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PAPER

Binucleating behaviour of a proximally-diphosphinated calix[4]arene†

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The long diphosphine 5,11-diphenylphosphanyl-25,26-dipropyloxy-27,28-bis(2-propenyloxy) calix[4]arene (*cone*) (**5**), in which the two phosphorus atoms are separated by a semi-rigid linking unit, was prepared in four steps starting from calix[4]arene. Reaction of **5** with $AuCl(SEt_2)$ or $[RuCl_2(p\text{-cymene})]_2$ led to calixarenes bearing two metallated pendant arms, $[\mathbf{5}\cdot(AuCl)_2]$ and $[\mathbf{5}\cdot\{RuCl_2(p\text{-cymene})\}_2]$, respectively. In the presence of $AgBF_4$ or $[Ni(C_5H_5)(1,5\text{-cyclooctadiene})]BF_4$, diphosphine **5** displayed a marked tendency to form oligomeric material, but under high dilution conditions dimeric species were obtained selectively. The inability of **5** to form chelate complexes was further illustrated by its reaction with $[PdCl_2(1,5\text{-cyclooctadiene})_2]$, which led quantitatively to a rare complex in which a diphosphine spans across the dinuclear $[PdCl(\mu\text{-}Cl)_2PdCl]$ unit.

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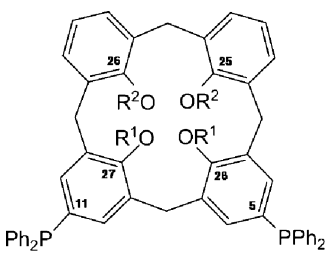
Introduction

The calix[4]arene skeleton has been recognised for over two decades as a priviliged, semi-rigid platform suitable for assembling a set of convergent ligands.[1–9] Among these a number of upper-rim phosphinated calix[4]arenes have been synthesised recently and used in transition metal chemistry.[10–19] Phosphines belonging to this class of ligands have led to a variety of complexes with unusual structural and catalytic properties exploiting the many interesting features of the macrocyclic platform, including its intrinsic dynamics[20] as well as its receptor properties.[21] While most studies dealing with upper-rim diphosphinated calix[4]arenes have focused on distally substituted macrocycles[13,22] that spontaneously form chelate complexes, the coordination behaviour of proximally-substituted versions of these ligands has been discussed in a unique publication.[23] The latter were shown to react with the cationic complexes $[M(cod)(thf)]PF_6$ (M = Rh(I) and Ir(I), cod = 1,5-cyclooctadiene; thf = tetrahydrofuran), thereby *selectively* forming dimers, as the rather rigid $ArCH_2Ar$ fragment that links the phosphorus atoms prevents formation of monomeric chelate complexes. Wondering whether the complexing behaviour of this large diphosphine towards cationic species is specific and whether other coordination modes are possible, we now synthesised diphosphine **5**, a new diphosphino-calixarene with a distal substitution pattern (Scheme 1), and investigated its complexation behaviour towards gold(I), silver(I), nickel(II) and palladium(II) complexes. Three X-ray studies carried out on complexes based on this ligand provide an understanding of the marked tendency of related ligands to behave as bridging rather than chelating ligands. Note that in diphosphine **5**, the phosphorus atoms are separated by eight chemical bonds.



5 $R^1 = CH_2CHCH_2$
$R^2 = CH_2CH_2CH_3$

Scheme 1 The proximally upper-rim substituted calixarene (cone conformation) used in this study.

Results and discussion

The route used for the synthesis of diphosphine **5** is summarised in Scheme 2. Its preparation began with a double alkylation of generic calixarene **1** (Scheme 2) using two equiv. of *n*-PrI in the presence of 3.6 equiv. of NaH. The resulting calixarene **2**, obtained in 66% yield, was reacted with Br_2 to produce selectively the distally dibrominated compound **3**. The hydroxyl groups of **3** were then alkylated with allylbromide, thus producing a calixarene bearing two allyl groups, which potentially allow further lower-rim functionalisation. The two phosphino groups were finally

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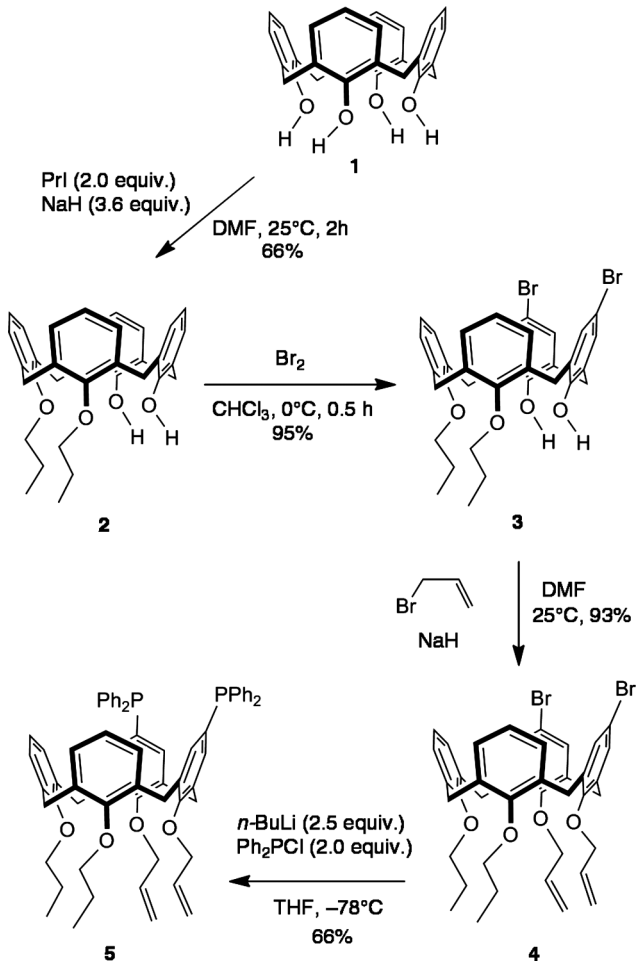
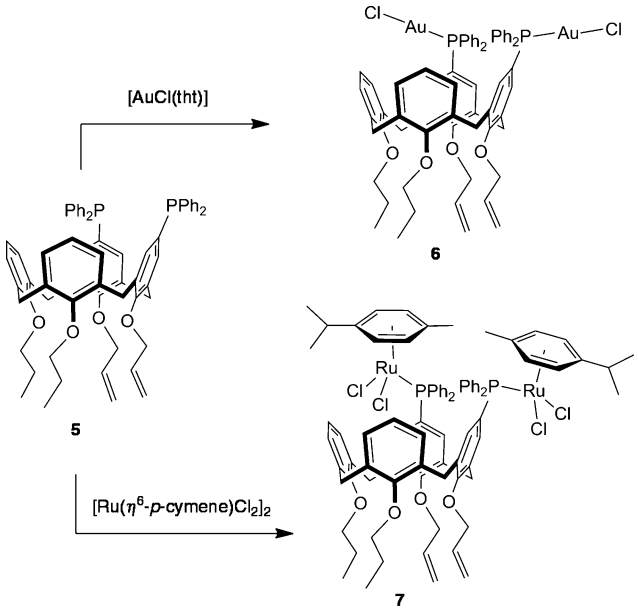


Scheme 2 Synthesis of diphosphine **5**.



Scheme 3 Formation of dinuclear complexes from diphosphine **5**.

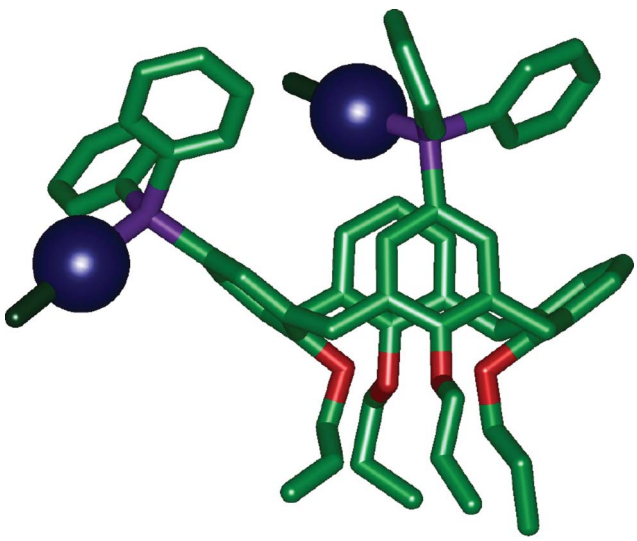


Fig. 1 X-Ray structure of the digold complex **6**. Important distances (Å): Au(1)–P(1) 2.227(2); Au(1)–Cl(2) 2.275(2); Au(2)–P(2) 2.232(2); Au(2)–Cl(1) 2.281(2); P(1)–Au(1)–Cl(2) 178.07(9); P(2)–Au(2)–Cl(1) 174.3(1).

introduced by treatment of intermediate **4** with *n*-BuLi in excess and subsequent reaction with two equivalents of Ph_2PCl. The ^1H NMR spectrum of the resulting diphosphine **5** displays three AB patterns for the methylenic Ar*CH*$_2$Ar groups (of relative intensity 2 : 4 : 2), with AB separations of 1.27, 1.29, and 1.42 ppm, respectively. These values are fully consistent with a calixarene backbone in the *cone* conformation.[24] In the ^{31}P NMR spectrum, the signal of the phosphorus atoms appears as a singlet at –4.1 ppm.

Reaction of diphosphine **5** with two equiv. of [AuCl(tht)] (tht = tetrahydrothiophene) afforded the dinuclear complex **6** in 71% yield (Scheme 3). As for the free ligand **5**, the ^1H NMR spectrum of **6** shows three distinct $ArCH_2$ patterns in keeping with a calixarene in the cone conformation. Consistent with a C_s-symmetrical complex, the ^{31}P NMR spectrum the phosphorus atoms appear as a unique peak (δ = 33.8 ppm). Crystals of **6** suitable for X-ray diffraction formed in a straightforward manner upon diffusion of pentane into a dichloromethane solution of the complex. In the solid state (Fig. 1) the calixarene skeleton adopts a typical flattened cone conformation, in which two phenoxy rings are nearly parallel (interplane angle 13.8°), while the angle between the other two phenoxy planes is 76.5°. One of the two gold atoms sits above the cavity entrance, the other one being pushed away from it.

A related complex, also containing two independent metal centres (**7**), was obtained by treatment of **5** with one equivalent of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (Scheme 3). The spectroscopic and analytical data of complex **7** are consistent with the proposed structure (see the Experimental section). Noteworthily, the ^1H NMR spectrum of **7** shows a singlet at 1.58 ppm for the $MeC_6H_4(^iPr)_2$ protons, a value that compares with that found in $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ complexes containing a conventional phosphine.[25,26] Some recent reports have shown that some calixarene monophosphines were able to position a $Ru(\eta^6\text{-}p\text{-cymene})$ moiety inside the cavity upon complexation, thereby inducing a significant highfield shift of the $MeC_6H_4(^iPr)_2$ signal, but this is not the case here.[12,17]

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Harvey *et al.* have carefully investigated the coordinative properties towards $[Rh(cod)(thf)_2)]^+$ and $[Ir(cod)(thf)_2)]^+$ of three proximally diphosphinated calixarenes closely related to **5**.[23] Based on ^{31}P spin–lattice relation time measurements, these authors proposed that their ligands resulted quantitatively in dimers in which two phosphorus atoms are *cis*-disposed about each metal centre. However, these studies were not corroborated by X-ray diffraction studies. Wondering whether this ligand type would also allow the formation of chelate complexes in the presence of a pseudo *trans*-orienting metal ion, we decided to study the reaction of **5** with $AgBF_4$. We first observed that when carried out at a metal concentration of 10^{-3} mol L^{-1}, the reaction with **5** led to a mixture of oligomeric complexes, which could not be separated. When repeating the reaction under high dilution conditions (see the Experimental section), only dimer **8** formed (Scheme 4). The ESI mass spectrum of this complex showed an intense peak at m/z 2165.6 having exactly the isotopic profile as that expected for $[M - 2BF_4 + K]^+$. In the corresponding ^{31}P NMR spectrum, the two phosphorus atoms appeared as two doublets centered at 11.2 ppm ($J(^{107}Ag,P)$ = 435 Hz, $J(^{109}Ag,P)$ = 505 Hz). The dimeric structure of **8** was confirmed by an X-ray diffraction study (Fig. 2). The molecule contains a centre of symmetry. Each silver atom, which adopts a Y-shaped coordination geometry, is bonded to two phosphorus atoms and a fluorine atom of a BF_4 anion, the corresponding AgP(1), AgP(2) and AgF bond distances being 2.416(1), 2.425(1), and 2.546(4) Å, respectively. The P–Ag–P angle is 150.9(3)° and the silver–silver separation 6.574 Å. The AgP and AgF bond lengths are comparable to those found in another chelated [Ag(diphosphine)](BF_4) complex in which the diphosphine gives rise to a similar wide P–Ag–P angle.[27] As in **6**, the two calixarenes display a typically flattened cone conformation, a geometry which renders the two P atoms of each calixarene unequivalent in the solid. The distances between

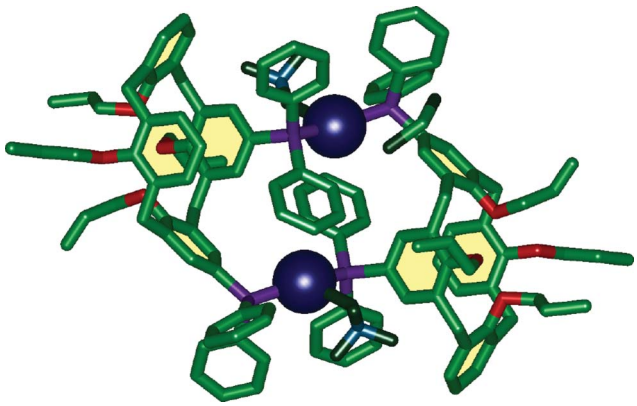
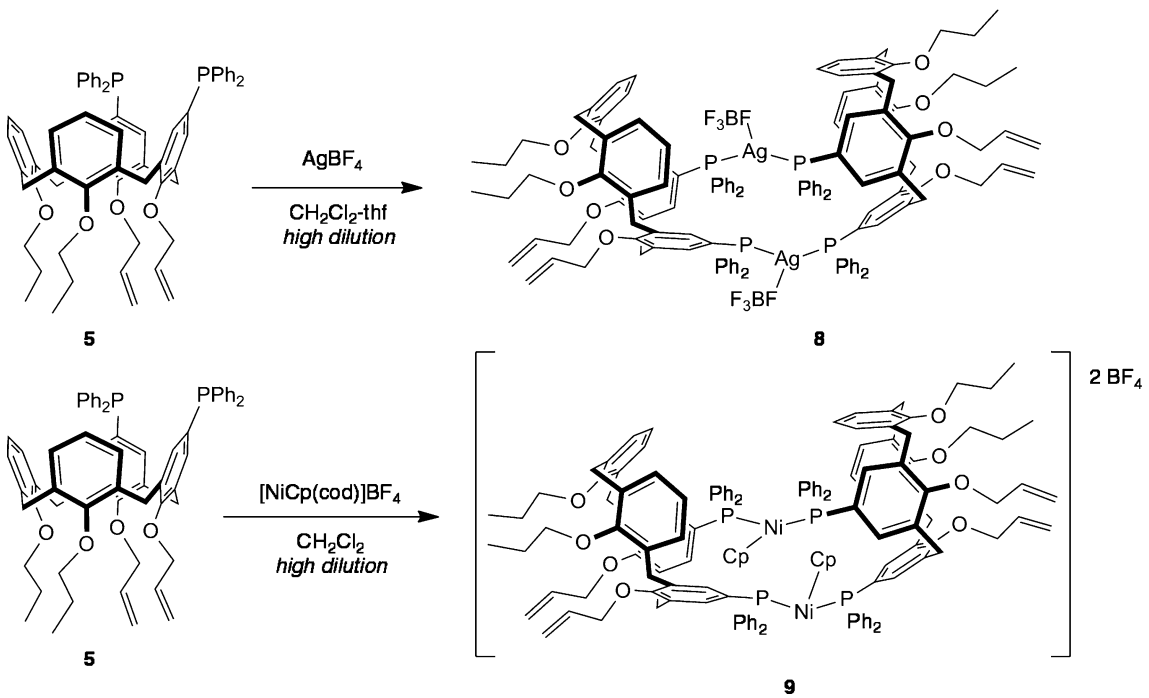


Fig. 2 Molecular structure of the silver complex **8**. Important distances (Å) and angles (°): Ag(1)–P(1) 2.4158(9); Ag(1)–P(2) 2.4248(9); Ag(1)–F(4) 2.546(4); P(1)–Ag–P(2) 150.89(3); P(1)–Ag(1)–F(4) 110.44(9).

the two (parallel) calixarene axes are 6.52 Å. The fact that in $CDCl_3$ a unique ^{31}P signal is observed reflects the classical breathing movement of the calixarene moieties in solution.[1]

The coordination properties of **5** were further assessed towards $[Ni(\eta^5\text{-}C_5H_5)(solvent)_2]BF_4$, the metal centre of which is expected to behave as a *cis*-orienting fragment towards two incoming two-electron donors. As previously observed with Ag^+, a *single* product formed with the cationic nickel precursor only when the reaction was performed under high dilution. This led to complex **9** (Scheme 4). The dimeric nature of **9** was inferred from the ESI TOF spectrum which showed a peak at m/z = 1080.4 (100%) having the isotopic profile of the dicationic species $[(M - 2BF_4)]^{2+}$. While the ^{31}P NMR spectra of dimer **8** and that of Harvey's dirhodium complex **10** showed equivalent phosphorus atoms, the spectrum of **9** unexpectedly revealed the presence of an AB spectrum



Scheme 4 Quantitative formation of dimers **8** and **9**.

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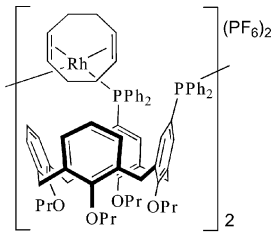
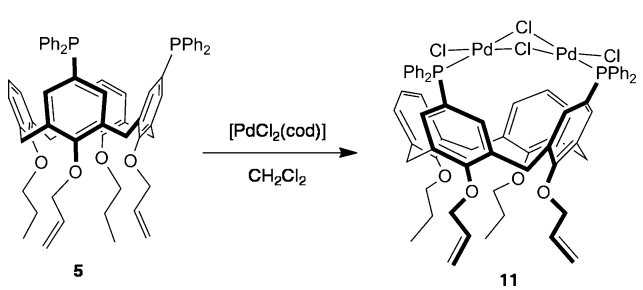
(J(AB) = 42 Hz). This reflects a rigid molecule with a non centrosymmetrical structure. This observation is corroborated by the presence in the ^{1}H NMR spectrum of four AB spin systems for the ArCH$_2$ protons.



10

Finally, we decided to examine the behaviour of **5** towards a metal fragment able to assemble two P(III) centres either in a *cis* or *trans* fashion. Thus, reaction of **5** with [PdCl$_2$(cod)] *quantitatively* gave the dinuclear complex **11** in which the diphosphine spans across a [PdCl(μ-Cl)$_2$PdCl] unit (Scheme 5). The "capping" behaviour of the diphosphine was deduced from the ESI TOF mass spectrum which showed a peak at m/z = 1334.08 with the isotopic profile expected for the [M + Na]$^+$ cation. All NMR data were consistent with the formation of a C_s-symmetrical complex. Thus, for example, the ^{31}P NMR spectrum showed a single peak at 31.2 ppm, while three AB patterns with an intensity ratio of 2 : 4 : 2 were found in the ^{1}H NMR spectrum for the ArCH_2 protons. As revealed by an X-ray diffraction study (Fig. 3), the molecule is no longer C_s symmetric in the solid state. This arises from the flattened structure adopted by the calixarene backbone, which makes the two phosphorus atoms unequivalent. Upon complexation, the Pd$_2$Cl$_4$ fragment has been positioned above the calixarene cavity, with the two phosphorus atoms being arranged in a cisoid manner. Both palladium centres are in a distorted square planar configuration with the bond angles ranging between 83.8° and 98.4° about Pd(1), and between 90.3° and 93.9° about Pd(2). Thus, the distortion is more significant for the palladium centre bonded to the phosphorus atom attached to the "pinched" part of the calixarene. Each Pd metal and the four atoms comprising its coordination sphere, three chlorines and one phosphorus, are planar within 0.06 Å. The Pd–Cl(terminal), Pd–Cl(bridging *trans* to P) and Pd–Cl (bridging *trans* to Cl), bond lengths average to 2.281, 2.408 and 2.320 Å, respectively, and fall within the usual ranges for these interactions. Unlike in most reported [(PR$_3$)PdCl(μ-Cl)$_2$PdCl(PR$_3$)] complexes,[28,29] the Pd$_2$Cl$_4$ unit displays a roof-shaped structure, the observed deviation from planarity reflecting the shortness and relative rigidity of the bidentate ligand. The angle between the two metal planes



5 **11**

Scheme 5 Synthesis of **11**.

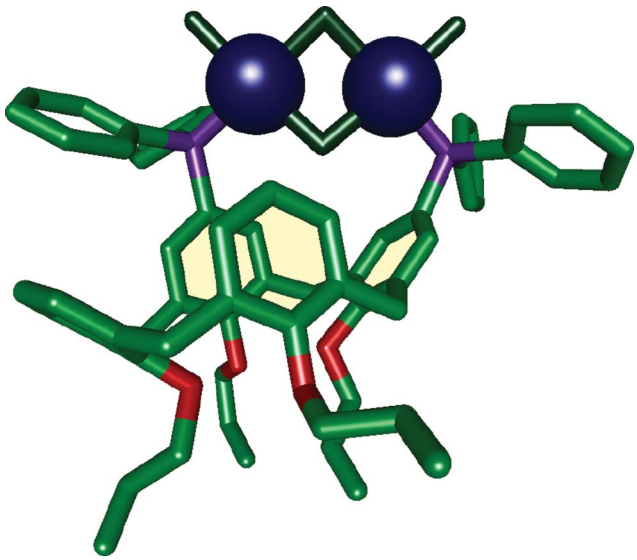


Fig. 3 Molecular structure of complex **11**. Important distances (Å) and angles (°): Pd(1)–P(1) 2.250(1); Pd(1)–Cl(1) 2.280(1); Pd(1)–Cl(2) 2.313(1); Pd(1)–Cl(3) 2.409(1); Pd(2)–P(2) 2.246(1); Pd(2)–Cl(4) 2.283(1); Pd(2)–Cl(2) 2.327(1); Pd(2)–Cl(3) 2.409(1); P(1)–Pd(1)–Cl(1) 85.97(3); P(1)–Pd(1)–Cl(2) 98.37(3); Cl(1)–Pd(1)–Cl(2) 175.36(3); P(1)–Pd(1)–Cl(3) 176.33(4); Cl(1)–Pd(1)–Cl(3) 91.94(4); Cl(2)–Pd(1)–Cl(3) 83.81(3); P(2)–Pd(2)–Cl(4) 90.36(4); P(2)–Pd(2)–Cl(2) 93.94(4).

is 23.2°. To the best of our knowledge there is only one other diphosphine enabling capping of M$_2$X$_4$ moieties, namely Gelman's 1,8-bis(diisopropylphosphino)triptycene (note that similar capping was also reported for a dinitrogen ligand[30]). The backbone of the latter is considerably less flexible than the calix[4]arene core of **5**, and not surprisingly the roof structure is more pronounced in the triptycene derivative (66.1°). Overall, the solid state structure of **5** provides a good understanding for why chelate formation is prevented with 5,11-diphosphinated calix[4]arenes.

Conclusions

In summary, we have shown that diphosphine **5** is a versatile ligand enabling the synthesis of three types of binuclear complex. In keeping with Harvey's studies dealing with rhodium and iridium complexes based on related ligands, **5** turned out to be suitable for the formation of dimeric species when opposed to cationic species. However, in contrast with the earlier studies, dimer formation is not selective in our cases, the corresponding dimers forming only when the reactions were performed under *high dilution*. The present study further established a new binding mode for calix[4]arenes having two distal PPh$_2$ substituents located at the upper rim. The crystallographic characterisation of the dipalladium complex **10** with a non planar Pd$_2$Cl$_4$ fragment in which one Pd atom strongly deviates from an ideal square planar configuration, nicely illustrates the limited flexibility of the calixarene core for forming a chelate complex.

Experimental

All commercial reagents were used as supplied. The syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents

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were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on FT Bruker AVANCE 300 (^1H: 300.1 MHz, ^{13}C: 75.5 MHz, ^{31}P: 121.5 MHz) and AVANCE 500 (*^1H: 500.1 MHz, ^{13}C: 125.8 MHz*) instruments at 25 °C. ^1H NMR spectral data were referenced to residual $CHCl_3$ (7.26 ppm) or CH_2Cl_2 (5.34 ppm), ^{13}C 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 either on a Bruker MicroTOF spectrometer (ESI-TOF) using CH_2Cl_2 as solvent, or on 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. Calix[4]arene (**1**),[31] [AuCl(tht)],[32] $[RuCl_2(p\text{-cymene})]_2$,[33] $[(\eta^5\text{-}C_5H_5)Ni(COD)]BF_4$[34] and $[PdCl_2(COD)]$[35] were prepared according to literature procedures. In the NMR data "C_q" denotes a quaternary carbon atom of the calixarene backbone.

25,26-Dihydroxy-27,28-dipropoxycalix[4]arene (2)

To a solution of calix[4]arene **1** (10.00 g, 23.55 mmol) in DMF (75 mL) was carefully added NaH (60% in mineral oil, 3.40 g, 84.81 mmol). After stirring for 15 min, propyliodide (8.61 g, 50.63 mmol) was added to the mixture. The solution was stirred for 2 h at room temperature, upon which the solvent was removed *in vacuo*. The residue was taken up in CH_2Cl_2 (150 mL), washed with HCl (1 M, 50 mL) then with water (2 × 100 mL). The organic layer was dried over $MgSO_4$. After filtration the solution was evaporated to dryness. The residue was purified by column chromatography on silica using CH_2Cl_2/cyclohexane (30 : 70, *v* : *v*) as solvent. Calixarene **2** was obtained as a white solid [R_f (SiO_2, CH_2Cl_2/cyclohexane (30 : 70, *v* : *v*) = 0.25]. Yield (7.90 g, 66%). Mp 192 °C. ^1H NMR ($CDCl_3$): δ 8.99 (s, 2H, OH), 7.07, 6.99 and 6.80 (ABC spin system, 6H, *m* and *p*-H of OAr, ^3J(AB) ≈ ^3J(AC) = 7.4 Hz, ^3J(BC) = 1.8 Hz), 7.00, 6.97 and 6.64 (ABC spin system, 6H, *m* and *p*-H of OAr, ^3J(AB) ≈ ^3J(AC) = 7.4 Hz, ^4J(BC) = 1.7 Hz), 4.56 and 3.41 (AB spin system, 2H, ArCH_2Ar, ^2J (AB) = 12.1 Hz), 4.35 and 3.40 (AB spin system, 4H, ArCH_2Ar, ^2J (AB) = 13.3 Hz), 4.33 and 3.36 (AB spin system, 4H, ArCH_2Ar, ^2J (AB) = 13.2 Hz), 4.14–4.06 and 3.95–3.86 (2 m, 8H, OCH_2CH$_2$), 2.15 (pseudo sext, 4H, OCH$_2$CH_2, ^3J = 7.0 Hz), 1.17 (t, 6H, CH$_3$, ^3J = 7.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.45 and 151.19 (2 s, arom. C_q–O), 134.69–120.53 (arom. C's), 78.30 (s, OCH$_2$CH$_2$), 31.92, 31.79 (2 s, ArCH$_2$Ar), 23.26 (s, OCH$_2$CH$_2$CH$_3$), 10.35 (s, OCH$_2$CH$_2$CH$_3$). Found: C, 79.90; H, 7.16. Calc. for $C_{34}H_{36}O_4$ (M_r = 508.65): C, 80.28; H, 7.13%.

5,11-Dibromo-25,26-dihydroxy-27,28-dipropoxy[4]calixarene (3)

To a cold (0 °C) solution of **2** (5.00 g, 9.83 mmol) in $CHCl_3$ (100 mL) was dropwise added a solution of Br_2 (3.37 g, 21.13 mmol) in $CHCl_3$ (100 mL). After stirring for 30 min at room temperature, the mixture was treated with Na_2SO_3 (1 M, 2 × 50 mL), then washed with water (2 × 100 mL). The organic layer was dried over $MgSO_4$. After filtration the solution was concentrated to *ca.* 5 mL. Addition of methanol afforded **3** as a white precipitate (6.03 g, 95%). Mp 261 °C. ^1H NMR ($CDCl_3$): δ 8.87 (s, 2H, OH), 7.11 and 7.06 (AB spin system, 4H, 6.99, *m*-H of OArBr, ^4J(AB) = 2.2 Hz), 7.10, 6.99 and 6.85 (ABC spin system, 6H, *m* and *p*-H of OAr, ^3J(AB) ≈ ^3J(AC) = 7.5 Hz, ^4J(BC) = 1.7 Hz), 4.51 and 3.43 (AB spin system, 2H, ArCH_2Ar, ^2J (AB) = 12.3 Hz), 4.30 and 3.22 (AB spin system, 2H, ArCH_2Ar, ^2J (AB) = 13.5 Hz), 4.27 and 3.36 (AB spin system, 4H, ArCH_2Ar, ^2J (AB) = 13.2 Hz), 4.13–4.05 and 3.92–3.83 (2 m, 8H, OCH_2CH$_2$), 2.12 (pseudo sext, 4H, OCH$_2$CH_2, ^3J = 7.5 Hz), 1.15 (t, 6H, CH$_3$, ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.26 and 150.52 (2 s, arom. C_q–O), 134.65–112.18 (arom. C's), 78.50 (s, OCH$_2$CH$_2$), 31.25 and 29.99 (2 s, ArCH$_2$Ar), 23.24 (s, OCH$_2$CH$_2$CH$_3$), 10.29 (s, OCH$_2$CH$_2$CH$_3$). Found: C, 61.20; H, 5.17. Calc. for $C_{34}H_{34}Br_2O_4$ (M_r = 666.44): C, 61.28; H, 5.14%.

5,11-Dibromo-27,28-diallyloxy-25,26-dipropoxycalix[4]arene (4)

To a solution of **3** (2.50 g, 3.7 mmol) in DMF (50 mL) was carefully added NaH (60% in mineral oil, 0.450 g, 11.25 mmol) and allyl bromide (1.40 g, 11.62 mmol). After stirring for 24 h, the mixture was evaporated to dryness. The residue was taken up in CH_2Cl_2 (150 mL), washed with HCl (1 M, 50 mL) and with water (2 × 100 mL). The organic layer was dried over $MgSO_4$ and concentrated to *ca.* 5 mL. Addition of methanol afforded a white precipitate (2.60 g, 93%). Mp 145 °C. ^1H NMR ($CDCl_3$): δ 6.75–6.58 (10H, arom. H's, *m* and *p*-H of OAr), 6.32–6.19 (m, 2H, OCH$_2$CH=CH$_2$), 5.26–5.17 (m, 4H, OCH$_2$CH=CH_2), 4.45–4.36 (m, 4H, OCH_2CH=CH$_2$), 4.43 and 3.19 (AB spin system, 4H, ArCH_2Ar, ^2J (AB) = 13.5 Hz), 4.38 and 3.12 (AB spin system, 2H, ArCH_2Ar, ^2J (AB) = 13.5 Hz), 4.30 and 3.04 (AB spin system, 2H, ArCH_2Ar, ^2J (AB) = 13.7 Hz), 3.77–3.92 (m, 4H, OCH_2CH$_2$), 1.89 (pseudo sext, 4H, OCH$_2$CH_2, ^3J = 7.5 Hz), 0.98 (t, 6H, CH$_3$, ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.51 and 155.03 (2 s, arom. C_q–O), 137.92–128.00 (arom. C's), 122.35 (s, OCH$_2$CH=CH$_2$), 117.53 (s, OCH$_2$CH=CH_2), 115.14 (s, arom. C_q-Br), 77.16 (s, OCH_2CH=CH$_2$), 75.80 (s, OCH_2CH$_2$), 31.06 (s, [x2], ArCH_2Ar), 23.48 (s, OCH$_2$CH_2CH$_3$), 10.73 (s, OCH$_2$CH$_2$CH_3). Found: C, 64.43; H, 5.86. Calc. for $C_{40}H_{42}Br_2O_4$ (M_r = 746.56): C, 64.35; H, 5.67%.

5,11-Bis(diphenylphosphino)-27,28-diallyloxy-25,26-dipropoxycalix[4]arene (5)

To a cold (–78°c) solution of **4** (0.65 g, 0.87 mmol) in THF was added a 1.6 M solution of *n*-BuLi/hexane (1.4 mL, 2.26 mmol). After stirring for 1 h, Ph_2PCl (0.46 mL, 2.30 mmol) was added dropwise. The solution was stirred for 10 h at room temperature. The solvent was removed and the residue was taken up with CH_2Cl_2. Addition of MeOH afforded **5** as a white precipitate (0.55 g, 66%). Mp 245 °C. ^1H NMR ($CDCl_3$): δ 7.31–7.03 (20H, PPh_2), 6.76–6.55 (10H, arom. H's, *m* and *p*-H of OAr), 6.38–6.24 (m, 2H, OCH$_2$CH=CH$_2$), 5.25–5.17 (m, 4H, OCH$_2$CH=CH_2), 4.46 and 3.19 (AB spin system, 2H, ArCH_2Ar, ^2J (AB) = 13.4 Hz), 4.50–4.43 (m, 4H, OCH_2CH=CH$_2$), 4.38 and 3.09 (AB spin system, 4H, ArCH_2Ar, ^2J (AB) = 13.1 Hz), 4.39 and 2.97 (AB spin system, 2H, ArCH_2Ar, ^2J(AB) = 13.1 Hz), 3.87 (m, 4H, OCH_2CH$_2$CH$_3$), 1.95 (pseudo sext, 4H, OCH$_2$CH_2CH$_3$, ^3J = 7.5 Hz), 0.99 (t, 6H, CH$_3$, ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.63 and 156.31 (2 s, arom. C_q–O), 138.27–128.19 (arom. C's),

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122.48 (s, $OCH_2CH{=}CH_2$), 117.16 (s, $OCH_2CH{=}CH_2$), 77.06 (s, $OCH_2CH{=}CH_2$), 76.93 (s, $OCH_2CH_2CH_3$), 31.36, 31.18, 31.03 (3 s, $ArCH_2Ar$), 23.35 (s, CH_2CH_3), 10.43 (s, CH_3). $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$): δ – 4.1 (s, PPh_2). Found: C, 78.09; H, 6.47%. Calc. for $C_{64}H_{62}O_4P_2{\cdot}2CH_3OH$ (M_r = 957.12 + 64.08): C, 77.62; H, 6.91.

(*P*,*P*)-Dichlorido-{5,11-bis(diphenylphosphino)-27,28-diallyloxy-25,26 dipropoxycalix[4]arene} digold(I) (6)

To a stirred solution of **5** (0.113 g, 0.120 mmol) in CH_2Cl_2 (10 mL) was added a solution of [AuCl(tht)] (0.076 g, 0.236 mmol) in thf (1 mL). After 2 h, the solution was concentrated to *ca.* 1 mL. Addition of hexane afforded **6** as a white precipitate (0.120 g, 71%). Mp 240 °C (dec.). ^1H NMR ($CDCl_3$): δ 7.67–7.09 (20H, PPh_2), 6.88–6.82, 6.67–6.61 and 6.49–6.44 (3 m, 10H, *m*-H of OArP and *m* and *p*-H of OAr), 6.33–6.21 (ddt, 2H, $OCH_2CH{=}CH_2$), 5.29–5.21 (4H, $OCH_2CH{=}CH_2$), 4.61–4.38 (m, 4H, $OCH_2CH{=}CH_2$), 4.48 and 3.24 (AB spin system, 2H, $ArCH_2Ar$, ^2J (AB) = 13.1 Hz), 4.44 and 3.15 (AB spin system, 4H, $ArCH_2Ar$, ^2J (AB) = 13.1 Hz), 4.39 and 2.99 (AB spin system, 2H, $ArCH_2Ar$, ^2J (AB) = 13.1 Hz), 3.96–3.79 (m, 4H, $OCH_2CH_2CH_3$), 1.95 (pseudo sext, 4H, $OCH_2CH_2CH_3$, ^3J = 7.4 Hz), 1.00 (t, 6H, $OCH_2CH_2CH_3$, ^3J = 7.4 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.81 and 156.36 (2 s, arom. C_q–O), 135.15–127.54 (arom. C's), 122.95 (s, $OCH_2CH{=}CH_2$), 118.42 (s, $OCH_2CH{=}CH_2$), 77.53 (s, $OCH_2CH{=}CH_2$), 76.29 (s, $OCH_2CH_2CH_3$), 31.47, 31.16, 30.93 (3 s, $ArCH_2Ar$), 23.39 (s, $OCH_2CH_2CH_3$), 10.40 (s, $OCH_2CH_2CH_3$). $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$): δ 33.8 (s, PPh_2). Found: C, 55.48; H, 4.68%. Calc. for $C_{64}H_{62}Au_2Cl_2O_4P_2{\cdot}C_6H_{14}$ (M_r = 1421.96 + 86.17): C, 55.75; H, 5.08. Slow diffusion of pentane into a dichloromethane solution of the complex yielded colorless crystals suitable for X-ray diffraction study.

Bis(η⁶-*p*-cymene)-tetrachlorido-*P*,*P*-[5,11-bis(diphenylphosphino)-27,28-diallyloxy-25,26-dipropoxycalix[4]arene] diruthenium(II) (7)

A solution of $[RuCl_2(p\text{-cymene})]_2$ (0.067 g, 0.110 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **5** (0.105 g, 0.11 mmol) in CH_2Cl_2 (20 mL). After stirring overnight, the solution was evaporated to dryness and the residue was taken-up with $CHCl_3$. Addition of Et_2O afforded **7** as an orange precipitate (0.120 g, 70%). Mp 220 °C. ^1H NMR ($CDCl_3$): δ 7.61–7.19 (24H, PPh_2 and *m*-H of OArP), 6.93–6.90, 6.83–6.77 and 6.55–6.50 (3 m, 6H, *m* and *p*-H of OAr), 6.36–6.23 (ddt, 2H, $OCH_2CH{=}CH_2$), 5.20, 4.97, 4.86 and 4.75 (ABCD spin system, 4H, $C_6H_4CH_3$, ^3J(AB) = 4.2 Hz, ^3J(CD) = 5.4 Hz), 5.19–5.16 (4H, $OCH_2CH{=}CH_2$), 4.57–4.46 (m, 4H, $OCH_2CH{=}CH_2$), 4.54 and 3.27 (AB spin system, 2H, $ArCH_2Ar$, ^2J (AB) = 13.2 Hz), 4.48 and 3.24 (AB spin system, 4H, $ArCH_2Ar$, ^2J (AB) = 13.1 Hz), 4.33 and 2.98 (AB spin system, 2H, $ArCH_2Ar$, ^2J (AB) = 13.1 Hz), 4.01–3.85 (m, 4H, $OCH_2CH_2CH_3$), 2.76 (quint., 2H, $C_6H_4CH(CH_3)_2$, ^3J = 6.9 Hz), 1.96 (pseudo sext, 4H, $OCH_2CH_2CH_3$, ^3J = 7.5 Hz), 1.58 (s, 3H, $CH_3C_6H_4$), 1.07 (d, 6H, $C_6H_4CH(CH_3)_2$, ^3J = 7.5 Hz), 1.05 (d, 6H, $C_6H_4CH(CH_3)_2$, ^3J = 7.5 Hz), 1.00 (t, 6H, $OCH_2CH_2CH_3$, ^3J = 7.4 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.75 and 156.47 (2 s, arom. C_q–O), 136.15–127.55 (arom. C's), 122.70 (s, $OCH_2CH{=}CH_2$), 117.95 (s, $OCH_2CH{=}CH_2$), 110.40 and 95.52 (2 s arom. C_q of C_6H_4), 77.25, 77.16 (2 s, $OCH_2CH_2CH_3$ and $OCH_2CH{=}CH_2$, exact assignment was not possible), 32.33 (s, $C_6H_4CH(CH_3)_2$), 31.56, 31.16 and 30.07 (3 s, $ArCH_2Ar$), 23.27 (s, $OCH_2CH_2CH_3$), 21.93 and 21.80 (s, $C_6H_4CH(CH_3)_2$), 17.52 (s, $CH_3C_6H_4$), 10.37 (s, $OCH_2CH_2CH_3$). $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$): δ 24.2 (s, PPh_2). Found: C, 55.48; H, 4.68%. Calc. for $C_{84}H_{90}Cl_2O_4P_2Ru_2$ (M_r = 1367.37): C, 73.78; H, 6.63.

Bis[(μ₂-5,11-bis(diphenylphosphanyl)-25,26-dipropoxy-27,28-bis(allyloxy)calix[4]arene-*P*:*P*′]disilver(I) bis(tetrafluoroborate) (8)

A three-necked flask containing CH_2Cl_2 (500 mL) was equipped with 2 addition funnels respectively containing a solution of $AgBF_4$ (0.012 g, 0.062 mmol) in CH_2Cl_2/THF (250 : 1 mL), and a solution of **5** (0.060 g, 0.062 mmol) in CH_2Cl_2 (250 mL). The latter two solutions were added dropwise over 2 h into the flask under vigorous stirring. After 12 h the solution was concentrated to *ca.* 5 mL. Addition of Et_2O afforded **8** as a white precipitate (0.060 g, 84%). ^1H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 7.58–7.44 and 7.33–7.24 (40H, PPh_2), 7.21–7.08, 6.75–6.70, 6.69–6.61 (3 broad signals, 2H, arom. H of calix), 6.30 (ddt, 4H, $OCH_2CH{=}CH_2$), 5.32–5.24 (m, 8H, $OCH_2CH{=}CH_2$), 4.60 and 4.54 (m, ABXYZ spin system, 8H, $OCH_2CH{=}CH_2$), 4.47 and 3.21 (AB spin system, 8H, $ArCH_2Ar$, ^2J (AB) = 13.0 Hz), 4.44 and 3.12 (two overlapping AB spin systems, 8H, $ArCH_2Ar$, ^2J (AB) = 12.5 Hz), 3.87 and 3.81 (ABX_3 spin system, 8H, $OCH_2CH_2CH_3$), 1.95 (pseudo sext, 8H, $OCH_2CH_2CH_3$, ^3J = 7.5 Hz), 1.01 (t, 12H, $OCH_2CH_2CH_3$, ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 157.11 and 156.78 (2 s, arom. C_q–O), 138.90–128.47 (arom. C's), 122.76 (s, $OCH_2CH{=}CH_2$), 117.41 (s, $OCH_2CH{=}CH_2$), 77.39 and 76.40 (2 s, $OCH_2CH_2CH_3$ $OCH_2CH{=}CH_2$, exact assignment was not made), 31.02, 30.98 and 30.83 (3 s, $ArCH_2Ar$), 23.45 (s, $OCH_2CH_2CH_3$), 10.39 (s, $OCH_2CH_2CH_3$). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): δ 11.2 (two d, PPh_2, $J(^{107}Ag,P)$ = 435 Hz, $J(^{109}Ag,P)$ = 505 Hz). Found: C, 66.80; H, 5.29%; calc. for $C_{128}H_{124}Ag_2B_2F_8O_8P_4$ (M_r = 2303.59): C, 66.74; H, 5.43. MS (ESI TOF): *m*/*z* (%) = 2165.6 (100) [M – $2BF_4$ + K]$^+$ (expected isotopic profile).

Bis(η⁵-cyclopentadienyl)-bis[μ₂-5,11-bis(diphenylphosphino)-27,28-diallyloxy-25,26-dipropoxycalix[4]arene] nickel(II) bis(tetrafluoroborate) (9)

A three-necked flask containing CH_2Cl_2 (500 mL) was equipped with two addition funnels containing a solution of [Ni(η⁵-C_5H_5)(cod)]BF_4 (0.018 g, 0.056 mmol) in CH_2Cl_2 (250 mL) and a solution of **5** (0.054 g, 0.056 mmol) in CH_2Cl_2 (250 mL), respectively. These solutions were added dropwise and simultaneously over 2 h into the flask under vigorous stirring. After 12h, the solution was concentrated to *ca.* 5 mL. Addition of Et_2O afforded **9** as a yellow precipitate (0.055 g, 85%). ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.73–5.57 (60H, arom. H), 6.48 (br signal, 4H, $OCH_2CH{=}CH_2$), 5.31–5.16 (m, 26H, C_5H_5, $OCH_2CH{=}CH_2$, and $OCH_2CH{=}CH_2$), 5.25 (m, 2H, $OCH_2CH{=}CH_2$), 4.62 and 3.55 (AB spin system, 4H, $ArCH_2Ar$, ^2J (AB) = 13.2 Hz), 4.53 and 3.31 (AB spin system, 4H, $ArCH_2Ar$, ^2J (AB) = 13.2 Hz), 4.51 and 3.20 (AB spin system, 4H, $ArCH_2Ar$, ^2J (AB) = 13.2 Hz), 4.50 and 3.17 (AB spin system, 4H, $ArCH_2Ar$, ^2J (AB) = 13.2 Hz), 4.12 (m, 4H, $OCH_2CH_2CH_3$), 3.87 (m, 4H, $OCH_2CH_2CH_3$), 1.99 (br signal, 8H, $OCH_2CH_2CH_3$), 1.11 (t, 6H, $OCH_2CH_2CH_3$, ^3J = 7.4 Hz), 0.95 (t, 6H, $OCH_2CH_2CH_3$, ^3J = 7.4 Hz). $^{31}P\{^1H\}$ NMR

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(121 MHz, $CDCl_3$, 25 °C): δ 39.2 (d, PPh_2, $J(PP') = 42.5$ Hz), 30.1 (d, PPh_2, $J(PP') = 42.5$ Hz). Found: C, 69.68; H, 6.30%. Calc. for $C_{138}H_{134}B_2F_8Ni_2O_8P_4{\cdot}2H_2O$ (M_r = 2335.43 + 36.02) C, 69.89; H, 5.87. MS (ESI TOF): m/z = 2052.8 (30%) $[M - 2BF_4 - 2C_5H_5 + Na]^+$ (expected isotopic profile), 1080.4 (100%) $[(M - 2BF_4)]^{2+}$ (expected isotopic profile).

Di(μ-chlorido)-dichlorido-{[5,11-bis(diphenylphosphino)-27,28-diallyloxy-25,26-dipropoxycalix[4]arene]-κP}dipalladium(II) (11)

A solution of $[PdCl_2(cod)]$ (0.071 g, 0.250 mmol) in CH_2Cl_2 (200 mL) was dropwise added to a solution of **5** (0.120 g, 0.125 mmol) in CH_2Cl_2 (200 mL). After stirring for one night, the solution was evaporated to dryness and the residue was dissolved in $CHCl_3$. Addition of Et_2O afforded **11** as a yellow precipitate (0.120 g, 70%). Mp 199–200 °C. ^{1}H NMR ($CDCl_3$): δ 7.99–7.21 (24H, PPh_2 and *m*-H of OArP), 6.80, 6.55 and 6.42 (ABC spin system, 6H, *m* and *p*-H of OAr, $^3J(AB) \approx {}^3J(AC) = 7.1$ Hz, $^3J(BC) < 1$ Hz), 6.31 (ddt, 2H, $OCH_2CH{=}CH_2$), 5.28–5.21 (2 overlapping ddt, 4H, $OCH_2CH{=}CH_2$), 4.47–4.41 (m, 4H, $OCH_2CH{=}CH_2$), 4.42 and 3.22 (AB spin system, 2H, $ArCH_2Ar$, ^2J (AB) = 13.4 Hz), 4.41 and 3.18 (AB spin system, 2H, $ArCH_2Ar$, ^2J (AB) = 13.3 Hz), 4.34 and 2.96 (AB spin system, 4H, $ArCH_2Ar$, ^2J (AB) = 13.3 Hz), 3.89–3.71 (m, 4H, $OCH_2CH_2CH_3$), 1.93 (broad signal, 4H, $OCH_2CH_2CH_3$), 0.97 (t, 6H, $OCH_2CH_2CH_3$, ^3J = 7.4 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.18 and 155.80 (2 s, arom. C_q—O), 143.09—128.24 (arom. C's), 117.96 (s, $OCH_2CH{=}CH_2$), 116.87 (s, $OCH_2CH{=}CH_2$), 76.86 and 76.45 (2 s, $OCH_2CH_2CH_3$ or $OCH_2CH{=}CH_2$, exact assignment was not made), 31.16, 31.05 and 30.56 (3 s, $ArCH_2Ar$), 23.24 (s, $OCH_2CH_2CH_3$), 10.31 (s, $OCH_2CH_2CH_3$). ^{31}P{^{1}H} NMR (120 MHz, $CDCl_3$): δ 31.2 (s, PPh_2). Found: C, 58.60; H, 4.81%. Calc. for $C_{64}H_{62}Cl_4O_4P_2Pd_2$ (M_r = 1311.77) C, 58.60; H, 4.76. MS (ESI TOF): m/z (%) = 1334.08 (67) $[M + Na]^+$ (expected isotopic profile), 1275.12 (21) $[M - Cl]^+$.

Crystal data for 6

Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of the complex: $C_{64}H_{62}Au_2Cl_2O_4P_2$, M = 1421.91, monoclinic, space group $P2_1/c$, a = 22.808(7), b = 15.115(5), c = 17.830(6) Å, β = 95.811(10), V = 6115(3) Å^3, Z = 4, μ = 4.976 mm^{-1}, $F(000)$ = 2800. Crystals of the compound were mounted on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). 107496 reflections were collected ($0.9 < \theta < 27.6°$), 14099 being found to be unique (merging R = 0.116). The structure was solved with SHELXS.[36] Final results: R_1 = 0.056, wR_2 = 0.110, goodness of fit = 0.981, 667 parameters, residual electron density: min./max. = –1.030/1.006 e Å^{-3}. Some important bond lengths and angles are given in Fig. 1. Crystallographic data in *.cif* format have been deposited with the Cambridge Crystallographic Data Centre, CCDC 809315.†

Crystal data for 8

Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of the complex: $C_{64}H_{62}AgBF_4O_4P_2{\cdot}2CH_2Cl_2$, M = 1321.61, triclinic, space group $P\bar{1}$, a = 14.0076(2), b = 16.3137(2), c = 17.0857(3) Å, α = 63.705(2), β = 70.812(2), γ = 66.189(2), V = 3148.53(8) Å^3, Z = 4, μ = 0.599 mm^{-1}, $F(000)$ = 1360. Crystals of the compound were mounted on a Oxford Diffraction CCD Saphire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (λ = 0.71073 Å) was carried out at 130 K. 43063 reflections were collected ($2.7 < \theta < 27.0°$), 12667 being found to be unique (merging R = 0.020). The structure was solved with SIR-97.[37] Final results: R_1 = 0.056, wR_2 = 0.172, goodness of fit = 1.081, 739 parameters, residual electron density: min./max. = –1.489/2.145 e Å^{-3}. The alerts level A are mainly due to a large thermal motion of the dichloromethane molecules. Some important bond lengths and angles are given in Fig. 2. Crystallographic data in *.cif* format have been deposited with the Cambridge Crystallographic Data Centre, CCDC 753229.†

Crystal data for 11

Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a $CHCl_3$ solution of the complex: $C_{64}H_{62}Cl_4O_4P_2Pd_2{\cdot}CHCl_3$, M = 1371.36, triclinic, space group $P\bar{1}$, a = 11.9880(3), b = 13.2820(3), c = 22.6990(5) Å, α = 95.162(2), β = 103.609(2), γ = 113.390(2), V = 3155.24(13) Å^3, Z = 2, μ = 0.899 mm^{-1}, $F(000)$ = 1394. Crystals of the compound were mounted on a Oxford Diffraction CCD Saphire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (λ = 0.71073 Å) was carried out at 143 K. 44507 reflections were collected ($2.6 < \theta < 27.0°$), 13748 being found to be unique (merging R = 0.037). The structure was solved with SIR-97.[37] Final results: R_1 = 0.037, wR_2 = 0.123, goodness of fit = 0.834, 756 parameters, residual electron density: min./max. = –1.380/1.217 e Å^{-3}. Two propyl chains were treated as disordered. Crystallographic data in *.cif* format has been deposited with the Cambridge Crystallographic Data Centre, CCDC 796779.†

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