Calix[4]arene Ligands with Phosphorus-Containing Groups Tethered at the Upper Rim

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The preparation and coordinative properties of two upper-rim functionalized calixarenes, 5,17-bis(*tert*-butyl)-11,23-bis(diethoxyphosphinomethoxy)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix [4] arene (**4**) and 5,17-bis(*tert*-butyl)-11,23-bis(diphenylphosphinomethyl)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene (**6**) are presented. Diphosphine **6** was oxidized by air to the corresponding di(phosphine oxide) **7**. The molecular structure of **7**·2$CHCl_3$ was elucidated by X-ray crystallography: $C_{78}H_{94}O_{10}P_2$·2$CHCl_3$, $a = 16.313$ (5) Å, $b = 16.553(5)$ Å, $c = 17.068(6)$ Å, $\alpha = 108.04(2)°$, $\beta = 93.13(2)°$, $\gamma = 100.27(2)°$, $Z = 2$. The calixarene matrix displays a pinched cone conformation, with the two ^{t}Bu-phenoxy rings of the macrocycle lying almost perpendicular (interplanar angle 84.7°) and the other two phenoxy rings making an angle of 20.9°. Reaction of **6** with 2 equiv of [AuCl(SC_4H_8)] (SC_4H_8 = tetrahydrothiophene) in CH_2Cl_2 afforded the digold complex **6**·$(AuCl)_2$ (**8**). Reaction of **6** with $[RuCl_2(p\text{-cymene})]_2$ resulted in formation of the dinuclear complex **6**·$[RuCl_2(p\text{-cymene})]_2$ (**9**) while the rhodium complex **6**·$[RhCl(norbornadiene)]_2$ (**10**) was formed by reaction of **6** with $[RhCl(norbornadiene)]_2$. Complex **10** catalyzes hydroformylation of styrene ($CO/H_2 = 1$, $P = 40$ bar, 70 °C, styrene/Rh ∼ 585) in the presence of NEt_3, from which linear and branched aldehydes were obtained in a 9:91 ratio. Diphosphite **4** was found to be suitable for chelate formation; thus $[Pd(\eta^3\text{-}MeC_3H_4)(thf)_2]BF_4$ (thf = tetrahydrofuran) reacts with **4** to yield the mononuclear complex [**4**·{$Pd(\eta^3\text{-}MeC_3H_4)$}]$BF_4$ (**11**), where the metal is located at the mouth of the cavity. All complexes were characterized by elemental analyses and by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

Introduction

The calix[4]arene matrix is a versatile, cavity-containing building block frequently used as a tool for the construction of organized polytopic ligands.[1−3] Its extensive use in supramolecular chemistry[4,5] started after Gutsche's pioneering work on synthetic methods for making this synthon readily accessible.[6] Many current studies focus on the functionalization of the calixarene platform, the main aim being to identify applications for the resultant circularly arranged binding units.[7,8] This strategy has already led to the discovery of a number of highly selective receptor molecules and of novel sensors for polyanionic species.[9,10] The idea of combining calixarene cavities with catalytic centers, notably transition metals, has emerged more recently.[3,11−13] One potentiality of such systems is to provide novel materials where the catalytic center operates inside a spatially confined environment.[14] This research is intended to identify catalysts displaying shape-selectivity and/or high regioselectivity.

Of particular interest in this area are the so-called phosphacalixarenes,[15] *i.e.* calixarenes that bear pendant P(III) atoms (notably phosphines, phosphites, phosphinites, etc.) able to form complexes with most transition metals. A synthetic methodology has already been developed that allows positioning of metallo fragments near the mouth of phosphacalix[4]arene tunnels, a feature that appears to be essential for achieving supramolecular catalysis.[14,16−19] To date, most studies have concerned calix[4]-

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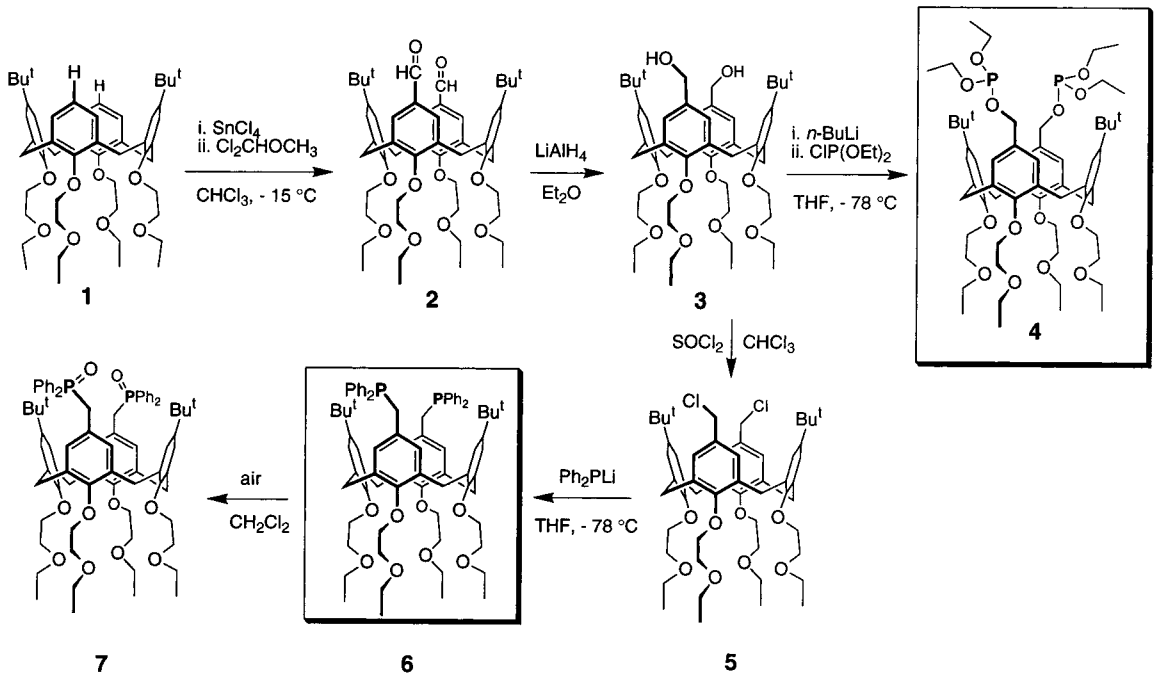
Scheme 1. Synthesis of Compounds **4**, **6**, and **7**



arenes with P(III) centers located at the lower rim of the macrocycle,[16,20−24] although some upper-rim functionalized P(III) compounds have been reported recently.[25,26] We now describe some new phosphorus-containing calix[4]arenes obtained by upper-rim functionalization of calixarene **1**, and report their coordinative behavior toward various platinum metals. The X-ray structure of a di(phosphine oxide) in which the phosphorus atoms are separated from the upper rim by $-CH_2O-$ spacers is also described.

Results and Discussion

Phosphorylation of 1. The key compound for the present study, diol **3**, was prepared in two steps from compound **1**. Its preparation (Scheme 1) was significantly improved with respect to the original procedure.[27] In the first step, formylation of **1** was achieved with $SnCl_4/Cl_2CHOCH_3$. We found that the highest yield was obtained by operating at −18 °C and by using a stoichiometry of **1**/$SnCl_4$/Cl_2CHOCH_3 of 1:10:4. Under these conditions, dialdehyde **2** was obtained in 88% yield after workup (original synthesis 60%). Reduction of **2** with $LiAlH_4$ in Et_2O gave **3** in quantitative yield. Reaction of **3** with 2 equiv of *n*-BuLi in THF at −78 °C and subsequent treatment with diethylchlorophosphite afforded diphosphite **4** in 93% yield. The NMR data of **4** are fully consistent with a C_2-symmetrical structure. The observed chemical shift of the ArCH_2Ar carbon atoms (31.3 ppm) indicate that the calixarene retains the original cone conformation.[28] To the best of our knowledge, only one other calix[4]arene-derived phosphite has been reported to date.[29] Compound **4** can be handled in air. Note that no hydrolysis was observed when the compound was dissolved in wet $CDCl_3$; this ligand stability contrasts with that of the calix[4]-phosphinites that have been reported previously by our group.[30]

Diphosphine **6** was prepared via compound **5**, itself obtained in high yield by reacting **3** with thionyl chloride. The phosphinylation of **5** was performed using 2 equiv of Ph_2PLi in THF at −78 °C. Compound **6**, after purification by column chromatography is a viscous oil that is highly soluble in common organic solvents. It is air stable in the solid state. The ^{31}P NMR spectrum shows a solitary signal at −10.1 ppm, while the PCH_2 signal appears as a singlet at 2.76 ppm in the ^1H NMR spectrum.

Compound **6** was readily oxidized in solution (see Experimental Section), affording the corresponding di(phosphine oxide) **7** for which molecular structure was established by an X-ray diffraction study and is shown in Figure 1. The compound obtained from a $CHCl_3$ solution crystallizes with two molecules of trichloromethane. The calixarene matrix adopts a "pinched cone" conformation[31] for which two opposite phenoxy rings are almost perpendicular (84.7°) and the other two subtend a dihedral angle of 20.9°. The distance between the centroids of the phosphorus-bearing phenoxy rings is 5.90 Å while that between the other two phenoxy rings is 7.28 Å. The dihedral angles between neighboring phenyls range from 81.2 to 84.7°, while the distances between neighboring phenyl group centers lie between 4.70 and 4.75 Å. The PC−H bonds are oriented toward the center of the bowl while the two PO vectors of the

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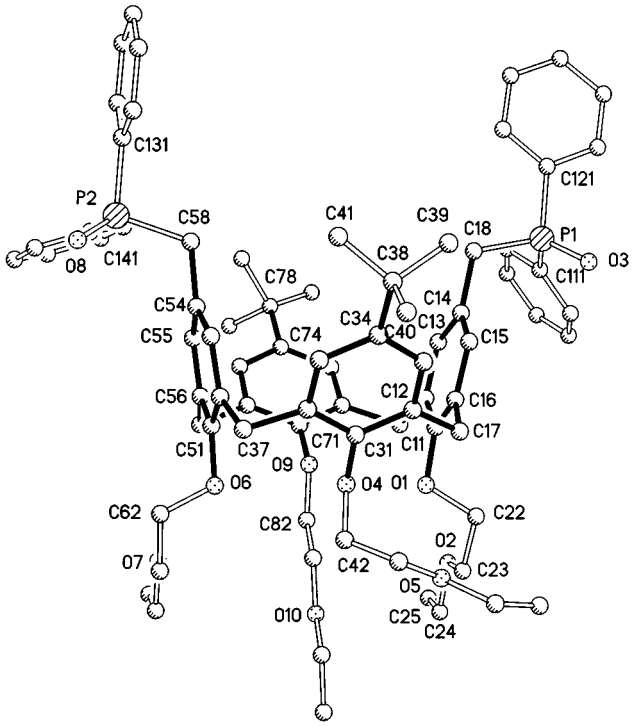


Figure 1. Molecular structure of **7** showing the atom-labeling scheme.

Table 1. Crystallographic Data for **7**·2 $CHCl_3$

empirical formula: $C_{80}H_{96}Cl_6O_{10}P_2$	fw: 1492.21
$a = 16.313(5)$ Å	space group $P\bar{1}$
$b = 16.553(5)$ Å	$T = -100$ °C
$c = 17.068(6)$ Å	$\lambda = 0.710\ 73$ Å
$\alpha = 108.04(2)°$	$\rho_{calcd} = 1.157$ g/cm^{-3}
$\beta = 93.13(2)°$	μ, mm^{-1} = 0.289
$\gamma = 100.27(2)°$	$R_{int} = 0.029$
$V = 4283(2)$ Å^3	$wR(F^2)^a = 0.309$
$Z = 2$	$R(F)^b = 0.094$

^{a} $wR(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ (all reflections). ^{b} $R = \sum||F_o| - |F_c||/\sum|F_o|$ $[F > 4\sigma(F)]$.

Table 2. Selected Atomic Distances (Å) and Bond Angles (deg) for Compound **7**·2$CHCl_3$

P(1)−O(3)	1.501(4)	C(11)−O(1)	1.387(7)
P(1)−C(121)	1.794(6)	C(51)−O(O6)	1.389(6)
P(1)−C(111)	1.809(6)	C(31)−O(4)	1.396(7)
P(1)−C(18)	1.813(5)	C(71)−O(9)	1.397(6)
P(2)−O(8)	1.484(4)	O(1)···O(6)	5.162(5)
P(2)−C(131)	1.803(6)	O(4)···O(9)	3.610(6)
P(2)−C(141)	1.814(6)	C(14)···C(54)	6.450(8)
P(2)−C(58)	1.823(5)	C(34)···C(74)	9.206(8)
P(1)−C(18)−C(14)	112.5(4)	P(2)−C(58)−C(54)	114.3(4)
C(18)−P(1)−O(3)	113.7(3)	C(54)−P(2)−O(8)	113.3(2)

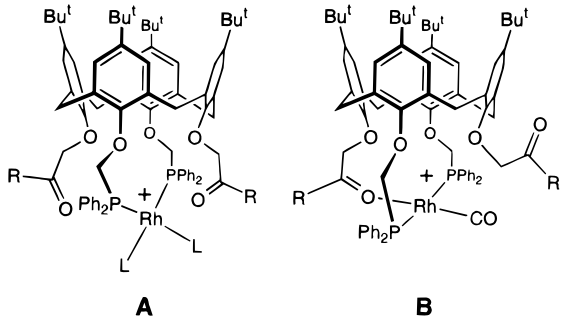
phosphoryl groups point to the exterior of the cavity, so as to minimize steric repulsion between the $Ph_2P(O)$- groups and the adjacent Bu^t substituents. Other important structural data can be drawn from Table 2.

Coordinative Properties. Reaction of **6** with 2 equiv of $[AuCl(SC_4H_8)]$ (SC_4H_8 = tetrahydrothiophene) in CH_2Cl_2 afforded the digold complex **8**. The FAB MS spectrum of **8** exhibits an intense signal at 1650.6 displaying the expected isotopic profile of the corresponding $[M - Cl]^+$ cation. In the ^{1}H NMR spectrum, the ArCH_2Ar bridges give rise to a single AB spin system, while in the ^{31}P NMR spectrum the phosphorus atoms appear as a singlet (at 33.4 ppm).

Treatment of **6** with $[RuCl_2(p\text{-cymene})]_2$ in CH_2Cl_2 gave the binuclear complex **9**, which according to all available NMR data possesses a C_2-symmetrical structure. The chemical shift difference between the two nonequivalent ArCH_2 protons ($\Delta_{AB} = \delta_A - \delta_B = 1.50$) is comparable with those of **6** ($\Delta_{AB} = 1.32$ ppm), **7** ($\Delta_{AB} = 1.33$ ppm), and **8** ($\Delta_{AB} = 1.44$ ppm), indicating that the flattening of the calix matrix is similar in each structure. We note, however, that the signals of the C(CH_3)$_3$, ArCH_2, and *m*-Ar*H*($ArBu^t$) hydrogen atoms of **9** are considerably highfield-shifted with respect to the corresponding signals of **6**, **7**, and **8**. This is because the two bulky "$RuCl_2$(*p*-cymene)" units force the PPh_2 groups to a position above the calixarene cavity so that the above-mentioned H atoms now lie within the shielding zone of the P−Ph aryl rings which close the calixarene cavity.

The dinuclear rhodium complex **10** was obtained by reacting **6** with 2 equiv of $[RhCl(norbornadiene)]_2$ in CH_2Cl_2. The NMR data unambiguously establish the C_2 symmetry of the molecule but in contrast to the observations made for **9** (see above) the ^{1}H NMR chemical shifts of the C(CH_3)$_3$, ArCH_2, and *m*-Ar*H*($ArBu^t$) hydrogen atoms appear to be "normal". Since the RhCl(norbornadiene) fragments are sterically less demanding than the "$RuCl_2$(*p*-cymene)" units found in **9**, free rotation about the P−CH_2 bonds can occur in **10**.

Complex **10** catalyzes the hydroformylation of styrene ($CO/H_2 = 1$, $P = 40$ bar, 70 °C, styrene/Rh ∼ 585) in the presence of NEt_3. The catalytic species shows a high regioselectivity for the branched aldehyde (n/iso = 9:91) while the turnover frequency was 31 mol of alkene/mol of Rh/h. These results are not unusual, lying close to those reported for many Rh/P(III)-systems.[32,33] Addition of 1 equiv of diphosphine **6** to the catalytic system maintains the selectivity but the activity is increased by ca. 60%. The added phosphine probably induces the formation of species where two P(III) atoms are bonded to each rhodium center, thus increasing the electron density of the metal atoms and hence favoring the aldehyde elimination step. It is noteworthy that no decomposition of the catalytic species was observed during these experiments. Hydroformylation experiments with lower-rim functionalized phosphacalixarenes of type **A** and **B** have recently been reported. These were found less



active, probably because the rhodium center is partially encapsulated during the catalytic process.[14,17] The conventional selectivity and activity observed for **10** in styrene hydroformylation suggests that the aromatic substrate is kept from entering the cavity during catalysis by the bulky ^{t}Bu groups. In other terms, the cavity is probably not able to entrap and hence orientate the substrate so as to favor the formation of a specific aldehyde, although this assumption remains somewhat speculative. Removal of the Bu^t groups could possibly also favor synergetic action of the two metal centers, as recently found

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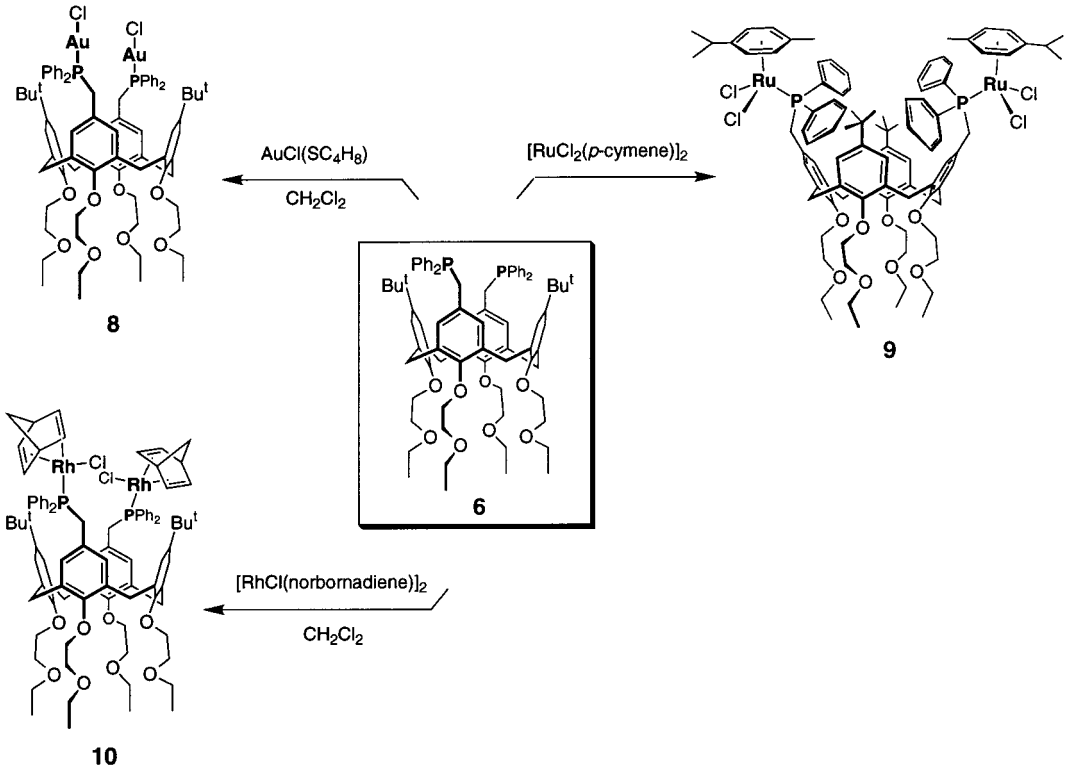
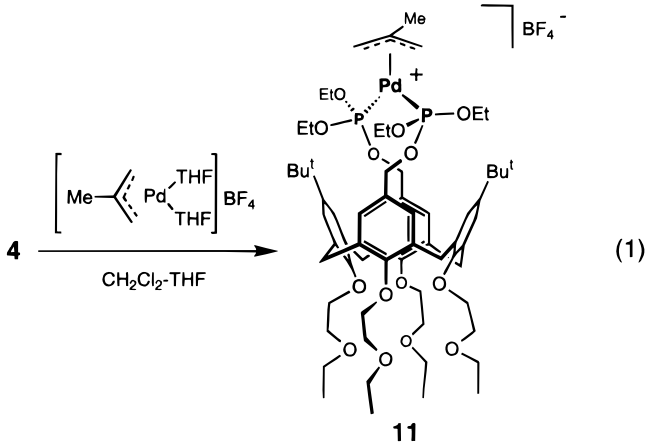
Scheme 2. Dinuclear Complexes Obtained from Diphosphine **6**



by Engbersen et al. in the catalytic phosphate diester cleavage by dinuclear calix[4]arenes bearing two copper(II) centers at the upper rim.[34]

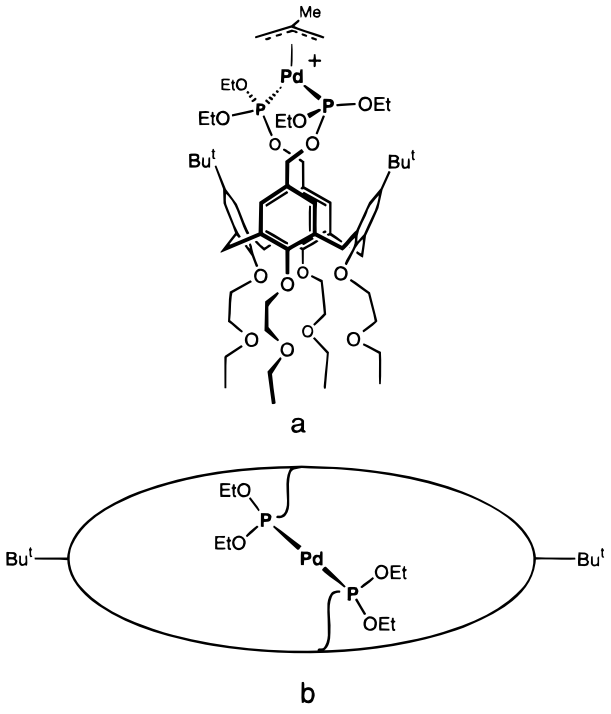
Attempts to prepare well-defined chelate complexes of ligand **6** were hampered by formation of polymeric species. Indeed examination of molecular models suggests that the PPh_2 groups are not well-suited to form stable chelates. In contrast, phosphite **4**, having longer pendant arms, reacts with [Pd(η^3-Me-allyl)-$(thf)_2$]BF_4 to afford the cationic chelate complex **11** in high yield (eq 1). The FAB mass spectrum exhibits an intense signal at



(1)

1285.1, having the expected isotopic profile of the $(\mathbf{11} - BF_4)^+$ cation. The ^{31}P NMR spectrum displays a solitary peak at 127.8 ppm, consistent with phosphite coordination. Interestingly, the ^1H NMR spectrum (300 MHz) shows that the *m*-ArH atoms of the P-substituted aryl rings appear as two distinct broad signals. A COSY experiment established that this nonequivalence is related to H atoms of a same aryl ring. Furthermore, the ^{13}C NMR spectrum displays two $POCH_2CH_3$ signals, indicating that the molecule no longer has C_{2v} symmetry. Examination of molecular models shows that the least-strained and sterically most favorable conformation of the bridge is that with the palladium, phosphorus, and oxygen(P) atoms adopting a twisted arrangement as shown in Scheme 3. Here phosphorus atoms lie on either side of the plane constituted by two aryl *C*-CH_2OP atoms and the metal atom, thus leading to nonequivalent

Scheme 3. Views of the Bridging P−Pd−P Unit in **11** (*a*, Perspective View; *b*, Partial View from the Top)



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m-ArH atoms. However, the fact that the allyl unit generates nonequivalence of the two palladium faces could also account for the observed dissymmetry.

In conclusion, this work describes a new strategy for preparation of upper-rim functionalized calix[4]arenes bearing distal P-containing substituents. It therefore constitutes the starting point for the synthesis of entire families of calixarenes having metals across the upper rim. Two new P(III) ligands have been presented. Ligand **4**, in which the phosphorus atoms are separated from the cavity by $-CH_2O-$ spacers, was found suitable for formation of chelates having a palladium center located above the calix cavity. Diphosphine **6** facilitated the preparation of complexes containing two metal centers that are maintained in close proximity and lie close to a cavity-shaped receptor. The dinuclear rhodium complex **10** displays useful catalytic activity for the hydroformylation of olefins, its activity being that of conventional Rh/PPh_3 systems. Increased selectivity is expected from debutylated analogues which could facilitate access of aromatic substrates to the cavity. The reported complexes open the way to new and important shape-selective catalysts.

Experimental Section

General Procedure. All compounds were handled using Schlenk techniques under a dry nitrogen atmosphere. The solvents were dried and distilled by standard methods. ^{1}H NMR spectra were recorded in $CDCl_3$ (293 K) either on a Bruker AC-200 spectrometer (200 MHz) or on a Bruker AC-300 (300 MHz) instrument. All $^{13}C\{^1H\}$ spectra were recorded in $CDCl_3$ (293 K) at 50.32 MHz, using a Bruker AC-200 spectrometer. ^{31}P spectra were recorded at 121.51 MHz on a Bruker AC-300 spectrometer. The ^{1}H NMR data are referenced to residual $CHCl_3$ (7.25 ppm), ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm), and the ^{31}P NMR data are given relative to external H_3PO_4. Mass spectra were recorded on a ZAB HF VG analytical spectrometer using *m*-nitrobenzyl alcohol as matrix. Column chromatography was performed on silica gel 60 (particle size 40−63 μm, 230−240 mesh). Calixarene **1**,[35] $[AuCl(SC_4H_8)]$,[36] $[RuCl_2(p\text{-cymene})]_2$,[37] $[RhCl(norbornadiene)]_2$,[38] and $[PdCl(\eta^3\text{-2-Me-allyl})]$[39] were synthesized according to procedures reported in the literature. The preparations reported below for **2**,[27] **3**,[27] and **5**[27] correspond to improved methods, and therefore only important spectroscopic data are given for these compounds. Microanalytical data have not been given for these compounds.

Hydroformylation of styrene with complex **10** was performed in a 100 mL glass-lined steel autoclave containing a Teflon-coated magnetic stirrer bar.

5,17-Diformyl-11,23-bis(*tert*-butyl)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene (2). To a solution of **1** (1.940 g, 2.35 mmol) in cold $CHCl_3$ (70 mL, −15 °C) was added $SnCl_4$ (6.183 g, 2.78 mL, 23.50 mmol), followed by Cl_2CHOCH_3 (1.103 g, 0.87 mL, 9.40 mmol). The mixture was stirred vigorously at room temperature for 1 h before being quenched with water (100 mL). The organic layer was separated, washed twice with water, and evaporated under vacuum to afford a yellow oil. Compound **2** was purified by column chromatography using hexane/ethyl acetate (1:1, v/v) as eluant. Compound **2** elutes first (R_f = 0.50; hexane/ethyl acetate, 2:1, v/v). Yield: 1.820 g, 88%. ^{1}H NMR (200.13 MHz): δ 9.22 (s, 2H, CHO), 7.02 and 6.70 (2s, 4H each, *m*-ArH), 4.49 and 3.15 (AB quartet, 8H, $ArCH_2$, J(AB) = 13.5 Hz), 4.17 and 4.05 (2t, 4H each, $ArOCH_2$, ^3J = 7 Hz), 3.82 and 3.77 (two overlapping t, 8H, $ArOCH_2CH_2$), 3.53 and 3.49 (two overlapping q, 8H, OCH_2CH_3, ^3J = 7 Hz), 1.29 (s, 18H, Bu^t), 1.20 and 1.17 (2t, 6H each, OCH_2CH_3, ^3J = 7 Hz each). $^{13}C\{^1H\}$ NMR (50.32 MHz): δ 191.5 (s, CHO), 160.5 and 154.8 (2s, arom. C_q-O), 145.5 (s, C_q-CHO), 135.3 and 134.8 (2s, arom. C_q-CH_2), 131.3 (s, arom. C_q-Bu^t), 129.4 and 126.0 (2s, arom. CH), 73.8 and 73.6 (2s, $ArOCH_2$), 69.6 (s, $ArOCH_2CH_2$), 66.5 and 66.2 (2s, OCH_2CH_3), 34.2 (s, $C(CH_3)_3$), 31.6 (s, $C(CH_3)_3$), 31.1 (s, $ArCH_2$), 15.3 (s, OCH_2CH_3).

5,17-Bis(*tert*-butyl)-11,23-bis(hydroxymethyl)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene (3). To a solution of **2** (1.820 g, 2.07 mmol) in Et_2O (80 mL) was added $LiAlH_4$ (0.314 g, 8.28 mmol). After stirring for 30 min, the mixture was quenched with 0.01 M HCl (100 mL). The organic layer was extracted with CH_2Cl_2 (300 mL), washed twice with water, and dried over $MgSO_4$. The solvent was removed under vacuum to afford a colorless oil. Yield: 1.790 g, 98%. ^{1}H NMR (200.13 MHz): δ 7.09 (s, 4H, *m*-ArH), 6.17 (s, 4H, *m*-ArH), 4.50 and 3.11 (AB quartet, 8H, $ArCH_2Ar$, J(AB) = 13.5 Hz), 4.28 (t, 4H, $ArOCH_2$, ^3J = 7 Hz), 4.01 (s, 4H, CH_2OH), 3.92 and 3.89 (two overlapping t, 8H, $ArOCH_2CH_2$), 3.78 (t, 4H, $ArOCH_2$, ^3J = 7 Hz), 3.58 and 3.53 (two overlapping q, 8H, OCH_2CH_3), 1.37 (s, 18H, Bu^t), 1.25 and 1.18 (2t, 12H, OCH_2CH_3, ^3J = 7 Hz). $^{13}C\{^1H\}$ NMR (50.32 MHz): δ 155.3 and 154.2 (2s, arom. C_q-O), 144.7 (s, arom. C_q-CH_2-OH, tent. assignment), 135.6 (s, arom. C_q-Bu^t, tent. assignment), 134.5 and 133.2 (2s, arom. C_q-CH_2), 125.6 (s, arom. CH), 73.8 and 72.1 (2s, $ArOCH_2$), 69.5 ($ArOCH_2CH_2$), 66.4 and 66.0 (2s, OCH_2CH_3), 64.4 (s, CH_2OH), 34.1 (s, $C(CH_3)_3$), 31.6 (s, $C(CH_3)_3$), 31.0 (s, $ArCH_2Ar$), 15.2 (OCH_2CH_3).

5,17-Bis(*tert*-butyl)-11,23-bis(diethoxyphosphinomethoxy)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene (4). To a solution of **3** (2.000 g, 2.26 mmol) in THF (50 mL) at −78 °C was added *n*-BuLi (1.49 M, 3.18 mL, 4.8 mmol). The solution was maintained for 1 h at −78 °C, and then a solution of $PCl(OEt)_2$ (0.740 g, 4.52 mmol) in THF (5 mL) was added dropwise via a cannula. The solution was brought to room temperature, stirred for 12 h, and evaporated to dryness. The residue was taken up with toluene, and the resultant suspension was filtered over Celite. Evaporation of the solvent gave an analytically pure colorless oil. Yield: 2.360 g, 93%. FAB MS: 1132.3 [85, $(M + Li)^+$]. Anal. Calcd for $C_{62}H_{94}O_{14}P_2$ (M_r = 1125.38): C, 66.17; H, 8.42. Found: C, 65.96; H, 8.37. ^{1}H NMR (300.17 MHz): δ 6.94 (s, 4H, *m*-ArH), 6.30 (s, 4H, *m*-ArH), 4.45 and 3.09 (AB spin system, 8H, $ArCH_2Ar$, ^2J(AB) = 13 Hz), 4.23 (d, 4H, $POCH_2Ar$, ^3J(PH) = 7.7 Hz), 4.19 and 3.97 (2t, 4H each, $ArOCH_2$, ^3J = 7 Hz each), 3.87 (t, 8H, $ArOCH_2CH_2$, ^3J = 7 Hz), 3.82 (m, 8H, $POCH_2CH_3$), 3.56 and 3.51 (two overlapping q, 8H, OCH_2CH_3, ^3J = 7 Hz each), 1.25 (s, 18H, Bu^t), 1.19 (several overlapping m, 24H, $POCH_2CH_3$ and $CH_2OCH_2CH_3$). $^{31}P\{^1H\}$ NMR (121.51 MHz): δ 139.4. $^{13}C\{^1H\}$ NMR (50.32 MHz): δ 154.8 (s, arom. C_q-O), 144.7 (s, arom. C_q-CH_2OP), 134.9 and 134.0 (2s, arom. C_q-CH_2Ar), 131.7 (s, arom. C_q-Bu^t), 127.5 and 125.5 (2s, arom. CH), 73.6 and 72.6 (2s, $ArOCH_2$), 69.6 (s, $ArOCH_2CH_2$), 66.4 and 66.2 (2s, OCH_2CH_3), 63.8 (d, $POCH_2Ar$, ^2J(PC) = 9 Hz), 58.1 (d, $POCH_2CH_3$, ^2J(PC) = 12 Hz), 34.0 (s, $C(CH_3)_3$), 31.5 (s, $C(CH_3)_3$, 31.3 (s, $ArCH_2Ar$), 16.9 (s, $POCH_2CH_3$), 15.3 (s, OCH_2CH_3).

5,17-Bis(*tert*-butyl)-11,23-bis(chloromethyl)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene (5). To a solution of **3** (3.500 g, 3.95 mmol) in $CHCl_3$ (40 mL) was added $SOCl_2$ (1.199 g, ca. 0.74 mL, 9.88 mmol). After stirring for 45 min at room temperature, the solvent and residual $SOCl_2$ were evaporated under vacuum. The oily residue did not require further purification. Yield: 3.567 g, 98%. ^{1}H NMR (200.13 MHz): δ 7.01 (s, 4H, *m*-ArH), 6.28 (s, 4H, *m*-ArH), 4.46 and 3.10 (AB quartet, 8H, $ArCH_2Ar$, ^2J = 13 Hz), 4.22 (t, 4H, $ArOCH_2$, ^3J = 7 Hz), 4.00 (s, 4H, CH_2Cl), 3.98 and 3.88 (two triplets, 4H each, $ArOCH_2CH_2$), 3.80 (t, 4H, $ArOCH_2$), 3.58 and 3.50 (two overlapping q, 8H, OCH_2CH_3), 1.31 (s, 18H, Bu^t), 1.24 and 1.17 (2t, 12H, OCH_2CH_3, ^3J = 7 Hz).

5,17-Bis(*tert*-butyl)-11,23-bis(diphenylphosphinomethyl)-25,26,-27,28-tetrakis(2-ethoxyethoxy)calix[4]arene (6). To a solution of Ph_2PH (1.210 g, 6.50 mmol) in cold THF (10 mL, −78 °C) was added *n*-BuLi (1.49 M, 4.36 mL, 6.5 mmol). The resultant red solution was transferred via a cannula to a stirred solution of **5** (3.000 g, 3.25 mmol) in THF (50 mL, −78 °C). The mixture was stirred overnight at room temperature. Evaporation of the solvent yielded a pale yellow oil which

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was dissolved in toluene so that precipitated LiCl could be removed by filtration over a bed of Celite. The yellow filtrate was evaporated to dryness and purified by column chromatography (hexane/ethyl acetate 2:1) under N_2. Ph_2PH elutes first ($R_f = 0.78$, hexane/ethyl acetate 2:1, v/v), then **6** ($R_f = 0.63$). Yield: 3.360 g, 85%. Mp: 164−166 °C. FAB MS: 1253.4 [72, $(M + 2O + H)^+$], 1237.4 [85, $(M + O + H)^+$], 1221.4 [100, $(M + H)^+$]. Anal. Calcd for $C_{78}H_{94}O_8P_2$ ($M_r = 1221.56$): C, 76.69; H, 7.76. Found: C, 76.32; H, 7.54. ^{1}H NMR (300.17 MHz): δ 7.35−7.28 (20H, PPh_2), 6.78 (s, 4H, *m*-Ar*H*), 5.97 (d, 4H, *m*-Ar*H*, ^4J(PH) 1 Hz), 4.24 and 2.92 (AB spin system, 4H each, ArCH_2Ar, $^2J = 13$ Hz), 4.13 (t, 4H, ArOCH_2, $^3J = 6.7$ Hz), 3.97 (t, 4H, ArOCH_2, $^3J = 7$ Hz), 3.87 (t, 4H, $ArOCH_2CH_2$, $^3J = 7$ Hz), 3.82 (t, 4H, $ArOCH_2CH_2$, $^3J = 7$ Hz), 3.54 and 3.52 (two overlapping q, 8H, OCH_2CH_3, $^3J = 7$ Hz each), 2.76 (s, 4H, PCH_2), 1.22 (t, 6H, OCH_2CH_3, $^3J = 7$ Hz), 1.19 (s, 18H, Bu^t), 1.17 (t, 6H, OCH_2CH_3, $^3J = 7$ Hz). ^{31}P{^{1}H} NMR (121.51 MHz): δ −10.1. ^{13}C{^{1}H} NMR (50.32 MHz): δ 154.8 and153.7 (arom. C_q-O), 144.4−125.3 (arom. C), 73.4 and 72.5 (2s, ArOCH_2), 69.6 (s, $ArOCH_2CH_2$), 66.5 and 66.2 (2s, OCH_2CH_3), 35.3 (d, PCH_2, J(PC) = 15 Hz), 34.0 (s, $C(CH_3)_3$), 31.7 (s, $C(CH_3)_3$), 31.1 (s, ArCH_2Ar), 15.4 (OCH_2CH_3).

5,17-Bis(*tert*-butyl)-11,23-bis(diphenylphosphinoylmethyl)-25,26,-27,28-tetrakis(2-ethoxyethoxy)calix[4]arene (7). A solution of **6** (0.800 g, 0.62 mmol) in CH_2Cl_2 was stirred for 2 h under air. The solution was concentrated, and hexane was added to give a white powder. Yield: 0.656 g, 80%. Mp: 208−210 °C. FAB MS: 1253.5 [100, $(M + H)^+$]. Anal. Calcd for $C_{78}H_{94}O_{10}P_2$ ($M_r = 1252.63$): C, 74.72; H, 7.56. Found: C, 74.85; H, 7.36. ^{1}H NMR (200.13 MHz): δ 7.55−7.29 (20H, PPh_2), 6.73 (s, 4H, *m*-ArH), 5.87 (d, 4H, *m*-ArH, ^4J(PH) = 2.2 Hz), 4.31 and 2.98 (AB spin system, 8H, ArCH_2Ar, J(AB) = 13.7 Hz), 4.11 and 3.93 (2t, 4H each, $ArOCH_2$, $^3J = 7$ Hz each), 3.81 and 3.76 (2t, 4H each, $ArOCH_2CH_2$, $^3J = 7$ Hz each), 3.53 and 3.48 (2q, 4H each, OCH_2CH_3, $^3J = 7$ Hz each), 2.87 (d, 4H, PCH_2, $J = 11$ Hz), 1.22 (t, 6H, OCH_2CH_3, $^3J = 7$ Hz), 1.21 (s, 18H, Bu^t), 1.15 (t, 6H, OCH_2CH_3, $^3J = 7$ Hz). ^{31}P{^{1}H} NMR (121.51 MHz): δ 29.5. ^{13}C{^{1}H} NMR (50.32 MHz): δ 154.8 and 154.0 (2s, arom. C_q-O), 144.4−123.4 (arom. C), 73.4 and 72.5 (2s, ArOCH_2), 69.5 (s, $ArOCH_2CH_2$), 66.4 and 66.2 (2s, OCH_2CH_3), 38.2 (d, PCH_2, J(PC) = 66.3 Hz), 34.0 (s, $C(CH_3)_3$), 31.6 (s, $C(CH_3)_3$), 31.0 (s, ArCH_2Ar), 15.3 (s, OCH_2CH_3).

Bischloro-[5,17-bis(*tert*-butyl)-11,23-bis(diphenylphosphinomethyl)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene]digold(I) (8). A mixture of **6** (0.180 g, 0.147 mmol) and [AuCl(SC_4H_8)] (0.095 g, 0.296 mmol) in CH_2Cl_2 was stirred for 1 h and then filtered over a bed of Celite. The solution was evaporated to dryness under vacuum. The residue was dissolved in CH_2Cl_2; addition of hexane precipitated **8** as a white powder. Yield: 0.182 g, 73%. Mp: 110 °C (decomp) FAB MS: 1650.6 [100, $(M - Cl)^+$]. Anal. Calcd for $C_{78}H_{94}Au_2Cl_2O_8P_2 \cdot CH_2Cl_2$ ($M_r = 1686.40$): C, 53.61; H, 5.47. Found: C, 53.22; H, 5.50. ^{1}H NMR (200.13 MHz): δ 7.57−7.30 (20H, PPh_2), 6.84 (s, 4H, *m*-ArH), 5.90 (d, 4H, *m*-ArH, ^4J(PH) = 2.5 Hz), 4.36 and 2.92 (AB spin system, 4H each, ArCH_2Ar, $^2J = 13$ Hz), 4.15 and 3.97 (2t, 4H each, ArOCH_2, $^3J = 7$ Hz each), 3.83 and 3.76 (two overlapping t, 4H each, $ArOCH_2CH_2$), 3.58 and 3.55 (two overlapping q, 4H each, OCH_2CH_3), 3.10 (d, 4H, PCH_2, $^2J = 10$ Hz), 1.29 (s, 18H, Bu^t), 1.26 and 1.18 (2t, 6H each, OCH_2CH_3, $^3J = 7$ Hz). ^{31}P{^{1}H} NMR (121.51 MHz): δ 33.4. ^{13}C{^{1}H} NMR (50.32 MHz): δ 154.9 (arom. C_q-O), 144.7−124.0 (arom. C), 73.7 and 72.4 (2s, ArOCH_2), 69.5 (s, $ArOCH_2CH_2$), 66.5 and 66.2 (2s, OCH_2CH_3), 35.5 (d, PCH_2, J(PC) = 30 Hz), 34.1 (s, $C(CH_3)_3$), 31.8 (s, $C(CH_3)_3$), 31.1 (s, ArCH_2Ar), 15.4 (s, OCH_2CH_3).

Tetrachlorobis(η^6-1-isopropyl-4-methylbenzene)-[5,17-bis(*tert*-butyl)-11,23-bis(diphenylphosphinomethyl)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene]diruthenium(II) (9). To a solution of **6** (0.200 g, 0.163 mmol) in CH_2Cl_2 (100 mL) was added a solution of [$RuCl_2(\eta^6$-*p*-cymene)]$_2$ (0.100 g, 0.163 mmol) in CH_2Cl_2 (20 mL). The solution was stirred overnight at 50 °C. The red solution was concentrated to ca. 2 mL and hexane was added, yielding a brown powder. Yield: 0.211 g, 71%. Mp: 168−172 °C. FAB MS: 1798.6 [8%, $(M - Cl)^+$]. Anal. Calcd for $C_{98}H_{122}Cl_4O_8P_2Ru_2$ ($M_r = 1832.54$): C, 64.17; H, 6.71. Found: C, 64.07; H, 6.61. ^{1}H NMR (300.17 MHz): δ 7.75−7.66 and 7.38−7.30 (20H, PPh_2), 6.08 (s, 4H, *m*-ArH of ArBu^t), 6.04 (d, 4H, *m*-ArH, ^4J(PH) = 1.9 Hz), 5.26 and 5.12 (2d, AA′BB′ spin system, 8H, arom. CH of *p*-cymene, ^3J(AB) = 6 Hz), 4.07 (t, 4H, $ArOCH_2$, $^3J = 7$ Hz), 4.00 and 2.50 (AB spin system, 8H, ArCH_2Ar, ^2J(AB) = 13 Hz), 3.88 (t, 4H, $ArOCH_2CH_2$, $^3J = 7$ Hz), 3.87 (d, 4H, PCH_2, ^2J(PH) = 7.5 Hz), 3.73 (t, 4H, ArOCH_2, $^3J = 7$ Hz), 3.64 (t, 4H, $ArOCH_2CH_2$, $^3J = 7$ Hz), 3.52 and 3.50 (two overlapping q, 8H, OCH_2CH_3, $^3J = 7$ Hz each), 2.49 (septet, 2H, C*H*$(CH_3)_2$, $^3J = 7$ Hz), 1.84 (s, 6H, *p-Me*-C_6H_4−Pr^i), 1.24 and 1.14 (2t, 6H each, OCH_2CH_3, $^3J = 7$ Hz), 0.90 (d, $CH(CH_3)_2$, 12H, $^3J = 7$ Hz), 0.68 (s, 18H, Bu^t). ^{31}P{^{1}H} NMR (121.51 MHz): δ 30.1. ^{13}C{^{1}H} NMR (50.32 MHz): δ 156.0 and 151.7 (arom. C_q-O), 144.8−124.6 (arom. C), 108.0 and 94.3 (2s, C_q of *p*-cymene), 90.0 and 85.7 (2s, arom. CH of *p*-cymene), 73.7 and 72.3 (2s, $ArOCH_2$), 69.8 and 69.6 (2s, $ArOCH_2CH_2$), 66.3 (s, OCH_2CH_3), 33.5 (s, $C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 30.5 (s, $ArCH_2Ar$), 30.0 (s, $CH(CH_3)_2$), 21.6 (s, $CH(CH_3)_2$), 17.3 (s, *p-*CH_3-C_6H_4-Pr^i), 15.5 and 15.2 (2s, OCH_2CH_3). The PCH_2 signal was not detected.

Bischlorobis(norbornadiene)-[5,17-bis(*tert*-butyl)-11,23-bis(diphenylphosphinomethyl-25,26,27,28-tetrakis(2-ethoxyethoxy)calix-[4]arene]dirhodium(I) (10). To a solution of **6** (0.100 g, 0.082 mmol) in CH_2Cl_2 (100 mL) was added a solution of [Rh(norbornadiene)Cl]$_2$ (0.038 g, 0.082 mmol) in CH_2Cl_2 (20 mL). After stirring for 2 h at room temperature, the yellow solution was concentrated and hexane was added, yielding a pale yellow powder. Yield: 0.082 g, 60%. Mp: 145−147 °C. FAB MS: 1646.4 [100, $(M - Cl)^+$]. Anal. Calcd for $C_{92}H_{110}Cl_2O_8P_2Rh_2$ ($M_r = 1682.56$): C, 65.69; H, 6.60. Found: C, 65.66; H,6.52. ^{1}H NMR (300.17 MHz): δ 7.40−7.27 (20H, PPh_2), 6.64 (s, 4H, *m*-ArH), 6.12 (s, 4H, *m*-ArH), 4.29 and 2.83 (AB spin system, 8H, ArCH_2Ar, ^2J(AB) = 13 Hz,), 4.03 and 4.00 (two overlapping t, 8H, ArOCH_2, $^3J = 7$ Hz each), 3.85 and 3.80 (2t, 4H each, $ArOCH_2CH_2$, $^3J = 6.4$ Hz), 3.68 (s br, 4H, C*H*, NBD), 3.59 and 3.56 (two overlapping q, 8H, OCH_2CH_3, $^3J = 7$ Hz each), 3.37 (d, 4H, PCH_2, $^2J = 8$ Hz,), 1.33 (s, 4H, CH_2 of NBD), 1.20 and 1.18 (two overlapping t, 12H, OCH_2CH_3, $^3J = 7$ Hz each), 1.15 (s, 18H, Bu^t). The olefinic CH signals have not been detected. ^{31}P{^{1}H} NMR (121.51 MHz): δ 31.1 (d, J(RhP) = 168 Hz). ^{13}C{^{1}H} NMR (50.32 MHz): δ 154.2 and 153.8 (2s, arom. C_q-O), 145.0−125.3 (arom. C), 83.9 and 84.9 (2s, HC═CH of NBD, tent. assignment), 74.5−72.0 (several overlapping signals, ArOCH_2 and PCH_2), 69.6 (s, $ArOCH_2CH_2$), 66.4 and 66.3 (2s, OCH_2CH_3), 64.0 (s, CH_2 of NBD), 50.8 (s, CH of NBD), 34.0 ($C(CH_3)_3$), 31.7 (s, $C(CH_3)_3$), 31.0 (s, ArCH_2Ar), 15.3 (s, OCH_2CH_3).

η^3-Methylallyl-[5,17-bis(*tert*-butyl)-11,23-bis(diethoxyphosphinomethoxy)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene]-palladium Tetrafluoroborate (11). To 6 mL of a CH_2Cl_2/THF solution (5:1 v/v) of [Pd(η^3-MeC_3H_4)Cl]$_2$ (0.022 g, 0.059 mmol) was added $AgBF_4$ (0.024 g, 0.12 mmol). After stirring for 5 min, the suspension was filtered over Celite and the filtrate was added to a solution of calixarene **4** (0.133 g, 0.119 mmol) in CH_2Cl_2 (5 mL). After 15 h, the solution was concentrated and pentane was added. Cooling to −20 °C afforded **11** as a yellow powder. Yield: 0.082 g, 70%. FAB MS: 1285.1 [100, M^+]. Anal. Calcd for $C_{66}H_{101}BF_4O_{14}P_2Pd$ ($M_r = 1373.68$): C, 57.71; H, 7.41. Found: C, 58.00; H, 7.71. ^{1}H NMR (300.17 MHz): δ 7.07 (s br, 4H, *m*-ArH of Bu^{t}ArO ring), 6.03 and 5.94 (two s br, 4H, *m*-ArH of P-linked ArO ring, ^5J(PH) < 1 Hz, ^4J(HH) ~ 1 Hz), 4.49 and 3.09 (AB spin system, 8H, ArCH_2Ar, ^2J(AB) = 13 Hz), 4.21 (t, 2H, H_{syn}-allyl), 4.27 (t, 4H, ArOCH_2, $^3J = 7$ Hz), 4.15−3.90 (m, $POCH_2$), 3.90 (t, 4H, ArOCH_2, $^3J = 7$ Hz), 3.86 (t, 4H, $ArOCH_2CH_2$, $^3J = 7$ Hz), 3.76 (t, 4H, $ArOCH_2CH_2$, $^3J = 7$ Hz), 3.57 and 3.47 (two q, 4H each, OCH_2CH_3, $^3J = 7$ Hz each), 3.48 (t, 2H, H_{syn}-allyl), 1.82 (s, 3H, Me of allyl), 1.35 (s, 18H, Bu^t), 1.32 and 1.31 (two t, 12H, $POCH_2CH_3$), 1.24 and 1.14 (two t, 12H, $CH_2OCH_2CH_3$, $^3J = 7$ Hz). ^{31}P{^{1}H} NMR (121.51 MHz): δ 127.8. ^{13}C{^{1}H} NMR (50.32 MHz): δ 155.0 (s, arom. C_q-O), 144.2 (s, arom. C_q-CH_2OP), 135.2−125.7 (arom. C's), 74.1 and 72.1 (2s, ArOCH_2), 69.6 (s, $ArOCH_2CH_2$), 66.7 (s, $POCH_2Ar$), 66.6 and 66.2 (2s, $CH_2OCH_2CH_3$), 62.5 (s, $POCH_2$-CH_3), 61.6 (s, $POCH_2CH_3$), 34.1 (s, $C(CH_3)_3$), 31.8 (s, $C(CH_3)_3$, 31.3 (s, ArCH_2Ar), 23.6 (s, Me of allyl), 16.3 (s, $POCH_2CH_3$), 15.3 (s, $CH_2OCH_2CH_3$).

Hydroformylation Experiments with 10. Experiment without Added Phosphine. In a typical experiment, 10 mL of a solution of **10** (0.012 g, 0.0071 mmol) in toluene/CH_2Cl_2 (9:1 v/v) was introduced under argon into the steel autoclave followed by addition of NEt_3 (0.1 mL, ca. 0.7 mmol) also under argon. The autoclave was pressurized with a 1:1 mixture of CO−H_2 (40 bar) and the temperature was raised

to 70 °C. After 2 h, the autoclave was cooled to room temperature and slowly depressurized. Styrene was introduced (0.5 mL, 0.453 g, 4.33 mmol). The autoclave was then pressurized with $CO-H_2$ (1:1, 40 bar) and heated to 70 °C. After 9 h the autoclave was cooled and the contents analyzed by GC. At this stage, the extent of styrene conversion was 90%. The linear/branched aldehyde ratio was 9:91. The calculated TOF was 30.5 mol of styrene/mol of Rh/h. No ethylbenzene was detected in this experiment.

Experiment with Added Phosphine. In a typical experiment, 20 mL of a solution of **10** (0.025 g, 0.0148 mmol) in toluene/CH_2Cl_2 (19:1) were introduced under argon into the steel autoclave followed by addition, also under argon, of NEt_3 (0.2 mL, ca. 1.4 mmol). The autoclave was pressurized with a 1:1 mixture of $CO-H_2$ (40 bar) and the temperature was raised to 70 °C. After 2 h, the autoclave was cooled to room temperature and slowly depressurized. Styrene was introduced (1.0 mL, 0.906 g, 8.67 mmol). The autoclave was then pressurized with $CO-H_2$ (1:1, 40 bar) and heated to 70 °C. After 6 h the autoclave was cooled and the contents analyzed by GC. At this stage the extent of styrene conversion was 100%. The linear/branched aldehyde ratio was 9:91. The calculated tof was 48.8 mol of styrene/mol of Rh/h. No ethylbenzene was detected.

Structural Determination. Single crystals of **7**·2 $CHCl_3$ were obtained by slow evaporation of a $CHCl_3$ solution. Crystallographic data are summarized in Table 1. Data were collected with Mo Kα radiation (λ = 0.710 73 Å) at low temperature on a Siemens P4 diffractometer. The structure was solved by direct methods and refined anisotropically on F^2, using the program SHELXL-97.[40] H atoms were included using a riding model or rigid methyl groups. The weighting scheme was of the form $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and a and b are constants optimized by the program. Various regions of poorly resolved electron density indicate the presence of further disordered solvent molecules, but no appropriate model could be refined.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for **7**·2 $CHCl_3$ is available free of charge via the Internet at http://pubs.acs.org.

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