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Unusually Large Bite Angle of a Distally Diphosphanylated Calix[4]arene Chelator

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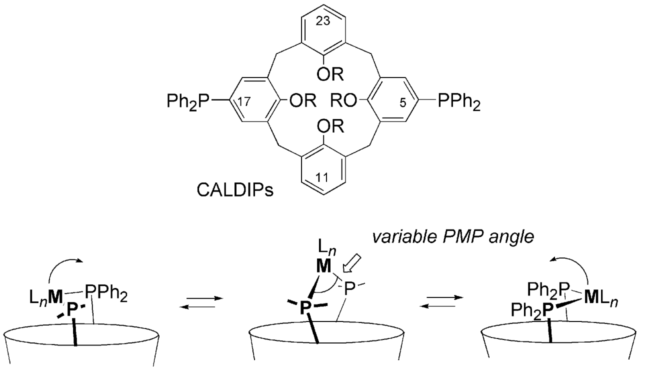
5,17-Diphenylphosphanyl-11,23-bis(4-tolyl)-25,26,27,28-tetrapropoxycalix[4]arene (**6**), a semi-rigid, calixarene-based diphosphane in which the phosphorus atoms are separated by 12 chemical bonds, reacts with [Ni(η^5-C_5H_5)(1,5-cyclooctadiene)]BF_4 or $AgBF_4$ to afford the corresponding chelate complexes [Ni(η^5-C_5H_5)(**6**)]BF_4 and [Ag(**6**)]BF_4 quantitatively. These complexes were both characterised by a single-crystal X-ray diffraction study. In the nickel complex the ligand shows a bite angle of 104.5°, which lies in the range expected for this kind of diphosphane with a large P···P separation. In the silver(I) complex the diphosphane displays a much larger bite angle of 138.8°, which was unexpected and reflects the flexilibilty of the calix[4]arene skeleton. Furthermore, in solution the silver complex shows dynamic behaviour. One of the observed motions corresponds to the silver atom switching reversibly from a linear to a bent AgP_2 cordination geometry.

Introduction

The bite angle and flexibility of diphosphane ligands are important parameters, especially when considering their use in homogeneous catalysis.[1–14] In recent studies we have investigated the coordination of several calix[4]arenes bearing two phosphanyl groups on the distal positions, C5 and C17, of the calixarene backbone.[15,16] We found that with Ni^{II} and Pd^{II} these ligands (CALDIPs) resulted in *cis*-chelate complexes in which the P–M–P angles were significantly larger than 90°. These complexes were found to operate as remarkably efficient catalysts in carbon–carbon coupling reactions.[17–22] Their high reactivity was attributed to the relatively large ligand bite angle (100–110°), which may favour a reductive elimination step in the catalytic cycle through steric effects involving the phosphorus substituents. A factor likely to enhance this effect is the fanning motion of the P–M–P plane in solution. These dynamics are characterised by a periodic increase of the P–M–P angle (Scheme 1).[16,23] For *cis*-[MX_2(CALDIP)] complexes (M = Ni^{II}, Pd^{II}, Pt^{II}), the highest bite angle observed to date in the solid state was 110°,[19] this value possibly corresponds to a minimum in solution. Pursuing our efforts to define the limits of the flexibility of CALDIPs, and in particular to examine whether bite angles significantly larger than 110° remain compatible with chelation in this class of ligands, we have investigated the coordination behaviour of **6** towards Ag^+. Silver(I) was chosen for its ability to readily form bent as well as linear arrangements when coordinated to two phosphanes, i.e., to potentially accept chelating ligands with large bite angles. Calix[4]arene backbones constitute semi-rigid platforms ideally suited for the synthesis of podands with convergent ligand arms.[24–26] Several recent studies have shown how the presence of a cavity in these podants may drastically influence the coordinative and catalytic ligand properties.[27–30]



Scheme 1. Typical dynamics of CALDIP complexes.

Results and Discussion

The ligand **6** used for this study was prepared in five steps shown in Scheme 2. The synthesis began with a selective distal dilithiation of tetrabromocalixarene (**1**) with

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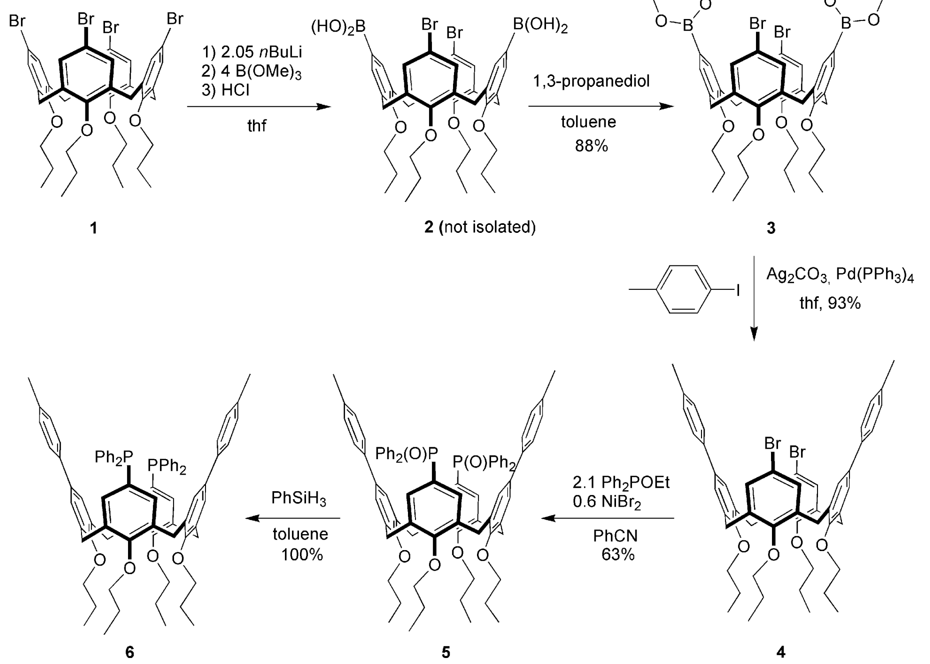


Scheme 2. Synthesis of diphosphane **6**.

*n*BuLi.[31] Quenching with $B(OMe)_3$ followed by treatment with HCl gave the diboronic acid **2**, which was not isolated. Compound **2** was directly converted into the corresponding 1,3-propanediol ester **3** (yield 88 %). Suzuki–Miyaura coupling of **3** with *p*-iodotoluene in the presence of Ag_2CO_3 and $Pd(PPh_3)_4$ afforded the expanded calixarene **4** in 93 % isolated yield. Phosphorus was then introduced through a nickel-catalysed Arbuzov reaction using Ph_2POEt.[15] The bis(phosphane oxide) **5** obtained was finally reduced with $PhSiH_3$ giving the diphosphane **6** quantitatively. The ^{31}P NMR spectrum of **6** shows a peak at –6.4 ppm which is in keeping with the formation of a triarylphosphane (cf. –4.5 ppm for PPh_3). The ^{1}H NMR spectrum displays a conventional AB pattern for the four methylenic ArCH_2Ar groups, with an AB separation of 1.27 ppm, in accord with a calixarene backbone in the cone conformation.[32]

Reaction of **6** with $[Ni(\eta^5\text{-}C_5H_5)(1,5\text{-cyclooctadiene})]BF_4$ gave complex **7** (Figure 1) in high yield (Scheme 3). The chelating behaviour of the ligand was confirmed by an X-ray diffraction study (Figure 2). In the solid state, the metal atom is oriented towards one side of the cavity. The dihedral angle between the P–Ni–P plane and the calixarene reference plane, defined as the average plane containing the four ArCH_2 carbon atoms, is 19.2°. The value of the P–Ni–P angle, 104.6°, is close to that found in two related $[Ni(\eta^5\text{-}C_5H_5)(CALDIP)]BF_4$ complexes.[17,22] The room temperature ^{1}H and ^{31}P NMR spectra are in accord with C_{2v} symmetry, which actually reflects a fast fanning motion of the P–Ni–P plane about the P···P axis similar to that previously reported for several $[MX_2(CALDIP)]$ (X = halide) and $[M(\eta^5\text{-}C_5H_5)(CALDIP)]$ complexes.[16,17] In this process the nickel atom moves between two positions on either side of the calixarene axis.

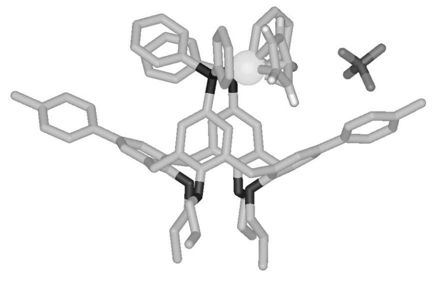
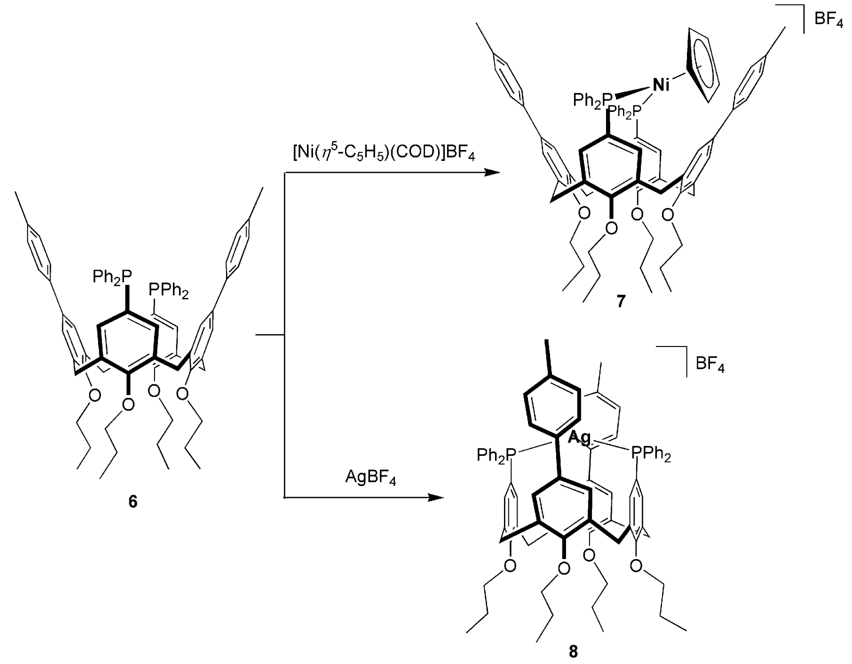


Figure 1. A view of the molecular structure of $[Ni(\eta^5\text{-}C_5H_5)(\mathbf{6})]BF_4$ (**7**). The complex crystallises with one molecule of chloroform (omitted for clarity). Bond lengths [Å] and angle [°]: P–Ni 2.184(2); P′–Ni 2.214(2); P–Ni–P′ 104.6(1). Only the hydrogen atoms of the Cp ring are shown.

Reaction of **6** with $AgBF_4$ gave complex **8** (Figure 2) as the sole product. As for **7**, all room temperature NMR spectroscopic data were in accord with C_{2v} symmetry. A single-crystal X-ray diffraction study revealed that in the solid state the AgP_2 moiety adopts a bent form with a P–Ag–P angle of 138.8°. The metal atom lies “higher” above the cavity than that in **7**, the P–Ag–P plane forming an angle of 47.4° with the calix reference plane (cf. 19.2° in **7**). An interaction between the silver atom and the neighbouring BF_4 moiety can be ruled out, as the closest F atom lies at a distance of 2.86 Å from the metal. We note that short F···HC(aromatic) contacts can be seen for two fluorine atoms (2.39 and 2.53 Å). A survey of the CCDC revealed that in the vast majority of complexes of general formula $[Ag(phosphane)_2]BF_4$ the P–Ag–P angle lies between 150°–180°, regardless of whether an interaction between the silver atom and the BF_4 unit exists or not.[33–36] The above bite angle of “only” 138.8° is therefore likely to reflect the strain



Scheme 3. Synthesis of complexes **7** and **8**.

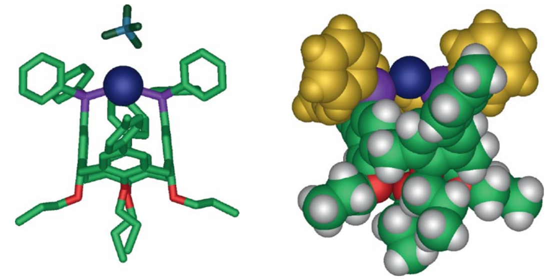
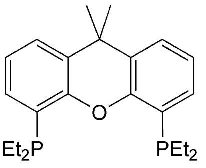


Figure 2. Two views of the molecular structure of the silver complex **8**. The CPK model (right; BF_4 anion omitted), showing P-aryl rings in yellow, illustrates the steric crowding *trans* to the metal–phosphorus bonds. Important bond lengths [Å] and angle [°]: Ag–P1 2.4260(12); Ag–P2 2.4297(13); P1–Ag–P2 138.76(4).

within the calix backbone, which prevents the ligand from reaching a larger bite angle. This strain becomes apparent in the markedly unsymmetrical orientation of the two phenoxy rings bearing the tolyl groups (the dihedral angles of the latter with the calixarene reference plane are 25° and 44°). Note that strained diphosphanes able to create bite angles near 140° are quite rare, a recently reported ligand for which such a value was found is EtXantphos.[37]



EtXantphos

A further interesting aspect of this structure concerns the bending of the two phenyl rings towards the metal centre, thereby resulting in a sterically crowded environment about the silver atom (Figure 2, bottom). Our previous studies of the solution dynamics of [MX$_2$(CALDIP)] complexes have led to the conclusion that during the fanning motion of the P–M–P plane, the ligand bite angle should periodically increase and thus transiently push two phosphorus substituents towards the two X ligands. The present study not only confirms that bite angles much larger than 110° are accessible for CALDIPs, but also that in the corresponding complexes a virtual metal embrace takes place. This phenomenon should, of course, strongly favor a reductive elimination step in a catalytic C–C bond formation reaction.

The ^{31}P NMR (121 MHz) and ^{1}H NMR (300 MHz) room temperature spectra of **8** (Figure 3) show an apparent C_{2v} symmetry of the complex, which is inconsistent with the solid-state structure. These findings taken together with the crystallographic study imply that in solution the silver atom moves rapidly from one side of the calixarene axis to the other, the position of the metal ion seen in the solid

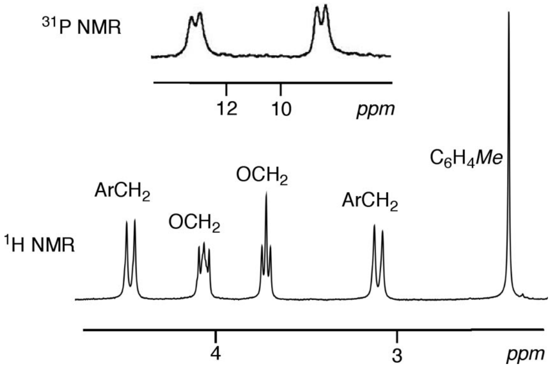
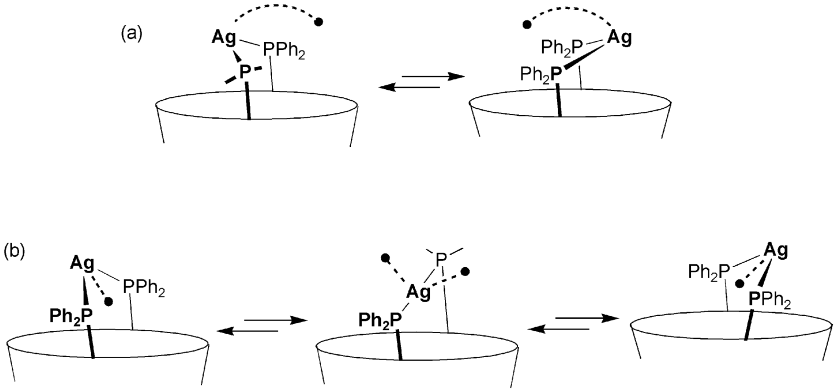


Figure 3. Room temperature ^{31}P NMR (121 MHz, $CDCl_3$) and ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **8**.



Scheme 4. Proposed dynamics of the cationic complex **8**. The dotted lines (red) indicate the trajectory of the silver ion in each type of movement.

state corresponds to its maximal separation from the calixarene axis. On lowering the temperature, the ^{31}P NMR (202 MHz) spectrum first broadens (Figure 4), then coalesces and finally splits into two AX patterns (X = ^{107}Ag/^{109}Ag) of relative intensity 1:4. The presence of two equilibrating species (denoted A and B in the ^{31}P NMR spectrum, Figure 4) was further confirmed by a variable temperature ^{1}H NMR study measured over the same temperature range (–65 °C to +20 °C). Two concommitant phenomena may be considered to account for the observed spectra: a) a rapid fanning motion of the P–Ag–P plane about the P···P axis, displacing the silver atom along an arc, as previously observed for other metal ions in [MX$_2$(CALDIP)] complexes (Scheme 4, a);[16,23] b) a switch from a bent to a linear coordination mode of the silver atom (Scheme 4, b). Interestingly, the ^{1}H NMR spectrum (500 MHz) measured at –65 °C revealed that the two species in equilibrium have C_{2v} symmetry (only one ArCH_2Ar AB pattern is seen), an observation which implies that the fanning motion is not frozen out at that temperature. As the J(P^{107},Ag) coupling constant (see Exp. Section) is smaller in the minor species A seen at low temperatures, we tentatively assign a bent structure to it.[36,38] Overall, the fluxional behaviour of the calixarene silver complex **8** contrasts with that previously seen in Pd^{II} and Pt^{II} complexes containing similar diphosphanes, in which only one type of displacement was detected.[16,17,23] This simply reflects the relatively easy change in coordination geometry from linear to bent of silver(I). Fluxional silver(I) complexes in which the metal ion switches in an analogous manner between two coordination geometries have recently been shown to occur in molecular rotors.[39]

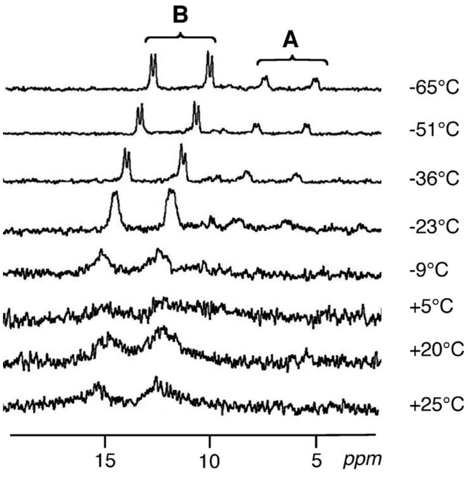


Figure 4. Variable temperature ^{31}P NMR study (202 MHz, CD$_2$Cl$_2$) of **8** showing the appearance of two species at low temperature. The peaks arising from the two equilibrating species are labelled A and B.

Conclusions

From previous studies[16,17,19,22,23] it is apparent that CALDIPs preferentially behave as chelating ligands with a bite angle lying in the range 100°–110° (in square planar or tetrahedral complexes), although an authentic *trans* chelating binding mode has also been reported.[15] This study shows, for the first time, that despite the rigidity of CALDIPs, the calixarene skeleton remains compatible with bite angles near 140°. Overall, within the family of chelators with wide bite angles, CALDIPs constitute rare examples[6,40] of diphosphanes giving access to bite angles not only lying at both ends of the range 100–180°, but also in the middle. Furthermore, it should be emphasised that our findings confirm that in CALDIP chelate complexes characterised by a P–M–P angle significantly larger than 110°, the steric pressure exerted by the PPh substituents on the first coordination sphere is drastically enhanced with respect to that seen in the resting state. In our previously reported C–C bond forming catalysts based on such ligands, all resulting in fast reaction rates, we have proposed that the P–M–P angle undergoes a periodic increase in the catalytic intermediates, which consequently favours the coupling step. This study clearly shows that if angles near 140° are reached during these dynamics, this would then significantly contribute to the high reaction rates observed.

Experimental Section

General Procedures: All commercial reagents were used as supplied. The syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed through an alumina column (5 cm length) and stored under nitrogen over molecular sieves (4 Å). Routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded with FT Bruker AVANCE 300 (^1H: 300.1 MHz, ^{13}C: 75.5 MHz, ^{31}P: NMR 121.5 MHz) and AVANCE 500 (^1H: NMR 500.1 MHz, ^{13}C: 125.8 MHz) instruments at 25 °C. ^1H NMR spectroscopic data were referenced to residual $CHCl_3$ (δ = 7.26 ppm) or CH_2Cl_2 (δ = 5.34 ppm). ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (δ = 77.0 ppm), and the ^{31}P NMR spectroscopic data are given relative to external H_3PO_4. Mass spectra were recorded either with a Bruker MicroTOF spectrometer (ESI-TOF) using CH_2Cl_2 as solvent, or with a Bruker MaldiTOF spectrometer (MALDI-TOF) using α-cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting point apparatus. 5,7,11,17-Tetrabromo-25,26,27,28-tetrapropoxycalix[4]arene (**1**)[31] and $[(\eta^5\text{-}C_5H_5)Ni(COD)]BF_4$[41] were prepared according to literature procedures.

5,17-Dibromo-11,23-(1,3,2-dioxaborinanyl)-25,26,27,28-tetrapropoxycalix[4]arene (3): To a cold (–78 °C) solution of **1** (10.00 g, 11.01 mmol) in THF (350 mL) was added a 1.6 M solution of *n*-BuLi/hexane (14.1 mL, 22.6 mmol). After stirring for 15 min, $B(OMe)_3$ (4.9 mL, 44.0 mmol) was added rapidly. The solution was stirred overnight at room temperature and then poured into a cold HCl solution (3 M, 500 mL, 0 °C). The product was extracted into $CHCl_3$ (2 × 400 mL). The organic phase was washed with water (2 × 500 mL), dried with $MgSO_4$, and the solvent was removed. The crude boronic acid **2** obtained was introduced into a Dean–Stark apparatus containing toluene (350 mL) and 1,3-propanediol (3.0 mL, 41.3 mmol). After elimination of water (heating for ca. 1 h), the solvent was removed. The solid residue was recrystallised from $CHCl_3$/*n*-heptane to afford a white solid (8.89 g, 88%). Mp > 250 °C. ^1H NMR ($CDCl_3$): δ = 7.54 (s, 4 H, *m*-H of OArB), 6.30 (s, 4 H, *m*-H of OArBr), 4.37 and 3.15 [AB spin system, $^2J(AB)$ = 13.4 Hz, 8 H, ArCH_2Ar], 4.22 (t, ^3J = 5.4 Hz, 8 H, BOCH_2CH_2), 4.05 (pseudo t, ^3J = 8.2 Hz, 4 H, OCH_2CH_2CH_3), 3.63 (t, ^3J = 6.8 Hz, 4 H, OCH_2CH_2CH_3), 2.12 (quint., ^3J = 5.2 Hz, 4 H, BOCH_2CH_2), 1.98–1.80 (two overlapping m, 8 H, OCH_2CH_2CH_3), 1.09 (t, ^3J = 7.4 Hz, 3 H, CH_3), 0.84 (t, ^3J = 7.5 Hz, 3 H, CH_3) ppm. $^{13}C\{^1H\}$NMR ($CDCl_3$): δ = 160.28 and 154.41 (2s, C_q-O), 135.59 and 134.99 (arom. C atoms), 130.34 (s, C_q-B), 115.32 (s, C_q-Br), 77.33 and 76.56 (2s, OCH_2CH_2CH_3), 62.14 (s, BOCH_2CH_2), 31.03 (s, ArCH_2Ar), 27.61 (s, BOCH_2CH_2), 23.59 and 23.00 (2s, OCH_2CH_2CH_3), 10.90 and 9.90 (2s, CH_3) ppm. $C_{46}H_{56}B_2Br_2O_8$ (*M*r = 918.36): calcd. C 60.16, H 6.15; found C 60.25, H 6.30.

5,17-Dibromo-11,23-bis(*p*-tolyl)-25,26,27,28-tetrapropoxycalix[4]arene (4): A mixture of **3** (4.00 g, 4.36 mmol), 4-iodotoluene (4.75 g, 21.78 mmol), Ag_2CO_3 (4.80 g, 17.42 mmol) and $Pd(PPh_3)_4$ (1.50 g, 0.44 mmol) was heated in refluxing THF (100 mL) for 24 h. The solution was filtered through Celite and the solvents evaporated to dryness. The residue was chromatographed on silica gel using CH_2Cl_2/cyclohexane (15:85, v/v), yielding **4** as a white solid [R_f (SiO_2, CH_2Cl_2/cyclohexane, 15:85, v/v) = 0.2]; yield 3.77 g, 93%; m.p. >250 °C. ^1H NMR ($CDCl_3$): δ = 7.30 and 7.11 [C_6H_4Me, $^3J(AB)$ = 8.2 and $^4J(AA')$ ≈ $^4J(BB')$ ≈ 2.0 Hz, 8 H, AA′BB′ spin system], 7.10 (s, 4 H, *m*-H of O*Ar*C_6H_4Me), 6.62 (s, 4 H, *m*-H of OArBr), 4.46 and 3.19 [AB spin system, $^2J(AB)$ = 13.2 Hz, 4 H, ArCH_2Ar], 3.97 (pseudo t, ^3J = 8.2 Hz, 4 H, OCH_2), 3.78 (m, 4 H, OCH_2), 2.37 (s, 6 H, C_6H_4CH_3), 2.03–1.86 (m, 8 H, OCH_2CH_2), 1.06 (t, ^3J = 7.4 Hz, 3 H, OCH_2CH_2CH_3), 0.95 (t, ^3J = 7.4 Hz, 3 H, OCH_2CH_2CH_3) ppm. $^{13}C\{^1H\}$NMR ($CDCl_3$): δ = 156.59 and 155.16 (2s, C_q-O), 138.05–126.60 (arom. C atoms), 115.23 (s, C_q-Br), 77.26 and 76.98 (2s, OCH_2CH_2CH_3), 31.26 (s, ArCH_2Ar), 23.49 and 23.22 (2s, OCH_2CH_2CH_3), 21.24 (s, C_6H_4CH_3), 10.68 and 10.17 (2s, OCH_2CH_2CH_3) ppm. $C_{54}H_{58}Br_2O_4$ (*M*r = 930.84): calcd. C 69.68, H 6.28; found C 69.70, H 6.29.

5,17-Diphenylphosphanyl-11,23-bis(4-tolyl)-25,26,27,28-tetrapropoxycalix[4]arene (5): A suspension of **4** (2.00 g, 2.15 mmol) and anhydrous $NiBr_2$ (0.28 g, 1.29 mmol) in PhCN (20 mL) was heated at 180 °C for 1 h. After addition of Ph_2POEt (2.8 mL, 12.9 mmol) at 180 °C the reaction mixture was refluxed for a further 1 h. The solvent was evaporated to dryness. The residue was taken up in toluene (20 mL) and washed with NH_3/H_2O (5%, 4 × 50 mL) and H_2O (2 × 50 mL). The organic layer was separated and dried with $MgSO_4$. The solvent was evaporated to dryness and the product was purified by column chromatography using acetone/cyclohexane (30:70, v/v). Calixarene **5** was obtained as a white solid [R_f (SiO_2, acetone/cyclohexane, 20:80, v/v) = 0.16]; yield 1.60 g, 63%, m.p. > 250 °C, ^1H NMR ($CDCl_3$): δ = 7.70–7.63, 7.53–7.46 and 7.34–7.27 (20 H, PPh_2), 7.50 (s, 4 H, *m*-H of OArP), 6.69 and 6.53 [AA′BB′ spin system, $^3J(AB)$ = 7.8; $^4J(AA')$ and $^4J(BB')$ < 1 Hz, 8 H, OArC_6H_4Me,], 6.34 (s, 4 H, *m*-H of O*Ar*C_6H_4Me), 4.49 and 3.19 [AB spin system, $^2J(AB)$ = 13.2 Hz, 8 H, ArCH_2Ar,], 4.17 (pseudo t, ^3J = 8.2 Hz, 4 H, OCH_2), 3.65 (t, ^3J = 7.0 Hz, 4 H, OCH_2), 2.33 (s, 6 H, C_6H_4CH_3), 2.09–1.97 (m, 4 H, OCH_2CH_2CH_3), 1.93–1.81 (m, 4 H, OCH_2CH_2CH_3), 1.07 (t, ^3J = 7.5 Hz, 6 H, OCH_2CH_2CH_3), 0.92 (t, ^3J = 7.5 Hz, 6 H, OCH_2CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 161.32 and 154.72 (2s, arom. C_q-O), 137.91–124.28 (arom. C atoms), 77.50 and 76.82 (2s, OCH_2), 31.17 (s, ArCH_2Ar), 23.65 and 23.24 (2s, CH_2CH_3), 21.28 (s, C_6H_4CH_3), 10.90 and 9.95 (2s, OCH_2CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 29.6 (s, PPh_2) ppm. $C_{78}H_{78}O_6P_2\cdot0.5CH_2Cl_2$ (*M*r = 1172.50 + 42.46): calcd. C 77.54, H 6.55; found C 77.57, H 6.61.

5,17-Diphenylphosphanyl-11,23-bis(4-tolyl)-25,26,27,28-tetrapropoxycalix[4]arene (6): A solution of **5** (1.20 mg, 1.02 mmol) and $PhSiH_3$ (1.0 mL, 8.18 mmol) in toluene (10 mL) was heated to reflux for 2 d. The solvent was evaporated to dryness and the residue was taken up in CH_2Cl_2. Addition of MeOH afforded pure **6** as a white powder; yield 1.17 g, 100%, m.p. 219.5–220.5 °C. ^1H NMR ($CDCl_3$): δ = 7.35–7.26 and 7.20–7.13 (24 H, PPh_2 and *m*-H of OArP), 6.74 and 6.62 [AA′BB′ spin system, $^3J(AB)$ = 7.8; $^4J(AA')$ and $^4J(BB')$ < 1 Hz, 8 H, OArC_6H_4Me], 6.39 (s, 4 H, *m*-H of O*Ar*C_6H_4Me), 4.47 and 3.12 [AB spin system, $^2J(AB)$ = 13.1 Hz, 8 H, ArCH_2Ar], 4.13 (pseudo t, ^3J = 8.1 Hz, 4 H, OCH_2), 3.65 (t, ^3J = 6.9 Hz, 4 H, OCH_2), 2.34 (s, 6 H, C_6H_4CH_3), 2.12–1.99 (m, 4 H, OCH_2CH_2CH_3), 1.94–1.82 (m, 4 H, OCH_2CH_2CH_3), 1.08 (t, ^3J = 7.5 Hz, 6 H, OCH_2CH_2CH_3), 0.93 (t, ^3J = 7.5 Hz, 6 H, OCH_2CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 158.85 and 154.77 (2s, arom. C_q-O), 138.48–126.06 (arom. C atoms), 77.37 and 76.68 (2s, OCH_2CH_2CH_3), 31.28 (s, ArCH_2Ar), 23.65 and 23.23 (2s, OCH_2CH_2CH_3), 21.29 (s, C_6H_4CH_3), 10.94 and 9.97 (2s, OCH_2CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –6.4 (s, PPh_2) ppm. $C_{78}H_{78}O_4P_2\cdot CH_3OH$ (*M*r = 1141.40 + 32.04): calcd. C 80.86, H 7.04; found C 80.93, H 7.12.

***cis*-*P*,*P′*-(η^5-Cyclopentadienyl)-{5,11-diphenylphosphanyl-17,23-bis(4-tolyl)-25,26,27,28-tetrapropoxycalix[4]arene}nickel(II) Tetrafluoroborate (7):** To a solution of **6** (0.082 g, 0.072 mmol) in CH_2Cl_2 (15 mL) was added a solution of $[(\eta^5\text{-}C_5H_5)Ni(COD)]BF_4$ (0.025 g, 0.079 mmol) in CH_2Cl_2 (3 mL). After stirring for 12 h, the solution was concentrated to ca. 2 mL. Addition of Et_2O afforded **7** as an orange powder; yield 0.070 g, 72%, m.p. 230 °C (dec.). Crystals suitable for X-ray diffraction were obtained by cooling a $CHCl_3$ solution of the complex. ^1H NMR ($CDCl_3$): δ = 7.28–7.20 (28 H, PPh_2 and C_6H_4Me), 6.92, 6.78 and 6.53 (broad signals, 16 H, *m*-H of OAr), 4.83 (s, 5 H, C_5H_5), 4.60 and 3.30 [AB spin system, ^2J(AB) = 14.2 Hz, 8 H, ArCH_2Ar], 4.08 (br. t, ^3J = 8.1 Hz, 4 H, O$CH_2CH_2CH_3$), 3.82 (t, ^3J = 6.6 Hz, 4 H, O$CH_2CH_2CH_3$), 2.28 (s, 6 H, $C_6H_4CH_3$), 1.99–1.83 (m, 8 H, $OCH_2CH_2CH_3$), 1.14 (t, ^3J = 7.2 Hz, 6 H, $OCH_2CH_2CH_3$), 0.83 (t, ^3J = 7.3 Hz, 6 H, $OCH_2CH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 158.84 and 157.46 (2s, arom. C_q-O), 137.33–126.88 (arom. C′s), 77.49 and 76.63 (2s, $OCH_2CH_2CH_3$), 31.68 (s, ArCH_2Ar), 23.64 and 22.70 (2s, $OCH_2CH_2CH_3$), 21.09 (s, $C_6H_4CH_3$), 10.91 and 9.65 (2s, $OCH_2CH_2CH_3$) ppm. ^{31}P NMR ($CDCl_3$): δ = 31.3 (s broad, PPh_2) ppm. $C_{83}H_{83}BF_4NiO_4P_2\cdot CHCl_3$ (*M*r = 1351.99 + 119.38): calcd. C 68.57, H 5.75; found C 68.31, H 6.03.

{5,11-Diphenylphosphanyl-17,23-bis(4-tolyl)-25,26,27,28-tetrapropoxycalix[4]arene}silver(I) Tetrafluoroborate (8): To a solution of $AgBF_4$ (0.016 g, 0.081 mmol) in THF (1 mL) was added a solution of **6** (0.093 g, 0.081 mmol) in CH_2Cl_2 (15 mL). After stirring for 1 h, the solution was concentrated to ca. 2 mL. Addition of pentane afforded **8** as a white powder; yield 0.082 g, 75%, m.p. 238–239 °C (dec.). ^1H NMR ($CDCl_3$, 25 °C, 300 MHz): δ = 7.49–7.20 (28 H, PPh_2 and C_6H_4Me), 7.04 (s, 4 H, *m*-H of OArC_6H_4Me), 6.25 [virtual t, *J*(PH) = 6 Hz, 4 H, *m*-H of OArP], 4.48 and 3.13 [AB spin system, ^2J(AB) = 12.9 Hz, 8 H, ArCH_2Ar], 4.11–4.05 (m, 4 H, O$CH_2CH_2CH_3$), 3.74 (t, ^3J = 6.90 Hz, 4 H, O$CH_2CH_2CH_3$), 2.43 (s, 6 H, $C_6H_4CH_3$), 2.07–1.87 (m, 8 H, $OCH_2CH_2CH_3$), 1.13 (t, ^3J = 7.5 Hz, 6 H, $OCH_2CH_2CH_3$), 0.90 (t, ^3J = 7.5 Hz, 6 H, $OCH_2CH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 156.91 and 156.65 (2s, arom. C_q-O), 137.84–126.90 (arom. C atoms), 77.79 and 77.37 (2s, $OCH_2CH_2CH_3$), 31.15 (s, ArCH_2Ar), 23.71 and 22.99 (2s, $OCH_2CH_2CH_3$), 21.29 (s, $C_6H_4CH_3$), 10.92 and 9.93 (2s, $OCH_2CH_2CH_3$) ppm. ^{31}P NMR ($CDCl_3$, 25 °C, 121 MHz): δ = 10.9 [two d, $J(^{107}Ag,P)$ = 506 and $J(^{109}Ag,P)$ = 578 Hz, PPh_2] ppm. In the ^{31}P NMR (202 MHz, CD_2Cl_2) spectrum measured at –65 °C, the following $J(^{107}Ag,P)$ coupling constants were found: 506 Hz (major species, δ = 11.6 ppm), 458 Hz (minor species, δ = 6.5 ppm). $C_{78}H_{78}AgBF_4O_4P_2\cdot 0.5CH_2Cl_2$ (*M*r = 1336.07 + 41.97): calcd. C 68.39, H 5.78; found C 68.50, H 5.80. MS (ESI TOF): *m*/*z* = 1249.39 $[M - BF_4]^+$ (expected isotopic profile).

Crystallographic Data for 7: Crystals suitable for X-ray diffraction were obtained by cooling a $CHCl_3$ solution of the complex: $C_{83}H_{83}BF_4NiO_4P_2\cdot CHCl_3$, M = 1471.32, triclinic, space group $P\bar{1}$, a = 14.475(1), b = 18.216(1), c = 18.746(1) Å, α = 108.222(10), β = 98.628(10), γ = 98.628(10), V = 4449.4(5) Å^3, Z = 2, μ = 0.395 mm^{-1}, $F(000)$ = 1540. Crystals of the compound were mounted on a Nonius Kappa CCD. Data collection with Mo-K_α radiation (λ = 0.71073 Å) was carried out at 173 K using the Nonius collect suite.[42] 56295 reflections were collected ($1.2 < \theta < 29.9°$), 25292 being found to be unique (merging R = 0.16). The structure was solved with SIR-97.[43] Final results: R_1 = 0.1158, wR_2 = 0.2953, goodness of fit = 1.128, 821 parameters, residual electron density: min./max. = –1.703/1.582 e Å^{-3}. Some important bond lengths and angles are given in Figure 1.

Crystallographic Data for 8: Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex: $C_{78}H_{78}AgBF_4O_4P_2$, M = 1336.07, monoclinic, space group $P\ 2_1/c$, a = 19.616(4), b = 16.093(4), c = 24.952(5) Å, β = 107.753(1), V = 7502(3) Å^3, Z = 4, μ = 0.366 mm^{-1}, $F(000)$ = 2784. Crystals of the compound were mounted on a Nonius Kappa CCD. Data collection with Mo-K_α radiation (λ = 0.71073 Å) was carried out at 173 K using the Nonius collect suite.[42] 46435 reflections were collected ($1.5 < \theta < 27.5°$), 17106 being found to be unique (merging R = 0.082). The structure was solved with SIR-97.[43] Final results: R_1 = 0.0814, wR_2 = 0.2345, goodness of fit = 1.063, 758 parameters, residual electron density: min./max. = –1.174/1.216 e Å^{-3}. Some important bond lengths and angles are given in Figure 2.

CCDC-771492 (for **7**) and -771518 (for **8**) 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.

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