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Phosphine Ligands

Arylcalixarenyl Phosphines in Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling Reactions

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Abstract: Two electron-rich arylcalixarenylphosphines have been synthesized in three steps from the appropriate 5-bromocalix[4]arene precursor **1**. The combination of 5-(2-diisopropylphosphinophenyl)-25,26,27,28-tetrapropyloxycalix[4]arene (**5**) and 5-(2-dicyclohexylphosphinophenyl)-25,26,27,28-tetrapropyloxycalix[4]arene (**6**), respectively, with $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) generated effective catalysts for the cross-coupling reactions of hindered aryl chlorides and arylboronic acids. Dicyclohexylphosphino-substituted ligand **6** had a higher activity that that of **5**, and the structures of ligand **5** and [AuCl·**5**] were determined by single-crystal X-ray diffraction studies. The solid-state structure of [AuCl·**5**] revealed that the gold atom lies above the outer face of the calixarene unit, with distances of 3.08 and 3.28 Å between the gold atom and the two closest aromatic carbon atoms of the calixarene moiety.

Introduction

Electron-rich dialkylbiarylphosphines, in particular Buchwald-type phosphines (which contain an *o*-substituted remote aryl ring),[1] are known to improve the reactivity of many palladium-catalyzed coupling reactions, including Suzuki–Miyaura coupling (SMC),[2] aryl amination[3] and amidation,[4] enolate arylation,[5] and Sonogashira coupling reactions.[6] Ligands of this family have been extensively applied to the syntheses of liquid crystalline materials, pharmaceuticals, biologically active compounds, natural products, and polymers, and the efficiency of the catalysts that contain these ligands is directly correlated with their structure.[1c] It is now well-recognized that the remarkable performance of such ligands in a SMC reaction arises from their ability to behave as hemilabile *P,C*-chelators, involving the *ipso* carbon atom of the remote aryl ring, which favors the formation of monoligand palladium intermediates over that of bis(ligand) complexes.[7] This property, together with the presence of a strong phosphorus donor, positively affects the rate of the oxidative addition step.[8] If such phosphines strongly sterically hinder the catalytic center, then the reductive elimination step may also be facilitated.

As an extension of our studies on cavity-shaped phosphines,[9] we now describe the synthesis of a new class of biarylphosphines, namely, 5-(2-diorganylphosphinophenyl)calix[4]arenes, which are hereafter referred to as arylcalixarenylphosphines (Figure 1), and report their use in Pd-catalyzed coupling reactions of bulky aryl chlorides and sterically hindered aryl boronic acids. In contrast to classical Buchwald-type biarylphosphines, the ligands described herein contain a biaryl unit that has one arene ring with two unsymmetrical faces because it is part of the calixarene skeleton.[10]

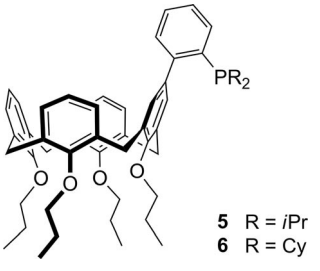

Figure 1. The two arylcalixarenylphosphines synthesized and examined in the present study.

Results and Discussion

Phosphines **5** and **6** were prepared in three steps from bromocalixarene **1**[11] according to Scheme 1. Calixarene **1** was first converted into a boronic acid derivative, which was subsequently transformed in situ to give arylated calixarene **2** by employing a Suzuki–Miyaura coupling with 1,2-dibromobenzene. Compound **2** was obtained in 56 % isolated yield. The dialkylphosphino moieties were then introduced by a halogen/lithium exchange reaction followed by treatment with the appropriate chlorophosphine at 65 °C. As the resulting phosphines can be readily oxidized to give the corresponding phosphine

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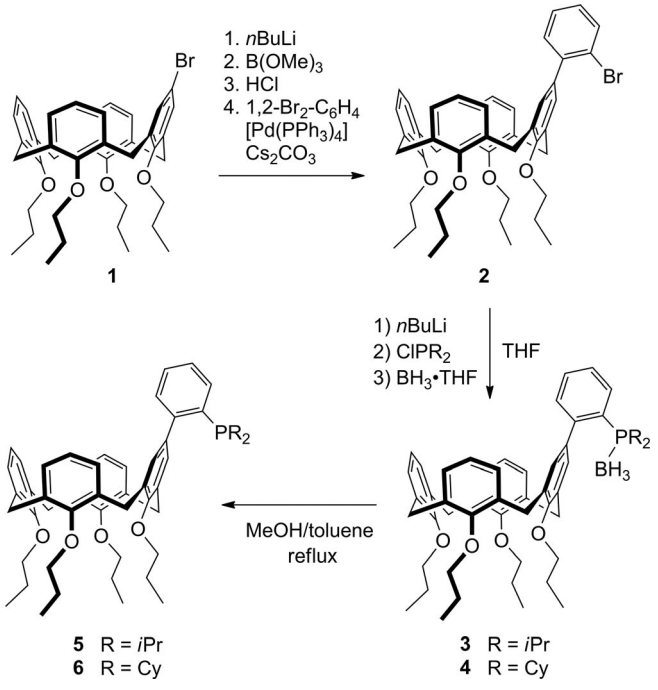
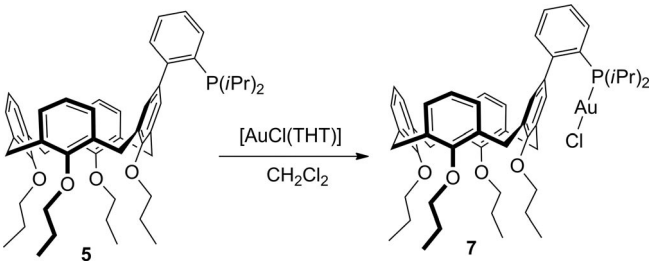
oxides, the crude reaction mixtures were first treated with BH_3 to produce the borane adducts, which were conveniently purified by chromatography [70 % yield (for **3**) and 65 % yield (for **4**)]. The free phosphines were then quantitatively formed upon heating the purified borane adducts in a MeOH/toluene (1:4) mixture at reflux for 5 h.



Scheme 1. Stepwise preparation of phosphines **5** and **6** (THF = tetrahydrofuran, Cy = cyclohexyl).

Each phosphine was characterized by a singlet found in the corresponding ^{31}P NMR spectrum [δ = –4.0 ppm (for **5**) and –13.5 ppm (for **6**)]. As expected, the ^1H NMR spectra of **5** and **6** are in agreement with those of C_s-symmetrical molecules, as both have two distinct AB patterns for the diastereotopic ArCH_2Ar protons. The large AB separations ($\Delta\delta$ > 1 ppm) unambiguously show that the calixarene core has maintained its conical shape in the tranformation of **1** into **5** or **6**.[12] The structure of **5** was confirmed by a single-crystal X-ray diffraction study (Figure 2). Interestingly, in the solid state, the phosphorus atom is oriented in such as way that its lone pair is only slightly skewed away from being directed into the calixarene cavity. The calixarene unit in this conformation has greater steric influence on reactions that take place at the phosphorus atom compared with that in which the phosphorus atom is turned towards the exterior of the cavity. A SPARTAN calculation revealed that the cone angle increases by approximately 10° upon changing from the conformation with the *exo*-oriented lone pair to that in which the lone pair of the phosphorus atom is directed towards the interior of the cavity (Tolman cone angle of the latter conformer: Θ = 150 °C).[13] Clearly, given the free rotation of the biaryl axis, ligand **5** should be regarded as a ligand with variable bulk.

To gain some insight into the coordination behavior of these biarylphosphines, phosphine **5** was treated with 1 equiv. of [AuCl(THT)] (THT: tetrahydrothiophene), which quantitatively led to complex **7** (Scheme 2). As for **5**, the ^1H NMR spectrum of **7** was in accord with a calixarene moiety in a cone conformation (see Exp. Section). An X-ray study (Figure 3) revealed that in the solid state, the gold and phosphorus atoms lie outside



Scheme 2. Synthesis of complex **7**.

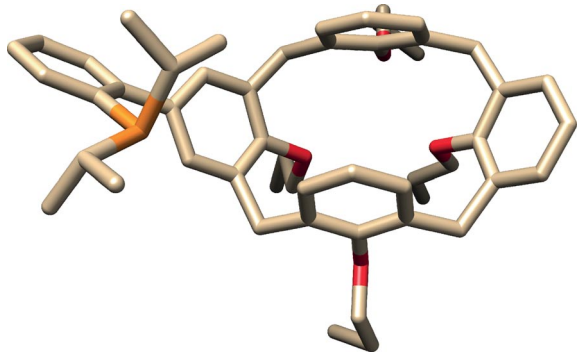


Figure 2. Molecular structure of **5**. Interplanar angles between opposite phenolic rings: 25.8° and 76.4°. Dihedral angle between the two rings of the biaryl subunit: 49.1°.

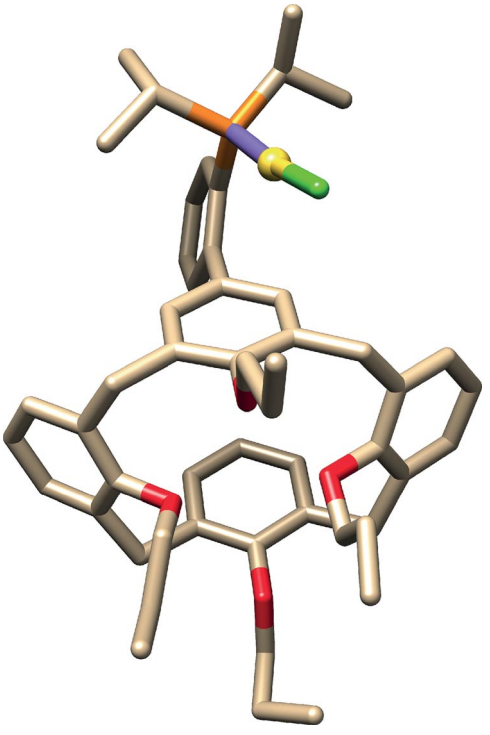


Figure 3. Molecular structure of **7**. Interplanar angles between opposite phenolic rings: 13.2° and 72.5°. Dihedral angle between the two rings of the biaryl subunit: 73.3°. Selected bond lengths [Å] and angle [°]: P–Au 2.239(1), Au–Cl 2.291(1); PAuCl 179.69(2).

the cone, which is defined by the calixarene core. The gold ion is exactly above a C–C bond of the remote biaryl unit with Au···C distances of 3.083 Å (Au···C-24) and 3.285 Å (Au···C-25; C-24 is the *ipso* carbon atom of the remote aryl ring). These values are close to those found in Echavarren's biarylphosphine gold complex **8** (3.02 and 3.25 Å) and typically reflect weak η^2-Au···arene interactions (Figure 4).[14] At this stage, we are unable to state whether a conformer of **7** with the gold atom η^2-bonded to the interior of the cavity exists in solution. However, we anticipate that filling the cavity with a chlorogold moiety would certainly result in strong repulsions between the chlorine atom and the cavity walls.

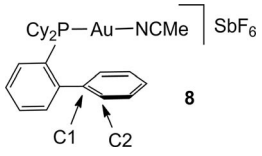
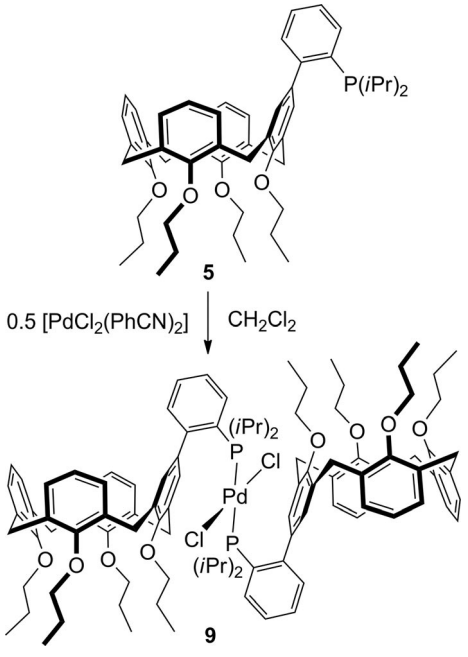


Figure 4. Echevarren's gold complex **8**. Important distances: 3.02 Å (Au···C-1) and 3.25 Å (Au···C-2).

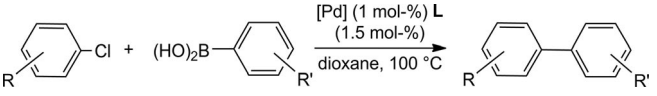
Ligand **5** also readily forms complexes with palladium(II). For example, the reaction of $[PdCl_2(PhCN)_2]$ with 2 equiv. of **5** in CH_2Cl_2 quantitatively gave the complex *trans*-$[PdCl_2(\mathbf{5})_2]$ (**9**; Scheme 3). The *trans*-selectivity of this reaction is a reflection of the high steric encumbrance of phosphine **5**. The *trans* configuration of the palladium complex was unambiguously inferred from the ^{13}C NMR spectrum, which shows a virtual triplet for the P*C*HMe$_2$ carbon atoms ($|^1J_{P,C} + {}^3J_{P,C}| = 20.5$ Hz).[15]



Scheme 3. Synthesis of palladium complex **9**.

Catalytic Suzuki–Miyaura Cross-Coupling with 5 and 6

The two phosphines were then employed in palladium-catalyzed Suzuki–Miyaura cross-coupling reactions (Scheme 4). The catalysts were generated in situ by combining different palladium precursor complexes with 1.5 equiv. of phosphine.



Scheme 4. Suzuki–Miyaura cross-coupling reactions of aryl chlorides with aryl boronic acids (L = phosphine ligand).

To determine the optimal catalytic conditions, $[Pd(OAc)_2]$ and ligand **5** were used in the cross-coupling reaction of 4-chloroanisole and phenylboronic acid at 100 °C in 1,4-dioxane. Each experiment was stopped after 1 h. In the first series of reactions, we determined the optimal base by employing either NaH, KOH, Cs_2CO_3, or *t*BuOK. As can be inferred from the results (Table 1 Entries 1–4), the most efficient base was *t*BuOK, which led to a conversion of 62.6 %. When $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) was used as the palladium precursor instead of $[Pd(OAc)_2]$, the conversion increased from 62.6 to 71.1 % (Table 1, Entry 5).

Table 1. Suzuki–Miyaura cross-coupling reaction of 4-chloroanisole with phenylboronic acid – a search for optimal catalytic conditions.[a] The conversions were determined by GC analysis with the calibrations based on decane.

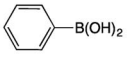
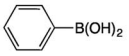
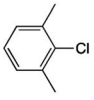
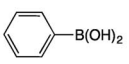
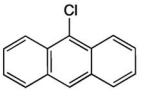
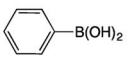
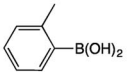
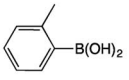
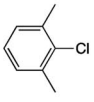
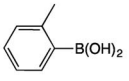
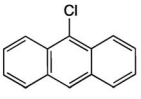
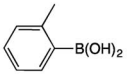
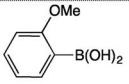
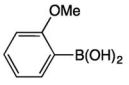
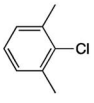
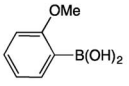
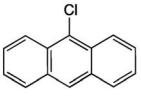
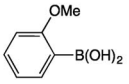
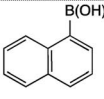
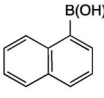
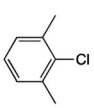
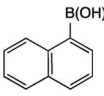
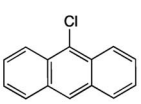
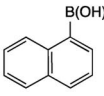
Entry	[Pd]	Phosphine	Base	Conversion (%)
1	$[Pd(OAc)_2]$	**5**	NaH	32.8
2	$[Pd(OAc)_2]$	**5**	KOH	33.0
3	$[Pd(OAc)_2]$	**5**	Cs_2CO_3	11.7
4	$[Pd(OAc)_2]$	**5**	*t*BuOK	62.6
5	$[Pd_2(dba)_3]$	**5**	*t*BuOK	71.1
6	$[Pd(OAc)_2]$	**6**	*t*BuOK	84.8
7	$[Pd_2(dba)_3]$	**6**	*t*BuOK	91.5

[a] Reagents and conditions: [Pd] (1.0 mol-%), phosphine (1.5 mol-%), 4-MeOC$_6$H$_4$Cl (0.25 mmol), PhB(OH)$_2$ (0.37 mmol), base (0.37 mmol), decane (0.025 mL), dioxane (0.75 mL), 100 °C, 1 h.

Under the determined optimal conditions {i.e., with $[Pd_2(dba)_3]$ and *t*BuOK}, the conversion reached 91.5 % by using phosphine **6**, the activity of which was approximately 30 % higher than that of **5** (Table 1, Entry 7). Reducing the palladium loading to 0.05 mol-% and carrying out the reaction for 22 h at 100 °C gave a conversion of 89.6 %. This corresponds to a turnover number (TON) of 1790 mol(ArCl)/mol(Pd), which was found to be 30 % higher than that obtained with the Buchwald ligand (*o*-biphenyl)PCy$_2$ {TON = 1440 mol(ArCl)/mol(Pd)}.[16] The difference in reactivity between the latter and **6** may be a reflection of the greater, time-averaged steric encumbrance of the calixarenylphosphine (see above).

The catalytic system $[Pd_2(dba)_3]$/**6** was further examined in the cross-coupling reactions of phenyl boronic acid with four sterically hindered aryl chlorides, namely, 2-chlorotoluene, 2-chloroanisole, chloro-2,6-dimethylbenzene, and 9-chloroanthracene. 2-Chlorotoluene and 2-chloroanisole were converted into the corresponding biaryls in high yields within 2 h (94.5 and 88.4 % conversion; Table 2, Entries 1 and 2). As expected, essentially complete conversion with the bulkier 2,6-dimethylchlorobenzene and 9-chloroanthracene required longer reaction times (Table 2, Entries 3 and 4). A similar trend was observed when the latter substrates were treated with the three encumbered reagents (2-methylphenyl)boronic acid, (2-methoxy-

Table 2. Suzuki–Miyaura cross-coupling of aryl chlorides catalyzed by using $[Pd_2(dba)_3]$/**6**.[a] The conversions were determined by GC analysis with the calibrations based on decane.

Entry	ArCl	Ar'B(OH)$_2$	Time [h]	Conv. (%)
1			2	94.5
2			2	88.4
3			8	94.9
4			5	98.1
5			16	99.8
6			16	65.9
7			24	68.2
8			16	80.5
9			16	99.7
10			16	92.6
11			24	78.5
12			16	95.1
13			8	73.9
14			8	88.6
15			16	90.2
16			8	97.3

[a] Reagents and conditions: $[Pd_2(dba)_3]$ (0.5 mol-%), **6** (1.5 mol-%), ArCl (0.25 mmol), ArB(OH)$_2$ (0.37 mmol), *t*BuOK (0.37 mmol), decane (0.025 mL), dioxane (0.75 mL), 100 °C.

phenyl)boronic acid, and naphthalene-1-boronic acid. These reactions with the combination of $[Pd_2(dba)_3]$ and phosphine **6** resulted in *ortho*-trisubstituted biphenyls in moderate to good yields. For example, the reactions of chloroanthracene and each of the three boronic acids gave the corresponding *ortho*-trisubstituted biphenyls in 80.5, 95.1, and 97.3 % yield, respectively, after 16, 16, and 8 h (Table 2, Entries 8, 12, and 16).

Overall, arylcalixarenylphosphine **6** in combination with palladium acts as an efficient cross-coupling catalyst towards aryl chlorides, especially for the synthesis of encumbered biaryls. However, the activity of the Pd/**6** system remains approximately 500 times lower than that of the Buchwald ligands, which incorporate additional methoxy groups at the *ortho*-carbon atoms of the remote aryl group.[1c] These ligands assist the oxidative addition step by forming intermediate electron-enriched *P,O*-chelate complexes, but they also possibly sterically favor the reductive elimination step.[17]

Conclusions

Herein, we have described the synthesis of the first conical calix[4]arenes, in which the upper rim is substituted by an *o*-phosphinated phenyl group and, therefore, belong to the class of ligands commonly designated as biarylphosphines. The structure of **5** was established by an X-ray diffraction study, which revealed that in the solid form, the phosphorus atom is placed on the inner side of the cavity delineated by the calixarene core. In contrast, in complex [AuCl•**5**], the P–Au–Cl rod is turned outwards from the cavity with a neighboring phenoxy ring weakly π-interacting with the gold ion. Arylcalixarenylphosphine **6** was more active as a catalyst ligand in the SMC reaction than Buchwald ligand (*o*-biphenyl)PCy_2. This result was a direct consequence of its greater bulkiness, which is imposed by the presence of the calixarene cavity. Ligand **6** was also employed in the effective cross-coupling reaction of a variety of *o*-substituted aryl chlorides with encumbered boronic acids. Its activity, however, remained lower than that of those Buchwald phosphines equipped with methoxy groups attached at the *o*-carbon atoms of the remote aryl ring, which may anchimerically assist in the reaction. With regard to this, it would be of interest to extend our studies to related arylcalixarenylphosphines that have both rims substituted with weak donors.

Experimental Section

General Methods: All manipulations that involve phosphorus derivatives were performed in Schlenk-type flasks under argon. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed through a 5 cm thick alumina column and stored under nitrogen over molecular sieves (4 Å). The routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic data were recorded with Bruker FT spectrometers (AVANCE 400 and 500). The chemical shifts in the ^1H NMR spectra are referenced to the residual protiated solvent (δ = 7.26 ppm for $CHCl_3$ and 7.11 ppm for C_6D_5H). The chemical shifts of the ^{13}C NMR spectra are reported relative to the deuteriated solvents (δ = 77.16 ppm for $CDCl_3$ and 128.06 ppm for C_6D_6). The chemical shifts of the ^{31}P NMR spectroscopic data are given relative to external H_3PO_4. Chemical shifts and coupling

constants are reported in ppm and Hz, respectively. Cq denotes a quaternary carbon atom. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, CNRS-Université de Strasbourg. 5-Bromo-25,26,27,28-tetrapropyloxycalix[4]arene (**1**),[11] [AuCl(THT)],[18] and $[PdCl_2(PhCN)_2]$[19] were prepared according to literature procedures.

5-(2-Bromophenyl)-25,26,27,28-tetrapropyloxycalix[4]arene (2): *n*BuLi (1.6 M in hexane, 0.53 mL, 0.86 mmol) was slowly added to a solution of 5-bromo-25,26,27,28-tetrapropyloxycalix[4]arene (**1**, 0.460 g, 0.78 mmol) in THF (15 mL) at –78 °C. After 0.5 h, the resulting carbanion was quenched by the addition of $B(OMe)_3$ (1.67 mL, 1.56 mmol), and the mixture was stirred at room temperature for 12 h. The reaction mixture was hydrolyzed with a solution of HCl (1 M, 50 mL). The product was then extracted into CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried with Na_2SO_4 and reduced under vacuum. The crude 5-boronic-25,26,27,28-tetrapropyloxycalix[4]arene acid was used without any further purification in the next step. A 100 mL Schlenk tube was filled with the crude boronic acid, 1,2-dibromobenzene (2.77 mL, 11.78 mmol), $[Pd(PPh_3)_4]$ (0.050 g, 0.40 mmol), and Cs_2CO_3 (0.300 g, 0.94 mmol). [1,2-Dibromobenzene was used in an excess amount to avoid formation of the corresponding 1,2-dicalixarenylbenzene]. *N*,*N*-dimethylformamide (DMF, 50 mL) was then added, and the resulting mixture was heated at 110 °C for 24 h. The solvent was evaporated under vacuum, and the residue was dissolved in CH_2Cl_2 (50 mL). The resulting solution was washed with water (4 × 25 mL), and the organic layer was dried with Na_2SO_4 and reduced under vacuum. The crude product was purified by column chromatography (petroleum ether) to afford **2** (0.280 g, 56 % yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1 H, arom. CH, C_6H_4), 7.28 (td, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 1 H, arom. CH, C_6H_4), 7.12 (td, ^3J = 7.6 Hz, ^4J = 1.8 Hz, 1 H, arom. CH, C_6H_4), 7.03 (dd, ^3J = 7.5 Hz, ^4J = 1.8 Hz, 1 H, arom. CH, C_6H_4), 6.78 (m, 4 H, arom. CH, calixarene), 6.74 (s, 2 H, arom. CH, calixarene), 6.68–6.65 (m, 4 H, arom. CH, calixarene), 6.57 (dd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, 1 H, arom. CH, calixarene), 4.56 and 3.24 (AB spin system, ^2J = 13.5 Hz, 4 H, ArCH_2Ar), 4.54 and 3.22 (AB spin system, ^2J = 13.2 Hz, 4 H, ArCH_2Ar), 3.97 (t, ^3J = 7.5 Hz, 4 H, OCH_2), 3.94 (t, ^3J = 7.5 Hz, 2 H, OCH_2), 3.90 (t, ^3J = 7.5 Hz, 2 H, OCH_2), 2.09–1.96 (m, 8 H, CH_2CH_3), 1.10 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.07 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 1.06 (t, ^3J = 7.5 Hz, 6 H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 156.72 (s, arom. Cq-O), 156.51 (s, arom. Cq-O), 156.15 (s, arom. Cq-O), 142.81–121.99 (arom. carbons), 76.97 (s, OCH_2), 76.91 (s, OCH_2), 76.81 (s, OCH_2), 31.12 (s, ArCH_2Ar), 23.50 (CH_2CH_3), 23.44 (CH_2CH_3), 23.35 (CH_2CH_3), 10.55 (CH_2CH_3), 10.42 (CH_2CH_3) ppm. MS (ESI): *m*/*z* = 769.28 $[M + Na]^+$ (expected isotopic profiles). $C_{46}H_{51}BrO_4$ (747.80): calcd. C 73.88, H 6.87; found C 73.91, H 6.90.

General Procedure for the Synthesis of [5-(2-Phosphinophenyl)-25,26,27,28-tetrapropyloxycalix[4]arene]boranes 3 and 4: *n*-Butyllithium (1.6 M in hexane, 0.68 mL, 1.08 mmol) was slowly added to a solution of 5-(2-bromophenyl)-25,26,27,28-tetrapropyloxycalix[4]arene (0.600 g, 0.87 mmol) in THF (50 mL) at –78 °C. After 0.5 h, the resulting carbanion was quenched with $ClPR_2$ (1.30 mmol), and the mixture was stirred at 65 °C for 16 h. The reaction was cooled to 0 °C, and BH_3·THF (1 M in THF, 2 mL, 2 mmol) was added. After stirring for 5 h at room temperature, the solvents were evaporated under reduced pressure, and the crude product was purified by column chromatography (see below).

[5-(2-Diisopropylphosphinophenyl)-25,26,27,28-tetrapropyloxycalix[4]arene]borane (3): Purification by column chromatography (CH_2Cl_2/petroleum ether, 20:80 v/v) afforded compound **3** (70 % yield). ^{1}H NMR (400 MHz, C_6D_6, 341 K): δ = 8.46–8.40 (m, 1 H, arom. CH, C_6H_4), 7.16–7.09 (m, 2 H, arom. CH, C_6H_4), 6.96–6.93 (m, 1 H, arom. CH, C_6H_4), 6.83–6.75 (m, 5 H, arom. CH, calixarene), 6.61–6.54 (m, 6 H, arom. CH, C_6H_4), 4.58 and 3.13 (AB spin system, ^2J = 13.6 Hz, 4 H, ArCH_2Ar), 4.55 and 3.13 (AB spin system, ^2J = 13.6 Hz, 4 H, ArCH_2Ar), 3.98 (t, ^3J = 7.0 Hz, 2 H, OCH_2), 3.90 (t, ^3J = 7.0 Hz, 2 H, OCH_2), 3.81 (t, ^3J = 6.8 Hz, 4 H, OCH_2), 2.21–2.06 [m, 2 H, $CH(CH_3)_2$], 1.95–1.84 (m, 8 H, CH_2CH_3), 1.23 [dd, $^3J_{P,H}$ = 14.8 Hz, ^3J = 6.8 Hz, 6 H, $CH(CH_3)_2$], 0.99 [dd, $^3J_{P,H}$ = 14.8 Hz, ^3J = 6.8 Hz, 6 H, $CH(CH_3)_2$], 0.95 (t, ^3J = 7.2 Hz, 9 H, CH_2CH_3), 0.93 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 0.88–0.80 (m, 3 H, BH_3) ppm. ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 341 K): δ = 157.46 (s, arom. Cq-O), 157.24 (s, arom. Cq-O), 156.81 (s, arom. Cq-O), 146.90–122.63 (arom. carbons), 77.20 (s, OCH_2), 77.12 (s, OCH_2), 31.78 (s, ArCH_2Ar), 31.67 (s, ArCH_2Ar), 24.67 [d, $^1J_{P,C}$ = 32.3 Hz, $CH(CH_3)_2$], 23.73 (CH_2CH_3), 23.67 (CH_2CH_3), 23.57 (CH_2CH_3), 19.30 [s, $CH(CH_3)_2$], 18.77 [s, $CH(CH_3)_2$], 10.61 (CH_2CH_3), 10.56 (CH_2CH_3), 10.49 (CH_2CH_3) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 341 K): δ = 45.8 [s, $P(BH_3)iPr_2$] ppm. $C_{52}H_{68}BO_4P$ (798.88): calcd. C 78.18, H 8.58; found C 78.22, H 8.68.

[5-(2-Dicyclohexylphosphinophenyl)-25,26,27,28-tetrapropyloxycalix[4]arene]borane (4): Purification by column chromatography (CH_2Cl_2/pentane, 20:80 v/v) afforded compound **4** (65 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02–7.97 (m, 1 H, arom. CH, C_6H_4), 7.37–7.30 (m, 2 H, arom. CH, C_6H_4), 6.89 (d, ^3J = 6.0 Hz, 2 H, arom. CH, calixarene), 6.81 (d, ^3J = 6.0 Hz, 2 H, arom. CH, calixarene), 6.74–6.68 (m, 3 H, arom. CH, calixarene), 6.59–6.53 (m, 3 H, arom. CH, calixarene and C_6H_4), 6.31 (s, 2 H, arom. CH, calixarene), 4.61 and 3.19 (AB spin system, ^2J = 13.2 Hz, 4 H, ArCH_2Ar), 4.53 and 3.19 (AB spin system, ^2J = 13.2 Hz, 4 H, ArCH_2Ar), 4.08–3.98 (m, 4 H, OCH_2), 3.89 (t, ^3J = 6.0 Hz, 2 H, OCH_2), 3.82 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 2.08–1.92 (m, 8 H, CH_2CH_3), 1.78–1.65 (m, 8 H, Cy), 1.58–1.42 (m, 4 H, Cy), 1.28–1.08 (m, 16 H, CH_2CH_3 and Cy), 1.01 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 0.80–0.35 (m, 3 H, BH_3) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 157.13 (s, arom. Cq-O), 156.15 (s, arom. Cq-O), 146.38–122.07 (arom. carbons), 77.63 (s, OCH_2), 77.13 (s, OCH_2), 76.79 (s, OCH_2), 34.06 [d, $^1J_{P,C}$ = 34.1 Hz, $CH(CH_2)_5$], 31.28 (s, ArCH_2Ar), 31.16 (s, ArCH_2Ar), 28.72 [s, $CH(CH_2)_5$], 27.94 [s, $CH(CH_2)_5$], 27.23 [d, $^2J_{P,C}$ = 13.3 Hz, $CH(CH_2)_5$], 26.92 [d, $^2J_{P,C}$ = 11.6 Hz, $CH(CH_2)_5$], 25.87 [s, $CH(CH_2)_5$], 23.52 (CH_2CH_3), 23.26 (CH_2CH_3), 10.70 (CH_2CH_3), 10.22 (CH_2CH_3) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 35.4 [s, $P(BH_3)Cy_2$] ppm. $C_{58}H_{76}BO_4P$ (879.01): calcd. C 79.25, H 8.71; found C 79.36, H 8.85.

General Procedure for the Synthesis of 5-(2-Phosphinophenyl)-25,26,27,28-tetrapropyloxycalix[4]arenes 5 and 6: A solution of the appropriate [5-(2-phosphinophenyl)-25,26,27,28-tetrapropyloxycalix[4]arene]borane (0.60 mmol) in MeOH/toluene (1:4, 15 mL) was heated at reflux for 5 h. After cooling to room temperature, the reaction mixture was evaporated to dryness, and the residue was dried overnight at 40 °C under vacuum to afford the corresponding phosphine quantitatively.

5-(2-Diisopropylphosphinophenyl)-25,26,27,28-tetrapropyloxycalix[4]arene (5): ^{1}H NMR (500 MHz, C_6D_6): δ = 7.45 (d, ^3J = 7.5 Hz, 1 H, arom. CH, C_6H_4), 7.35–7.33 (m, 1 H, arom. CH, C_6H_4), 7.22–7.17 (m, 4 H, arom. CH, C_6H_4, calixarene), 6.96–6.87 (m, 5 H, arom. CH, calixarene), 6.65 (t, ^3J = 7.5 Hz, 2 H, arom. CH, calixarene), 6.60 (d, ^3J = 7.0 Hz, 2 H, arom. CH, C_6H_4), 4.61 and 3.27 (AB spin system, ^2J = 13.0 Hz, 4 H, ArCH_2Ar), 4.58 and 3.18 (AB spin system, ^2J = 13.5 Hz, 4 H, ArCH_2Ar), 3.99 (t, ^3J = 7.7 Hz, 4 H, OCH_2), 3.73 (t, ^3J = 7.2 Hz, 4 H, OCH_2), 2.04–1.92 [m, 6 H, CH_2CH_3 and $CH(CH_3)_2$], 1.88–1.80 (m, 4 H, CH_2CH_3), 1.07 [dd, $^3J_{P,H}$ = 14.0 Hz, ^3J = 6.5 Hz, 6 H, $CH(CH_3)_2$], 1.01 [dd, $^3J_{P,H}$ = 11.5 Hz, ^3J = 7.0 Hz, 6 H, $CH(CH_3)_2$], 0.94 (t, ^3J = 7.5 Hz, 6 H, CH_2CH_3), 0.90 (t, ^3J = 7.5 Hz, 6 H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 157.78 (s, arom. Cq-O), 156.69 (s,

arom. Cq-O), 156.32 (s, arom. Cq-O), 151.00–122.55 (arom. carbons), 77.05 (s, OCH_2), 76.86 (s, OCH_2), 31.65 (s, $ArCH_2Ar$), 31.60 (s, $ArCH_2Ar$), 25.16 [d, $^1J_{P,C}$ = 16.1 Hz, $CH(CH_3)_2$], 23.76 (CH_2CH_3), 23.67 (CH_2CH_3), 23.55 (CH_2CH_3), 20.58 [d, $^2J_{P,C}$ = 19.9 Hz, $CH(CH_3)_2$], 20.40 [d, $^2J_{P,C}$ = 12.6 Hz, $CH(CH_3)_2$], 10.76 (CH_2CH_3), 10.36 (CH_2CH_3), 10.35 (CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = –4.0 (s, P*i*Pr$_2$) ppm. $C_{52}H_{65}O_4P$ (785.05): calcd. C 79.56, H 8.35; found C 79.38, H 8.30.

5-(2-Dicyclohexylphosphinophenyl)-25,26,27,28-tetrapropyloxycalix[4]arene (6): ^1H NMR (400 MHz, C_6D_6): δ = 7.77–7.74 (m, 1 H, arom. CH, C_6H_4), 7.58–7.53 (m, 1 H, arom. CH, C_6H_4), 7.42–7.38 (m, 4 H, arom. CH, calixarene, C_6H_4), 7.35 (s, 2 H, arom. CH, calixarene), 7.13 (s, 2 H, arom. CH, calixarene), 7.09–7.04 (m, 1 H, arom. CH, calixarene), 6.86 (t, ^3J = 7.5 Hz, 2 H, arom. CH, calixarene), 6.77 (d, ^3J = 7.2 Hz, 2 H, arom. CH, calixarene), 4.82 and 3.49 (AB spin system, ^2J = 13.5 Hz, 4 H, $ArCH_2Ar$), 4.77 and 3.37 (AB spin system, ^2J = 13.2 Hz, 4 H, $ArCH_2Ar$), 4.23–4.16 (m, 4 H, OCH_2), 3.91 (t, ^3J = 7.2 Hz, 4 H, OCH_2), 2.25–1.84 (m, 18 H, CH_2CH_3 and Cy), 1.78–1.74 (m, 2 H, Cy), 1.55–1.33 (m, 10 H, Cy), 1.14 (t, ^3J = 7.5 Hz, 6 H, CH_2CH_3), 1.10 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 1.09 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 157.85 (s, arom. Cq-O), 156.75 (s, arom. Cq-O), 156.31 (s, arom. Cq-O), 151.51–122.53 (arom. carbons), 77.05 (s, OCH_2), 76.83 (s, OCH_2), 35.75 [d, $^1J_{P,C}$ = 16.8 Hz, $CH(CH_2)_5$], 31.70 (s, $ArCH_2Ar$), 31.54 [d, $^2J_{P,C}$ = 12.4 Hz, $CH(CH_2)_5$], 31.21 (s, $ArCH_2Ar$), 30.35 [d, $^2J_{P,C}$ = 10.5 Hz, $CH(CH_2)_5$], 27.53 [s, $CH(CH_2)_5$], 27.38 [s, $CH(CH_2)_5$], 26.91 [s, $CH(CH_2)_5$], 23.78 (CH_2CH_3), 23.70 (CH_2CH_3), 23.55 (CH_2CH_3), 10.79 (CH_2CH_3), 10.37 (CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = –13.5 (s, PCy$_2$) ppm. MS (ESI): *m/z* = 865.53 $[M + H]^+$ (expected isotopic profiles). $C_{58}H_{73}O_4P$ (865.17): calcd. C 80.52, H 8.50; found C 80.61, H 8.64.

Chlorido[5-(2-diisopropylphosphinophenyl)-25,26,27,28-tetrapropyloxycalix[4]arene] Gold(I) (7): A solution of [AuCl(THT)] (0.063 g, 0.2 mmol) in CH_2Cl_2 (25 mL) was added to a stirred solution of **5** (0.155 g, 0.2 mmol) in CH_2Cl_2 (25 mL). After stirring at room temperature for 0.5 h, the reaction mixture was concentrated to about 2 mL, and then *n*-hexane (20 mL) was added. A white precipitate formed, which was then separated by filtration and dried under vacuum to give compound **7** (0.124 g, 95 % yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.48–7.44 (m, 1 H, arom. CH, C_6H_4), 7.35–7.31 (m, 2 H, arom. CH, C_6H_4), 6.91 (d, ^3J = 7.0 Hz, 2 H, arom. CH, calixarene), 6.87 (d, ^3J = 7.0 Hz, 2 H, arom. CH, calixarene), 6.73 (t, ^3J = 7.0 Hz, 2 H, arom. CH, calixarene), 6.61–6.57 (m, 1 H, arom. CH, C_6H_4), 6.41 (s, 3 H, arom. CH, calixarene), 6.18 (s, 2 H, arom. CH, calixarene), 4.53 and 3.25 (AB spin system, ^2J = 13.5 Hz, 4 H, $ArCH_2Ar$), 4.49 and 3.17 (AB spin system, ^2J = 13.0 Hz, 4 H, $ArCH_2Ar$), 4.03 (t, ^3J = 7.0 Hz, 4 H, OCH_2), 3.99 (t, ^3J = 7.5 Hz, 2 H, OCH_2), 3.75 (t, ^3J = 6.0 Hz, 2 H, OCH_2), 2.35–2.28 [m, 2 H, $CH(CH_3)_2$], 2.05–1.88 (m, 8 H, CH_2CH_3), 1.23 [dd, $^3J_{P,H}$ = 18.5 Hz, ^3J = 6.5 Hz, 6 H, $CH(CH_3)_2$], 1.12 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3), 1.07 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.01 [dd, $^3J_{P,H}$ = 17.5 Hz, ^3J = 7.0 Hz, 6 H, $CH(CH_3)_2$], 0.95 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 157.52 (s, arom. Cq-O), 156.44 (s, arom. Cq-O), 155.97 (s, arom. Cq-O), 149.95–121.95 (arom. carbons), 78.19 (s, OCH_2), 77.19 (s, OCH_2), 76.75 (s, OCH_2), 31.28 (s, $ArCH_2Ar$), 31.13 (s, $ArCH_2Ar$), 27.23 [d, $^1J_{P,C}$ = 33.8 Hz, $CH(CH_3)_2$], 23.78 (CH_2CH_3), 23.54 (CH_2CH_3), 23.16 (CH_2CH_3), 20.36 [s, $CH(CH_3)_2$], 19.71 [s, $CH(CH_3)_2$], 10.94 (CH_2CH_3), 10.76 (CH_2CH_3), 10.13 (CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 49.4 (s, P*i*Pr$_2$) ppm. $C_{52}H_{65}AuClO_4P$ (1017.46): calcd. C 61.38, H 6.44; found C 61.45, H 6.52.

***trans*-*P*,*P*-Dichlorido-bis[5-(2-diisopropylphosphinophenyl)-25,26,27,28-tetrapropyloxy-calix[4]arene]palladium(II) (9):** A solution of $[PdCl_2(PhCN)_2]$ (0.012 g, 0.03 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of **5** (0.050 g, 0.06 mmol) in CH_2Cl_2 (10 mL). After stirring for 0.5 h, the reaction mixture was concentrated to about 1 mL, and *n*-hexane (20 mL) was added. The yellow precipitate was separated by filtration and dried under vacuum to give compound **9** (0.053 g, 97 % yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.99–7.95 (m, 1 H, arom. CH, C_6H_4), 7.31–7.24 (m, 2 H, arom. CH, C_6H_4), 6.90–6.79 (m, 5 H, arom. CH, C_6H_4, calixarene), 6.72 (t, ^3J = 7.2 Hz, 1 H, arom. CH, calixarene), 6.49–6.44 (m, 6 H, arom. CH, calixarene), 4.46 and 3.16 (AB spin system, ^2J = 13.5 Hz, 4 H, $ArCH_2Ar$), 4.41 and 3.05 (AB spin system, ^2J = 13.5 Hz, 4 H, $ArCH_2Ar$), 3.90 (t, ^3J = 7.0 Hz, 2 H, OCH_2), 3.89 (t, ^3J = 7.5 Hz, 2 H, OCH_2), 3.81 (t, ^3J = 6.2 Hz, 4 H, OCH_2), 2.45–2.40 [br. signal, 2 H, $CH(CH_3)_2$], 2.00–1.85 (m, 8 H, CH_2CH_3), 1.26 [dd, $^3J_{P,H}$ = 15.0 Hz, $^3J_{HH}$ = 7.5 Hz, 6 H, $CH(CH_3)_2$], 1.10 [dd, $^3J_{P,H}$ = 14.5 Hz, ^3J = 7.5 Hz, 6 H $CH(CH_3)_2$], 1.01 (t, ^3J = 7.5 Hz, 6 H, CH_2CH_3), 0.99 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 0.98 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 157.08 (s, arom. Cq-O), 156.49 (s, arom. Cq-O), 156.20 (s, arom. Cq-O), 146.86–121.97 (arom. carbons), 76.86 (s, OCH_2), 76.82 (s, OCH_2), 31.11 (s, $ArCH_2Ar$), 31.03 (s, $ArCH_2Ar$), 24.07 [virtual t, $|^1J_{P,C} + {}^3J_{P,C}|$ = 20.1 Hz, $CH(CH_3)_2$], 23.47 (CH_2CH_3), 23.34 (CH_2CH_3), 23.18 (CH_2CH_3), 21.15 [s, $CH(CH_3)_2$], 19.66 [s, $CH(CH_3)_2$], 10.67 (CH_2CH_3), 10.60 (CH_2CH_3), 10.37 (CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 46.3 (s, P*i*Pr$_2$) ppm. $C_{104}H_{130}Cl_2O_8P_2Pd$ (1747.42): calcd. C 71.48, H 7.50; found C 71.55, H 7.61.

X-ray Crystal Structure Analysis of 5: Single crystals of **5** suitable for X-ray analysis were obtained by slow diffusion of hexane into a chloroform solution of phosphine **5**. Crystal data: *Mr* = 785.01 g mol^{-1}, monoclinic, space group $P2_1/c$, *a* = 17.7981(15) Å, *b* = 15.3224(14) Å, *c* = 19.0158(13) Å, β = 117.920(6)°, *V* = 4582.2(7) Å^3, *Z* = 4, D_x = 1.138 mg m^{-3}, μ = 0.103 mm^{-1}, *F*(000) = 1696, *T* = 173(2) K. The sample (0.500 × 0.350 × 0.300 mm) was studied on a Kappa APEX II diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å). The data collection ($2\theta_{max}$ = 55.9°, omega scan frames by using 0.7° omega rotation and 30 s per frame, range *hkl*: *h* –19,23 *k* –20,20 *l* –25,11) gave 11043 reflections. The structure was solved with SIR-97,[20] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all of the hydrogen atoms were found with a Fourier difference map. The structure was refined with SHELXL97[21] by the full-matrix least-square techniques (use of *F* square magnitude; *x*, *y*, *z*, βij for C, O, and P atoms; *x*, *y*, *z* in riding mode for H atoms); 536 variables and 8258 observations with $I > 2.0\,\sigma(I)$; calcd. $w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 3.8030P]$ where $P = (F_o^2 + 2F_c^2)/3$, with the resulting $R = 0.0531$, $R_W = 0.1380$, and $S_W = 1.020$, $\Delta\varrho < 0.878$ e Å^{-3}.

X-ray Crystal Structure Analysis of 7: Single crystals of **7** suitable for X-ray analysis were obtained by slow diffusion of methanol into a chloroform solution of the complex. Crystal data: *Mr* = 1017.42 g mol^{-1}, triclinic, space group $P\bar{1}$, *a* = 11.2854(7) Å, *b* = 12.4261(8) Å, *c* = 19.8280(13) Å, α = 87.284(2)°, β = 79.750(1)°, γ = 66.829(1)°, *V* = 2514.7(3) Å^3, *Z* = 2, D_x = 1.344 mg m^{-3}, μ = 3.051 mm^{-1}, *F*(000) = 1040, *T* = 173(2) K. The sample (0.320 × 0.180 × 0.160 mm) was studied on a Kappa APEX II diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å). The data collection ($2\theta_{max}$ = 61.8°, omega scan frames by using 0.7° omega rotation and 30 s per frame, range *hkl*: *h* –16,9 *k* –17,17 *l* –28,28) gave 60478 reflections. The structure was solved with SIR-97,[20] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all of the hydrogen atoms were found with a Fourier difference map. The structure was refined with SHELXL97[21] by the full-matrix least-square techniques (use of *F* square magnitude; *x*, *y*, *z*, βij for Au; C, Cl, O and P atoms; *x*, *y*, *z* in riding mode for H atoms); 540 variables and 13416 observations with $I > 2.0\,\sigma(I)$; calcd. $w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 1.0409P]$ where

$P = (F_o^2 + 2F_c^2)/3$, with the resulting $R = 0.0289$, $R_W = 0.0608$ and $S_W = 1.055$, $\Delta\rho < 1.692$ e Å^{-3}.

CCDC 1447135 (for **5**) and 1447135 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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