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Multinuclear Calixarene Synthons with Covalently Linked Aryl-Palladium(II) Complexes

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New synthetic procedures have been developed for potentially useful metallacalixarene building blocks. The metal sites were covalently connected to calix[*n*]arenes ($n = 4$, 6) by oxidative addition of 4-iodobenzyl precursors to either $Pd(PPh_3)_4$ or $Pd_2(dba)_3$/tmeda (dba = dibenzylideneacetone) to furnish calixarene-modified aryl-Pd(II)I(L_n) complexes [L_n = bis-PPh_3 or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda)]. Methods were explored for the selective preparation of mono-Pd(II)-calix[4]arene and di-Pd(II)-calix[*n*]arenes ($n = 4$ or 6) complexes and also for bifunctional calix[4]arene synthons with two Pd(II) complexes accompanied by 4-pyridylmethyl or 4-cyanobenzyl groups. The properties of the Pd(II)-calix[*n*]arenes were studied in detail by one- and two-dimensional NMR and mass spectrometric techniques. The X-ray molecular structures of two 4-iodobenzylcalix[4]arene precursors were also determined.

Introduction

Calix[4]- and calix[6]arenes[1] have been widely used as building blocks in supramolecular synthesis.[2] On one hand, calixarenes can possess a basket-shaped conformation useful for molecular recognition.[3] On the other hand, calixarenes have provided platforms for the immobilization of (transition) metal centers that are useful in catalysis,[4] among other applications.[5] Most of the previously reported approaches toward the synthesis of metallacalixarenes are based on coordination of calixarene scaffolds endowed with N- or P-donor motifs for metal coordination.[6] The formation of less dynamic metal-to-carbon (M−C) bonds[7] can be a highly attractive feature from a stability point of view (for example, metal leaching), an aspect that may be preferred in long-term (catalytic) applications. More importantly, a detailed control over the relative positions of multiple organometallic groups enables a precise manipulation of the metallacalixarene structure. From this point of view, calixarenes are highly useful, rigid carrier molecules and their topology should allow the introduction of functional groups at preselected positions.This could give access to catalyst systems displaying cooperative effects (e.g., enzymes), such as bimetallic activation of substrates.

Here, we present a general strategy toward lower rim functionalized metallacalix[*n*]arenes ($n = 4$, 6) that possess organometallic groups covalently attached to the calixarene support. Methods for the selective introduction of a single or multiple Pd(II) center(s) will be described as well as for novel metallacalixarene synthons with potentially useful auxiliary groups.

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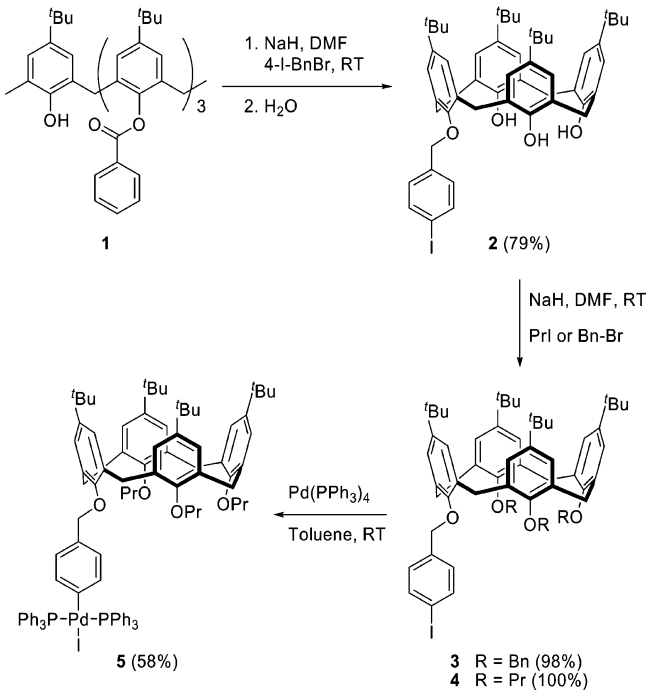
SCHEME 1. Synthesis of Mono-Pd(II) Calix[4]arene 5



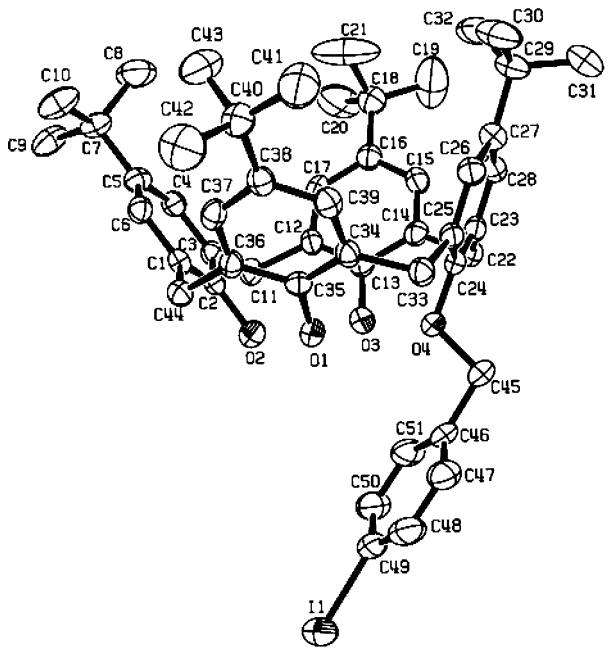


FIGURE 1. X-ray molecular structure of **2** with adopted numbering scheme. For clarity, hydrogen atoms and cocrystallized solvent molecules have been omitted and thermal ellipsoids are shown at 30% probability.

Results and Discussion

Synthesis of Monosubstituted Calix[4]arenes. Selective introduction of a single organometallic group at the lower rim of the calix[4]arene backbone was achieved by use of a recently disclosed methodology reported by Ungaro and co-workers.[8] One of the intermediate components in their studies was a de-*tert*-butylated, tribenzoylcalix[4]arene, first described by Gutsche and Lin.[9] At a later stage, Chawla and Pathak[10] reported the synthesis of tribenzoyl derivative **1** (Scheme 1), and this species was selected as starting point for the monofunctionalized calixarene compounds in this work.

4-Iodobenzyltetra-*tert*-butylcalix[4]arene **2**[11] could be directly obtained (79% isolated yield) via a one-pot alkylation−deprotection sequence,[12] starting from a mixture of conformers of **1**,[13] 4-iodobenzyl bromide, and excess sodium hydride, the principal quenching reagent here being H_2O.[14] Monosubstitution in **2** was confirmed by NMR spectroscopy and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. The conformation and structural details were revealed by single-crystal X-ray crystallography (Figure 1; for selected bond angles and distances see Table S1 in Supporting Information).

The structure shows a monofunctionalized calix[4]arene in an almost ideal, rather open cone conformation. All aromatic rings of the calixarene framework are pointing outward as referred to the reference plane defined by the calixarene methylene carbons. As expected, the iodobenzyl moiety in **2** is situated below the lower rim cavity of the calixarene.

Attempts to prepare the corresponding Pd(II) derivative from **2** by standard procedures involving activation of the carbon−iodine bond by a suitable Pd(0) precursor [i.e., $Pd(PPh_3)_4$] were unsuccessful. Although ^1H NMR monitoring of the reaction indicated the initial formation of a new species, as suggested by the appearance of new sets of signals for the OH and OCH_2 groups, extensive decomposition of the intermediate product and/or the Pd(0) reagent takes place subsequently, probably because of the high acidity of the three free hydrogen-bonded phenol OH groups present in **2** ($\delta_{OH} = 9.97$ and 9.33 ppm, respectively).[15]

The free phenol positions in **2** were therefore protected. Benzylation with an excess of benzyl bromide in dimethylformamide (DMF), in the presence of NaH, afforded the corresponding compound **3** in high yield (Scheme 1). The symmetry of **3** was easily recognized in the NMR spectra. The two proximal benzyl groups with respect to the aryl iodide substituent gave rise to a neat AB pattern for the

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(12) Although this compound was previously reported (see ref 11a), we developed a slightly modified, simpler synthetic procedure that obviates the use of heavy metal reagents and tedious workup procedures.

(13) The tribenzoyl derivative **1** was prepared by a modified literature procedure (see ref 9). The conformational properties differed markedly from those reported earlier. For full details see Kleij, A. W.; Souto, B.; Pastor, C. J.; Prados, P.; de Mendoza, J. *J. Org. Chem.* **2003**, *68*, 8711−8714.

(14) Presumably, the excess NaH reacts with the quenching reagent (H_2O) to form NaOH in situ that gives rise to fast deprotection of the tribenzoyl intermediate (79% yield) under the employed conditions. This procedure was reproduced with an isolated yield of 80%.

(15) A further demonstration of the acid instability of the Pd(II)-calixarenes was given by attempting column chromatography with silica stationary phases. This gave a fast decomposition of the products as indicated by darkening of the material.

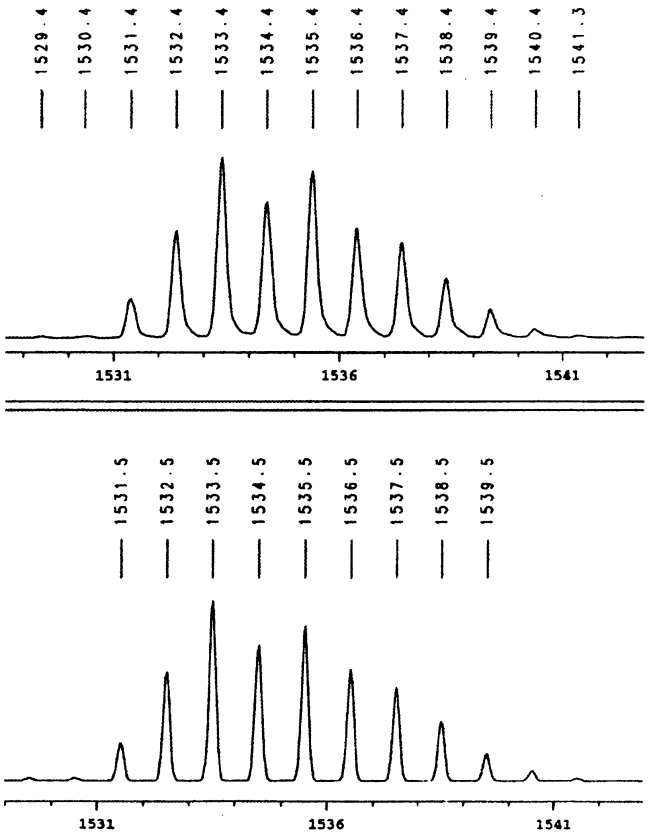


FIGURE 2. Part of the MALDI-TOF-MS spectrum of compound **5** showing the observed (upper spectrum) and calculated (lower spectrum) isotopic distribution for the fragment ion [(M − $2PPh_3$ + K + dppe)$^+$].

OCH_2 unit, while the remaining OCH_2 groups were observed as singlets. Additionally, the $^{13}C\{^1H\}$ NMR spectrum showed three separate signals for the OCH_2 carbons. Tripropyl derivative **4** was obtained analogously in quantitative yield (Scheme 1). In agreement with the previous structure, the NMR spectrum of **4** showed the presence of two distinct propyl groups. Use of propyl instead of benzyl protection allowed a straightforward synthesis of the corresponding Pd(II) complex **5** as a yellow solid in moderate yield (58%).[16] Although a peak at m/z = 1397.3 (calcd 1397.5), assignable to the [(M − $2PPh_3$ + K)$^+$] fragment ion, was visible in the MALDI-TOF mass spectrum of **5**, phosphine exchange with 1,2-diphenylphosphinoethane (dppe) resulted in a more stable complex, as was confirmed by the presence of a sizable [(M − $2PPh_3$ + K + dppe)$^+$] fragment at m/z = 1533.4 (calcd 1533.5) (Figure 2).

Synthesis and Characterization of Disubstituted Calix[4]arenes. Treatment of the parent starting materials *p*-R-calix[4]arenes **6** (R = ^{t}Bu) and **7** (R = H) with 4-iodobenzyl bromide in acetonitrile, with K_2CO_3 as base, afforded the *syn*-1,3-bis(4-iodobenzyl)calix[4]arenes **8** (76%) and **9** (92%), respectively (Scheme 2). These compounds were subsequently used as starting materials for the preparation of the corresponding dipalladated derivatives **10** and **11** (Scheme 2).

(16) Palladation was unsuccessfully attempted with tribenzyl-protected derivative **3** (^{1}H NMR monitoring), probably due to steric reasons. Prolonged reaction times are unlikely to be beneficial due to Pd-reagent and/or Pd-calixarene decomposition in methanol.

Therefore, solution mixtures of **8** or **9** and a suitable Pd(0) precursor [e.g., $Pd(PPh_3)_4$] were stirred at ambient temperature until complete conversion (^{1}H NMR monitoring). The OCH_2 signals were particularly diagnostic, as they underwent large upfield shifts ($\Delta\delta \approx 0.5$ ppm) upon introduction of the metal center, as well as the aryl protons of the pendant arylmethyl groups (from ca. δ = 7.7 and 7.4 ppm to 6.5 and 6.3 ppm, respectively). These spectroscopic changes could be ascribed to the anisotropy of the close P-aryl groups. The resulting Pd(II) derivatives **10** and **11** were isolated as yellow solids in 72% and almost quantitative yield, respectively.[17] Although these Pd(II)-containing calix[4]arenes **10** and **11** are stable in the solid state as well as in solution in a number of solvents [tetrahydrofuran (THF), CH_2Cl_2, and acetone], particular care should be taken with long-term exposure to more acidic or protic solvents such as $CHCl_3$ and MeOH. Prolonged standing in either of these solvents caused solutions to darken, accounting for some decomposition, as was evidenced by NMR ($CDCl_3$) measurements.

Compounds **10** and **11** constitute useful examples of multicentered metallacalixarenes with direct M−C bonds and potentially tunable metal centers via electronic and/or steric modifications. The NMR spectroscopic data of the aryl-Pd(II) groups in **10** and **11** agree with the values reported for other nonsupported aryl-Pd(II) complexes of this type.[18]

The MALDI-TOF mass spectrum (ditranol matrix + NaI) of **10** exhibited an intense cluster at m/z = 1838.5 (calcd 1839.3) that was attributed to the fragment ion [(M − $2PPh_3$ + Na)$^+$]. Additional isotopic patterns could be detected, which were assigned to dipalladated calix[4]arenes. These clusters are probably a result of in situ fragmentation/decomposition processes under the applied conditions, as observed previously for complex **5**. Consequently, no molecular ion could be detected. This type of fragmentation behavior is thus a common feature in the mass spectra of all PPh_3-containing Pd(II)-calix[4]arenes presented in this investigation.

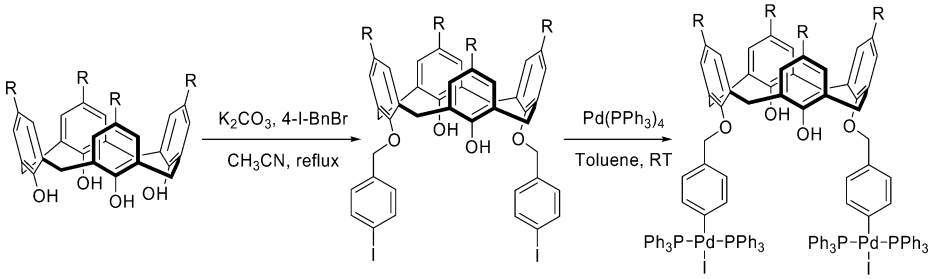
Synthesis and Characterization of Difunctional Calix[4]arenes. Disubstituted calix[4]arene **8** was used as starting point for the preparation of cone calix[4]arenes bearing two different functional groups at the lower rim. Apart from the 4-iodobenzyl groups, which can be converted into aryl-Pd(II)I complexes after treatment with $Pd(PPh_3)_4$ (vide supra), the possibility to introduce other functional groups was also explored. These could eventually be useful for the construction of catalytic species with proximal auxiliary groups aimed at the molecular recognition of specific substrates.

Treatment of **8** with NaH in DMF at room temperature, followed by slow addition of solid 4-chloromethylpyridine hydrochloride, yielded the difunctional derivative **12** in 62% yield, after crystallization from CH_2Cl_2/MeOH. A similar approach was used for the synthesis of **13** (90% yield) from 4-cyanobenzyl bromide (Scheme 3). The ^{1}H NMR spectra of these compounds showed the

(17) In this case, the diametrically opposite OH groups do not seem to interfere with metalation, probably due to their lower acidity as compared with the strongly chelated vicinal OH groups in **1**, causing a faster decomposition of acid-labile Pd-containing reagent/products.

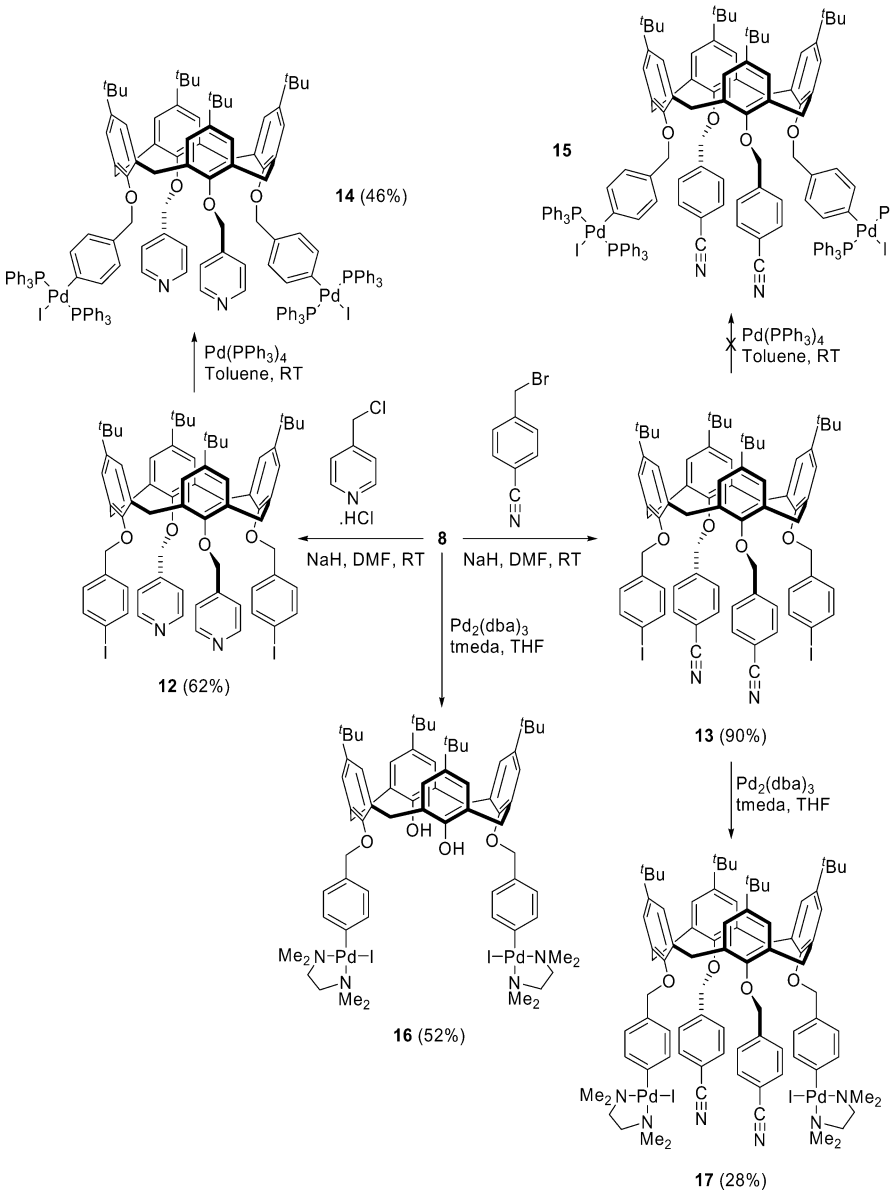
(18) Wallow, T. I.; Goodson, F. E.; Novak, B. M. *Organometallics* **1996**, *15*, 3708−3716.

SCHEME 2. Synthesis of Di-Pd(II) Calix[4]arenes 10 and 11



6 R = ^{t}Bu
7 R = H
8 R = ^{t}Bu (76%)
9 R = H (92%)
10 R = ^{t}Bu (72%)
11 R = H (98%)

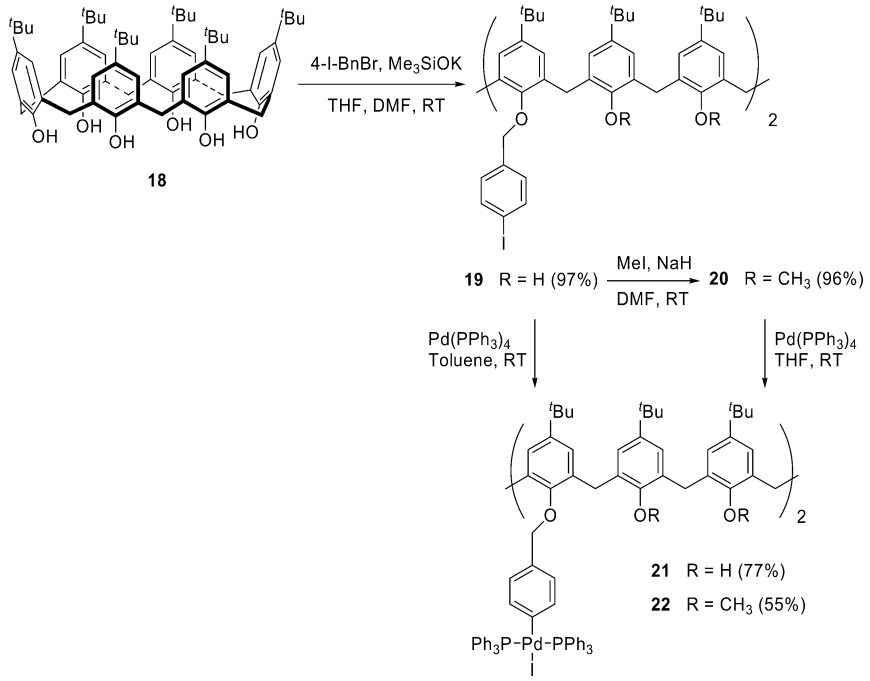
SCHEME 3. Synthesis of Difunctional Calix[4]arenes



presence of two separate singlet resonances for the OCH_2 as well as the *tert*-butyl groups and one AB system corresponding to the methylene CH_2 fragments, while the $^{13}C\{^1H\}$ spectra showed sets of two peaks for each of these compounds. The combined NMR data agrees with the presence of a single, C_{2v}-symmetrical species in a cone conformation.

Precursors **12** and **13** were then subjected to metalation as described for **8** and **9**. Dipalladium-dipyridylcalix[4]arene **14** was isolated as a bright yellow solid in a moderate yield (46%, Scheme 3). The most significant changes in the ^1H NMR spectrum of **14** (as compared to **12**) were found in the aromatic, OCH_2, and *tert*-butyl regions. Upon introduction of the Pd(II) centers, the aryl

SCHEME 4. Synthesis of Bis-Pd(II)-calix[6]arenes 21 and 22



protons of the initial aryl iodide moiety shifted from $\delta =$ 7.52 and 6.94 ppm to 6.53 and 6.30 ppm, respectively. Simultaneously, one of the OCH_2 resonances appeared at lower field ($\delta = 5.02$ ppm), whereas the other peak shifted to higher field ($\delta = 4.40$ ppm) as compared to the initial values of 4.87 and 4.71 ppm, respectively. Similar changes were noted for the *tert*-butyl groups and the aryl protons of the calix[4]arene backbone. MALDI-TOF mass spectra of **14** (ditranol matrix) gave rather similar results as reported for **10** and **11**, i.e., no molecular ions were detected and primary fragmentation processes involved loss of iodide and/or phosphine ligands. A reasonably resolved isotope pattern that was assigned to a dipalladium fragment ion was found at $m/z = 1561.4$ (calcd 1561.4) corresponding to $[(M - 4PPh_3 - I + \text{ditranol})^+]$.

Surprisingly, a similar palladation procedure involving **13** as a substrate did not give rise to formation of the bis-Pd(II) derivative **15** (Scheme 3), even after prolonged reaction times (>72 h) or elevated temperatures (up to 70 °C), and only a mixture of components could be isolated. This difference in reactivity toward $Pd(PPh_3)_4$ between **13** and the pyridine-containing precursor **12** could be explained by the more sterically demanding 4-cyanobenzyl groups present in **13**, which may give rise to a larger repulsion between the aryl iodide and the Pd(0) reagent during the oxidative addition. This assumption was clearly supported by CPK model inspection of the bis-Pd(II) targets **14** and **15**.

As an alternative Pd(0) source, we therefore turned to $Pd_2(dba)_3$ (dba = dibenzylideneacetone). Upon treatment of **8** with a stoichiometric amount of $Pd_2(dba)_3$[19] in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda), the bis-Pd(II)-calixarene **16** was formed in 52% yield within 15 min (cf. the syntheses of **10**, **11**, and **14**). A diagnostic neat color change of the reaction mixture from dark purple to orange/yellow was noted upon full consumption of the Pd(0) reagent, allowing an easy way to monitor the reaction. The success of this synthetic protocol prompted us to prepare the analogous derivative **17**, starting from **13** (Scheme 3), which was isolated in a rather low yield (28%). The latter results supported the earlier view that the steric requirements of the Pd(0) reagent seem to be of importance for the introduction of Pd(II) sites in this type of lower rim functionalized calix[4]arenes.

Once again, the mass spectrometric data for Pd(II)-containing calixarenes **16** and **17** proved to be quite helpful for molecular identification, as intensive $[(M - \text{tmeda})^+]$ and $[(M - \text{tmeda} + K)^+]$ fragment ions were observed, providing direct evidence for the formation of bis-Pd(II) species. More importantly, it can be assumed that fragment ions still comprising bidentate donor ligands (i.e., tmeda in compounds **16** and **17**) as compared to monodentate ligands (i.e., PPh_3 in **8**, **9**, and **14**) probably have higher stability properties and, consequently, give simpler and easy to interpret mass spectra.

Synthesis and Characterization of Calix[6]arene Derivatives. The parent *p-tert*-butylcalix[6]arene **18** was treated with an excess of 4-iodobenzyl bromide in THF/DMF (5:1) with Me_3SiOK as external base (Scheme 4).[20] This known protocol afforded the 1,4-bis(4-iodobenzyl) derivative **19** in excellent yield as a single species, contrary to an earlier report for a fairly similar compound.[21] Compound **19** probably exists as a cone conformer at room temperature in $CDCl_3$ solution, as sug-

(19) For the introduction of multiple Pd(II) centers in dendrimer systems by use of $Pd_2(dba)_3$ as reagent, see (a) Hoare, J. L.; Lorenz, K.; Hovestad, N. J.; Smeets, W. J. J.; Spek, A. L.; Canty, A. J.; Frey, H.; van Koten, G. *Organometallics* **1997**, *16*, 4167−4173. (b) Hovestad, N. J.; Hoare, J. L.; Jastrzebski, J. T. B. H.; Canty, A. J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1999**, *18*, 2970−2980.

(20) Kanamathareddy, S.; Gutsche, C. D. *J. Org. Chem*. **1994**, *59*, 3871−3879.

(21) A rather similar compound has previously been studied with 4-tolyl instead of 4-iodobenzyl groups connected to positions 1 and 4 of the lower rim of the calix[6]arene. This compound exhibited closely related spectroscopic features as reported here for **19**. See Kanamathareddy, S.; Gutsche, C. D. *J. Org. Chem*. **1992**, *57*, 3160−3166.

gested by the presence of two AB systems (2:1 integral ratio) for the methylene protons. Furthermore, only one set of singlet lines was observed for the OH and OCH_2 groups. The $^{13}C\{^1H\}$ NMR analysis was also in agreement with the assignment of a cone conformation, since only two separate signals were observed at $\delta = 32.5$ and 31.9 ppm (1:2 ratio), respectively.[20,22]

The OH groups in **19** were subsequently protected by treatment with methyl iodide, in the presence of NaH as a base, to furnish the dibenzyltetramethylcalixarene **20** in nearly quantitative yield. The ^1H NMR and $^{13}C\{^1H\}$ spectra collected for **20** unequivocally revealed the presence of two different conformational isomers through the presence of two sets of resonances for all groups. For the major isomer, three separate patterns were observed for the methylene protons at $\delta = 4.23$ (d), 3.84 (s), and 3.59 (d) ppm, whereas the minor isomer gave rise to two AB systems in a 2:1 ratio. Furthermore, two (broadened) singlet lines were found for OCH_2 as well as OCH_3 groups for the solution mixture (see Experimental Section). Remarkably, the $^{13}C\{^1H\}$ NMR spectrum of **20** displayed methylene signals only at $\delta = 30.2$, 30.1, and 30.0 ppm (partly overlapping), accounting for an all-syn orientation of the aromatic rings in both isomers.[20]

At higher temperatures (298−393 K, $C_2D_2Cl_4$; Supporting Information) the signals sharpened significantly and small shifts were noted for a number of groups, but the isomer ratio (1.8:1, as measured by signal integration) remained virtually unchanged, in agreement with the presence of two stable conformers under these conditions. Addition of MeOH-d_4 (up to 40% v/v) to a $CDCl_3$ solution of **20** caused preferential precipitation of the major isomer and thus enrichment in the solid state. Crystallization from $CHCl_3$/MeOH afforded suitable crystals for X-ray structure determination (Figure 3; for selected bond angles and distances, see Table S2 in Supporting Information).[23]

The molecular structure of **20** is defined by two anti-positioned iodobenzyl groups and alternating methoxy substituents at the lower and upper rims of the calixarene. The structure of **20** could best be described as a 1,2,3-alternate conformation with the aromatic groups of the calixarene backbone being neither purely syn- nor purely anti-oriented with respect to each other. In solution, a rotational process, accounting for the NMR observations, is likely.[24] This should involve a rapid interconversion between different conformations that primarily involve the methyl-substituted phenol rings. A nonrigid conformation with two anti-positioned iodobenzyl groups was further suggested by a nuclear Overhauser effect spectroscopy (NOESY) experiment (500 MHz, 323 K; Supporting Information), which, for instance, showed only weak through-space interactions

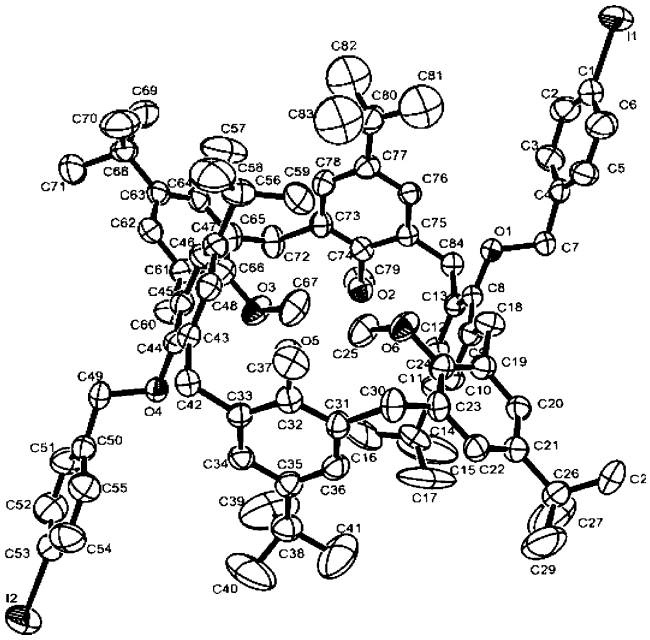


FIGURE 3. X-ray molecular structure of **20** with the adopted numbering scheme. For clarity, hydrogen atoms and cocrystallized solvent molecules have been omitted and thermal ellipsoids are shown at 30% probability.

between the OCH_3/CH_2 groups and the aromatic protons of the adjacent aryl rings. The minor isomer could likewise be correlated with a structure having a nonrigid conformation with two syn-positioned iodobenzyl groups.

Compound **19** (cone conformation) was submitted to a similar palladation procedure as for **8** and **9** with $Pd(PPh_3)_4$ as reagent in toluene. This furnished, after workup, the bis-palladated calixarene **21** in good yield (77%) as an orange solid. Analysis of the NMR data revealed that **21** was isolated as a mixture of components. Likely, compound **21** exists in solution as a mixture of two conformers in equilibrium. The "through-the-annulus" rotation of the unsubstituted phenol rings in **21** is slower than for **19** on the NMR time scale, probably due to the steric hindrance caused by the PPh_3 ligands, which partly occupy the lower rim cavity.

Similar spectroscopic findings (i.e., two sets of signals as noted for **20** and **21**) characterize compound **22** (55% yield), which was derived from the tetramethyl-substituted derivative **20** by treatment with $Pd(PPh_3)_4$ in THF. Bis-Pd(II) calixarene **22** was only moderately soluble in THF and (partly) precipitated from the mixture during synthesis. The NMR features of **22** were in close agreement with those reported for **20** and **21**; that is, the major component of **22** was associated with a nonrigid isomer with two anti-positioned Pd(II) metal centers as referred to the calixarene basal plane. Strong evidence for the structure of **22** was further provided by MALDI-TOF mass spectrometry, which demonstrated a reasonably intense peak at $m/z = 2236.6$ (calcd 2237.5) ascribed to the fragment ion $[(M - 2PPh_3 + K)^+]$.

Conclusions

In summary, we have presented methodologies for the functionalization of calixarene frameworks with useful 4-iodobenzyl groups, which can easily be converted into

(22) Jaime, C.; de Mendoza, J.; Prados, P.; Nieto, P. M.; Sánchez, C. *J. Org. Chem*. **1991**, *56*, 3372−3376.

(23) A separate measurement of another crystal gave again the 1,2,3-alternate conformation as a result, thereby supporting preferential crystallization of this isomer in the applied solvent combination.

(24) A rapid, full "lower-rim-through-the-annulus" rotation of the methyl-substituted phenol rings in the temperature range 298−393 K could provide an explanation for the noted spectroscopic patterns for the CH_2 groups of both isomers. An opposite position of both aryl iodide groups (major component with a nonrigid conformation) would then give rise to one AB pattern (8H) and a singlet resonance (4H), while a nonrigid conformer with two syn-related aryl iodide groups would afford two AB patterns in a 2:1 ratio.

organometallic groups that possess a direct and stable palladium−carbon bond. The electronic as well as steric features of the organometallic units can be altered by simple ligand exchange reactions after introduction of the metal sites. This is undoubtedly advantageous in cases where these changes could lead to modified or improved catalytic properties of these materials. On the other hand, calixarene derivatives reminiscent of **17** could be an excellent starting point for supramolecular, self-assembling capsule formation via halide abstraction procedures or for self-assembling dendrimer construction. Analogously, 1,3-alternate isomers of either **14** or **17** could also provide access to channel-like structures. Studies are currently underway to exploit the full potential of these metallacalixarene synthons.

Experimental Section

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25-(4-iodobenzyloxy)-26,27,28-trihydroxycalix[4]arene (2). A suspension of **1** (1.42 g, 1.48 mmol), NaH (60% on a dispersion oil, 1.04 g, 26.0 mmol), and 4-iodobenzyl bromide (0.50 g, 1.68 mmol) in dry DMF (30 mL) was stirred at room temperature for 2.5 h, after which the mixture was quenched with excess H_2O (60 mL) and stirred additionally for 1 h. The white solid precipitate was filtered off and dissolved in CH_2Cl_2 (100 mL), washed once with H_2O (100 mL), dried ($MgSO_4$), and filtered. Concentration in vacuo and treatment with MeOH yielded pure **2** (1.01 g, 79% overall). Crystals suitable for X-ray diffraction were obtained by crystallization from CH_2Cl_2/MeOH: mp 141−142 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.97 (s, 1H, OH), 9.33 (s, 2H, OH), 7.85 (d, ^3J = 7.8 Hz, 2H, ArH), 7.49 (d, ^3J = 8.6 Hz, 2H, ArH), 7.12 (s, 2H, ArH), 7.04 (s, 4H, ArH), 6.99 (s, 2H, ArH), 5.09 (s, 2H, OCH_2), 4.27 [apparent t, $^2J_{app}$(A−B) = 14.1 Hz, 4H, $2CH_2$], 3.42 [apparent d, $^2J_{app}$(A−B) = 13.3 Hz, 4H, CH_2], 1.22 [s, 9H, $C(CH_3)_3$], 1.21 [s, 27H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.1, 148.4, 147.6, 143.6, 143.1, 138.1, 135.3, 133.5, 130.8, 128.2, 127.8, 127.5, 126.6, 125.8, 125.7, 125.6 (ArC, ArCH), 94.9 (Ar−C−I), 78.3 (CH_2O), 34.3, 34.0, 33.9 [3*C*$(CH_3)_3$, ratio 1:1:2], 32.9, 32.4 ($2CH_2$, ratio 1:1), 31.5, 31.2 [2C(*C*$H_3)_3$, ratio 3:1]; MALDI-TOF MS (ditranol) *m*/*z* 865.2 [(M + H)$^+$] (calcd 865.4). Anal. Calcd for $C_{51}H_{61}IO_4$·0.5H_2O: C, 70.09; H, 7.15. Found: C, 70.28; H 6.86.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25-(4-iodobenzyloxy)-26,27,28-tribenzyloxycalix[4]arene (3). A mixture of **2** (0.32 g, 0.37 mmol), NaH (60% on a dispersion oil, 0.58 g, 14.5 mmol), and benzyl bromide (0.30 mL, 2.5 mmol) in dry DMF (20 mL) was stirred at room temperature for 64 h. The mixture was quenched with H_2O and the precipitate was filtered off. Trituration with methanol and drying in vacuo yielded **3** as a white solid (0.41 g, 98%). Crystallization from CH_2Cl_2/MeOH afforded white needles: mp 203−204 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, ^3J = 8.2 Hz, 2H, ArH), 7.30−7.20 (m, 8H, ArH), 6.93 (d, ^3J = 8.2 Hz, 2H, ArH), 6.80 (s, 2H, ArH), 6.77 (s, 2H, ArH), 6.65 (s, 2H, ArH), 6.62 (s, 2H, ArH), 4.90 (s, 2H, OCH_2), 4.82 [d, ^2J(A−B) = 11.7 Hz, 2H, OCH_2], 4.79 (s, 2H, OCH_2), 4.74 [d, ^2J(A−B) = 11.8 Hz, 2H, OCH_2], 4.23 [d, ^2J(A−B) = 12.9 Hz, 2H, CH_2], 4.09 [d, ^2J(A−B) = 12.3 Hz, 2H, CH_2], 2.91 [d, ^2J(A−B) = 12.9 Hz, 2H, CH_2], 2.82 [d, ^2J(A−B) = 12.9 Hz, 2H, CH_2], 1.13 [s, 9H, $C(CH_3)_3$], 1.12 [s, 9H, $C(CH_3)_3$], 1.06 [s, 18H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.0, 152.5, 144.7, 144.6, 144.5, 138.4, 138.2, 138.0, 136.9, 134.2, 133.3, 131.6, 129.6, 129.5, 128.0, 127.9, 127.7, 127.5, 125.2, 125.0, 124.8 (ArC, ArCH), 93.2 (ArC−I), 76.9, 76.5, 75.4 ($3OCH_2$), 33.9, 33.7 [2*C*$(CH_3)_3$], 31.9, 31.3 [2C(*C*$H_3)_3$], 31.4, 29.7 ($2CH_2$) (assignments based on COSY, HETCOR, and DEPT experiments); MALDI-TOF MS (ditranol + KI) *m*/*z* 1157.6 [(M + Na)$^+$] (calcd 1157.5), 1173.5 [(M + Na)$^+$] (calcd 1173.5). Anal. Calcd for $C_{72}H_{79}IO_4$·0.5H_2O: C, 75.57; H, 7.05. Found: C, 75.64; H, 6.91.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25-(4-iodobenzyloxy)-26,27,28-tripropyloxycalix[4]arene (4). This compound was prepared similarly as **3** starting from **2** (0.29 g, 0.335 mmol), NaH (60% on a dispersion oil, 0.70 g, 17.5 mmol), and propyl iodide (0.8 mL, 8.2 mmol) in dry DMF (20 mL), quantitative yield; mp 125−126 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.72 (d, ^3J = 7.8 Hz, 2H, ArH), 7.25 (d, ^3J = 7.8 Hz, 2H, ArH), 6.91 (s, 4H, ArH), 6.66 (s, 2H, ArH), 6.62 (s, 2H, ArH), 4.77 (s, 2H, OCH_2), 4.38 [d, ^2J(A−B) = 12.5 Hz, 2H, CH_2], 4.35 [d, ^2J(A−B) = 12.5 Hz, 2H, CH_2], 3.73 (m, 6H, $OCH_2CH_2CH_3$), 3.10 [d, ^2J(A−B) = 11.7 Hz, 2H, CH_2], 3.09 [d, ^2J(A−B) = 12.5 Hz, 2H, CH_2], 1.93 (m, 6H, $OCH_2CH_2CH_3$), 1.07 (m, 9H, $OCH_2CH_2CH_3$), 1.19 [s, 18H, $C(CH_3)_3$], 0.99 [s, 9H, $C(CH_3)_3$], 0.96 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.1, 153.2, 152.5, 144.6, 144.4, 144.1, 137.9, 137.2, 134.7, 134.3, 133.13, 133.10, 131.7, 125.3, 125.0, 124.9, 124.7 (ArC, ArCH), 93.5 (ArC−I), 77.1 ($OCH_2CH_2CH_3$), 76.8 (OCH_2), 76.7 ($OCH_2CH_2CH_3$), 33.9, 33.8, 33.7 [3*C*$(CH_3)_3$, ratio 2:1:1], 31.6, 31.38, 31.36 [3C(*C*$H_3)_3$], 31.2, 31.1 ($2CH_2$), 23.5, 23.1 ($2OCH_2CH_2CH_3$), 10.5, 10.0 ($2OCH_2CH_2CH_3$) (assignments based on DEPT, COSY, and HETCOR experiments); MALDI-TOF MS (ditranol + KI) *m*/*z* 887.6 [(M − I + Na)$^+$] (calcd 887.6), 903.5 [(M − I + K)$^+$] (calcd 903.6), 1013.4 [(M + Na)$^+$] (calcd 1013.5), 1029.4 [(M + K)$^+$] (calcd 1029.5). Anal. Calcd for $C_{60}H_{79}IO_4$·H_2O: C, 71.41; H, 8.09. Found: C, 71.66; H, 7.89.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25-{4-[PdI(PPh$_3$)$_2$]-benzyloxy}-26,27,28-tripropyloxycalix[4]arene (5). A solution of **4** (111.1 mg, 0.112 mmol) and $Pd(PPh_3)_4$ (131.3 mg, 0.114 mmol) in THF (30 mL) was stirred for 2 h at 50 °C and then concentrated in vacuo. Addition of MeOH furnished **5** as a bright, yellow solid (105.2 mg, 58%), which was directly isolated and dried: mp 118−120 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54−7.48 (m, 6H, P−ArH_{ortho}), 7.33−7.20 (m, 9H, P−Ar$H_{meta+para}$), 6.93 (d, ^4J = 2.4 Hz, 2H, ArH), 6.91 (d, ^4J = 2.2 Hz, 2H, ArH), 6.62 (s, 1H, ArH), 6.55 (s, 1H, ArH), 6.52 (s, 2H, ArH), 4.58 (s, 2H, OCH_2), 4.41 [d, ^2J(A−B) = 12.5 Hz, 2H, CH_2], 4.36 [d, ^2J(A−B) = 12.5 Hz, 2H, CH_2], 3.93−3.76 (m, 4H, OCH_2 propyl), 3.71 (t, ^3J = 7.6 Hz, 2H, OCH_2 propyl), 3.11 [d, ^2J(A−B) = 12.4 Hz, 2H, CH_2], 3.01 [d, ^2J(A−B) = 12.6 Hz, 2H, CH_2], 2.02−1.95 (m, 6H, CH_2CH_3), 1.21 [s, 18H, $C(CH_3)_3$], 0.97 [s, 9H, $C(CH_3)_3$], 0.93 [s, 9H, $C(CH_3)_3$], 0.79 (t, ^3J = 7.4 Hz, 9H, CH_2CH_3); ^{13}C{^{1}H} (75 MHz, $CDCl_3$) δ 154.1, 153.1, 144.3, 144.0, 143.9, 135.2, 134.9 (br), 132.8, 132.4, 132.1, 132.2, 130.0, 129.6, 128.5, 128.4, 127.7 (br), 126.7, 125.1 (br), 124.5 (ArC, ArCH), 77.1, 76.43 ($2OCH_2CH_2CH_3$, ratio 1:2), 76.38 (OCH_2), 33.9, 33.7 [2*C*$(CH_3)_3$], 31.6, 31.3 [2C(*C*$H_3)_3$], 31.3, 31.1 ($2CH_2$), 23.4, 23.1 ($2OCH_2CH_2CH_3$, ratio 1:2), 10.5, 10.0 ($2OCH_2CH_2CH_3$, ratio 1:2); ^{31}P{^{1}H} (121.5 MHz, $CDCl_3$) δ 22.8 (PPh_3); MALDI-TOF MS (ditranol + KI) *m*/*z* 1381.3 [(M − 2PPh$_3$ + Na)$^+$] (calcd 1381.5), 1397.3 [(M − 2PPh$_3$ + K)$^+$] (calcd 1397.5); MALDI-TOF MS (ditranol + KI + dppe) *m*/*z* 1517.4 [(M − 2PPh$_3$ + Na + dppe)$^+$] (calcd 1517.5), 1533.4 [(M − 2PPh$_3$ + K + dppe)$^+$] (calcd 1533.5). Anal. Calcd for $C_{96}H_{109}IO_4P_2Pd$·0.5H_2O: C, 70.69; H, 6.80. Found: C, 70.54; H, 6.68.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-bis(4-iodobenzyloxy)-26,28-dihydroxycalix[4]arene (8). A suspension of *p-tert*-butylcalix[4]arene **6** (0.88 g, 1.36 mmol), 4-iodobenzyl bromide (0.96 g, 3.23 mmol), and K_2CO_3 (0.71 g, 5.14 mmol) in acetonitrile (100 mL) was refluxed for 17 h. Then the mixture was filtered hot and concentrated in vacuo. To the residue were added CH_2Cl_2 (100 mL) and H_2O (100 mL). After thorough mixing, the aqueous layer was discarded and the organic layer was dried on anhydrous K_2CO_3, filtered, and concentrated under reduced pressure. The remaining oil was triturated with MeOH to give **8** as a white solid (1.12 g, 76%). Crystallization from CH_2Cl_2/MeOH afforded white needles: mp 228−229 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.73 (d, ^3J = 7.8 Hz, 4H, ArH), 7.42 (d, ^3J = 8.6 Hz, 4H, ArH), 7.18 (s, 2H, OH), 7.05 (s, 4H, ArH), 6.79 (s, 4H, ArH), 5.00 (s, 4H, CH_2O), 4.24 [d, ^2J(A−B) = 12.5 Hz, 4H, CH_2], 3.29 [d, ^2J(A−B) = 13.3 Hz, 4H, CH_2], 1.29 [s, 18H, $C(CH_3)_3$], 0.95 [s, 18H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.5, 149.4, 147.2, 141.5,

137.7, 136.7, 132.4, 129.1, 127.5, 125.5, 125.0 (ArC, ArCH), 93.6 (Ar−C−I), 77.1 (CH_2O), 33.9, 33.8 [2*C*(CH_3)$_3$], 31.7, 30.9 [2C(CH_3)$_3$], 31.6 (CH_2) (spectroscopic assignment was derived from a DEPT analysis); MALDI-TOF MS (ditranol) *m*/*z* 1081.3 [(M + H)$^+$] (calcd 1081.3), 1103.3 [(M + Na)$^+$] (calcd 1103.3), 1119.3 [(M + K)$^+$] (calcd 1119.3). Anal. Calcd for $C_{58}H_{66}I_2O_4\cdot 0.5H_2O$: C, 63.91; H, 6.20. Found: C, 63.82; H, 6.14.

25,27-Bis(4-iodobenzyloxy)-26,28-dihydroxycalix[4]arene (9). A suspension of calix[4]arene **7** (0.47 g, 1.11 mmol), 4-iodobenzyl bromide (0.73 g, 2.46 mmol) and K_2CO_3 (0.70 g, 5.06 mmol) in acetonitrile (30 mL) was refluxed for 15 h. After a similar workup procedure as for **8**, compound **9** was isolated as a white solid (0.87 g, 92%): mp 247−248 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.73 (d, ^3J = 8.6 Hz, 4H, ArH), 7.69 (s, 2H, OH), 7.42 (d, ^3J = 8.6 Hz, 4H, ArH), 7.18 (s, 2H, OH), 7.07 (d, ^3J = 7.5 Hz, 4H, ArH from calixarene), 6.89 (d, ^3J = 7.0 Hz, 4H, ArH from calixarene), 6.77−6.64 (m, 8H, ArH from calixarene), 5.01 (s, 4H, CH_2O), 4.27 [d, ^2J(A−B) = 12.9 Hz, 4H, CH_2], 3.37 [d, ^2J(A−B) = 12.9 Hz, 4H, CH_2]; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.1, 151.6, 137.8, 136.3, 133.0, 129.1, 128.5, 127.8, 125.6, 119.1 (ArC, ArCH), 93.8 (Ar−C−I), 77.5 (CH_2O), 31.3 (CH_2); MALDI-TOF MS (ditranol) *m*/*z* 857.1 [(M + H)$^+$] (calcd 857.1), 879.1 [(M + Na)$^+$] (calcd 879.0), 895.0 [(M + K)$^+$] (calcd 895.0). Anal. Calcd for $C_{42}H_{34}I_2O_4\cdot 0.5H_2O$: C, 58.28; H, 4.08. Found: C, 58.19; H, 4.32.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-bis{4-[PdI(PPh$_3$)$_2$]benzyloxy}-26,28-dihydroxycalix[4]arene (10). A solution of **8** (140.4 mg, 0.130 mmol) and $Pd(PPh_3)_4$ (297.7 mg, 0.258 mmol) in toluene (25 mL) was stirred for 66 h at room temperature. The solvent was removed under reduced pressure and the residue was triturated with hot MeOH to give **10**, after drying, as a yellow solid (220 mg, 72%): mp 126−128 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49 (br m, 14H, OH + P−ArH_{ortho}), 7.22 (br m, 36H, P−ArH), 7.02 (br s, 4H, ArH), 6.61 (br s, 4H, ArH), 6.52 (br d, ^3J = 7.0 Hz, 4H, ArH), 6.26 (br d, ^3J = 7.0 Hz, 4H, ArH), 4.47 (br s, 4H, CH_2O), 4.20 [br d, ^2J(A−B) = 12.9 Hz, 4H, CH_2], 3.12 [d, ^2J(A−B) = 12.9 Hz, 4H, CH_2], 1.32 [s, 18H, C(CH_3)$_3$], 0.86 [s, 18H, C(CH_3)$_3$]; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.8 (ArC_{ipso}), 150.8 [d, ^1J(P−C) = 18.8 Hz, P−ArC_{ipso}], 146.2, 141.1 (ArC), 135.7 (br, ArC), 134.8 (apparent t, J_{app} = 6.3 Hz, ArC), 132.2, 132.1, 131.9, 131.8, 131.6 (P−ArC and ArC), 130.4 (ArC), 129.9 (br, ArC), 128.3 (ArC), 127.8 (br, ArC), 125.1 [J(P−C) = 27.2 Hz, P−ArC], 79.0 (OCH_2), 33.8 and 33.7 [2*C*(CH_3)$_3$], 31.7, 30.9 [2C(CH_3)$_3$], 31.6 (CH_2); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$) δ 23.2 (PPh_3); MALDI-TOF MS (ditranol, NaI) *m*/*z* 1838.5 [(M − 2PPh$_3$ + Na)$^+$] (calcd 1839.3). Anal. Calcd for $C_{130}H_{126}I_2O_4P_4Pd_2\cdot H_2O$: C, 66.07; H, 6.23. Found: C, 65.95, H, 5.86.

25,27-Bis{4-[PdI(PPh$_3$)$_2$]benzyloxy}-26,28-dihydroxycalix[4]arene (11). This compound was prepared similarly as for **10**, starting from **9** (194.5 mg, 0.227 mmol), $Pd(PPh_3)_4$ (531.2 mg, 0.460 mmol), and toluene (25 mL) to finally furnish **11** as a yellow solid (0.48 g, >98%): mp 154−156 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.52 (br m, 14H, OH + P−ArH_{ortho}), 7.25−7.13 (br m, 36H, P−ArH), 7.01 (d, ^3J = 7.0 Hz, 8H, ArH from calixarene), 6.74−6.56 (m, 8H, ArH), 6.26 (br d, ^3J = 7.8 Hz, 4H, ArH), 4.49 (br s, 4H, CH_2O), 4.18 [br d, ^2J(A−B) = 13.3 Hz, 4H, CH_2], 3.17 [d, ^2J(A−B) = 13.3 Hz, 4H, CH_2]; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.9 (ArC_{ipso}), 153.1 [d, ^1J(P−C) = 23.4 Hz, P−ArC_{ipso}], 136.0 (br, ArC), 134.8 (apparent t, J_{app} = 6.1 Hz, P−ArC), 132.6, 132.3, 132.0, 131.7, 129.9, 128.7, 128.4, 128.2 (ArC, ArCH), 127.8 (apparent t, J_{app} = 5.0 Hz, P−ArC), 124.6, 118.7 (ArC), 79.1 (OCH_2), 31.6 (CH_2) [missing ArC signal probably caused by coalescence with other(s)]; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$) δ 23.2 (PPh_3); MALDI-TOF MS (ditranol, NaI) *m*/*z* 1614.6 [(M − 2PPh$_3$ + Na)$^+$] (calcd 1615.0). Anal. Calcd for $C_{114}H_{94}I_2O_4P_4Pd_2\cdot H_2O$: C, 64.09, H, 4.53. Found: C, 63.66; H, 4.55.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-bis(4-iodobenzyloxy)-26,28-bis[(4-pyridyl)methyloxy]calix[4]arene (12). A mixture of **8** (0.831 g, 0.768 mmol) and NaH (60% on a dispersion oil, 23.5 mmol) in DMF (30 mL) was stirred at room temperature for 25 min. Then, 4-chloromethylpyridine hydrochloride (1.00 g, 6.10 mmol) was added as a solid over a period of 30 min. The resultant brownish suspension was stirred for another 1.5 h and quenched with MeOH. Subsequently, H_2O was added and the precipitate was filtered off and dissolved in CH_2Cl_2 (100 mL). The resulting solution was washed once with H_2O (100 mL) and dried ($MgSO_4$). After filtration and concentration, the residue was treated with MeOH to yield **12** as a white solid (0.60 g, 62%). Analytically pure **12** was obtained from crystallization in CH_2Cl_2/MeOH, as white needles: mp 204−206 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, ^3J = 4.7 Hz, 4H, PyH), 7.52 (d, ^3J = 8.6 Hz, 4H, ArH), 7.22 (^3J = 4.7 Hz, 4H, PyH), 6.94 (d, ^3J = 7.8 Hz, 4H, ArH), 6.84 (s, 4H, ArH), 6.67 (s, 4H, ArH), 4.87 (s, 4H, OCH_2), 4.71 (s, 4H, OCH_2), 4.12 [d, ^2J(A−B) = 12.5 Hz, 4H, CH_2], 2.93 [d, ^2J(A−B) = 12.5 Hz, 4H, CH_2], 1.14 [s, 18H, C(CH_3)$_3$], 1.00 [s, 18H, C(CH_3)$_3$]; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 152.4, 149.6, 146.7, 145.4, 145.1, 137.3, 137.3, 133.9, 133.0, 131.0, 125.5, 125.1, 123.6, 118.6 (ArC, ArCH, PyC, PyCH), 93.7 (ArC−I), 76.4, 75.0 (2OCH_2), 33.9, 33.8 [2*C*(CH_3)$_3$], 31.5, 31.3 [2C(*C*H_3)$_3$], 31.2 (CH_2); FAB-MS (*m*-NBA) *m*/*z* 1263.5 (100) [(M + H)$^+$] (calcd 1263.4), 1171.4 (38) [(M − py)$^+$] (calcd 1171.4), 1045.5 (21) [(M − arylI)$^+$] (calcd 1045.4). Anal. Calcd for $C_{70}H_{76}I_2N_2O_4\cdot CH_2Cl_2$: C, 63.26; H, 5.83; N, 2.08. Found: C, 63.32; H, 6.00; N, 1.98.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-bis(4-iodobenzyloxy)-26,28-bis(4-cyanobenzyloxy)calix[4]arene (13). A mixture of **8** (0.85 g, 0.786 mmol), 4-cyanobenzyl bromide (0.48 g, 2.45 mmol), and NaH (60% on a dispersion oil, 0.59 g, 14.8 mmol) in DMF (20 mL) was stirred for 2 h at room temperature. The initial gray/black suspension turned into brownish. The reaction mixture was quenched with MeOH/H_2O and worked up similarly as for **12**. Trituration with MeOH yielded **13** as a white solid (0.93 g, 90%). Analytically pure **13** was obtained by crystallization from CH_2Cl_2/MeOH as white needles: mp 225−226 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.54 (d, ^3J = 7.8 Hz, 4H, ArH), 7.46 (d, ^3J = 8.6 Hz, 4H, ArH), 7.31 (d, ^3J = 8.6 Hz, 4H, ArH), 6.98 (d, ^3J = 7.6 Hz, 4H, ArH), 6.76 (s, 4H, ArH), 6.72 (s, 4H, ArH), 4.85 (s, 4H, OCH_2), 4.73 (s, 4H, OCH_2), 4.06 [d, ^2J(A−B) = 12.5 Hz, 4H, CH_2], 2.89 [d, ^2J(A−B) = 12.5 Hz, 4H, CH_2], 1.09 [s, 18H, C(CH_3)$_3$], 1.05 [s, 18H, C(CH_3)$_3$]; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 152.1, 152.0, 145.4, 145.2, 143.0, 137.4, 137.2, 133.3, 132.6, 131.8, 131.1, 129.6, 125.4, 125.3 (ArC, ArCH), 118.8 (ArC−*C*≡N), 111.6 (Ar*C*−C≡N), 93.7 (ArC−I), 76.3, 75.6 (2OCH_2), 33.9 [*C*(CH_3)$_3$], 31.3 [C(*C*H_3)$_3$], 31.2 (CH_2) (missing signals probably due to overlap); FAB-MS (*m*-NBA) *m*/*z* 1309.5 (44) [(M)$^+$] (calcd 1310.4), 1195.5 (28) [(M − arylnitrile)$^+$] (calcd 1195.4), 1093.5 (100) [(M − arylI)$^+$] (calcd 1093.4). Anal. Calcd for $C_{74}H_{76}N_2O_4\cdot H_2O$: C, 66.87, H, 5.91; N, 2.11. Found: C, 66.83; H, 5.77; N, 2.05.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-bis{4-[PdI(PPh$_3$)$_2$]benzyloxy)}-26,28-bis[(4-pyridyl)methyloxy]calix[4]arene (14). A yellow/orange solution of **12** (140.8 mg, 0.111 mmol) and $Pd(PPh_3)_4$ (257.8 mg, 0.223 mmol) in toluene (40 mL) was stirred at room temperature for 20 h. The volatiles were then removed in vacuo and the product **14** was isolated, as reported for **10** and **11**, as a yellow solid (129.8 mg, 46%): mp 124−126 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.40 (d, ^3J = 5.5 Hz, 4H, PyrH_{ortho}), 7.47−7.50 (br m, 24H, P−ArH_{ortho}), 7.18−7.34 (m, 40H, P−ArH + PyrH), 6.95 (s, 4H, ArH), 6.53 (d, ^3J = 7.0 Hz, 4H, ArH), 6.43 (s, 4H, ArH), 6.30 (d, ^3J = 7.0 Hz, 4H, ArH), 5.02 (s, 4H, O*C*H_2−Pyr), 4.40 (s, 4H, O*C*H_2−ArPd), 4.11 (d, ^2J = 12.5 Hz, 4H, CH_2), 2.87 (d, ^2J = 13.3 Hz, 4H, CH_2), 1.29 [s, 18H, C(CH_3)$_3$], 0.86 [s, 18H, C(CH_3)$_3$]; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 156.5 (ArC_{ipso}), 152.6 [d, ^1J(P−C) = 8.4 Hz, P−ArC_{ipso}], 149.4, 146.8, 145.3, 144.2, 136.0, 135.2, 135.2, 135.1 (ArC, ArCH), 134.8 [apparent t, J(P−C) = 6.3 Hz, P−ArC], 134.6, 132.4, 132.1, 132.0, 131.8, 131.6, 130.2, 129.7, 128.5, 128.4, 127.8 127.7, 127.6, 127.1, 125.7, 124.7, 123.9 (ArC, ArCH, P−ArC), 76.8 (OCH_2), 74.0

(OCH_2), 34.0, 33.6 [2*C*(CH_3)$_3$], 31.6, 31.1 [2C(*C*H_3)$_3$], 31.0 (CH_2); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ 22.7 (PPh_3); MALDI-TOF MS (ditranol + NaI) *m*/*z* 2023.1 [(M − 2PPh_3 + Na)$^+$] (calcd 2024.4), 1874.1 [(M − 2PPh_3 − I)$^+$] (calcd 1875.5), 1561.4 [(M − 4PPh_3 − I + ditranol)$^+$] (calcd 1561.4). Anal. Calcd for $C_{142}H_{136}I_2N_2O_4P_4Pd_2\cdot 2H_2O$: C, 66.59; H, 5.51; N, 1.09. Found: C, 66.22, H, 5.10; N, 0.98.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-bis{4-[PdI(tmeda)]benzyloxy}-26,28-dihydroxycalix[4]arene (16). A mixture of **8** (235.6 mg, 0.218 mmol), $Pd_2(dba)_3$ (203.8 mg, 0.223 mmol), and tmeda (108.6 mg, 0.935 mmol) in THF (25 mL) was stirred at room temperature for 15 min. Then the mixture was filtered to remove traces of Pd(0) and the resulting clear, bright orange solution was concentrated under reduced pressure. The residue was treated with Et_2O/hexane (20 mL, v/v = 1:1) and the precipitate was filtered off and dried in vacuo, giving **16** as a yellow solid (172.6 mg, 52%). Off-white, needle-shaped crystals were obtained by crystallization from CH_2Cl_2/MeOH: mp 178−180 °C (decomp); ^1H NMR (200 MHz, $CDCl_3$) δ 7.46 (d, ^3J = 7.8 Hz, 4H, ArH), 7.37 (s, 2H, OH), 7.22 (d, ^3J = 7.8 Hz, 4H, ArH), 7.01 (s, 4H, ArH), 6.73 (s, 4H, ArH), 4.91 (s, 4H, OCH_2), 4.25 (d, ^2J = 12.5 Hz, 4H, CH_2), 3.22 (d, ^2J = 13.3 Hz, 4H, CH_2), 2.81 (br m, 4H, part of AA′BB′ system, NCH_2CH_2N), 2.74 (s, 6H, NCH_3), 2.62 (br m, 4H, part of AA′BB′ system, NCH_2CH_2N), 2.37 (s, 6H, NCH_3), 1.27 [s, 18H, C(CH_3)$_3$], 0.92 [s, 18H, C(CH_3)$_3$]; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 150.8, 150.2, 146.5, 145.0, 141.0, 136.4, 132.5, 131.5, 127.8, 125.7, 125.3, 124.8 (ArC, ArCH), 78.3 (OCH_2), 62.2, 58.3 (2N*C*H_2*C*H_2N), 50.2, 49.9 (2NCH_3) 33.8, 33.7 [2*C*(CH_3)$_3$], 31.74 (CH_2), 31.68, 31.0 [2C(*C*H_3)$_3$] (assignment based on DEPT experiments); MALDI-TOF MS (ditranol) *m*/*z* 1410.1 [(M − tmeda)$^+$] (calcd 1410.2), 1399.3 [(M − I)$^+$] (calcd 1399.5), 1283.2 [(M − I − tmeda)$^+$] (calcd 1283.3). Anal. Calcd for $C_{70}H_{89}I_2N_4O_4Pd_2\cdot H_2O$: C, 53.87; H, 6.38; N, 3.70. Found: C, 54.14, H, 6.29, N, 3.74.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-bis{4-[PdI(tmeda)]benzyloxy}-26,28-bis(4-cyanobenzyloxy)calix[4]arene (17). A mixture of **13** (168.3 mg, 0.128 mmol), $Pd_2(dba)_3$ (125.7 mg, 0.137 mmol), and tmeda (102.0 mg, 0.878 mmol) in THF (40 mL) was stirred at room temperature for 45 min. Then the product was isolated as reported for **16** and crystallized from CH_2Cl_2/hexane to afford **17** as a yellow solid (63.0 mg, 28%): mp 158−160 °C (decomp); ^1H NMR (200 MHz, $CDCl_3$) δ 7.48 (d, ^3J = 7.8 Hz, 4H, ArH), 7.30 (d, ^3J = 7.8 Hz, 4H, ArH), 7.18 (d, ^3J = 7.8 Hz, 4H, ArH), 6.93 (d, ^3J = 7.8 Hz, 4H, ArH), 6.89 (s, 4H, ArH), 6.52 (s, 4H, ArH), 4.99 (s, 4H, OCH_2), 4.56 (s, 4H, OCH_2), 4.19 (d, ^2J = 12.5 Hz, 4H, CH_2), 2.96 (d, ^2J = 12.5 Hz, 4H, CH_2), 2.73 (br m, 4H, part of AA′BB′ system, NCH_2CH_2N), 2.67 (s, 6H, NCH_3), 2.55 (br m, 4H, part of AA′BB′ system, NCH_2CH_2N), 2.16 (s, 6H, NCH_3), 1.19 [s, 18H, C(CH_3)$_3$], 0.92 [s, 18H, C(CH_3)$_3$]; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 152.6, 152.3, 145.1, 145.0, 144.4, 143.8, 136.2, 134.6, 132.6, 131.9, 130.1, 129.8, 127.6, 125.5, 124.7 (ArC, ArCH), 119.3 (Ar*C*−C≡N), 110.8 (ArC−*C*≡N), 77.6, 74.7 (2OCH_2), 62.0, 58.3 (2N*C*H_2*C*H_2N), 49.7 (overlapping NCH_3) 33.9, 33.7 [2*C*(CH_3)$_3$], 31.6 (CH_2), 31.5, 31.2 [2C(*C*H_3)$_3$] (assignment based on DEPT analysis); MALDI-TOF MS (ditranol + NaI) *m*/*z* 1679.4 [(M − tmeda + K)$^+$] (calcd 1679.3), 1663.4 [(M − tmeda + Na)$^+$] (calcd 1663.3), 1640.4 [(M − tmeda)$^+$] (calcd 1640.3) (the cluster peaks with highest intensity are given). Anal. Calcd for $C_{86}H_{108}I_2N_6O_4Pd_2\cdot CH_2Cl_2$: C, 56.75, H, 6.02, N, 4.56. Found: C, 57.08, H, 5.85; N, 4.58.

5,11,17,23,29,35-Hexakis(1,1-dimethylethyl)-39,42-bis(4-iodobenzyloxy)-37,38,40,41-tetrahydroxycalix[6]arene (19). To a suspension of *p-tert*-butylcalix[6]arene **18** (1.38 g, 1.42 mmol) in a mixture of anhydrous THF/DMF (50:7) was added Me_3SiOK (90%, 1.19 g, 9.28 mmol). The resultant reddish solution was stirred at room temperature for 50 min. Then, a solution of 4-iodobenzyl bromide (1.13 g, 3.81 mmol) in anhydrous THF (5 mL) was added in one portion, upon which an orange suspension was obtained. The mixture was stirred at room temperature for 2 h and concentrated in vacuo. The residue was treated with excess aqueous 1 M HCl to give a yellowish suspension. The solid was filtered off and triturated with MeOH to yield **19** as a slightly yellow solid (1.93 g, 97%). Analytically pure **19** was obtained by crystallization from MeOH/CH_2Cl_2 giving white needles: mp 194−196 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (s, 4H, OH), 7.59 (d, ^3J = 8.2 Hz, 4H, ArH), 7.21 (d, ^3J = 8.2 Hz, 4H, ArH), 7.10 (s, 8H, ArH), 6.96 (s, 4H, ArH), 5.05 (s, 4H, OCH_2), 4.30 [d, ^2J(A−B) = 14.1 Hz, 4H, CH_2], 3.83 [d, ^2J(A−B) = 13.5 Hz, 2H, CH_2], 3.61 [d, ^2J(A−B) = 14.1 Hz, 2H, CH_2], 3.54 [d, ^2J(A−B) = 14.1 Hz, 4H, CH_2], 1.27 [s, 36H, C(CH_3)$_3$], 1.09 [s, 18H, C(CH_3)$_3$]; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 149.9, 149.6, 147.8, 142.5, 137.6, 135.9, 132.2, 129.0, 126.8, 126.6, 125.9, 125.8, 125.6 (ArC, ArCH), 76.7 (OCH_2), 34.2, 33.9 [2*C*(CH_3)$_3$, ratio 1:2], 32.5, 31.9 (2CH_2, ratio 1:2), 31.6, 31.1 [2C(*C*H_3)$_3$, ratio 2:1] (the assignment of the carbon resonances corresponding to the ^{t}Bu and CH_2 groups was based on a separate DEPT experiment); MALDI-TOF MS (ditranol + KI) *m*/*z* 1443.2 [(M + K)$^+$] (calcd 1443.5). Anal. Calcd for $C_{80}H_{96}I_2O_6\cdot 3H_2O$: C, 65.84, H, 6.91. Found: C, 66.01; H, 6.78.

5,11,17,23,29,35-Hexakis(1,1-dimethylethyl)-39,42-bis(4-iodobenzyloxy)-37,38,40,41-tetramethoxycalix[6]arene (20). A mixture of **19** (0.65 g, 0.462 mmol) and NaH (60% on a dispersion oil, 0.61 g, 15.3 mmol) in DMF (20 mL) was stirred for 10 min at room temperature. After this period, excess MeI (2.0 mL, 32.1 mmol) was added and the resultant white suspension was stirred for another 18 h. The reaction mixture was carefully quenched with H_2O and subsequently mixed with 1 M HCl (100 mL). After 0.5 h, the product was extracted with CH_2Cl_2 (2 × 50 mL) and the organic layers were washed with H_2O (100 mL), dried ($MgSO_4$), filtered, and concentrated to a minimal volume (∼5 mL). Addition of MeOH caused precipitation of **20** as a white solid, which was collected by filtration and dried (0.65 g, 96%). Analytically pure **20** was obtained by crystallization from CH_2Cl_2/MeOH: mp 308−309 °C; ^1H NMR (300 MHz, $CDCl_3$, mixture of isomers) δ 7.72 (d, *J* not resolved, ArH, minor), 7.70 (d, ^3J = 8.2 Hz, 4H, ArH, major), 7.29 (d, ^3J = 7.6 Hz, 4H, ArH, major + minor), 7.19 (s, 4H, ArH, major), 7.01 (s, 4H, ArH, major), 6.98 (s, 6H, ArH, minor), 6.92 (s, 6H, ArH, minor), 6.88 (s, 4H, ArH, major), 4.80 (s, 4H, OCH_2, major), 4.51 [d, ^2J(A−B) = 15.3 Hz, 4H, CH_2, minor], 4.45 (s, 4H, OCH_2, minor), 4.39 [d, ^2J(A−B) = 15.2 Hz, 2H, CH_2, minor], 4.23 [d, ^2J(A−B) = 14.1 Hz, 4H, CH_2, major], 3.84 (s, 4H, CH_2, major), 3.59 [d, ^2J(A−B) = 14.1 Hz, 4H, CH_2, major], 3.52 [d, ^2J(A−B) = 15.2 Hz, 2H, CH_2, minor], 3.43 [d, ^2J(A−B) = 15.2 Hz, 4H, CH_2, minor], 2.83 (s, 12H, OCH_3, minor), 2.66 (br s, 12H, OCH_3, major), 1.15 [s, 36H, C(CH_3)$_3$, major], 1.10 [s, 36H, C(CH_3)$_3$, minor], 1.09 [s, 18H, C(CH_3)$_3$, minor], 1.07 [s, 18H, C(CH_3)$_3$, major]; ^{13}C NMR$\{^1H\}$ (125 MHz, $CDCl_3$, mixture of isomers) δ 154.2, 153.8, 151.9, 146.1, 145.7, 145.6, 137.7, 137.5, 137.5, 137.4, 133.6, 133.5, 133.3, 133.2, 133.1, 130.1, 129.4, 126.8, 125.9, 125.6, 125.2 (ArC, ArCH), 93.1 (ArC−I), 73.7 (OCH_2, major), 73.4 (OCH_2, minor), 60.1 (OCH_3, minor), 59.6 (OCH_3, major), 34.12, 34.07 [2*C*(CH_3)$_3$], 31.4, 31.3 [2C(*C*H_3)$_3$], 30.2, 30.1, 30.0 (3CH_2) [assignment was fully supported by DEPT, COSY (H,H), and HETCOR (C,H) experiments]; MALDI-TOF MS (ditranol + KI) *m*/*z* 1483.4 [(M + K)$^+$] (calcd 1483.6). Anal. Calcd for $C_{84}H_{104}I_2O_6\cdot 0.5H_2O$: C, 68.61; H, 7.06. Found: C, 68.45; H, 7.26.

5,11,17,23,29,35-Hexakis(1,1-dimethylethyl)-39,42-bis{4-[PdI(PPh_3)$_2$]benzyloxy}-37,38,40,41-tetrahydroxycalix[6]arene (21). A solution of **19** (247.0 mg, 0.176 mmol) and $Pd(PPh_3)_4$ (423.3 mg, 0.366 mmol) in toluene (40 mL) was stirred for 22 h at room temperature and then worked up as reported for **10** and **11** to give **21** as a light-orange solid (0.36 g, 77%): mp 164−166 °C (decomp); ^1H NMR (300 MHz, $CDCl_3$, mixture of isomers) δ 7.67 (br s, OH), 7.48 (br m, P−ArH_{ortho}), 7.26 (br m, P−ArH), 7.08 (br s, ArH), 7.00 (br s, ArH), 6.59−6.53 (m, ArH), 6.43−6.36 (m, ArH), 6.21 (m, ArH), 5.01 (br, OCH_2), 4.75 (br, *J* unresolved, CH_2), 4.65 (br s, OCH_2), 4.25 (d, ^2J = 15.2 Hz, CH_2), 4.18 (d, ^2J = 15.2 Hz, CH_2), 4.06 (d, ^2J

= 14.7 Hz, CH_2), 3.82 (br s + unresolved signal, two CH_2 patterns), 3.51 (d, ^2J = 14.7 Hz, CH_2), 3.35 [d, ^2J(A−B) = 14.9 Hz, CH_2], 1.29 [s, $C(CH_3)_3$], 1.25 [s, $C(CH_3)_3$], 1.11 [s, $C(CH_3)_3$], 0.75 [s, $C(CH_3)_3$]; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, mixture of isomers) δ 160.7 (ArC_{ipso}), 150.0 (br, ArC), 148.1 (ArC), 142.2 (br, ArC), 136.0 (ArC), 135.2−134.6 (br, ArC), 132.2, 131.9, 131.6, 130.2, 129.8, 128.9 (ArC), 127.8 (br, ArC), 127.6, 126.5, 126.3, 125.8, 125.6, 125.3, 124.5 (ArC, ArCH), 78.5 (br, OCH_2), 34.2, 33.9 [br, $2C(CH_3)_3$], 32.3, 32.0, 31.2, 30.8, 30.6 [CH_2 + $C(CH_3)_3$]; $^{31}P\{^1H\}$ NMR (121.5 MHz, major isomer) δ 22.8 (PPh_3); MALDI-TOF MS (2-amino-4-methyl-5-nitropyridine) *m*/*z* 2276.2 [(M − PPh_3 − I)$^+$] (calcd 2275.7), 2013.4 [(M − 2PPh_3 − I)$^+$] (calcd 2013.6), 1489.7 [(M − 4PPh_3 − I)$^+$] (calcd 1489.4). Anal. Calcd for $C_{152}H_{154}I_2O_6P_4Pd_2 \cdot 2H_2O$: C, 67.53; H, 5.89. Found: C, 67.34; H, 6.01.

5,11,17,23,29,35-Hexakis(1,1-dimethylethyl)-39,42-bis-{4-[PdI(PPh_3)$_2$]benzyloxy}-37,38,40,41-tetramethoxylcalix-[6]arene (22). A solution of **20** (171.0 mg, 0.117 mmol) and $Pd(PPh_3)_4$ (274.2 mg, 0.237 mmol) in THF (30 mL) was stirred at room temperature for 22 h. Then the white precipitate formed was isolated by filtration. The filtrate was concentrated in vacuo and treated with Et_2O to yield an off-white solid product. The two fractions were combined and dried to give compound **22** (174.6 mg, 55%); ^1H NMR (200 MHz, $CDCl_3$, data for the 1,2,3-alternate conformer) δ 7.50 (br m, P−ArH_{ortho}), 7.26 (br m, P−ArH), 6.92 (br s, ArH), 6.88 (br s, ArH), 6.54 (d, ^3J = 7.8 Hz, 2H, ArH), 6.48 (d, ^3J = 7.8 Hz, 2H, ArH), 4.47 (br s, 4H, OCH_2), 4.27 (d, ^2J = 14.9 Hz, 4H, CH_2), 3.81 (s, 4H, CH_2), 3.56 (d, ^2J = 13.3 Hz, CH_2), 2.63 (br s, 12H, OCH_3), 1.13 [s, 36H, $C(CH_3)_3$], 0.96 [s, 18H, $C(CH_3)_3$]; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, data for the 1,2,3-alternate conformer) δ 154.2 (ArC_{ipso}), 145.6, 135.9, 135.4, 135.2, 134.9, 134.8, 134.8, 134.6, 134.5, 133.5, 132.3, 132.1, 132.0, 131.7, 130.2, 129.7, 129.0, 128.2, 128.1, 127.9, 127.8, 127.7, 127.1, 125.8, 125.3, 124.6 (ArC, ArCH), 74.7 (br, OCH_2), 59.4 (OCH_3), 34.1 [br, $C(CH_3)_3$], 31.4, 31.3 [$2C(CH_3)_3$], 30.7 (br, CH_2, overlapping signals); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, data for the 1,2,3-alternate conformer) δ 23.0 (PPh_3); MALDI-TOF MS (ditranol + KI) *m*/*z* 2236.6 [(M − 2PPh_3 + K)$^+$] (calcd 2237.5). Anal. Calcd for $C_{156}H_{162}I_2O_6P_4Pd_2 \cdot H_2O$: C, 68.34; H, 6.03. Found: C, 68.09, H, 6.29.

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Supporting Information Available: General experimental methods, crystallographic studies and CIF files for **2** and **20**, variable-temperature ^1H NMR spectra (500 MHz) for **20**, NOESY spectrum for **20**, and tables with bond lengths/angles and crystallographic data for **2** and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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