for the cone (Figure 3b and e), and (u,di,u,d,ui,d)[18] for the 1,3,5-alternate conformation (Figure 3c and f). The energy calculations on these optimized structures at the same level (B3LYP/LANL2DZ) revealed that the energy difference between the 1,2,3-alternate and the cone conformations is very small: the latter is slightly more stable than the former but only by 0.36 (for **3**) and 0.96 kcal mol^{-1} (for **5**). However, the 1,3,5-alternate conformation is considerably less stable (11.93 kcal mol^{-1} for **3** and 12.67 kcal mol^{-1} for **5**) than the cone conformation. This result can explain why no 1,3,5-alternate conformations were observed for **3** and **5** and that facile conformational interconversion between the 1,2,3-alternate and the cone takes place to afford the 1,2,3-alternate conformation in the crystal structure, possibly by a preferential crystallization of this conformation.[30]

The ^{13}C NMR chemical shifts of **3** were calculated by the GIAO (Gauge-Independent Atomic Orbital)[31] method at the HF/6-31G(d) level of theory for the optimized cone (Figure 3b) and the 1,2,3-alternate (Figure 3a) structures. As shown in Table 2 and Figure 4, the calculated chemical shifts of the cone structure are in good correlation with the values observed in CD_2Cl_2 (r^2 = 0.996), thereby indicating that the calculation is reliable, although the calculated values are smaller than the observed ones by 1.5–5 ppm. It is noteworthy that among the six bridging methylene carbon atoms of the 1,2,3-altenate structure, the calculated chemical shifts of the four carbon atoms (δ = 28.04, 28.44, 28.45, and 28.46 ppm) of the *syn* orientation are definitely smaller than those of the two carbon atoms of the *anti* orientation (δ = 32.40 and 32.42 ppm). Such explicit differences would warrant the aforementioned diagnostic bridging methylene carbon resonances of the *syn* and *anti* orientations.

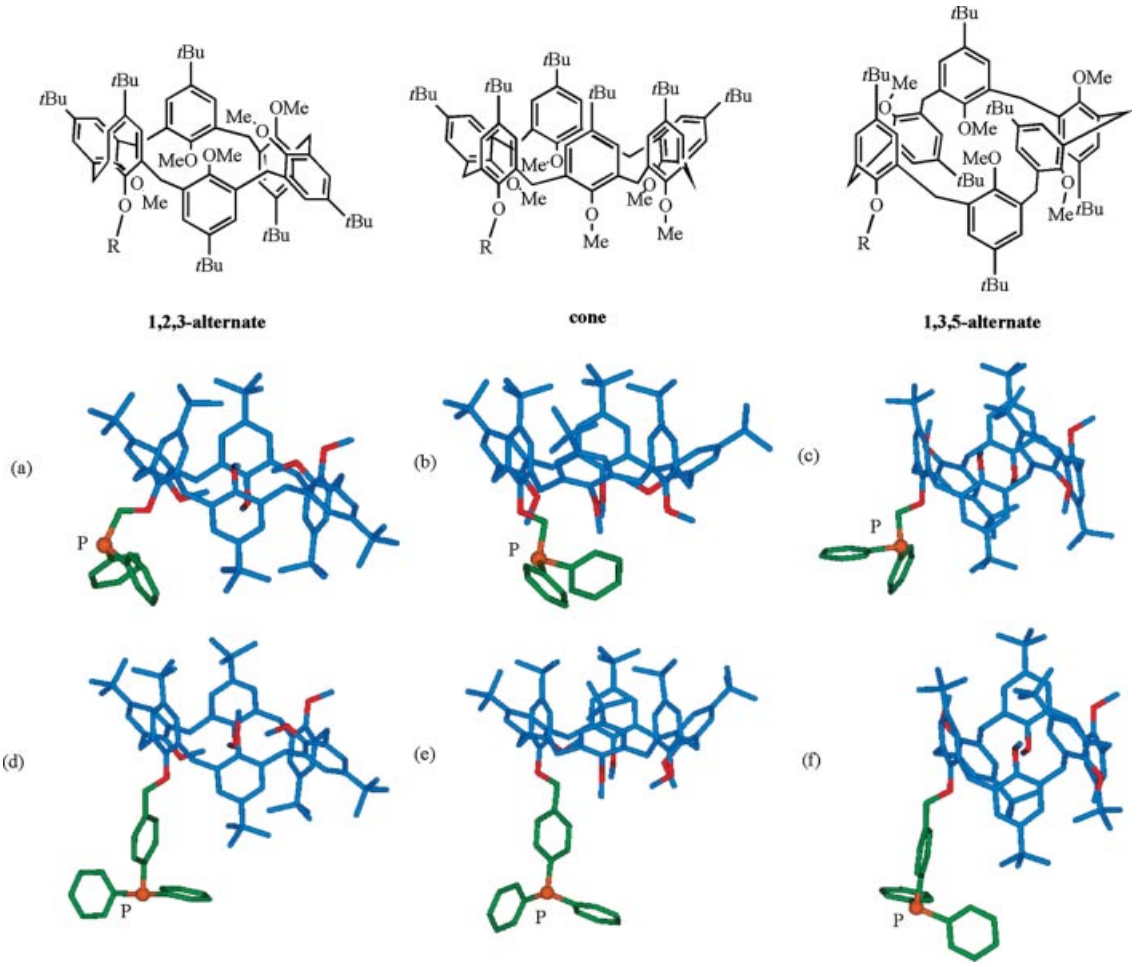


Figure 3. Conformers and optimized structures (B3LYP/LANL2DZ–CONFLEX5/MMFF94s) of **3** [(a) 1,2,3-alternate, (b) cone, (c) 1,3,5-alternate] and **5** [(d) 1,2,3-alternate, (e) cone, (f) 1,3,5-alternate].

Table 2. GIAO calculation of ^{13}C NMR chemical shifts [ppm] of **3** at the HF/6-31G(d) level for the cone and the 1,2,3-alternate conformers.

	Cone		1,2,3-Alternate
	Calculated	Experimental[a]	Calculated
Ar–CH_2–Ar	27.24 (*syn*)	30.81 (–3.57)	28.04 (*syn*), 28.44 (*syn*)
	28.65 (*syn*)	30.44 (–1.79)	28.45 (*syn*), 28.46 (*syn*)
	29.05 (*syn*)	30.53 (–1.48)	32.40 (*anti*), 32.42 (*anti*)
$(CH_3)_3C$–Ar	28.12	31.48 (–3.36)	
	28.23	31.38 (–3.15)	28.32, 28.33, 28.36
	28.68	31.68 (–3.00)	28.46, 28.68, 28.72
	28.69	31.63 (–2.94)	
$(CH_3)_3C$–Ar	31.21	34.34 (–3.13)	
	31.28	34.34 (–3.06)	31.38, 31.40, 31.41
	31.43	34.43 (–3.00)	31.43, 31.47, 31.65
	31.43	34.43 (–3.00)	
CH_3O–Ar	55.18	60.20 (–5.02)	54.09, 54.20
	55.76	60.24 (–4.48)	55.09, 55.31
	55.86	60.37 (–4.51)	55.33
O–CH_2–PPh_2	73.18	75.02 (–1.84)	70.80

[a] In CD_2Cl_2 at 25 °C (Figure 2a). The figures in parentheses show the difference between the calculated and experimental chemical shifts.

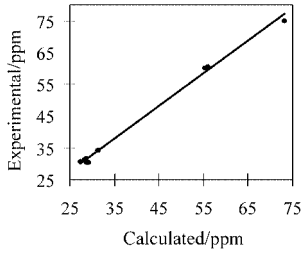


Figure 4. Correlation plots of the calculated vs. experimental ^{13}C NMR chemical shifts for the cone conformer.

Preparation of Platinum(II) and Rhodium(I) Complexes of 3

Pt^{II} and Rh^{I} complexes of **3** were prepared. Compound **3** (2 equiv.) was treated with [$PtCl_2$(COD)] (COD = 1,5-cyclooctadiene) to afford [$PtCl_2$(**3**)$_2$] in 78% yield [Equation (1)]. Characterization of [$PtCl_2$(**3**)$_2$] was performed by NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystal structure analysis. The ESI mass spectrum of [$PtCl_2$(**3**)$_2$] exhibits an intense signal for $[M + Na]^+$

(m/z = 2770). The structure of $[PtCl_2(\mathbf{3})_2]$ was unequivocally confirmed by X-ray diffraction. Figure 5 shows the molecular structure of $[PtCl_2(\mathbf{3})_2]$. The crystal data and selected bond lengths and angles are summarized in the Experimental Section and Table 3, respectively. In contrast to the structure of **3** (Figure 1), the two calix[6]arene moieties in $[PtCl_2(\mathbf{3})_2]$ adopt a cone conformation. The platinum atom is *cis*-coordinated by two phosphane groups and the P1–Pt–P2 bond angle is 97.6(5)°, which is comparable to the value of 98.1(3)° found in *cis*-$[PtCl_2(PMePh_2)_2]$.[32] The Cl(1)–Pt(1)–P(1) and Cl(2)–Pt(1)–P(2) angles are 170.82 (5)° and 172.15 (6)°, respectively. Thus, the geometry of the platinum center is approximately square-planar with a slightly tetrahedral distortion. The Pt–P bond lengths [2.255(1) and 2.247(2) Å] and the Pt–Cl bond lengths [2.359(2) and 2.349(1) Å] are similar to those in *cis*-$[PtCl_2(PMePh_2)_2]$[32] and other phosphanylcalixarene-based Pt^{II} complexes.[33]

$$[PtCl_2(COD)] + \mathbf{3} \xrightarrow[\text{r.t., 2 h}]{CH_2Cl_2} [PtCl_2(\mathbf{3})_2] \quad (1)$$

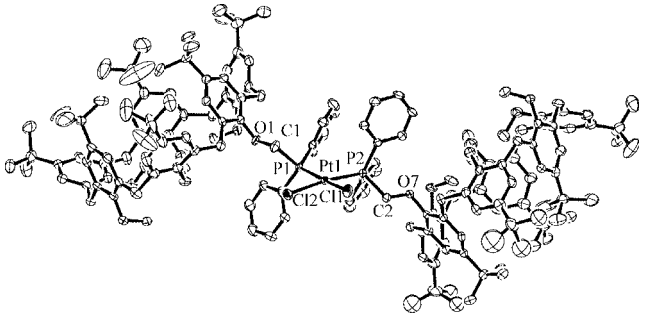


Figure 5. ORTEP drawing of $[PtCl_2(\mathbf{3})_2]$ with thermal ellipsoids at 50% probability levels. Hydrogen atoms have been omitted for clarity.

Table 3. Selected bond lengths [Å] and angles [°] for $[PtCl_2(\mathbf{3})_2]$.

Pt(1)–P(1)	2.255(1)	Pt(1)–P(2)	2.247(2)
Pt(1)–Cl(1)	2.350(2)	Pt(1)–Cl(2)	2.359(2)
P(1)–C(1)	1.847(7)	P(2)–C(2)	1.857(7)
O(1)–C(1)	1.430(8)	O(7)–C(2)	1.424(7)
P(1)–Pt(1)–P(2)	97.57(5)	Cl(1)–Pt(1)–Cl(2)	87.28(6)
Cl(1)–Pt(1)–P(1)	170.82(6)	Cl(2)–Pt(1)–P(2)	172.15(6)
O(1)–C(1)–P(1)	108.9(3)	O(7)–C(2)–P(2)	109.0(4)

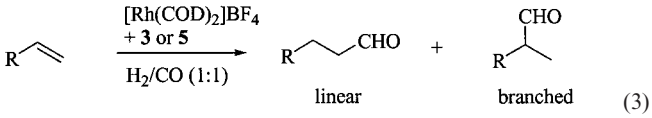
In solution, the ^1H NMR spectrum of $[PtCl_2(\mathbf{3})_2]$ shows the bridging methylene protons as five distinct doublets with geminal couplings of 15 Hz; the other doublet is overlapped by the methoxy proton resonances. The *tert*-butyl protons appear as four singlets in a 1:1:2:2 ratio and the methoxy protons exhibit three distinct resonances with a 1:2:2 ratio. The ^{13}C NMR resonances of the bridging methylene carbon atoms appear at δ = 29.84, 30.33, and 30.54 ppm in a ratio of 1:1:1. All these NMR spectroscopic data indicate that the calixarene moieties of $[PtCl_2(\mathbf{3})_2]$ remain in the cone conformation in solution, as is also the case in the crystalline state (Figure 5). The $^{31}P\{^1H\}$ NMR spectrum displays a singlet peak at δ = 6.0 ppm with a $^1J_{Pt,P}$ coupling constant of 3611 Hz, which indicates the *cis* coordination of the phosphane ligand.[5a,34] When the *cis* complex was heated at 60 °C for 24 h, no *cis*/*trans* isomerization[35] was observed.

Treatment of **3** with $[Rh(COD)_2]BF_4$ in CH_2Cl_2 afforded $[Rh(COD)(\mathbf{3})_2]BF_4$ in 68% yield [Equation (2)]. The ESI mass spectrum of this complex shows an intense peak at m/z = 2694 ($[M - BF_4^-]^+$). In the ^1H and $^{13}C\{^1H\}$ NMR spectra of $[Rh(COD)(\mathbf{3})_2]BF_4$ (see Experimental Section), the resonances for the bridging methylene protons and carbon atoms and the *tert*-butyl and methoxy protons indicate that the calix[6]arene moieties also maintain the cone conformation in the complex. The ^{31}P NMR spectrum of the complex shows a resonance at δ = 20.8 ppm ($^1J_{Rh,P}$ = 141 Hz), which is consistent with a *cis*-planar structure as was reported for $[Rh(COD)(DPPB)]BF_4$ [DPPB = 1,4-bis(diphenylphosphanyl)butane; δ =23.5 ppm ($^1J_{Rh-P}$ = 144 Hz)].[36]

$$[Rh(COD)_2]BF_4 + \mathbf{3} \xrightarrow[\text{r.t., 3 h}]{CH_2Cl_2} [Rh(COD)(\mathbf{3})_2]BF_4 \quad (2)$$

Hydroformylation Experiments

It is known that (phosphanylcalix[4]arene)rhodium complexes have been found to be active catalysts for the hydroformylation of olefins.[5c,5g,5k,5n,5o] Phosphanylcalix[6]arenes have a larger cavity than phosphanylcalix[4]arenes; therefore, in order to examine the catalytic performance (catalytic activity and regioselectivity) of the novel monophosphanylcalix[6]arene ligands **3** and **5**, Rh^I-catalyzed hydroformylations of four different terminal olefins were examined [Equation (3) and Table 4]. The hydroformylation reactions were carried out with a 1:1 mixture of CO/H_2 (10 atm) in the presence of $[Rh(COD)_2]BF_4$ combined with **3** or **5** (olefin/Rh/P ratio = 2000:1:4) in benzene at 70 °C. When 1-hexene was employed as substrate, 1-heptanal (linear) and 2-methylhexanal (branched) were formed in 79% (with **3**) and 85% (with **5**) total yields (Entries 1 and 2). The present catalysts also show high activity in hydroformylation of styrene to afford the branched aldehyde as the major product (Entries 3 and 4). These regioselectivities (linear/branched ratios) are similar to those reported with phosphanylcalix[4]-arene ligands[5c,5g,5k,5o,5n] and conventional phosphanes.[37] In the hydroformylation of vinyl acetate and vinyl benzoate, the rhodium catalyst with **3** shows a better catalytic activity than that with **5** and affords branched aldehydes exclusively (Entries 5–8). Thus, the rhodium catalyst system combined with **3** or **5** displays a high catalytic activity for the hydroformylation of various terminal alkenes.



(3)

Table 4. Rh^{I}-catalyzed hydroformylations of terminal olefins.[a]

Entry	Olefin	Ligand	Aldehydes [%]	Linear/branched[b]
1	1-hexene	**3**	79	66:34
2		**5**	85	71:29
3	styrene	**3**	81	8:92
4		**5**	91	10:90
5	vinyl acetate	**3**	67	–[c]
6		**5**	24	–[c]
7	vinyl benzoate	**3**	96	–[c]
8		**5**	57	–[c]

[a] Olefin (1.0 mmol), $[Rh(COD)_2]BF_4$ (0.005 mmol), ligand (**3** or **5**) (0.02 mmol) in benzene (2 mL) at 70 °C under 10 atm CO/H_2 (1:1). [b] Determined by GC. [c] No linear adduct was detected.

In conclusion, novel monophosphanylcalix[6]arene ligands having mono-*O*-diphenylphosphanylmethyl (**3**) and mono-*O*-(4-diphenylphosphanylphenyl)methyl (**5**) moieties have been prepared, and complexation of **3** with Pt^{II} and Rh^{I} complexes has been carried out. Conformational analysis of the ligands and complexes suggests that the cone is the most stable conformer in both solution and the solid state. However, in the crystalline state, due to a small energy difference between the cone and 1,2,3-alternate conformations, facile interconversion between these conformations takes place to afford the 1,2,3-alternate conformation by preferential crystallization of this conformer.

Experimental Section

General: All reactions were performed under argon using standard Schlenk techniques. Solvents were dried and purified before use by usual methods.[38] $[Rh(COD)_2]BF_4$,[39] $[PtCl_2(COD)]$,[40] and 5,11,17,23,29,35-hexa-*tert*-butyl-38,39,40,41,42-pentamethoxycalix-[6]aren-37-ol (**1**)[15] were prepared according to literature procedures. Medium-pressure column chromatography (Yamazen YFLC-540) was performed on silica gel (Wakogel C-400HG; particle size 20–40 μm) with a UV detector (Yamazen UV-10V). Preparative-scale GPC was carried out with a Japan Analytical Industry LC-9104 instrument equipped with Jaigel-1H-40 and Jaigel-2H-40. ^1H (400 MHz), $^{13}C\{^1H\}$ (100 MHz), and $^{31}P\{^1H\}$ NMR (162 MHz) spectra were recorded with a Bruker ARX 400 instrument. The ^1H NMR spectroscopic data are referenced relative to residual protonated solvent (δ = 5.32 and 7.26 ppm in CD_2Cl_2 and $CDCl_3$, respectively). ^{13}C NMR chemical shifts are reported relative to either CD_2Cl_2 (δ = 53.1 ppm) or $CDCl_3$ (δ = 77.0 ppm). The ^{31}P NMR spectroscopic data are given relative to external 85% H_3PO_4. HMBC[20] 2D NMR spectra were recorded with a JEOL α-500 or a JEOL ECX-400 instrument. CPMAS solid-state $^{13}C\{^1H\}$ NMR (100 MHz) spectra were recorded with a JEOL CMXP400 or a JEOL ECX-400 instrument with magic-angle spinning at 8 kHz (for **3**) or 5 kHz (for **5**); the ^{13}C NMR spectroscopic data are referenced relative to hexamethylbenzene (δ = 17.4 ppm). FD and ESI mass spectra were recorded with a JEOL JMS-SX102A instrument at the GC-MS & NMR Laboratory of the Faculty of Agriculture at Hokkaido University. Elemental analysis was performed at the Center for Instrumental Analysis of Hokkaido University. Molecular-orbital calculations were performed with the Gaussian 03 program[41] on a HIT HPC-IA642/SS 1.3/3D-4G.

5,11,17,23,29,35-Hexa-*tert*-butyl-37-(diphenylphosphanylmethoxy)-38,39,40,41,42-pentamethoxycalix[6]arene (2): $Ph_2P(O)CH_2OTs$[14] (0.44 g, 1.1 mmol) was added to a suspension of **1**[13] (1.04 g, 1.0 mmol) and NaH (24 mg, 10 mmol) in 24 mL of toluene. The reaction mixture was heated to 90 °C and stirred at this temperature for 2 d. After cooling, the unreacted NaH was neutralized carefully by adding aq. 3% HCl. The crude product was extracted with chloroform and dried with $MgSO_4$. Analytically pure product was obtained by medium-pressure column chromatography with ethyl acetate as an eluent, followed by recrystallization from dichloromethane/ethanol (1:5). Yield: 1.20 g (95%). M.p. 172–174 °C. ESI-MS: m/z = 1256 $[M]^+$. ^1H NMR ($CDCl_3$): δ = 0.83 (s, 9 H), 0.98 (s, 18 H), 1.26 (s, 9 H), 1.29 (s, 18 H), 2.23 (s, 6 H, OCH_3), 2.70 (s, 3 H, OCH_3), 3.32 (d, $^2J_{H,H}$ = 15 Hz, 2 H, ArCH_2Ar), 3.37 (s, 6 H, OCH_3), 3.62 (d, $^2J_{H,H}$ = 14 Hz, 2 H, ArCH_2Ar), 3.76 (d, $^2J_{H,H}$ = 14 Hz, 2 H, ArCH_2Ar), 4.12 (d, $^2J_{H,H}$ = 14 Hz, 2 H, ArCH_2Ar), 4.16 (d, $^2J_{H,H}$ = 15 Hz, 2 H, ArCH_2Ar), 4.25 (d, $^2J_{H,H}$ = 14 Hz, 2 H, ArCH_2Ar), 4.74 [d, $^2J_{P,H}$ = 7 Hz, 2 H, OCH_2P(O)Ph_2], 6.68 (s, 2 H), 6.77 (s, 2 H), 6.86 (s, 2 H), 7.13 (s, 2 H), 7.15 (s, 4 H), 7.45–7.58 (m, 6 H), 8.03–8.10 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 29.90, 30.14, 30.19, 31.05, 31.25, 31.48, 31.52, 33.97, 34.00, 34.13, 59.73, 59.86, 60.00, 71.20 [d, $^1J_{P,C}$ = 96 Hz, O*C*H$_2$P(O)Ph_2], 124.23, 124.47, 124.87, 126.78, 127.15, 127.43, 128.70 (d, $^2J_{P,C}$ = 11 Hz), 130.84 (d, $^1J_{P,C}$ = 110 Hz), 131.70 (d, $^2J_{P,C}$ = 9 Hz), 132.30, 132.86, 133.20, 133.24, 133.52, 133.58, 145.60, 145.64, 146.56, 151.95 (d, $^3J_{P,C}$ = 13 Hz), 153.34, 154.14, 154.32 ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 27.9 ppm. $C_{84}H_{105}O_7P{\cdot}H_2O$ (1275.7): calcd. C 79.08, H 8.45; found C 79.44, H 8.40.

5,11,17,23,29,35-Hexa-*tert*-butyl-37-(diphenylphosphanylmethoxy)-38,39,40,41,42-pentamethoxycalix[6]arene (3): $PhSiH_3$ (2.78 g, 25.8 mmol) was added to a solution of **2** (1.08 g, 0.86 mmol) in 20 mL of toluene. The reaction mixture was refluxed for 2 d and then cooled down. After evaporation of the volatiles, an analytically pure product was obtained by recrystallization from dichloromethane/ethanol (1:5). Yield: 0.96 g (90%). M.p. 117–119 °C. ESI-MS: m/z = 1264 $[M + Na]^+$. ^1H NMR ($CDCl_3$): δ = 0.92 (s, 9 H), 1.06 (s, 18 H), 1.27 (s, 9 H), 1.30 (s, 18 H), 2.50 (s, 6 H, OCH_3), 2.81 (s, 3 H, OCH_3), 3.26 (s, 6 H, OCH_3), 3.48 (d, $^2J_{H,H}$ = 15 Hz, 2 H, ArCH_2Ar), 3.70 (d, $^2J_{H,H}$ = 14 Hz, 2 H, ArCH_2Ar), 3.85 (d, $^2J_{H,H}$ = 15 Hz, 2 H, ArCH_2Ar), 4.03 (d, $^2J_{H,H}$ = 15 Hz, 2 H, ArCH_2Ar), 4.19 (d, $^2J_{H,H}$ = 14 Hz, 2 H, ArCH_2Ar), 4.35 (d, $^2J_{H,H}$ = 15 Hz, 2 H, ArCH_2Ar), 4.74 (d, $^2J_{P,H}$ = 4 Hz, 2 H, OCH_2PPh_2), 6.78 (s, 2 H), 6.87 (s, 2 H), 6.93 (s, 2 H), 7.11 (s, 2 H), 7.15 (s, 2 H), 7.24 (s, 2 H), 7.34–7.38 (m, 6 H), 7.60–7.63 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.38, 30.48, 30.64, 31.15, 31.30, 31.49, 31.53, 33.99, 34.04, 34.15, 59.88, 59.92, 60.00, 74.74 (d, $^1J_{P,C}$ = 9 Hz, O*C*H$_2$PPh_2), 124.20, 124.82, 125.11, 126.62, 126.78, 127.42, 128.50 (d, $^2J_{P,C}$ = 6.3 Hz), 128.83, 133.18, 133.30, 133.42, 133.45, 133.62, 136.37 (d, $^1J_{P,C}$ = 11 Hz), 145.57, 145.90, 153.25 (d, $^3J_{P,C}$ = 5 Hz), 153.56, 154.20, 154.38 ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.38, 30.48, 30.64, 31.15, 31.30, 31.49, 31.53, 33.99, 34.04, 34.15, 59.88, 59.92, 60.00, 74.74 (d, $^1J_{P,C}$ = 9 Hz, O*C*H$_2$PPh_2), 124.20, 124.82, 125.11, 126.62, 126.78, 127.42, 128.50 (d, $^2J_{P,C}$ = 6.3 Hz), 128.83, 133.18, 133.30, 133.42, 133.45, 133.62, 136.37 (d, $^1J_{P,C}$ = 11.4 Hz), 145.57, 145.90, 153.25 (d, $^3J_{P,C}$ = 5 Hz), 153.56, 154.20, 154.38 ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 30.44, 30.53, 30.81, 31.38, 31.48, 31.63, 31.68, 34.34, 34.43, 60.20, 60.24, 60.37, 75.02 (d, $^1J_{P,C}$ = 9 Hz, O*C*H$_2$PPh_2), 124.60, 125.09, 125.41, 127.19,

127.40, 127.89, 128.90 (d, $^2J_{P,C}$ = 6 Hz), 129.30, 133.57, 133.69, 133.88, 133.99, 136.83 (d, $^1J_{P,C}$ = 11 Hz), 146.06, 146.37, 153.50 (d, $^3J_{P,C}$ = 5 Hz), 153.85, 154.54, 154.70 ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –16.5 ppm. $C_{84}H_{105}O_6P{\cdot}CH_2Cl_2$ (1326.6): calcd. C 76.95, H 8.13; found C 76.91, H 8.14.

5,11,17,23,29,35-Hexa-*tert*-butyl-37-{(4-diphenylphosphanylphenyl)-methoxy}-38,39,40,41,42-pentamethoxycalix[6]arene (4): $Ph_2P(O)C_6H_4CH_2Br$[15] (0.782 g, 1.17 mmol) was added to a suspension of **1** (1.00 g, 0.95 mmol) and NaH (46 mg, 1.90 mmol) in DMF (25 mL). The reaction mixture was heated to 50 °C and stirred for 20 h. After cooling to room temperature, the unreacted NaH was slowly quenched with MeOH and H_2O. The crude product was extracted with Et_2O/toluene (3:1) and dried with $MgSO_4$. After filtration, the solvent was removed in vacuo and analytically pure product was obtained as a light-yellow solid by preparative GPC using chloroform as an eluent. Yield: 1.19 g (94%). FD-MS: *m*/*z* = 1334 $[M]^+$. ^1H NMR ($CDCl_3$): δ = 0.97 (s, 9 H), 1.01 (s, 18 H), 1.23 (s, 27 H), 2.50 (s, 6 H, OCH_3), 2.76 (s, 3 H, OCH_3), 3.21 (s, 6 H, OCH_3), 3.51 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 3.66 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 3.79 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 4.05 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 4.16 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 4.41 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 4.90 (s, 2 H), 6.82 (d, $^4J_{H,H}$ = 2 Hz, 2 H), 6.88 (s, 2 H), 6.89 (d, $^4J_{H,H}$ = 2 Hz, 2 H), 7.08 (d, $^4J_{H,H}$ = 3 Hz, 2 H), 7.11 (s, 2 H), 7.19 (d, $^4J_{H,H}$ = 3 Hz, 2 H), 7.44–7.72 (m, 14 H) ppm. $^{13}C\{^1H\}$NMR ($CDCl_3$): δ = 30.38, 30.79, 31.36, 31.43, 31.62, 31.70, 34.18, 34.22, 34.26, 59.95, 60.06, 60.11, 73.55, 124.84, 125.06, 125.31, 126.83, 127.07, 127.27, 127.37 (d, $^2J_{P,C}$ = 12 Hz), 128.63 (d, $^2J_{P,C}$ = 12 Hz), 131.27, 132.03, 132.22 (d, $^3J_{P,C}$ = 10 Hz), 132.45 (d, $^3J_{P,C}$ = 11 Hz), 133.11, 133.33, 133.52, 133.63, 133.69, 133.89, 142.17, 142.19, 145.76, 145.87, 146.34, 151.78, 153.68, 154.30, 154.38 ppm. $^{31}P\{^1H\}$NMR ($CDCl_3$): δ = 29.6 ppm. $C_{90}H_{109}O_7P{\cdot}CHCl_3$ (1453.2): calcd. C 75.21, H 7.63; found C 75.12, H 7.77.

5,11,17,23,29,35-Hexa-*tert*-butyl-37-{(4-diphenylphosphanylphenyl)-methoxy}-38,39,40,41,42-pentamethoxycalix[6]arene (5): A suspension of **4** (800 mg, 0.60 mmol) in toluene (12 mL) was refluxed in the presence of $PhSiH_3$ (2.2 mL, 18.0 mmol) for 2 d. The solvent was then removed under reduced pressure and the residue dissolved in CH_2Cl_2 (2 mL). Reprecipitation with MeOH afforded the product as a white solid. Analytically pure product was obtained by recrystallization from dichloromethane/MeOH (2:5). Yield: 646 mg (82%). FD-MS: *m*/*z* = 1318 $[M]^+$. ^1H NMR ($CDCl_3$): δ = 0.97 (s, 9 H), 1.02 (s, 18 H), 1.23 (s, 9 H), 1.24 (s, 18 H), 2.49 (s, 6 H, OCH_3), 2.76 (s, 3 H, OCH_3), 3.22 (s, 6 H, OCH_3), 3.51 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 3.68 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 3.81 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 4.04 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 4.16 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 4.43 (d, $^2J_{H,H}$ = 15 Hz, 2 H, $ArCH_2Ar$), 4.86 (s, 2 H, CH_2), 6.82 (d, $^4J_{H,H}$ = 2 Hz, 2 H), 6.87 (s, 2 H), 6.90 (d, $^2J_{H,H}$ = 2 Hz, 2 H), 7.08 (d, $^2J_{H,H}$ = 2 Hz, 2 H), 7.11 (s, 2 H), 7.22 (d, $^2J_{H,H}$ = 2 Hz, 2 H), 7.30–7.34 (m, 12 H), 7.49–7.52 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.42, 30.76, 30.80, 31.32, 31.39, 31.59, 34.15, 34.16, 34.24, 59.91, 60.01, 60.09, 73.94, 124.66, 125.02, 125.23, 126.86, 127.01, 127.38, 127.81 (d, $^2J_{P,C}$ = 8 Hz), 128.59 (d, $^2J_{P,C}$ = 7 Hz), 128.78, 130.19, 133.32, 133.44, 133.67, 133.72, 133.90, 133.93, 134.13, 145.71, 145.79, 146.10, 151.95, 153.64, 154.30, 154.39 ppm. ^{31}P NMR ($CDCl_3$): δ = –5.62 ppm. $C_{90}H_{109}O_6P{\cdot}CH_3OH$ (1349.8): calcd. C 80.97, H 8.44; found C 80.63, H 8.32.

$[PtCl_2(3)_2]$: A solution of ligand **3** (200 mg, 0.16 mmol) in CH_2Cl_2 (10 mL) was added to a solution of $[PtCl_2(COD)]$ (29.9 mg, 0.08 mmol) in 6 mL of CH_2Cl_2 over a period of 15 min. The solution was stirred at room temperature for 2 h. The resulting solution was then concentrated to about 0.5 mL under vacuum and the product was precipitated with ethanol (3 mL). The solid obtained was filtered and washed with ethanol to afford a pure product. Yield: 172 mg (78%). ESI-MS: *m*/*z* = 2770 $[M + Na]^+$. ^1H NMR ($CDCl_3$): δ = 0.76 (s, 18 H), 0.88 (s, 36 H), 1.31 (s, 18 H), 1.32 (s, 36 H), 2.03 (s, 12 H, OCH_3), 2.43 (s, 6 H, OCH_3), 3.05 (d, $^2J_{H,H}$ = 15 Hz, 4 H, $ArCH_2Ar$), 3.47–3.57 (m, 16 H, OCH_3 overlapped with $ArCH_2Ar$), 3.66 (d, $^2J_{H,H}$ = 15 Hz, 4 H, $ArCH_2Ar$), 3.72 (d, $^2J_{H,H}$ = 15 Hz, 4 H, $ArCH_2Ar$), 4.23 (d, $^2J_{H,H}$ = 15 Hz, 4 H, $ArCH_2Ar$), 4.30 (d, $^2J_{H,H}$ = 15 Hz, 4 H, $ArCH_2Ar$), 5.07 (br. s, 4 H, OCH_2PPh_2), 6.51 (br. s, 4 H), 6.69 (br. s, 4 H), 6.74 (br. s, 4 H), 7.06 (br. s, 4 H), 7.10–7.23 (m, 16 H), 7.27–7.37 (m, 4 H), 7.78–7.90 (m, 8 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 29.84, 30.33, 30.54, 31.40, 31.60, 31.98, 34.33, 34.38, 34.57, 59.82, 60.34, 77.27, 77.59, 124.24, 124.63, 125.40, 126.53, 127.49, 127.66, 128.22, 128.76, 131.90, 133.14, 133.44, 133.55, 133.93, 134.05, 135.06, 135.15, 136.37 145.87, 146.01, 146.91, 153.47, 154.70 ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 6.0 ($^1J_{Pt,P}$ = 3611 Hz) ppm. $C_{168}H_{210}Cl_2O_{12}P_2Pt{\cdot}CH_2Cl_2$ (2834.3): calcd. C 71.62, H 7.54; found C 71.45, H 7.57.

$[Rh(COD)(3)_2]BF_4$: A solution of ligand **3** (100 mg, 0.08 mmol) in CH_2Cl_2 (12 mL) was added to a solution of $[Rh(COD)_2]BF_4$ (17.2 mg, 0.04 mmol) in 6 mL of THF over a period of 15 min. The solution was stirred at room temperature for 3 h. Removal of the solvent gave a crude product as yellow solid, which was purified by reprecipitation from CH_2Cl_2 solution with hexane. Yield: 72.4 mg (68%). ESI-MS: *m*/*z* = 2694 $[M - BF_4^-]^+$. ^1H NMR ($CDCl_3$): δ = 0.76 (s, 18 H), 0.91 (s, 36 H), 1.30 (s, 18 H), 1.34 (s, 36 H), 2.09 (s, 12 H, OCH_3), 2.24–2.41 (m, 8 H), 2.46 (s, 6 H, OCH_3), 2.58 (br., 4 H), 2.66 (d, *J* = 15 Hz, 4 H, $ArCH_2Ar$), 3.51 (s, 12 H, OCH_3), 3.61 (d, *J* = 14 Hz, 4 H, $ArCH_2Ar$), 3.66 (d, $^2J_{H,H}$ = 15 Hz, 4 H, $ArCH_2Ar$), 4.23 (d, $^2J_{H,H}$ = 15 Hz, 4 H, $ArCH_2Ar$), 4.30 (d, $^2J_{H,H}$ = 15 Hz, 4 H, $ArCH_2Ar$), 4.54 (br., 4 H, OCH_2PPh_2), 5.10 (br., 4 H), 6.46 (br., 4 H), 6.72 (br., 4 H), 6.78 (br., 4 H), 6.99 (br., 4 H), 7.16 (br., 4 H), 7.19 (br., 4 H), 7.34–7.47 (m, 12 H), 7.86–7.98 (m, 8 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.04, 30.27, 30.45, 31.16, 31.42, 31.62, 31.96, 32.00, 34.32, 34.40, 34.61, 60.01, 60.39, 77.62, 99.10, 124.40, 124.84, 127.60, 127.92, 128.56, 129.60, 132.02, 132.78, 132.92, 133.53, 133.88, 133.97, 134.93, 146.09, 146.78, 152.45, 153.47, 154.60 ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.8 (d, $^1J_{Rh,P}$ = 141 Hz) ppm. $C_{176}H_{222}BF_4O_{12}P_2Rh{\cdot}CH_2Cl_2$ (2866.2): calcd. C 74.17, H 7.88; found C 74.27, H 7.91.

Hydroformylation: In a typical experiment, $[Rh(COD)_2]BF_4$ (2 mg, 0.005 mmol) and **3** (25 mg, 0.02 mmol) were introduced into a 50-mL stainless-steel autoclave (Toyo koatsu) under argon. Benzene (2 mL), decane (71 mg, 0.5 mmol, as an internal standard), and 1-hexene (84 mg, 1 mmol) were then added and the resulting solution was stirred under argon for 1 h. The autoclave was then pressurized to 10 atm with H_2/CO (1:1) and the reaction mixture was stirred at 70 °C for 16 h. The products were analyzed by GC and GC-MS and the structures were confirmed by spectral comparison with authentic aldehydes. The GC yields were determined by the internal standard method.

X-ray Crystallography: Details of the crystal data and a summary of intensity data collection parameters for **3** and $[PtCl_2(3)_2]$ are given in Table 5. Single crystals of **3** and $[PtCl_2(3)_2]$ were grown by slow diffusion of ethanol into a toluene solution of **3** and diffusion of methanol into a toluene solution of $[PtCl_2(3)_2]$. Data were collected with a Rigaku Saturn CCD diffractometer area detector with graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å) to a maximum 2θ value of 55.0°. The structures were solved by direct methods using the program SIR2002[42] and expanded using Fou-

Table 5. Crystal and structure refinement data for **3** and $[PtCl_2(\mathbf{3})_2]$.

Param	**3**	$[PtCl_2(\mathbf{3})_2]$
Empirical formula	$C_{84}H_{105}O_6P{\cdot}C_7H_8{\cdot}0.5C_2H_6O$	$C_{168}H_{210}Cl_2O_{12}P_2Pt{\cdot}4C_7H_8$
Formula mass	1356.90	3182.09
Temperature [°C]	–160(1)	–160(1)
Wavelength [Å]	0.71070	0.71070
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$(#2)	$P\bar{1}$(#2)
a [Å]	11.557(2)	21.50(7)
b [Å]	12.946(6)	24.63(10)
c [Å]	28.47(3)	18.83(7)
α [°]	81.4(1)	100.61(8)
β [°]	79.01(12)	106.98(5)
γ [°]	84.89(10)	97.96(7)
V [Å^3]	4126.7(46)	9174.8(60)
Z	2	2
$D_{calcd.}$ [g cm^{-3}]	1.092	1.152
μ [cm^{-1}]	0.85	8.66
Crystal size [mm]	0.30 × 0.10 × 0.06	0.30 × 0.20 × 0.16
No. of reflections measured	33429	90674
No. of unique reflections, R_{int}	16706, 0.045	90564, 0.085
R_1[a]	0.099[b]	0.098[c]
wR_2	0.107[d]	0.223[e]
GOF	1.145	1.164

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $I > 2.3\sigma(I)$. [c] $I > 2.0\sigma(I)$. [d] wR_2 $[I > 2.3\sigma(I)] = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = [0.0010F_o^2 + 3.0000\sigma(F_o^2) + 0.5000]^{-1}$. [e] wR_2 (all data) $= [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (0.0713P)^2 + 43.3300P]^{-1}$ where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

rier techniques.[43] For **3**, non-hydrogen atoms except some of the solvent molecules were refined anisotropically. Hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares refinement on F was based on 8953 observed reflections [$I > 2.3\sigma(I)$] and 881 variable parameters. A Sheldrick weighting scheme was used. For $[PtCl_2(\mathbf{3})_2]$, non-hydrogen atoms except some *tert*-butyl carbon atoms and solvent molecules were refined anisotropically. Some *tert*-butyl carbon atoms were disordered over multiple positions, which were refined isotropically at fixed positions with appropriate occupation factors without hydrogen atoms. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 41459 observed reflections (using all data) and 1785 variable parameters. Neutral-atom scattering factors were taken from Cromer and Waber.[44] Anomalous dispersion effects were included in F_c.[45] All calculations were performed with the CrystalStructure[46] crystallographic software package except for the refinement of $[PtCl_2(\mathbf{3})_2]$, which was performed with SHELXH-97.[47] CCDC-278415 (**3**) and -278416 $[PtCl_2(\mathbf{3})_2]$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): X-ray structure of **2** and ROESY spectrum of **3**.

[1] a) C. D. Gutsche, *Calixarenes Revisited; Monographs in Supramolecular Chemistry* (Ed.: J. F. Stoddart), Royal Society of Chemistry, Cambridge **1998**; b) V. Böhmer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 713; c) S. Shinkai, *Tetrahedron* **1993**, *49*, 8933; d) L. Mandolini, R. Ungaro, *Calixarenes in Action*, Imperial College Press, London, UK, **2000**.

[2] a) C. Wiser, C. B. Dielman, D. Matt, *Coord. Chem. Rev.* **1997**, *165*, 93; b) I. Neda, T. Kaukorat, R. Schmutzler, *Main Group Chem. News* **1998**, *6*, 4.

[3] a) L. Brandsma, S. F. Vasilevsky, H. D. Verkruijsse, *Applications of Transition Metals Catalysts, in Organic Synthesis*, Springer, Berlin, **1999**; b) *Homogeneous Catalysis with Metal Phosphine Complexes* (Ed.: L. H. Pignolet), Plenum, New York, **1983**.

[4] We have recently prepared a bowl-shaped phosphane and a phosphane-containing dendrimer unit, see: a) O. Niyomura, M. Tokunaga, Y. Obora, T. Iwasawa, Y. Tsuji, *Angew. Chem. Int. Ed.* **2003**, *42*, 1287; b) B. S. Balaji, Y. Obora, D. Ohara, S. Koide, Y. Tsuji, *Organometallics* **2001**, *20*, 5342.

[5] For selected recent examples of phosphanylcalix[4]arenes, see: a) S. Kim, J. S. Kim, O. J. Shon, S. S. Lee, K. M. Park, S. O. Kang, J. Ko, *Inorg. Chem.* **2004**, *43*, 2906; b) P. Kuhn, C. Jeunesse, D. Sémeril, D. Matt, P. Lutz, R. Welter, *Eur. J. Inorg. Chem.* **2004**, 4602; c) F. Plourde, K. Gilbert, J. Gagnon, P. D. Harvey, *Organometallics* **2003**, *22*, 2862; d) M. Lejeune, C. Jeunesse, D. Matt, N. Kyritsakas, R. Welter, J. P. Kintzinger, *J. Chem. Soc., Dalton Trans.* **2002**, 1642; e) C. Kunze, D. Selent, I. Neda, R. Schmutzler, A. Spannenberg, A. Börner, *Heteroatom Chem.* **2001**, *12*, 577; f) C. Dieleman, S. Steyer, C. Jeunesse, D. Matt, *J. Chem. Soc., Dalton Trans.* **2001**, 2508; g) C. Jeunesse, C. Dieleman, S. Steyer, D. Matt, *J. Chem. Soc., Dalton Trans.* **2001**, 881; h) M. Vénzina, J. Gagnon, K. Villeneuve, M. Drouin, P. D. Harvey, *Organometallics* **2001**, *20*, 273; i) M. Vénzina, J. Gagnon, K. Villeneuve, M. Drouin, P. D. Harvey, *Chem. Commun.* **2000**, 1073; j) S. Shimizu, S. Shirakawa, Y. Sasaki, C. Hirai, *Angew. Chem. Int. Ed.* **2000**, *39*, 1256; k) I. A. Bagatin, D. Matt, H. Thönnessen, P. G. Jones, *Inorg. Chem.* **1999**, *38*, 1585; l) C. B. Dieleman, C. Marsol, D. Matt, N. Kyritsakas, A. Harriman, J.-P. Kintzinger, *J. Chem. Soc., Dalton Trans.* **1999**, 4139; m) C. Wieser-Jeunesse, D. Matt, A. De Cian, *Angew. Chem. Int. Ed.* **1998**, *37*, 2861; n) C. Wieser, D. Matt, J. Fischer, A. Harriman, *J. Chem. Soc., Dalton Trans.* **1997**, 2391; o) X. Fang, B. L. Scott, J. G. Watkin, C. A. G. Carter, G. J. Kubas, *Inorg. Chim. Acta* **2001**, *317*, 276.

[6] a) K. Takenaka, Y. Obora, L. Jiang, Y. Tsuji, *Organometallics* **2002**, *21*, 1158; b) K. Takenaka, Y. Obora, L. Jiang, Y. Tsuji, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1709; c) K. Takenaka, Y. Obora, Y. Tsuji, *Inorg. Chim. Acta* **2004**, *357*, 3895.

[7] J. P. M. van Duynhoven, R. G. Janssen, W. Verboom, S. M. Franken, A. Casnati, A. Pochini, R. Ungaro, J. de Mendoza, P. M. Nieto, P. Prados, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1994**, *116*, 5814, and references cited therein.

[8] J. F. Malone, D. J. Marrs, M. A. McLervey, P. O'Hagan, N. Thompson, A. Walker, F. Arnaud-Neu, O. Mauprivez, M.-J. Schwing-Weill, J.-F. Dozol, H. Rouquette, N. Simon, *J. Chem. Soc., Chem. Commun.* **1995**, 2151.
[9] Y. Obora, Y. Liu, L. Jiang, K. Takenaka, M. Tokunaga, Y. Tsuji, *Organometallics* **2005**, *24*, 4.
[10] For monophosphorylated (P^V) calix[6]arenes, see: a) R. G. Janssen, W. Verboom, S. Harkema, G. J. van Hummel, D. N. Reinhoudt, A. Pochini, R. Ungaro, P. Prodos, J. de Mendoza, *J. Chem. Soc., Chem. Commun.* **1993**, 506; b) R. G. Janssen, J. P. M. van Duynhoven, W. Verboom, G. J. van Hummel, S. Harkema, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1996**, *118*, 3666.
[11] a) G. T. Grisp, *Chem. Soc. Rev.* **1998**, *27*, 427; b) T. Hayashi, *Acc. Chem. Res.* **2000**, *33*, 354.
[12] C. B. Dieleman, D. Matt, I. Neda, R. Schmutzler, A. Harriman, R. Yaftian, *Chem. Commun.* **1999**, 1911.
[13] J. de Mendoza, M. Carramolino, F. Cuevas, P. M. Nieto, P. Prados, D. N. Reinhoudt, W. Verboom, R. Ungaro, A. Casnati, *Synthesis* **1994**, 47.
[14] a) R. S. Marmor, D. Seyferth, *J. Org. Chem.* **1969**, *34*, 748; b) A. W. Spassov, Z. D. Raikov, *Z. Chem.* **1971**, *11*, 262.
[15] D. Gloyna, L. Alder, H. G. Henning, H. Koeppel, M. Siegmund, K. D. Schleinitz, *J. Prakt. Chem.* **1980**, *322*, 237.
[16] F. Pérez-Balderas, F. Santoyo-Gonzalés, *Synlett* **2001**, 1699.
[17] We also carried out an X-ray crystal structure analysis of **5**. However, partly due to crystal instability, good crystals of **5** for detailed X-ray analysis could not be obtained and the *R* value did not converge to an acceptable level. Nonetheless, a preliminary X-ray analysis showed that the structure of **5** is indeed in its 1,2,3-alternate conformation, as was observed in **3**.
[18] S. Kanamathareddy, C. D. Gutsche, *J. Am. Chem. Soc.* **1993**, *115*, 6572.
[19] a) L. N. Markovsky, V. I. Kalchenko, M. A. Vysotsky, V. V. Pirozhenko, Y. A. Simonov, A. A. Dvorkin, A. V. Iatsenko, J. Lipkowski, *Supramolecular Chem.* **1997**, *8*, 85; b) R. Ungaro, A. Pochini, G. D. Andreetti, P. Domiano, *J. Incl. Phenom.* **1983**, *1*, 135; c) F. Arnaud-Neu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. McKervey, E. Marques, B. L. Ruhl, M. J. Schwing-Weill, E. M. Seward, *J. Am. Chem. Soc.* **1989**, *111*, 8681.
[20] A. Bax, M. F. Summers, *J. Am. Chem. Soc.* **1986**, *108*, 2093.
[21] C. D. Gutsche, *Calixarenes; Monographs in Supramolecular Chemistry* (Ed.: J. F. Stoddart); Royal Society of Chemistry, London **1989**, pp 110–111.
[22] S. Kanamathareddy, C. D. Gutsche, *J. Org. Chem.* **1994**, *59*, 3871.
[23] C. Jaime, J. de Mendoza, P. Prados, P. M. Nieto, C. Sánchez, *J. Org. Chem.* **1991**, *56*, 3372.
[24] a) J. Magrans, A. M. Rincón, F. Cuevas, J. López-Prados, P. M. Nieto, M. Pons, P. Prados, J. de Mendoza, *J. Org. Chem.* **1998**, *63*, 1079; b) S. Kanamatharenddy, C. D. Gutsche, *J. Org. Chem.* **1992**, *57*, 3160; c) E. D. Silva, L. Memmi, A. W. Coleman, B. Rather, M. J. Zaworotko, *J. Supramol. Chem.* **2001**, *1* 135; d) E. A. Shokova, E. V. Khomich, N. N. Akhmetov, I. M. Vatsuro, Y. N. Luzikov, V. V. Kovalev, *Russ. J. Org. Chem.* **2003**, *39*, 368.
[25] A similar conformational difference between a crystalline and a solution state has also been observed for phosphane oxide analogs **2**. In the crystalline state, **2** adopts the 1,2,3-alternate structure (see Figure S1 and Table S1 in the Supporting Information), while the characteristic ^1H and $^{13}C\{^1H\}$ NMR resonances in $CDCl_3$ (see Exp. Sect.) show that **2** has a cone structure in the solution.
[26] a) H. Goto, E. Osawa, *J. Am. Chem. Soc.* **1989**, *111*, 8950; b) H. Goto, E. Osawa, *J. Chem. Soc., Perkin Trans. 2* **1993**, 187.
[27] a) T. A. Halgren, *J. Comput. Chem.* **1999**, *20*, 720; b) T. A. Halgren, *J. Comput. Chem.* **1996**, *17*, 490.
[28] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[29] a) T. H. Dunning, Jr., P. J. Hay, in *Modern Theoretical Chemistry* (Ed.: H. F. Schaefer III), Plenum, New York **1976**, vol. 3, p. 1; b) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270; c) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284; d) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
[30] A. W. Kleij, B. Souto, C. J. Pastor, P. Prados, J. de Mendoza, *J. Org. Chem.* **2004**, *69*, 6394.
[31] K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251.
[32] H. Kin-Chee, G. M. McLaughlin, M. McPartlin, G. B. Bobertson, *Acta Crystallogr., Sect. B* **1982**, *38*, 421.
[33] C. Loeber, C. Wieser, D. Matt, A. De Cian, J. Fischer, L. Toupet, *Bull. Soc. Chim. Fr.* **1995**, *132*, 166.
[34] a) R. Favcz, R. Roulet, A. A. Pinkerton, D. Schwarzenbach, *Inorg. Chem.* **1980**, *19*, 1356; b) P. S. Pregosin, R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Springer-Verlag, Berlin, **1976**, Vol. 16.
[35] a) G. K. Anderson, R. J. Cross, *Chem. Soc. Rev.* **1980**, *9*, 185; b) P. Haake, R. M. Pfeiffer, *J. Am. Chem. Soc.* **1970**, *92*, 4996.
[36] M. P. Anderson, L. H. Pignolet, *Inorg. Chem.* **1981**, *20*, 4101.
[37] a) F. Agbossou, J.-F. Carpentier, A. Mortreux, *Chem. Rev.* **1995**, *95*, 2485; b) S. Gladiali, J. C. Bayón, C. Claver, *Tetrahedron: Asymmetry* **1995**, *6*, 1453; c) T. Bartik, H. Ding, B. Bartik, B. E. Hanson, *J. Mol. Catal.* **1995**, *98*, 117.
[38] W. L. F. Armarego, D. D. Perrin, *Purification of Laboratory Chemicals*, 4th ed., Butterworth-Heinemann, Oxford, U. K. **1997**.
[39] T. G. Shenck, J. M. Downs, C. R. C. Milne, P. B. Mackenzie, H. Boucher, J. Whealan, B. Bosnich, *Inorg. Chem.* **1985**, *24*, 2334.
[40] J. X. McDermott, J. F. White, G. M. Whitesides, *J. Am. Chem. Soc.* **1976**, *98*, 6521.
[41] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03*, Revison A.1, Gaussian, Inc., Pittsburgh, PA, **2003**.
[42] M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, *SIR2002*, **2003**.
[43] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, *DIRDIF99, The DIRDIF-99 program system*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1999**..
[44] D. T. Cromer, J. T. Waber, in *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, U. K. **1974**, vol. IV.
[45] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.
[46] a) Crystal Structure Analysis Package, Rigaku and Rigaku/MSC, *CrystalStructure*, ver. 3.6.0., 9009 New Trails Dr., The Woodlands, TX 77381, USA, **2000**–**2004**; b) D. J. Watkin, C. K. Prout, J. R. Carruther, P. W. Betteridge, Chemical Crystallography Laboratory, Oxford, U. K., **1996**.
[47] G. M. Sheldrick, *SHELX97*, **1997**.

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