(η^5-Pentamethylcyclopentadienyl)rhodium Complexes of Upper-Rim Monophosphinated Calix[4]arene

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A new and convenient synthesis of the upper-rim monobrominated calix[4]arene Br-calixPR_2 is reported and has been used as the key precursor for the preparation of both the diphenyl- (**6a**) and diisopropylphosphine ligands (**6b**). Reactions of these new ligands with $[(C_5Me_5)RhCl_2]_2$ afford the complexes (calixPR_2)$(C_5Me_5)Rh(Cl)_2$ (**8a**,**b**), which can be converted into their corresponding dihydrides (calixPR_2)$(C_5Me_5)Rh(H)_2$ (**9a**,**b**) using $NaBH_4$. **6a** also reacts with $(C_5Me_5)Rh(CO)_2$ to form (calixPPh_2)$(C_5Me_5)Rh(CO)$ (**10**). The X-ray structures for both **8a** and **8b** confirm the cone geometry of the calix[4]arene bowl and reveal the presence of the phenyl and isopropyl groups over the cavity. With respect to the Rh−P bond, a gauche conformation is depicted in the solid state. Complexes **8a**,**b** and **9a**,**b** appear to be fluxional in solution, as demonstrated from VT ^1H and ^{31}P NMR measurements for **8a**,**b**. Molecular modelings confirm the presence of 13 conformers associated with the rotation around the C(calix)−P and P−Rh bonds and the cavity locking groups above it. The minimum energy conformation for the unsaturated (calixPPh_2)$(C_5Me_5)Rh$ complex exhibits the Rh atom well located at the opening of the free cavity.

Introduction

The basket-shaped calix[4]arene is a remarkable molecule, which exhibits a cyclic tetraphenolic structure giving rise to extremely rich chemistry, as pointed out by the pioneer works of Gutsche.[1] Because of the presence of ionophoric and hydrophobic cavities and the generally simple chemistry of the calix[4]arene, many useful applications in the area of cation binding and transport are now known, and many elegant highly selective receptors and novel sensors for polyanionic species have been designed with this host molecule.[2]

While attempting to successfully couple the very convenient host−guest behavior of calix[4]arene with interesting properties of transition-metal complexes, numerous researchers have performed the synthesis of complexes of this platform molecule.[3] The literature shows that functionalization of the lower-rim segment has been successfully exploited, due primarily to the relative ease with which the R−OH fragments can be manipulated chemically.[4] On the other hand, few upper-rim derivatizations has been reported. A list of electron donor groups that have been successfully anchored at the upper-rim includes $-SO_3-$,[5] $-NO_2$,[6] $-NH_2$,[7] $-N{=}NR$,[8] and $-PPh_2$,[9] among a few others.[10]

Atwood et al. have reported the preparation of the soft ligand 5,11,17,23-tetrakis(diphenylphosphino)-25,26,27,28-tetramethoxycalix[4]arene.[11] Unfortunately the spectroscopic data reveal that this molecule must exist with multiple conformations (cone, 1,2-alternated, 1,3-alternated, etc.), which in addition can be in equilibrium with each other. The use of propyl residues at the lower rim is known to prevent such behavior, and only the desired cone conformation is obtained.[12] So far the upper-rim functionalization mentioned above appears in the literature in two ways. These are the tetrasubstituted and 5,17-disubstituted calix[4]arenes.[5−10] The dramatic consequence of this chemistry is that the upper-rim opening giving access to the hosting hydrophobic cavity either is blocked if 5,17-chelation with transition metals occurs[10] or is seriously sterically hindered. Monofunctionalization of the upper rim of the calix[4]arene molecule appears to be a much more desirable approach in this case.

Recently, Shinkai et al.[13] reported a methodology to prepare the key precursor 5-bromo-25,26,27,28-tetra-

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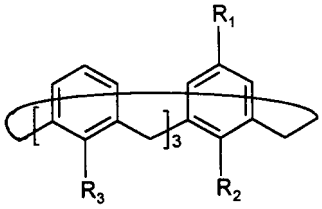
Table 1. List of Investigated Compounds and Complexes



compd	R_1	R_2	R_3
1	H	OH	OH
2	H	OH	O(CO)Ph
3	Br	OH	O(CO)Ph
4	Br	OH	OH
5	Br	OPr	OPr
6a	$P(Ph)_2$	OPr	OPr
6b	$P(i\text{-}Pr)_2$	OPr	OPr
7	$O{=}P(Ph)_2$	OPr	OPr
8a	$P(Ph)_2(C_5Me_5)Rh(Cl)_2$	OPr	OPr
8b	$P(i\text{-}Pr)_2(C_5Me_5)Rh(Cl)_2$	OPr	OPr
9a	$P(Ph)_2(C_5Me_5)Rh(H)_2$	OPr	OPr
9b	$P(i\text{-}Pr)_2(C_5Me_5)Rh(H)_2$	OPr	OPr
10	$P(Ph)_2(C_5Me_5)Rh(CO)$	OPr	OPr

propoxycalix[4]arene using the known 25,26,27,28-tetrapropoxycalix[4]arene and bromine. Although the desired molecule is formed as a major product, a certain amount of the dibromo derivatives are also formed. These products are difficult to separate due to similar solubilities and polarities. The unfortunate consequence is found in the poor yield. Alternative routes for the selective bromination of calix[4]arene in a cleaner fashion are clearly required.

We have elected to investigate the $(C_5Me_5)Rh$ complexes of monophosphinated calix[4]arene, because this metallic fragment is well-known for its ability to cleave C−H bonds,[14] a property that is crucial for the functionalization of saturated hydrocarbons. Branching a $(C_5Me_5)Rh$ moiety onto the upper rim of a monophosphinated calix[4]arene provides an unprecedented opportunity for coupling this very important C−H bond activation property with the supramolecular behavior of this bowl-shaped molecule. This way, very elegant regioselective C−H bond activation can be anticipated with such complexes, potentially leading toward an important impact in the field.

We now wish to report a novel and convenient synthesis of the monobromocalix[4]arene, along with the diphenyl- and diisopropylphosphine derivatives and a number of their corresponding $(C_5Me_5)Rh$ complexes. The X-ray structure for the diphenylphosphine calix[4]-arene complex of $(C_5Me_5)RhCl_2$ is also reported.[15] The complexes are found to be fluxional in solution, and the ^1H NMR data are analyzed and complemented with computer modelings. The list of investigated compounds and complexes is provided in Table 1.

Results and Discussion

1. Ligand Preparation. The monophosphinated ligands **6a**,**b** can be prepared in five steps from the nonsubstituted calix[4]arene **1** (Figure 1). The key step

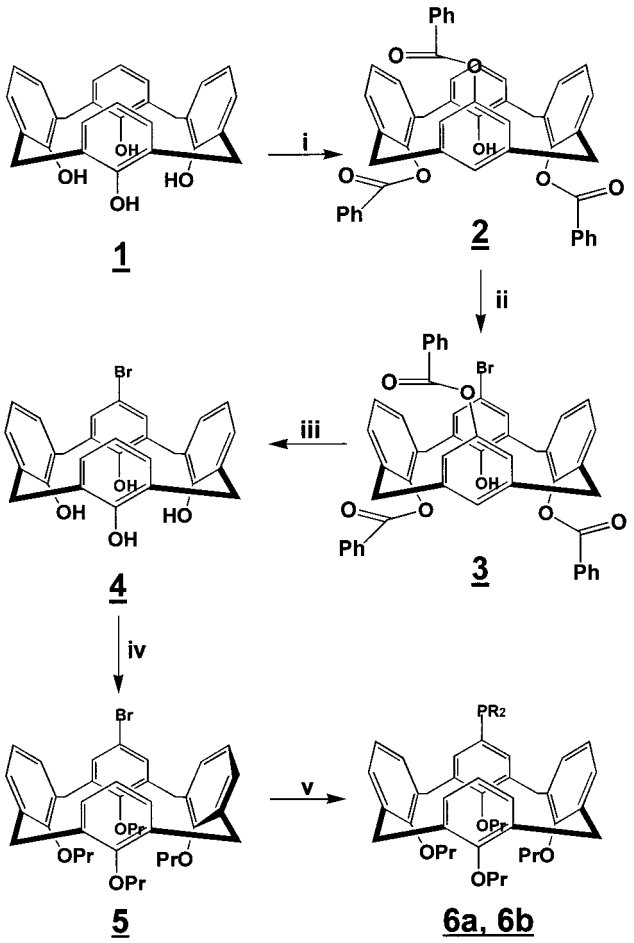


Figure 1. Reaction schemes for the preparation of compounds **6a**,**b**. Legend: (i) 1-methylimidazole/$PhCO_2Cl$/ACN, room temperature, 24 h; (ii) $Br_2/CHCl_3$, room temperature, 15 min; (iii) NaOH/THF, room temperature, 48 h; (iv) NaH/1-IPr/DMF, room temperature, 72 h; (v) *n*-BuLi/$ClPPh_2$ (**6a**)/$ClP(i\text{-}Pr)_2$ (**6b**)/THF, −78 °C, 24 h.

is the tribenzoylation of **1** to give the known compound **2**.[16] The literature procedure involves the use of pyridine as a base and solvent, with a reported chemical yield of 71%. By using 1-methylimidazole in acetonitrile, the isolated yield is increased to 88%. This compound **2** now exhibits two types of phenyl residues: an electron-rich phenolic one and three significantly poorer ones. This greater difference in electronic density allows a very good discrimination for the bromination reaction favoring the phenolic ring. As anticipated, the bromination of **2** affords **3** *cleanly*, as evidenced by the quasi-quantitative isolated yield. Both **2** and **3** exhibit ^1H NMR data that are indicative of a partial cone conformation.

The following two steps consist of standard benzoyl cleavage and propylation reactions in good (90%) and modest (65%) yields, respectively. In these cases intramolecular H bondings in **4** and large *n*-propyl groups in **5** favor the cone conformation, as confirmed by the ^1H NMR data (Experimental Section). Finally, the conversion of monobromotetrapropoxycalix[4]arene (**5**) into **6a**,**b** proceeds via lithiation of the bromophenyl fragment with *tert*-butyllithium, followed immediately by the phosphination reaction either with chlorodiphen-

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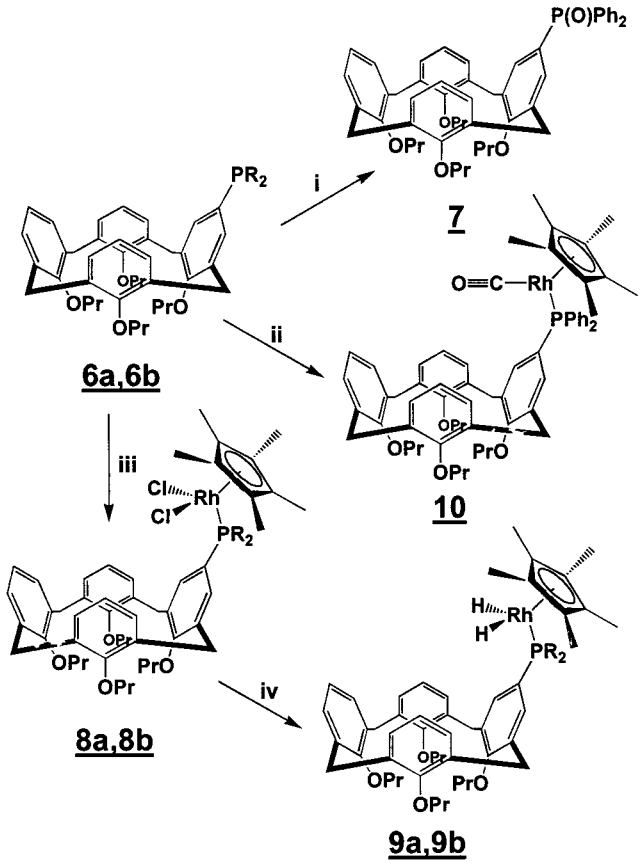

Figure 2. Reaction schemes for the preparation of compounds **9a**,**b** and **10**. Legend: (i) H_2O_2/THF, room temperature, 24 h; (ii) $Cp^*Rh(CO)_2/C_6H_6$, reflux, 24 h; (iii) $[(C_5Me_5)RhCl_2]_2$/EtOH/C_6H_6, reflux, 5 h; (iv) $NaBH_4$/EtOH, reflux, 1 h.

ylphosphine (**6a**) or chlorodiisopropylphosphine (**6b**). The overall yields are on the order of 30% and are explained by the difficult propylation reaction and air sensitivity of the phosphine compounds. The best results have been obtained when 1-iodopropane was used instead of 1-bromopropane for the propylation. While **6a** oxidizes slowly in air to give the crystallographically characterized phosphine oxide **7** (drawing provided in the Supporting Information), **6b** oxidizes readily. The ^{1}H NMR spectrum of **7** also confirms the cone conformation.[17]

2. Complex Synthesis. The complexation scheme for the preparation of the (η^5-pentamethylcyclopentadienyl)-rhodium complexes **9a**,**b** is presented in Figure 2. The mononuclear complexes **8a**,**b** can conveniently be obtained in good yield using the dimeric $[(C_5Me_5)RhCl_2]_2$ complex in the presence of the corresponding aryl- and alkylphosphine ligands **6a**,**b**. Both complexes are stable, and a single crystal suitable for X-ray crystal analysis (Tables 2 and 3) was obtained for **8a**. Figure 3 shows the ORTEP drawing for **8a** and confirms the expected upper-rim monofunctionalization of the calix[4]arene host. The coordination environment of the Rh(III) center is very similar to that reported for $[(C_5Me_5)RhCl_2]_2$ (μ-dmpe) (dmpe = bis(dimethylphosphino)ethane).[18] Indeed, the literature $d(Rh-C_{Cp^*})_{average}$, $d(Rh-P)$, and $d(Rh-Cl)$ values of 2.17(4), 2.29(1), and 2.41(1) Å, respectively, compare favorably to those listed for **8a** in Table 3. The slightly shorter 2.29(1) Å value for $d(Rh-P)$ in the $[(C_5Me_5)RhCl_2]_2$(μ-dmpe) dinuclear complex is consistent with the better π-back-bonding of this stronger phosphine base.

Table 2. X-ray Data for 8a

chem formula	$C_{62}H_{72}Cl_2O_4PRh$
habit	red rectangular cryst
space group	$P2_1/c$
a, Å	18.009(7)
b, Å	15.401(2)
c, Å	21.996(5)
β, deg	110.34(2)
V, Å^3	5720(3)
Z	4
ρ_{calcd}, g/cm^3	1.261
radiation	Cu Kα, graphite monochromated
$\lambda(K\alpha_{ax})$, Å	1.540 60
cryst dimens, mm^3	0.13 × 2.15 × 0.32
T, °C	293(2)
μ, cm^{-1}	16.35
index range	$-21 < h < 19$, $0 < k < 18$, $0 < l < 25$
diffractometer	Nonius
diff. geom	CAD-4
θ range, deg	2.61−64.84
no. of rflns collected	18919
no. of indep rflns	9703 (R(int) + 0.07)
R1[a]	0.0734
wR2[b]	0.1897

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{0.5}$.

Table 3. Selected Bond Distances and Angles[a] for 8a

P−C_{calix}	1.815(6)	Rh−Cl1	2.3835(18)
P−Rh	2.335(18)	Rh−Cl2	2.405(2)
Rh−$C_{C_5Me_5}$	2.194(29)	P−Rh−Cl2	93.50(7)
Rh−P−C_{calix}	110.00(19)	Cl1−Rh−Cl2	93.54(8)
P−Rh−Cl1	85.71(6)		

[a] Bond distances in Å and angles in deg.

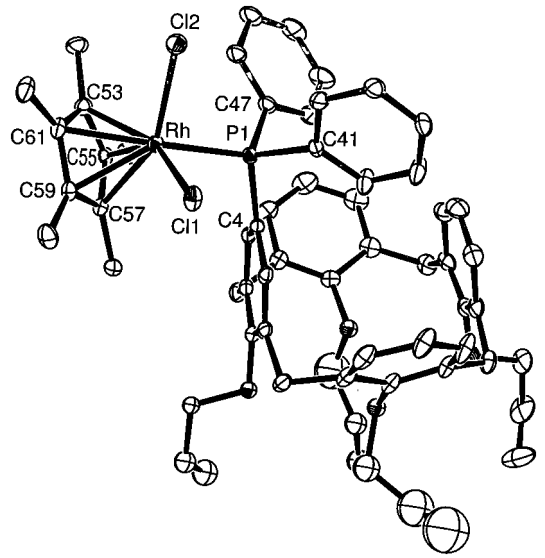

Figure 3. ORTEP drawing of compound **8a**. Ellipsoids are shown at 10% probability, and the H atoms are not shown for clarity.

(17) Single crystals suitable for X-ray analysis were obtained, but the residual was too high (R_w = 16%). Nonetheless, the structure was indeed as expected in its cone conformation. A picture of the ligand is provided in the Supporting Information.

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8a exhibits P−C_{Calix} and P−Rh single bonds, allowing many conformers to exist, as discussed below. This complex in the solid state adopts a geometry where the two phenyl groups are placed over the cavity, and the $(C_5Me_5)RhCl_2$ fragment is in a gauche conformation with respect to the PPh_2(calix) residue. Crystal packing may be at the origin of this conformation. The bowl-shaped calix[4]arene moiety does not adopt a symmetrical C_{4v} local point group but, rather, a local C_{2v}. More importantly, two of the phenyl groups are placed in a quasi face-to-face fashion. The phosphinated phenyl group and its facing ring slightly point toward each other with a plane-to-plane angle of 9.01(0.34)°. The other pair of phenyl rings forms an angle of 85.59(0.31)° and are open away from each other.

X-ray data for **8b** have been obtained and demonstrate the isostructurality with **8a**, but the quality of the crystal is poor, and the data cannot be formally reported. A picture of the complex is provided in the Supporting Information, and the presence of two of the methyl groups of the isopropyl substituents well above the cavity is obvious. The ^{1}H NMR spectrum for **8b** is very revealing: four different $(CH_3)_2CH$ groups are depicted. Indeed, a pair of doublets are observed at 1.6 ppm as expected, as well as another more shielded one at 0.8 ppm. The spectral feature can only be explained by the presence of two CH_3 groups locked over the cavity, in direct contact with the cone of anisotropy of the benzene ring. The spectral interpretation was confirmed by the 2D NMR technique HMBC.[19]

Complexes **8a**,**b** can easily and predictably be converted into their corresponding dihydride species **9a**,**b** via a direct reaction with sodium borohydride in refluxing ethanol. These new complexes turn out to be relatively unstable with time, particularly in the presence of light or air. Clearly these complexes must be freshly synthesized prior to use. The ^{1}H NMR spectra exhibit the expected doublet of doublets centered at −13.07 and −14.29 ppm for **9a**,**b**, respectively, with ^1J(Rh,H) ≈ 28 Hz and ^2J(P,H) ≈ 38 Hz, while the IR-active ν(Rh−H) bands are located at 2080 and 2008 cm^{-1}, respectively.

6a can also react with the mononuclear complex $(C_5Me_5)Rh(CO)_2$[20] via a simple thermally induced CO substitution to provide the basket molecule **10**. A single and characteristic ν(CO) absorption is readily observed at 1960 cm^{-1} in the solid state. The new complex has been confidently characterized by standard methods (chemical analysis, ^{1}H and ^{31}P NMR, IR, and FAB mass), which confirm its identity and purity. Although **10** is somewhat more stable than **9a** and **9b**, decomposition may be depicted when subjected to UV−visible light.

3. Fluxionality. Compounds, **8a** and **9a** exhibit ^{1}H NMR signals that are significantly larger than that found for the other investigated compounds in this work, at room temperature. A VT study of **8a** and **8b** (Supporting Information) clearly shows a progressive transformation of the spectra where a coalescence process appears at ∼268 K for **8a**, and ∼205 K for **8b** (somewhat limited by the freezing point of the toluene solvent). Compounds **9a**,**b** could not be investigated due to their limited stability in solutions as a function of time. Interestingly, the full width at half-maximum (fwhm) is variable vs temperature from one signal to another within the same sample. This observation indicates that in fact more than one fluxionality process occurs, as anticipated for these very flexible molecules (Chart 1). As a typical example, Figure 4 exhibits the 2.5−5.0 ppm region of the ^{1}H NMR spectra of **8a** in toluene. The 3.1 and 4.5 ppm signals are the equatorial and axial calix $-CH_2-$ protons, respectively. The slightly more shifted signals at 4.50 and 3.13 ppm correspond to the calix $-CH_2-$ groups located away from the phosphine residues, while the pair of shielded doublets found at 4.45 and 3.00−3.13 ppm (depending upon the temperature) are the calix $-CH_2-$ residues placed near the $P(C_6H_5)_2$ fragment. This assignment is based upon the comparison of the data of 25,26,27,28-tetra-*n*-propoxycalix[4]-arene (**11**) and 5,11,17,23-tetrakis(diphenylphosphino)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (**12**).[21] With the lowering of the temperature, the latter undergoes a coalescence process at a temperature in the neighborhood of 268 K as stated, where the shielded signals are larger than the deshielded ones. The unsubstituted propoxyaryl residue facing the phosphine group is less encumbered and experiences slightly faster molecular motions. The ∼3.8 ppm signal is attributed to the $O-CH_2$ protons and exhibits the same phenomena. Two pairs of triplets are depicted at higher temperature (see

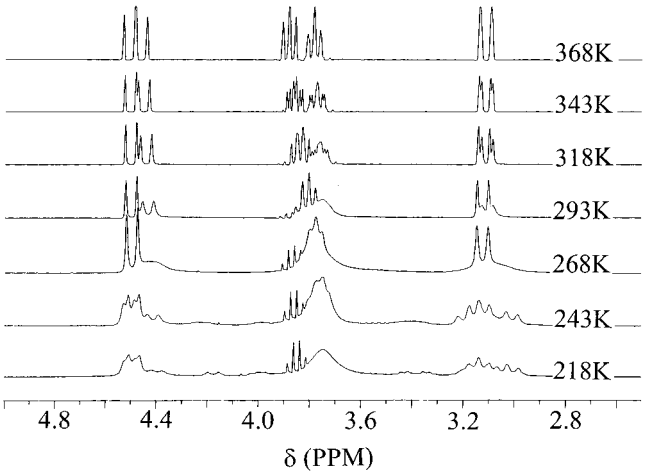
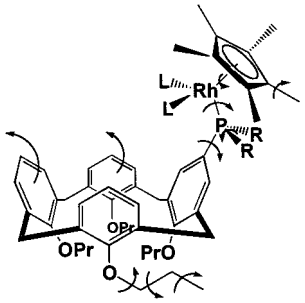


Figure 4. ^{1}H NMR spectra of **8a** in toluene-d_8 as a function of temperature. The quartet at 3.85 ppm is due to residual ethyl acetate impurity.

Chart 1



(19) The spectral interpretation was confirmed by the 2D NMR technique called Heteronuclear Multiple Bond Connectivity (HMBC). The description of this common technique can be found in the original paper by: Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093.

(20) Drolet, D. P.; Lees, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 4186.

(21) Gagnon, J.; Vezina, M.; Drouin, M.; Harvey, P. D. Unpublished results.

368 K). When the temperature is lowered (318 K), this region becomes complex and evolves into a triplet centered at 3.80 ppm and a broad envelope at 3.74 ppm. When the temperature is lowered further, the signal becomes a broad triplet, which progresses toward a single large signal at ~3.75 ppm (218 K). In this case, VT experiments are not reported below this temperature due to limited solubility below 218 K. However, it appears that 218 K must be close to the coalescence temperature based on the shape of this signal. The greater flexibility of the *n*-propyl chain can easily account for the lower coalescence temperature.

Similar observations can be made for the aromatic region, including signals associated with the (C_6H_5)−P groups. A coalescence process is evident at ~268 K (Supporting Information). Clearly, the (C_6H_5)−P group multiplet at ~8.0 ppm is also involved in the fluxional process. The latter broadens upon cooling and separates spectacularly into two signals at ~280 K. While the most deshielded signal becomes a multiplet, the shielded one at 7.95 ppm sharpens and then broadens further down at 218 K. Multiple fluxions occur, and molecular fragments appear to cooperate in various motions, in agreement with Chart 1.

The VT measurements for **8b** again reveal similar information (spectra provided in the Supporting Information). When the temperature is lowered, most of the signals become significantly broad, but at different rates. For instance, the signals associated with the methyl groups in C_5Me_5 are relatively narrow within this temperature range, while the very broad signals in the aromatic region practically vanish. Interestingly, the shielded P−CH−CH_3 signals (at ~0.75 ppm) broaden at a higher temperature (256 K), indicating that the relative steric hindrance is easily felt in the interior of the cavity. The deshielded P−CH−CH_3 resonances broaden at about 230 K, while the P−CH−$(CH_3)_2$ signals (at 3.22 ppm) become broad, somewhat similarly to that of the former ones. The O−CH_2 multiplet broadens in the 243−230 K range, while the −CH_2−CH_3 and −CH_2−CH_3 fragments of the *n*-propyl chains resonating at 2.1 and 1.9 ppm, respectively, undergo similar processes at lower temperatures. Clearly, the more flexible the fragments, the lower the broadening temperature will be (i.e., coalescence temperature). In contrast to **8a**, the calix −CH_2− signals broaden only at temperatures approaching 210 K, indicating that the bowl structure in **8b** is more flexible than that in **8a**. This observation is consistent with the fact that the PR_2 groups lie above the cavity, as demonstrated by the X-ray structure determination, including intramolecular steric hindrance.

The last comment about compounds **8a**,**b** concerns the signals at 7.55 (**8a**) and 7.30 ppm (**8b**) associated with the ortho hydrogens of the calix phosphinated aromatic ring. This assignment is also based upon the comparison of the ^{1}H NMR spectra of **11** and **12**[21] and their relative intensities. The doublet is due to ^3J(P,H). These peaks broaden at 318 and 256 K for **8a**,**b**, respectively. This large difference (~60 °C) strongly suggests that the motion of the larger (C_5Me_5)Rh(Cl)$_2$P(C_6H_5)$_2$ group must be slower than that of (C_5Me_5)Rh(Cl)$_2$P(CH(CH_3)$_2$)$_2$. In addition, the ^{31}P NMR spectra of **8a**,**b** exhibit a sharp doublet due to ^1J(Rh,P) coupling at room temperature,

Chart 2

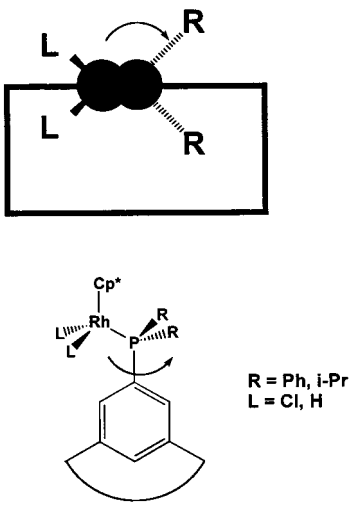
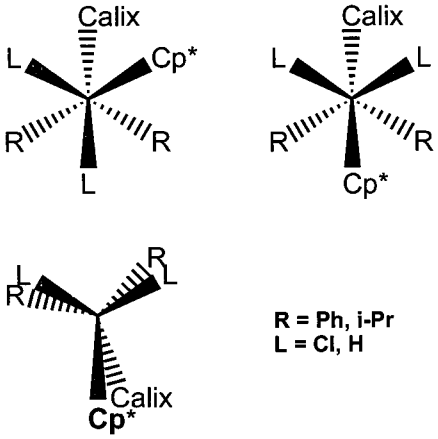


Chart 3



but this doublet becomes broad at lower temperatures. At 218 K, the fwhm are ~0.5 and 1.0 ppm for **8a** and **8b**, respectively, in comparison with ~0.2 ppm at 293 K. When **8a** is cooled further (193 K), a complex multiplet appears as witness to the presence of more than one conformer in solution.

4. Conformational Analysis. The VT NMR experiments clearly indicate that more than one conformer exists at higher temperatures for **8a**,**b**. The presence of C(calix)−P and Rh−P single bonds, and a cavity, controls the number of possible conformers (Chart 1). The C_5Me_5 motions are ignored, since no evidence for coalescence was observed between 210 and 368 K. X-ray structures reveal that the PR_2 residues were found locked above the cavity, as corroborated by ^{1}H NMR analysis for R = *i*-Pr. Using the program PC-model to qualitatively address the presence of multiple conformers, computations are performed for both **8a** and **8b**. The results are essentially identical for both complexes and will be discussed simultaneously.

Rotations around the C(calix)−P bond provides four possible minimum energy conformations where two groups, either C_6H_5 or Cl, sit over the cavity as shown in Chart 2. In addition, rotation around the Rh−P bond affords three more possibilities (two gauche and one anti; Chart 3), making a subtotal of 4 × 3 conformations. Finally, one eclipsed special case also occurs in theory, where the bulky C_5Me_5 falls inside the cavity (Chart 3,

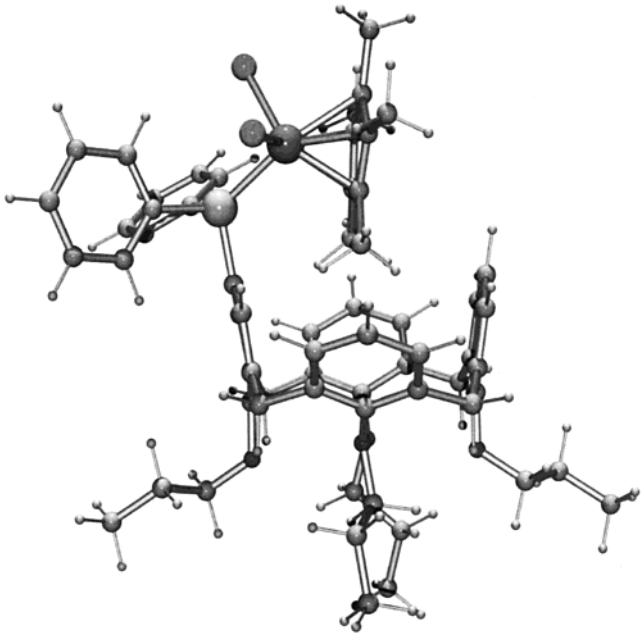


Figure 5. Ball and stick model of one of the 13 possible conformers of **8a**.

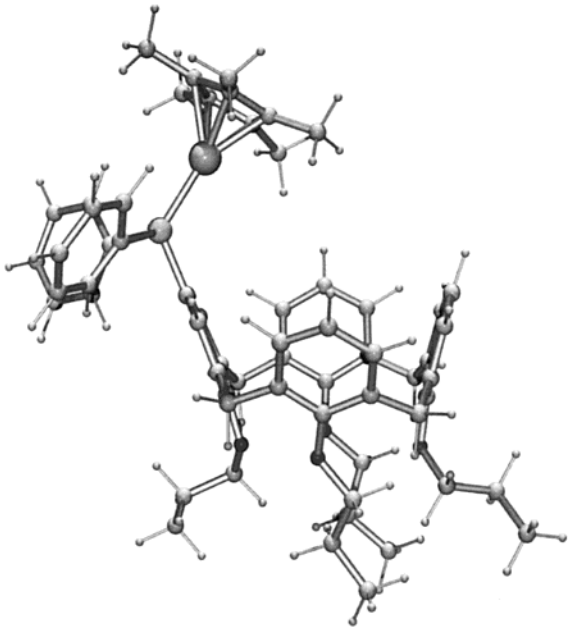


Figure 6. Ball and stick model of one of the possible conformers for the $[Ph_2P(calix)]Rh(C_5Me_5)$ reactive intermediate. The cavity is available for substrate binding.

bottom structure). Computer modelings predict that in fact 13 conformers are possible, 4 of which are equivalent because of the gauche geometries.

In all cases, CPK models indicate that access of guest molecules is precluded by the presence of the PR_2 groups, which is consistent with the tetrahedral geometry of the coordinated P atom. In addition, the gauche conformations depicted by the X-ray structures are two of the most stable conformations based upon the PC-model relative total energy (i.e., they are in fact the second most stable). Unexpectedly, the conformation where the C_5Me_5 fragment is located inside the cavity (Figure 5) is the least energetically demanding. One possible explanation for this interesting result is that there is a decrease in steric interactions between the $P(C_6H_5)_2$ groups with the large calix fragment in that particular conformation. In the gauche conformation, such as in Figure 3, the C_5H_6 groups do not fall inside the cavity but are just sitting above it, together being too large to penetrate the cavity. However, this special "C_5Me_5 in the cavity" geometry is not accessible, since the C_5Me_5 is much too bulky to hop over the calix aromatic groups, during the rotation aound the C(calix)−P bond. As anticipated, no evidence for this conformation is found in the ^{1}H NMR spectra in the $Rh(C_5Me_5)$ region. The conformer where the two Cl ligands lie above the bowl is the most energetic one but offers the most space near the cavity. This calculated higher energy conformation results from the fact that the $RhCl_2$ fragment does not fall into the cavity, forcing the other substituents, $Rh(C_5Me_5)$ and $P(C_6H_5)_2$, to occupy a more restricted area.

This observation is crucial. If the Cl ligands were to be completely removed from the Rh environment, then the cavity would become more available for host−guest interactions. Indeed, computer models (see Figure 6 as an example) illustrate well this behavior well. Again rotations around the C(calix)−P and P−Rh bonds give rise to multiple conformers as well. This time, only three rotamers would be available, since the P−Rh−(C_5Me_5) fragment is expected to be linear.[14] Therefore, steric hindrance is expected to be minimal.

Final Remarks

Preliminary results show that **9a**,**b** and **10** both thermally and photochemically eliminate H_2 and CO, respectively, to generate the very reactive postulated species $(calixPR_2)(C_5Me_5)Rh^I$; as briefly described above, C−H bond activation in benzene has been observed. This important species is expected to activate other C−H bonds, and regioselectivity due to host−guest interactions would be an unprecedented asset. Reactivities of this species will be reported in due course.

Experimental Section

Materials. 25,26,27,28-Tetrahydroxycalix[4]arene (**1**) was prepared according to standard procedures.[22] The solvents were purified according to general procedures.[23] Column chromatography was performed from silica gel 230−400 mesh (60A) and was used as received. All manipulations were carried out under N_2 or Ar atmospheres, using standard Schlenk techniques, or in a glovebox. All other reagents were used as received.

Apparatus. The NMR spectra were acquired on a 300 MHz Bruker instrument (^{1}H, 300.15 MHz; ^{13}C, 75.478 MHz; ^{31}P, 121.497 MHz). The chemical shifts (δ) are reported with respect to tetramethylsilane, TMS (^{1}H, ^{13}C), which were determined on the basis of residual proton solvent resonances and H_3PO_4 (^{31}P). The coupling constants are reported in ppm. The FT-IR data were obtained on a Perkin-Elmer spectrometer. Model 1600. The mass spectra (EI) were measured on a ZAB-1F instrument (VG model). All chemical analyses and FAB mass spectra were acquired at the Université de Montréal (Regional Services).

Computer Modeling. The calculations were performed using the commercially available program PC-model from

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Serena Software (version 7.0), which uses the MMX empirical model. The Rh−Cl and Cl−Cl separations were set as crystallographically found and remained fixed during the computations. For comparison purposes the Rh−C, Rh−Cl, Rh−P, C(calix)−P and Ph C−P distances are 2.19 vs 2.24 Å, 2.39 vs 2.36 Å, 2.34 vs 2.36 Å, 1.82 vs 1.86 Å, and 1.84 vs 1.90 Å for the X-ray and calculated data, respectively. The minimum energy conformations were found by calculating the total energy as a function of the dihedral angle of the C(calix)−P and P−Rh bonds. Then, each conformation was minimized individually around the minimum of the potential to take into account the presence of substituents (i.e., $-C_6H_5$, $-CH(CH_3)_2$, $-C_5Me_5$, −calix). These minimizations allowed the extraction of the relative total energy for each conformer.

Crystallography. Intensity data from a dark red prismatic crystal were collected at 293(2) K on an Enraf-Nonius CAD-4 automatic diffractometer, with graphite-monochromated Cu Kα radiation (1.541 84 Å). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 24 centered reflections in the range $40° < 2\theta < 50°$. Space group determination was based upon systematic absences, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure. The NRCCAD program[24] was used for centering, indexing, and data collection. The NRCVAX programs[25] were used for crystal structure solution by application of direct methods. The SHELX-97 program[26] was used for refinement by full-matrix least squares on F^2, with structure factors being taken from ref 27. The absorption coefficients (μ) are listed in the Supporting Information. A Gaussian integration absorption was made. No significant decay was observed during data collection. Isotropic extinction coefficients were included in the refinement to account for secondary extinction effects.[28] Three of the four *n*-propyl groups are disordered; these were refined using the SAME and SADI restraints available in SHELXL-97. Hydrogens were all geometrically placed, and the respective final refinements included anisotropic thermal parameters for the non-hydrogen atoms, except for the disordered atoms, and isotropic thermal parameters for the hydrogen atoms. Individual displacement parameters were fixed at $U(H) = 1.5[U_{eq}$(C-methyl)] or $U(H) = 1.2U_{eq}$ and were treated as rigid for refinement. The $R(F)$ and $R_w(F^2)$ final discrepancy indices at convergence for the $I_{net}{}^3$ $2.0\sigma(I_{net})$ significant reflections, the number of restraints and variables, and the GOF are listed in the Supporting Information.

25,26,27-Tribenzoyl-28-hydroxycalix[4]arene (2). A 30 g (71 mmol) amount of **1** was suspended in 1700 mL of dry acetonitrile under an N_2 atmosphere. To this suspension was added 15 equiv of 1-methylimidazole (84.5 mL, 1.06 mo), upon which solubilization of **1** occurred within a few minutes. After the solution was stirred for 15 min, 2.9 equiv of benzoyl chloride (24 mL, 200 mmol) was added and the solution was stirred for another 12 h, during which a white precipitate appeared. The latter was then filtered and was washed with 20 mL of cold acetonitrile. Yield: 51.7 g, 88%. Mp: 260−262 °C. Anal. Calcd for $C_{49}H_{36}O_7$: C, 79.88; H, 4.92. Found: C, 79.43; H, 4.89. ^{1}H NMR ($CDCl_3$): δ 8.12 (d, 4H, $^3J_{H-H} = 7.35$, Ph), 7.75 (t, 2H, $^3J_{H-H} = 7.44$, Ph), 7.59 (t, $^3J_{H-H} = 7.45$, 1H, Ph), 7.55 (t, $^3J_{H-H} = 7.45$, 4H, Ph), 7.30−7.20 (m, 4H, Ph), 7.08 (d, 2H, $^3J_{H-H} = 7.45$, Ph), 7.03 (dd, 2H, $^3J_{H-H} = 6.67$ and 2.66, Ph), 6.92 (d, 2H, $^3J_{H-H} = 7.50$, Ph), 6.79 (t, 1H, $^3J_{H-H} = 7.36$, Ph), 6.76 (t, 1H, $^3J_{H-H} = 7.44$, Ph), 6.65−6.55 (dd + t, 4H, Ph), 5.49 (s, 1H, OH), 3.95 (d, 2H, $^2J_{H-H} = 14.34$, CH_2−Ar), 3.85 (d, 2H, $^2J_{H-H} = 15.55$, CH_2−Ar), 3.75 (d, 2H, $^2J_{H-H} = 15.37$, CH_2−Ar), 3.53 (d, 2H, $^2J_{H-H} = 14.23$, CH_2−Ar). ^{13}C NMR ($CDCl_3$): δ 164.34, 163.76, 152.67, 148.17, 146.60, 133.68, 133.39, 133.10, 132.13, 132.51, 131.19, 130.67, 130.17, 129.78, 129.42, 128.54, 127.95, 126.18, 125.89, 125.01, 119.64, 37.31, 32.30. MS (EI): *m/z* 736 (M^+, relative intensity 20%).

25,26,27-Benzoyl-5-bromo-28-hydroxycalix[4]arene (3). A 20 g (27 mmol) portion of **2** was dissolved in 400 mL of $CHCl_3$ in the presence of an excess of Br_2 (10 mL, 180 mmol), and the mixture was stirred for 30 min at room temperature. The reaction was quenched with an aqueous $Na_2S_2O_3$ solution (4 g/100 mL). The organic layer was extracted once more with this aqueous $Na_2S_2O_3$ solution and then twice with a 1 N aqueous HCl solution and once with water. This organic layer was then dried over $MgSO_4$ and then filtered and evaporated. The resulting light yellow powder was then washed overnight with 1000 mL of methanol. The solution was filtered, and an off-white solid was obtained. Yield: 21 g, 95%. Mp: dec >250 °C. Anal. Calcd for $C_{49}H_{35}O_7Br$: C, 72.15; H, 4.32. Found: C, 71.95; H, 4.28. ^{1}H NMR ($CDCl_3$): δ 8,05 (d, 4H, $^3J_{H-H} = 7.30$, Ph), 7.77 (t, 2H, $^3J_{H-H} = 7.43$, Ph), 7.60−7.55 (2t, 1H + 4H, Ph), 7.35−7.32 (m, 4H, Ph), 7.10 (s, 2H, Ph), 7.07 (dd, 2H, $^3J_{H-H} = 6.56$ and 2.74, Ph), 6.87 (d, 2H, $^3J_{H-H} = 7.50$, Ph), 6.75−6.60 (3t + dd, 5H, Ph), 5.27 (s, 1H, OH), 3.85−3.65 (3d, 3 × 2H, CH_2−Ar), 3.53 (d, 2H, $^2J_{H-H} = 14.48$, CH_2−Ar). ^{13}C NMR ($CDCl_3$): δ 164.27, 163.83, 151.99, 148.17, 146.92, 133.76, 133.61, 133.23, 133.11, 131.84, 131.55, 131.26, 130.80, 130.68, 129.70, 129.44, 129.04, 128.78, 128.55, 127.93, 127.80, 125.95, 125.01, 37.22, 32.96. MS (IE): *m/z* 816 (M^+, relative intensity 10%).

5-Bromo-25,26,27,28-tetrahydroxycalix[4]arene (4). A 20 g (25 mmol) amount of **3** and 1000 mL of THF were treated with 100 mL of a 70% NaOH aqueous solution for 48 h at room temperature, during which the mixture turned deep purple. The THF solvent was then evaporated, and the pink solid was redissolved in 700 mL of CH_2Cl_2. The organic phase was then extracted twice with a 1 N NaOH aqueous solution, twice with 1 N HCl aqueous solution, and twice with water. Finally, the organic layer was dried over $MgSO_4$, filtered, and evaporated, resulting in a white product. Yield: 11 g, 90%. Mp: dec >250 °C. Anal. Calcd for $C_{28}H_{23}O_4Br$: C, 66.81; H, 4.61. Found: C, 65.22; H, 4.62. ^{1}H NMR ($CDCl_3$): δ 10.13 (s, 4H, OH), 7.15 (s, 2H, Ph), 7.10−7.03 (m, 6H, Ph), 6.79−6.73 (m, 3H, Ph), 4.25 (br s, 4H, CH_2−Ar), 3.50 (br s, 4H, CH_2−Ar). ^{13}C NMR ($CDCl_3$): δ 148.76, 148.53, 148.03, 131.48, 130.36, 129.28, 129.02, 128.31, 128.02, 127.36, 122.37, 113.84, 31.64, 31.49. MS (IE): *m/z* 502 (M^+, relative intensity 30%).

5-Bromo-25,26,27,28-tetra-*n*-propoxycalix[4]arene (5). A 5.0 g (9.9 mmol) amount of **4** was dissolved in 275 mL of dry DMF under an N_2 atmosphere. Then an excess of NaH (4.77 g, 197 mmol) was slowly added, and gas evolution was noticed. After the mixture was stirred for 1 h, an excess of 1-iodopropane (24 mL, 247 mmol) was added. The solution was stirred for an extra 72 h, and the solvent was subsequently evaporated. The yellow residue was redissolved in 300 mL of CH_2Cl_2, and the organic layer was extracted twice with 300 mL of a 1 N HCl aqueous solution and twice with water. The CH_2Cl_2 solution was then dried over $MgSO_4$ and was filtered and evaporated. The white product was purified by column chromatography (SiO_2) using a CH_2Cl_2/hexanes mixture (20:80) as solvents. Yield: 4.3 g, 65%. Mp: 144−146 °C. Anal. Calcd for $C_{40}H_{47}O_4Br$: C, 71.52; H, 7.05. Found: C, 71.74; H, 7.11. ^{1}H NMR ($CDCl_3$): δ 6.83−6.68 (m, 5H, Ph), 6.60 (t, 2H, $^3J_{H-H} = 7.59$, Ph), 6.49 (s, 2H, Ph), 6.41 (d, 2H, $^3J_{H-H} = 7.47$, Ph), 4.45 (d, 2H, $^2J_{H-H} = 14.80$, CH_2−Ar), 4.40 (d, 2H, $^2J_{H-H} = 13.80$, CH_2−Ar), 3.92−3.83 (m, 4H, CH_2O), 3.81−3.72 (m, 4H, CH_2O), 3.16 (d, 2H, $^2J_{H-H} = 13.66$, CH_2−Ar), 3.09 (d, 2H, $^2J_{H-H} = 13.55$, CH_2−Ar), 1.95−1.84 (m, 8H, CH_2−CH_3), 1.06−

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0.97 (m, 6H, CH_2-CH_3), 0.94 (t, 6H, $^3J_{H-H} = 7.36$, CH_2-CH_3). ^{13}C NMR ($CDCl_3$): δ 157.10, 155.30, 136.88, 137.07, 134.37, 130.77, 130.48, 128.86, 128.41, 128.27, 128.13, 127.84, 122.13, 114.74, 76.79, 76.67, 31.00, 30.88, 23.29, 23.14, 10.54, 10.12. MS (IE): *m/z* 670 (M^+, relative intensity 20%).

5-(Diphenylphosphino)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (6a). A 3.0 g (4.5 mmol) amount of **5** was placed in a flame-dried 100 mL flask. Then 20 mL of dry THF was transferred into the flask under N_2. The reaction mixture was cooled to −78 °C (acetone/dry ice), and 0.29 g (4.5 mmol) of *tert*-butyllithium in solution in hexane was added. After 1 h of reaction, 0.98 mL (5.4 mmol) of $ClPPh_2$ was added to the solution using a syringe and the solution was stirred for 10 h at the same temperature. The solution was then warmed to room temperature and evaporated down until an oily residue appeared. The crude product was then purified by column chromatography (SiO_2) using a CH_2Cl_2/hexane (20:80) mixture as solvents. A white solid was obtained. Yield: 2.0 g, 60%. Mp: 138−140 °C. Anal. Calcd for $C_{52}H_{57}O_4P$: C, 80.38; H, 7.39. Found: C, 80.17; H, 7.64. ^1H NMR ($CDCl_3$): δ 7.31−7.26 (m, 6H, Ph), 7.19−7.13 (m, 4H, Ph), 6.75 (d, 2H, $^3J_{H-H} = 7.26$, Ph), 6.69−6.63 (m, 5H, Ph), 6.58−6.48 (m, 4H, Ph), 4.49 (d, 2H, $^2J_{H-H} = 13.58$, CH_2−Ar), 4.44 (d, 2H, $^2J_{H-H} = 13.67$ CH_2−Ar), 3.91−3.85 (m, 8H, CH_2O), 3.20 (d, 2H, $^2J_{H-H} = 13.20$, CH_2−Ar), 3.08 (d, 2H, $^2J_{H-H} = 13.16$, CH_2−Ar), 2.01−1.91 (m, 8H, CH_2-CH_3), 1.05−0.98 (m, 12H, CH_2-CH_3). ^{13}C NMR ($CDCl_3$): δ 157.20, 156.25, 138.10, 135.16, 134.95, 134.59, 133.74, 133.49, 133.26, 128.49, 128.10, 122.09, 121.98, 76.80, 76.62, 30.87, 30.74, 23.17, 10.27. ^{31}P NMR ($CDCl_3$): δ −3.96. MS (IE): *m/z* 776 (M^+, relative intensity 100%).

5-(Diisopropylphosphino)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (6b). A 0.10 g (0.15 mmol) amount of **5** was placed in a flame-dried 100 mL Schlenk flask. Then 10 mL of dry benzene was transferred into the flask under N_2. The solution was then stirred for a few minutes, and 11.5 mg (0.180 mmol) of *tert*-butyllithium in solution in hexane was added using a syringe. The solution turned orange-brown over a period of 30 min, and then 0.048 mL (0.30 mmol) of $ClP(CH(CH_3)_2)_2$ was added to the solution using a syringe. The solution was stirred for 24 h, and a yellow solution was obtained. Then 40 mL of benzene was added and the entire solution was extracted twice with 50 mL of water inside the glovebox. The organic phase was dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo at room temperature. The oily residue was washed twice with 5 mL of methanol, and a white powder appeared on the wall of the flask. The product was very air-sensitive and oxidized easily. Yield: 0.08 g, 80%. ^1H NMR (C_6D_6): δ 7.20 (d, 2H, $^3J_{H-H} = 6.59$, Ph), 6.86−6.63 (m, 9H, Ph), 4.54 (d, 2H, $^2J_{H-H} = 12.98$, CH_2−Ar), 4.53 (d, 2H, $^2J_{H-H} = 13.02$, CH_2−Ar), 3.88−3.75 (m, 8H, CH_2O), 3.19 (d, 2H, $^2J_{H-H} = 13.16$, CH_2−Ar), 3.15 (d, 2H, $^2J_{H-H} = 13.17$, CH_2−Ar), 2.02−1.85 (m, 10H, CH_2-CH_3 and P−CH−$(CH_3)_2$), 1.19 and 1.09 (d + d, 3H, $^3J_{H-H} = 6.96$ and 6.95, P−CH−CH_3), 1.09 and 1.04 (d + d, 9H, $^3J_{H-H} = 6.98$ and 6.99, P−CH−CH_3), 1.00−0.80 (m, 12H, CH_2-CH_3). ^{13}C NMR (C_6D_6): δ 156.94, 156.73, 156.22, 137.09, 135.68, 135.40, 135.26, 135.11, 134.89, 134.67, 134.46, 130.84, 128.86, 128.33, 127.69, 127.39, 122.42, 122.17, 76.79, 76.58, 31.09, 23.27, 22.92, 20.05, 19.83, 18.87, 18.72, 10.19, 10.08. ^{31}P NMR (C_6D_6): δ 10.04 (s). MS (EI): *m/z* 708 (M^+, relative intensity 15%).

5-(Diphenylphophine oxide)-25,26,27,28-tetrapropoxycalix[4]arene (7). In a 100 mL Schlenk flask, 0.10 g (0.13 mmo1) of **6a** was dissolved in 15 mL of tetrahydrofuran. Then 10 mL of an aqueous solution of hydrogen peroxide (30%) was added. The solution was stirred for 24 h at room temperature. Then, the solvent was evaporated and 50 mL of CH_2Cl_2 was added. The organic solution was extracted twice with 50 mL of water. The organic phase was dried over $MgSO_4$, filtered, and evaporated. The oily residue was then purified by column chromatography (SiO_2) using an acetone/hexane mixture (40:60) as solvent. Compound **7** was obtained in quantitative yield (>95%) as a white-yellow solid. Mp: 117−119 °C. Anal. Calcd for $C_{52}H_{57}O_5P$: C, 78.76; H, 7.24. Found: C, 77.82; H, 7.11. IR (cm^{-1}): ν(P═O), 1194 (s). ^1H NMR ($CDCl_3$): δ 7.50−7.45 (m, 2H, Ph), 7.40−7.32 (m, 8H, Ph), 6.91−6.87 (m, 2H, Ph), 6.80 (d, 2H, $^3J_{H-H} = 12.38$, Ph), 6.68 (d, 2H, $^3J_{H-H} = 7.50$, Ph), 6.62−6.59 (m, 4H, Ph), 6.44 (t, 1H, $^3J_{H-H} = 7.48$, Ph), 4.50 (d, 2H, $^2J_{H-H} = 13.37$, CH_2−Ar), 4.46 (d, 2H, $^2J_{H-H} = 14.65$, CH_2−Ar), 4.00−3.90 (m, 4H, CH_2O), 3.80 (td, 4H, $^3J_{H-H} = 7.21$ and 2.32, CH_2O), 3.22 (d, 2H, $^2J_{H-H} = 13.14$, CH_2−Ar), 3.11 (d, 2H, $^2J_{H-H} = 13.20$, CH_2−Ar), 2.06−1.86 (m, 8H, CH_2-CH_3), 1.09−1.01 (m, 6H, CH_2-CH_3), 0.98 (t, 6H, $^3J_{H-H} = 7.46$, CH_2-CH_3). ^{13}C NMR ($CDCl_3$): δ 159.42, 156.07, 135.77, 135.11, 134.96, 134.82, 134.52, 133.34, 132.76, 132.61, 131.94, 131.19, 128.49, 128.26, 128.00, 127.84, 124.89, 123.50, 122.54, 122.10, 77.18, 76.66, 30.92, 30.79, 23.37, 23.14, 10.48, 10.12. ^{31}P NMR ($CDCl_3$): δ 30.39 (s). MS (IE): *m/z* 792 (M^+, relative intensity 100%).

Dichloro(η^5-pentamethylcyclopentadienyl)(5-(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene)-rhodium(III), $(C_5Me_5)[(C_6H_5)_2P(calix)]RhCl_2$ (8a). In a 100 mL flask, 1.0 g (1.3 mmol) of **6a** was placed under N_2 in the presence of 0.4 g (0.65 mmol) of $[(C_5Me_5)RhCl_2]_2$. Then 25 mL of freshly distilled ethanol was added to the mixture. The solution was refluxed for 5 h and then cooled to room temperature. The solvent was then evaporated, and the crude product was purified by column chromatography using an ethyl acetate/dichloromethane mixture (30:70) as solvent. Red crystals suitable for crystallography were obtained from recrystallization in ethanol. Yield: 1.19 g, 85%. Mp: dec >280 °C. Anal. Calcd for $C_{62}H_{72}O_4PCl_2Rh$: C, 68.57; H, 6.68. Found: C, 68.01; H, 6.78. ^1H NMR ($CDCl_3$): δ 7.58 (br t, 4H, Ph), 7.37−7.00 (m, 8H, Ph), 6.76−6.66 (m, 4H, Ph), 6.55−6.41 (m, 5H, Ph), 4.47 (d, 2H, $^2J_{H-H} = 13.19$, CH_2−Ar), 4.43 (d, 2H, $^2J_{H-H} = 14.42$, CH_2−Ar), 3.91−3.78 (m, 8H, CH_2O), 3.19 (d, 2H, $^2J_{H-H} = 13.20$, CH_2−Ar), 3.09 (d, 2H, $^2J_{H-H} = 13.12$, CH_2−Ar), 2.00−1.86 (m, 8H, CH_2CH_3), 1.30 and 1.29 (s + s, 15H, CH_3−Cp), 1.03−0.95 (m, 12H, CH_2-CH_3). ^{13}C NMR (CD_2Cl_2): δ 171.14, 158.87, 156.88, 156.58, 136.01, 134.98, 131.44, 130.10, 128.72, 128.58, 128.41, 127.87, 122.83, 122.24, 99.27, 77.85, 77.48, 77.10, 60.56, 31.21, 24.10, 23.73, 23.50, 10.59, 10.35, 8.74. ^{31}P NMR ($CDCl_3$): δ 29.95 (d, $^1J_{P-Rh} = 137$). MS (FAB^+): *m/z* 1083 (M^+, relative intensity 10%).

Dichloro(η^5-pentamethylcyclopentadienyl)(5-(diisopropylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene)-rhodium(III), $(C_5Me_5)[(CH(CH_3)_2)_2P(calix)]RhCl_2$ (8b). In a 100 mL flask, 0.1 g (0.15 mmol) of **6b** was placed under N_2 in the presence of 46 mg (0.075 mmol) of $[(C_5Me_5)RhCl_2]_2$. Then 15 mL of benzene and 20 mL of ethanol was added to the mixture. The solution was refluxed for 5 h and then cooled to room temperature. The solvent was then evaporated, and the crude product was purified by column chromatography (SiO_2) using a ethyl acetate/dichloromethane mixture (25:75) as solvent. A red solid was obtained. Yield: 0.13 g, 85%. Mp: dec >280 °C. Anal. Calcd for $C_{56}H_{76}O_4PCl_2Rh$: C, 66.14; H, 7.48. Found: C, 65.07; H, 7.81. ^1H NMR ($CDCl_3$): δ 7.03 (d, 2H, $^3J_{H-H} = 8.55$, Ph), 6.77 (d, 4H, $^3J_{H-H} = 7.47$, Ph), 6.66 (t, 2H, $^3J_{H-H} = 7.43$, Ph), 6.60 (d, 2H, $^3J_{H-H} = 7.44$, Ph), 6.46 (t, 1H, $^3J_{H-H} = 7.44$, Ph), 4.47 (d, 2H, $^2J_{H-H} = 12.91$, CH_2−Ar), 4.45 (d, 2H, $^2J_{H-H} = 12.90$, CH_2−Ar), 4.00−3.85 (m, 4H, CH_2O), 3.80−3.73 (m, 4H, CH_2O), 3.17 (d, 2H, $^2J_{H-H} = 13.00$, CH_2−Ar), 3.16 (d, 2H, $^2J_{H-H} = 12.99$, CH_2−Ar), 3.00−2.92 (m, 2H, P−CH−$(CH_3)_2$), 2.10−1.98 (m, 4H, CH_2CH_3), 1.97−1.83 (m, 4H, CH_2CH_3), 1.39 (d, 3H, $^3J_{H-H} = 7.26$, P−CH−CH_3), 1.34 (d, 3H, $^3J_{H-H} = 7.29$, P−CH−CH_3), 1.22 and 1.21 (s + s, 15H, CH_3−Cp), 1.06−0.96 (m, 12H, CH_2-CH_3), 0.76 (d, 3H, $^3J_{H-H} = 7.23$, P−CH−CH_3), 0,72 (d, 3H, $^3J_{H-H} = 7.22$, P−CH−CH_3), ^{13}C NMR (CD_2Cl_2): δ 157.61, 156.94, 156.14, 136.06, 135.33, 134.67, 134.47, 132.50, 128.94, 128.57, 128.35, 125.49, 124.97, 122.69, 98.48, 77.98, 77.69, 77.03, 31.22, 31.08, 26.82, 26.60, 23.67, 23.51, 21.11, 20.12, 10.79, 10.64, 10.27, 8.73. ^{31}P NMR

($CDCl_3$): δ 34.85 (d, $^1J_{P-Rh} = 137$). MS (FAB^+): *m*/*z* 1016 (M^+, relative intensity 10%).

Dihydrido(η^5-pentamethylcyclopentadienyl)(5-(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene)-rhodium(III), (C_5Me_5)[(C_6H_5)$_2$P(calix)]RhH_2 (9a). The complete procedure was performed in the dark and under N_2. In a 100 mL Schlenk flask, 0.050 g (0.046 mmol) of **8a** was dissolved in 15 mL of freshly distilled ethanol. The solution was refluxed for a few minutes, and then 0.03 g (0.8 mmol) of $NaBH_4$ was quickly added via a 5 mL suspension in dry ethanol. The reaction mixture was then stirred for 1 h, and the volatiles were removed in vacuo at room temperature. Then the crude product was redissolved in a minimum of benzene and this solution filtered and reevaporated, also under vacuum at room temperature. Compound **9a** was obtained in quantitative yield (>98%) as a red solid. Anal. Calcd for $C_{62}H_{74}O_4PRh$: C, 73.25; H, 7.33. Found: C, 73.14; H, 7.47. IR (cm^{-1}): ν(Rh−H), 2080. ^{1}H NMR (C_6D_6): δ 7.71−7.64 (m, 4H, Ph), 7.18−7.10 (m, 8H, Ph), 6.90 (d, 2H, $^3J_{H-H} = 7.46$, Ph), 6.85−6.51 (m, 7H, Ph), 4.55 (d, 2H, $^2J_{H-H} = 13.12$, CH_2−Ar), 4.43 (d, 2H, $^2J_{H-H} = 12.66$, CH_2−Ar), 3.87−3.78 (m, 8H, CH_2O), 3.17 (d, 2H, $^2J_{H-H} = 12.76$, CH_2−Ar), 3.01 (d, 2H, $^2J_{H-H} = 13.05$, CH_2−Ar), 1.95 (s, 15H, CH_3−Cp), 1.95−1.74 (m, 8H, CH_2−CH_3), 0.94−0.86 (m, 12H, CH_2−CH_3), −13.07 (dd, 2H, $^2J_{H-P} = 37.94$ and $^1J_{H-Rh} = 28.70$, Rh−H). ^{31}P NMR (C_6D_6): δ 30.49 (d, $^1J_{P-Rh} = 145$). MS (FAB^+): *m*/*z* 1015 ($M^+ - H_2$, relative intensity 10%, M^+ not observed).

Dihydrido(η^5-pentamethylcyclopentadienyl)(5-(diisopropylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene)-rhodium(III), (C_5Me_5)[($CH(CH_3)_2$)$_2$P(calix)]RhH_2 (9b). The complete procedure was performed in the dark and under N_2. In a 100 mL Schlenk flask, 30 mg (0.030 mmol) of **8b** was dissolved in 15 mL of freshly distilled ethanol. The solution was refluxed for a few minutes, and then 30 mg (0.8 mmol) of $NaBH_4$ was quickly added via a 5 mL suspension in dry ethanol. The reaction mixture was then stirred for 1 h, and the volatiles were removed in vacuo at room temperature. Then the crude product was redissolved in a minimum of benzene and the solution filtered and re-evaporated, also under vacuum at room temperature. Compound **9b** was obtained in quantitative yield (>98%) as a red solid. Anal. Calcd for $C_{56}H_{78}O_4PRh$: C, 70.89; H, 8.28. Found: C, 71.12; H, 8.24. IR (cm^{-1}): ν(Rh−H), 2008. ^{1}H NMR (C_6D_6): δ 7.46 (d, 2H, $^3J_{H-H} = 8.82$, Ph), 6.95 (d, 2H, $^3J_{H-H} = 7.29$, Ph), 6.84 (t, 1H, $^3J_{H-H} = 7.27$, Ph), 6.65 (d, 2H, $^3J_{H-H} = 7.45$, Ph), 6.60−6.51 (m, 4H, Ph), 4.63 (d, 2H, $^2J_{H-H} = 13.13$, CH_2−Ar), 4.53 (d, 2H, $^2J_{H-H} = 13.14$, CH_2−Ar), 4.02−3.92 (m, 4H, CH_2O), 3.71 (t, 4H, $^3J_{H-H} = 7.02$, CH_2O), 3.35 (d, 2H, $^2J_{H-H} = 13.17$, CH_2−Ar), 3.34−3.26 (m, 2H, P−CH−(CH_3)$_2$), 3.15 (d, 2H, $^2J_{H-H} = 13.15$, CH_2−Ar), 2.06−1.79 (m, 8H, CH_2CH_3), 1.09 (d, 3H, $^3J_{H-H} = 6.75$, P−CH−CH_3), 1.04 (d, 3H, $^3J_{H-H} = 6.68$, P−CH−CH_3), 0.95 and 0.93 (s + s, 15H, CH_3−Cp), 0.95−0.80 (m, 18H, CH_2CH_3 and P−CH−(CH_3)$_2$), −14.29 (dd, 2H, $^2J_{H-P} = 38.81$ and $^1J_{H-Rh} = 28.21$, Rh−H). ^{31}P NMR (C_6D_6): δ 83.08 (d, $^1J_{P-Rh} = 152.88$). MS (FAB^+): *m*/*z* 947 ($M^+ - H_2$, relative intensity 1%, M^+ not observed).

(η^5-pentamethylcyclopentadienyl)carbonyl(5-(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene)-rhodium(I), (C_5Me_5)[Ph_2P(calix)]Rh(CO) (10). An 11.4 mg (36.6 mmol) amount of (C_5Me_5)$RhCO_2$ and 30.2 mg (36.6 mmol) of **6a** were dissolved in 10 mL of dry benzene in the dark under an N_2 atmosphere. The solution was then refluxed for 24 h, and the volatiles were removed in vacuo at room temperature. The red solid was purified in the dark from column chromatography using silaned silica gel and a 25:75 THF/hexane mixture. Yield: 0.032 g (80%). Anal. Calcd for $C_{63}H_{72}O_5PRh$: C, 72.50; H, 6.96. Found: C, 72.41; H, 6.89. IR (cm^{-1}): ν(Rh−CO), 1960. ^{1}H NMR (C_6D_6): δ 7.75−7.60 (m, 2H, Ph), 7.25 (d, 2H, $^3J_{H-H} = 10.71$, Ph), 7.20−7.05 (m, 8H, Ph), 6.85−6.70 (m, 5H, Ph), 6.58 (t, 2H, $^3J_{H-H} = 7.57$, Ph), 6.51 (dd, 2H, $^3J_{H-H} = 7.57$ and 1.14, Ph), 4.52 (d, 2H, $^2J_{H-H} = 12.99$, CH_2−Ar), 4.45 (d, 2H, $^2J_{H-H} = 13.1$, CH_2−Ar), 3.95−3.75 (m, 8H, CH_2O), 3.15 (d, 2H, $^2J_{H-H} = 13.20$, CH_2−Ar), 3.06 (d, 2H, $^2J_{H-H} = 13.10$, CH_2−Ar), 1.85 and 1.84 (s + s, 15H, CH_3−Cp), 2.00−1.70 (m, 8H, CH_2−CH_3), 0.95−0.80 (m, 12H, CH_2−CH_3). ^{31}P NMR (C_6D_6): δ 52.81 (d, $^1J_{P-Rh} = 199$). MS (FAB^+): *m*/*z* 1043 (M^+, relative intensity 10%).

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Supporting Information Available: Tables giving detailed crystallographic data, atomic positional parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles, and least-squares planes and deviations and ORTEP figures for compound **8a** and figures giving the structures of **7** and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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