DOI: 10.1002/ejoc.200901201

Regioselective Grafting of Two $-CH_2P(X)Ph_2$ Units (X = O, Lone Pair) onto a Resorcin[4]arene-Derived Cavitand

Hani El Moll,[a] David Sémeril,*[a] Dominique Matt,*[a] and Loïc Toupet[b]

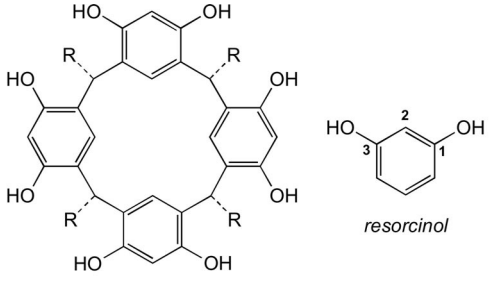
Keywords: Resorcinarene / Cavitands / Phosphanes / Phosphane oxides / Ruthenium

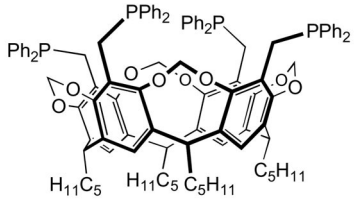
The first diphosphanes based on a resorcinarene-derived cavitand were obtained in six steps starting from 5,11,17,23-tetrabromo-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene. The synthesis of these bulky ligands was based on the selective C-2 functionalisation either of two proximal resorcinolic units or of two distal ones. The ligands, both of which were characterised by X-ray diffraction, readily react with $[RuCl_2(p\text{-cymene})]_2$ to form the corresponding bimetallic complexes $[RuCl_2(p\text{-cymene})]_2$·L in which the cavitand shape remains unchanged with respect to that of the free phosphanes.

Introduction

Cavitands are cavity-shaped receptors characterised by high structural rigidity.[1] Among the most useful precursors of such compounds are the resorcin[4]arenes, a class of tetrameric molecules conveniently obtainable through acid-catalysed condensation between a resorcinol and an aldehyde.[2] The rigidity of resorcinarene-derived cavitands is ensured by the presence of two links between each pair of neighbouring aromatic rings, in comparison with only one in the more flexible parent compounds.[3] The C2-positions in the resorcinol units can be easily modified, a property that makes the corresponding cavitands valuable platforms for the attachment of four ligands closely positioned near to a receptor unit.[3,4] Ligands with cavities, especially phosphanes and phosphane oxides, are currently the subjects of intensive study because of their potential use both in catalysis[5–10] and in separation science.[11–16] Mainly for synthetic reasons, only one phosphane ligand derived from a resorcinarene – the tetraphosphane **1**[4] – has been described in the literature, but a number of other phosphorus-functionalised resorcinarenes have already been reported.[17–22] Diphosphanes based on the same skeleton, which are potential precursors of bimetallic and chelate complexes, and therefore of complexes of catalytic relevance, have not yet been reported.

As an extension of our previous work on resorcinarene-based ligands,[4] we now describe the synthesis of cavitands related to **1**, but bearing only two $-CH_2PPh_2$ podand arms. The study incidentally also allowed the preparation of the corresponding phosphane oxides, as well as that of a cavitand with a single P-substituent. Some complexation properties of the new resorcinarenes are also reported.



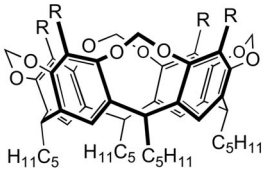


1

Results and Discussion

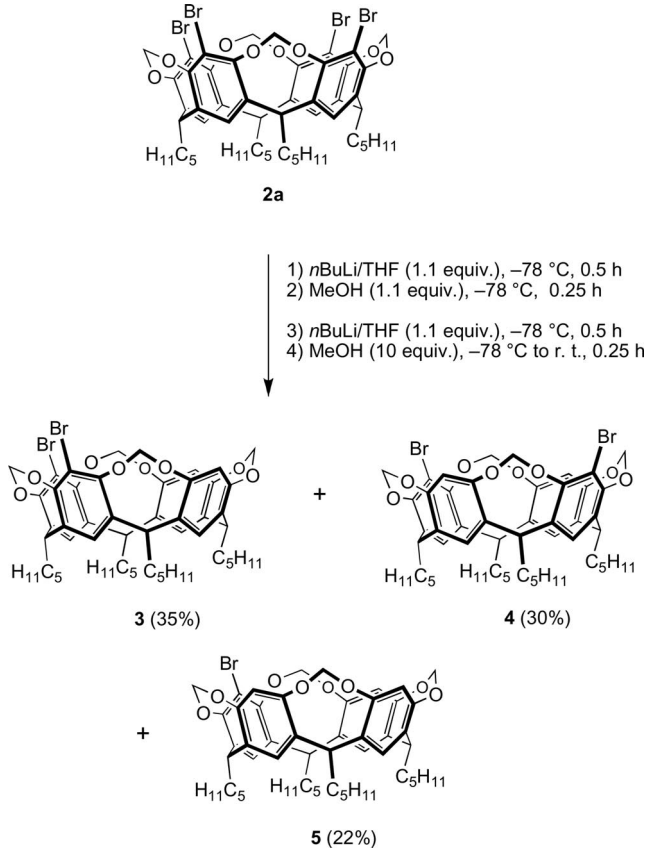
For the preparation of the diphosphanes **10** and **15** (Scheme 2, below, and also of the corresponding phosphane oxides), the partially brominated resorcinarenes **3** and **4** were needed. To gain access to these precursors we gave priority to a synthetic route involving dehalogenation of the tetrabrominated precursor **2a**,[4] rather than attempting a dibromination step starting from the parent cavitand **2b**.

[a] Laboratoire de Chimie Inorganique Moléculaire et Catalyse, Université de Strasbourg, Institut de Chimie, UMR 7177 CNRS,
1 rue Blaise Pascal, 67008 Strasbourg cedex, France
E-mail: dsemeril@chimie.u-strasbg.fr
dmatt@chimie.u-strasbg.fr
[b] Groupe Matière Condensée et Matériaux UMR 6626, Université de Rennes 1,
Campus de Beaulieu, 35042, Rennes cedex, France



2a R = Br
2b R = H

This choice was mainly dictated by the relatively easy synthesis of **2a**, relative to that of its nonbrominated counterpart. The dibromo cavitands **3** and **4** (Scheme 1), already described by Sherburn et al.,[23,24] were obtained by the following simplified one-pot procedure: **2a** was first treated with *n*BuLi (1.1 equiv.), after which the resulting solution was quenched with methanol (1.1 equiv.). The same sequence was repeated after 15 min, leading to a mixture of **3** and **4**. The monobrominated compound **5** was also produced during this synthesis. Rigorous separation of **3** and **4**, which have quite similar polarities, required two successive chromatography steps (see Exp. Sect.). The three compounds were eventually obtained in 35% (**3**), 30% (**4**) and 22% (**5**) yields. It should also be mentioned here that lithiation of **2a** with two equivalents of *n*BuLi gave only poor amounts of **3**, with the reaction mainly leading to **4**.



Scheme 1. Synthesis of the brominated cavitands **3**–**5**.

The syntheses of the two target molecules **10** and **15** (Scheme 2) were basically identical (see Exp. Sect.), so only that of **10** is detailed here. In the first step, compound **3** was subjected to bromine/lithium exchange (*t*BuLi), after which ethyl chloroformate was added to yield the diester **6**. Reduction of **6** with $LiAlH_4$ gave the diol **7**, which was subsequently treated with PBr_3 to afford **8**. Solvent-free Arbuzov phosphorylation of **8** with Ph_2POEt then gave the bis(phosphane oxide) **9**. The last step was the reduction of **9** with $PhSiH_3$, resulting in **10**. The overall yield of this synthesis was 52%. Application of the same sequence of reactions to the dibromo-cavitand **4** gave the diphosphane **15** in 52% yield. Because the monobrominated compound **5** was also to hand, the whole reaction sequence was, logically, also applied to this precursor, resulting in the monophosphane **20** (55% yield). The three new phosphanes were unambiguously characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy and elemental analysis. The ^{31}P NMR spectrum of each compound shows a single phosphorus signal near $\delta = -9$ ppm. In the following discussion, only some spectroscopic features of the diphosphane **10** are discussed. The data for the other compounds, as well as those for the corresponding intermediates, can be found in the Exp. Sect. As a result of the C_s symmetry of the diphosphane **10**, the corresponding ^1H spectrum shows three AB patterns (intensity 1:2:1) for the four OCH_2O groups. It further reveals three methine triplets, as well as an ABX pattern for the signals of the PCH_2 groups (Figure 1). Furthermore, a $^6J(P,H)$ coupling of ca. 2 Hz (see Exp. Sect.) can be seen between the resorcinolic *p*-CH proton and the corresponding P atom. In the ^{13}C NMR spectrum of **10** the three methylenic OCH_2O carbon atoms appear at $\delta = 99.46$, 99.44 and 99.35 ppm. The NMR spectra of the corresponding phosphane oxide **9** are consistent, as in the case of **10**, with a C_s-symmetrical molecule. The P=O signal of **9** appears at $\delta = 28.4$ ppm in its ^{31}P NMR spectrum.

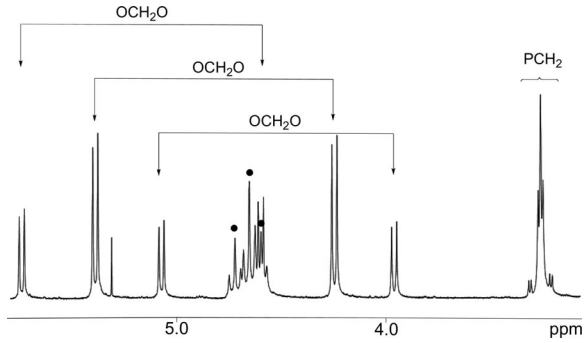
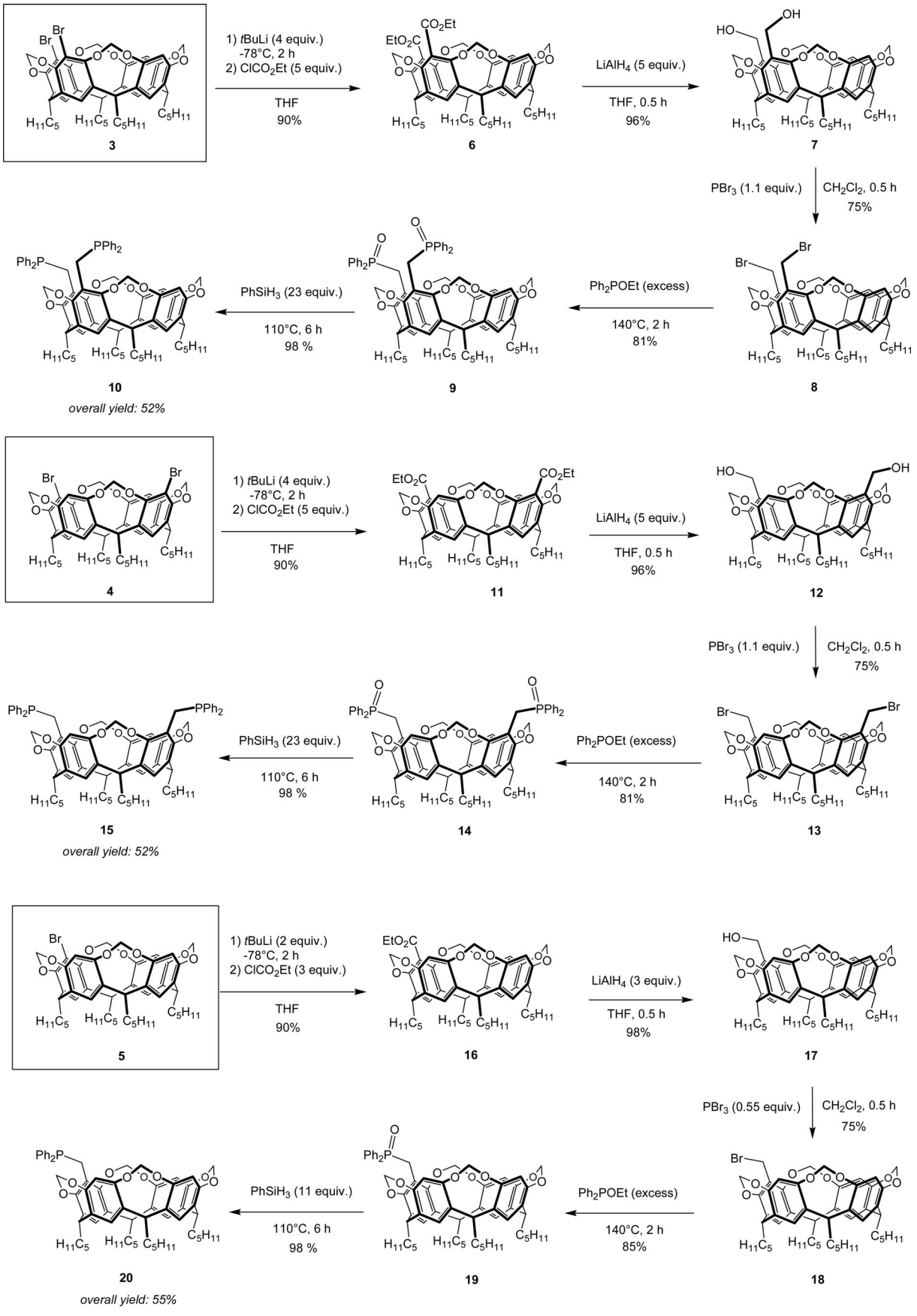


Figure 1. Part of the ^1H NMR ($CDCl_3$) of **10**. The dots represent the centres of the methine triplets.

The solid-state structures of the diphosphanes **10** and **15** were established by single-crystal X-ray diffraction analyses (Figure 2). Whereas the unit cell of **10** contains two insignificantly different molecules, only one type of molecule is present in that of **15**. In each structure the core of the cavitand adopts the usual bowl-shaped structure of a resorcin[4]arene-derived cavitand containing OCHRO linkers.[4,25] The top rim diameters (i.e., the segments linking the C-2 aromatic carbon atoms of opposite resorcinolic rings) are 8.06 and 8.01 Å (aver.) in **10** and 7.95 and 8.14 Å in **15**.



Scheme 2. Stepwise construction of phosphanes **10**, **15** and **20**.

Only one of the phosphorus lone pairs of **10** is directed towards the cavitand axis, the other one being oriented towards the exterior of the cavity. Those of **15** are both turned to the cavity axis. A similar *endo* orientation is observed for the two phosphoryl groups in the bis(phosphane oxide) **14** (Figure 3). In this case the two phosphoryl oxygen atoms are separated by 5.87 Å.

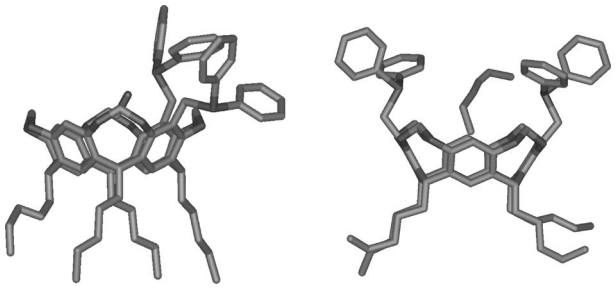


Figure 2. X-ray structures of the diphosphanes **10** (left) and **15** (right), containing a molecule of methanol and hexane, respectively, embedded in the cavity. Top rim diameters: 8.06 (aver.) and 8.01 Å (aver.) in **10**; 7.95 and 8.14 Å in **15**. Only one of the two resorcinarenes present in the unit cell of **10** is shown.

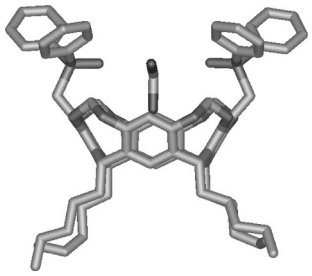
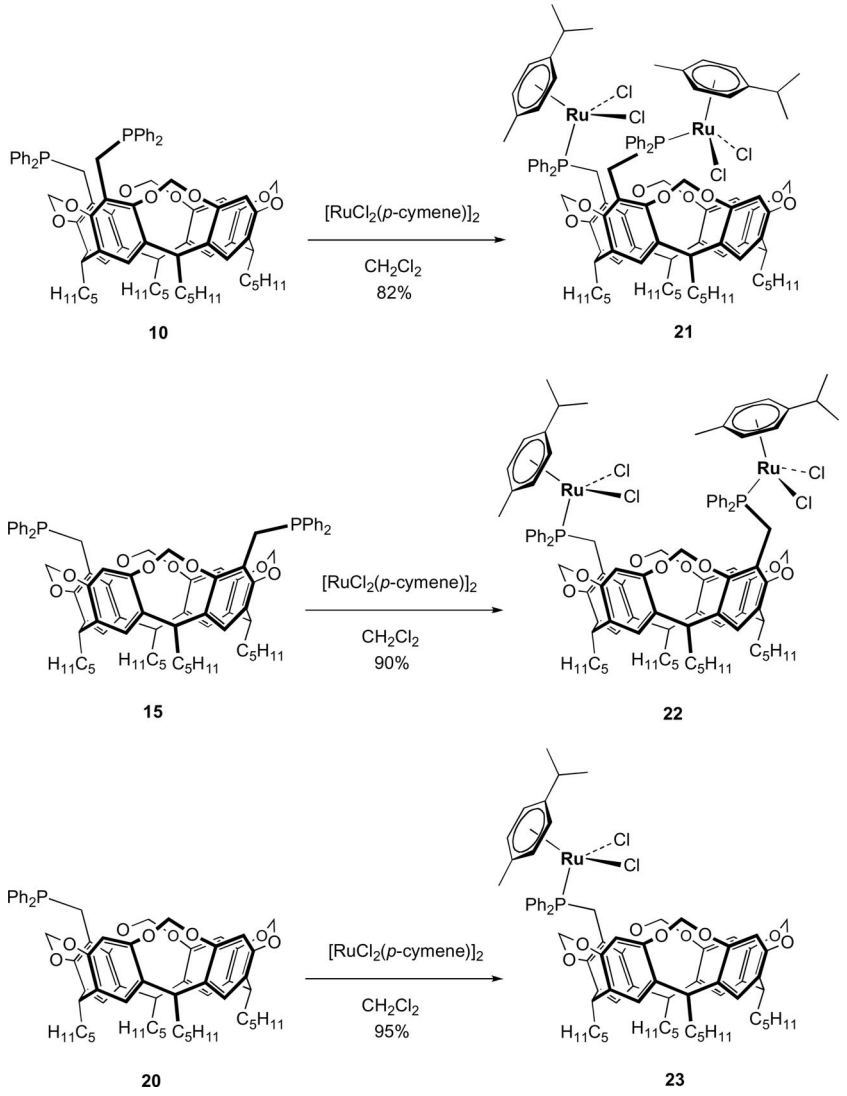


Figure 3. X-ray structure of the bis(phosphane oxide) **14**. A molecule of CH_2Cl_2 sits inside the cavity. Top rim diameters: 8.01 and 8.18 Å.

Treatment of the phosphanes **10**, **15** and **20** with $[RuCl_2(p\text{-cymene})]_2$ gave the ruthenium complexes **21**–**23**, respectively, in quantitative manner (Scheme 3). In each



Scheme 3. Syntheses of complexes **21**–**23**.

case the symmetry of the complex is identical with that of the corresponding free ligand. Interestingly, the ^{1}H NMR spectrum of **21** (with a plane as the sole element of symmetry) shows an ABCD spectrum for the aromatic protons of the *p*-cymene units, whereas that of the C_{2v}-symmetrical **22** shows the conventional AA′BB′ pattern for the corresponding protons.

The solid-state structure of the mononuclear complex **23** was also established by a single-crystal X-ray diffraction study (Figure 4). The complex crystallised with three molecules of MeOH, one of which sits in the cavity. The structural features of the cavity are almost identical with those of the metal-free resorcinarenes described above. The phosphane arm is folded back towards the external cavity wall, with one of the two P-phenyl groups and a resorcinolic ring clearly being engaged in π–π stacking interactions (shortest associated C···C distances: 3.054, 3.32, 3.28, 3.58 Å). As a consequence of this particular P–Ph orientation, the P–Ru vector is pointing towards the exterior of the cavity.

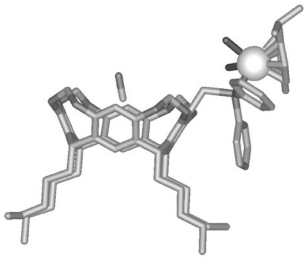


Figure 4. X-ray structure of the monoruthenium complex **23** showing the *exo* orientation of the P–Ru(*p*-cymene) unit. Important bond lengths [Å]: Ru–P 2.3493(6), Ru–Cl(1) 2.4177(6) Ru–Cl(2) 2.4055(6) Å. Top rim diameters: 7.93 and 7.96 Å. The two molecules of methanol lying out of the cavity are not shown.

Conclusions

In summary, we have described the synthesis of the first resorcin[4]arene-derived diphosphanes together with that of the corresponding phosphane oxides. The methodology used is based on the C-2 functionalisation of two distal or two proximal resorcinolic units, starting from a tetrabrominated resorcinarene precursor. Overall, the study gives access to new bulky diphosphanes that have been shown to be suitable for the preparation of bimetallic complexes without alteration of the shape of the generic cavitand core. Further studies will focus on the use of these bulky, cavity-shaped ligands in catalytic reactions.

Experimental Section

General Procedure: All manipulations involving phosphorus derivatives were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} spectra were recorded with Bruker FT instruments (AC 300). ^{1}H spectra were referenced to residual protonated solvents (δ = 7.26 ppm for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuterated solvents (δ = 77.16 ppm for $CDCl_3$), whereas the ^{31}P NMR spectroscopic data are given relative to external H_3PO_4. Chemical shifts and coupling constants are reported in ppm and in Hz, respectively. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Université de Strasbourg. $[RuCl_2(p\text{-cymene})]_2$,[26] $[PdCl(o\text{-}C_6H_4CH_2NMe_2)_2]$[27] and the tetrabrominated cavitand **1**[4] were prepared by literature procedures.

Syntheses of 5,11-Dibromo-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (3) and of 4 and 5: The tetrabromo-resorcinarene **1** (7.000 g, 6.18 mmol) was dissolved in dry THF (100 cm^3). The resulting solution was cooled to –78 °C, after which a solution of *n*BuLi (1.6 M, 4.25 mL, 6.80 mmol) was added. After 0.5 h, methanol (0.25 cm^3, 6.8 mmol) was added, and stirring was continued at the same temperature for 10 min. A second aliquot of *n*BuLi (4.25 cm^3, 6.80 mmol) was added, and the reaction mixture was stirred at –78 °C for 0.5 h. An excess of methanol (3 mL) was then added. The solution was allowed to warm to room temperature. The organic solution was washed with brine (3 × 100 mL) and the aqueous layers were extracted with ethyl acetate (2 × 100 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuum. The crude product was purified by column chromatography (CH_2Cl_2/petroleum ether 50:50, *v*/*v*) to afforded successively 5,11,17-tribromo-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]-arene (0.455 g, 7%; R_f = 0.71, Et_2O/petroleum ether 10:90, *v*/*v*), a mixture of the dibromo-resorcinarenes **3** and **4**, and the monobromo-resorcinarene **5** (1.210 g, 22%; R_f = 0.21, Et_2O/petroleum ether 10:90, *v*/*v*). For the separation of **3** and **4**, a second chromatographic separation was needed (**3**: 2.110 g, 35%; **4**: 1.810, 30%). This was carried out with a Et_2O/petroleum ether mixture (5:95, *v*/*v*): R_f (**3**) = 0.39, Et_2O/petroleum ether 10:90; R_f (**4**) = 0.50, Et_2O/petroleum ether 10:90. The NMR spectroscopic data of these precursor were identical with those reported in the literature.[28]

Diethyl 4(24),6(10),12(16),18(22)-Tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene-5,11-dicarboxylate (6): A solution of *t*BuLi in pentane (1.7 M, 7.24 mL, 12.31 mmol) was slowly added to a cold (–78 °C) solution of **3** (3.000 g, 3.08 mmol) in THF (70 mL). After the system had been stirred for 2 h, ethyl chloroformate was added (1.47 mL, 15.39 mmol). The solution was then allowed to warm to room temperature and stirred for a further 16 h. The solution was washed with brine (100 mL) and the organic phase was separated. This operation was repeated twice. The aqueous layer was treated with ethyl acetate (2 × 100 mL). The combined organic layers were then dried with Na_2SO_4, filtered and concentrated in vacuo. The crude product was recrystallised from EtOAc/EtOH to afford pure **6** (2.66 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.17 (s, 2 H, arom. CH), 7.08 (s, 2 H, arom. CH), 6.53 (s, 2 H, arom. CH), 5.73 and 4.61 (AB spin system, ^2J = 7.1 Hz, 2 H, OCH_2O), 5.68 and 4.49 (AB spin system, ^2J = 7.3 Hz, 4 H, OCH_2O), 5.64 and 4.41 (AB spin system, ^2J = 7.3 Hz, 2 H, OCH_2O), 4.77–4.70 (m, 4 H, $CHCH_2$), 4.31 (ABX_3 spin system, 4 H, $CO_2CH_2CH_3$), 2.25–2.17 (m, 8 H, $CHCH_2$), 1.45–1.28 (m, 30 H, $CH_2CH_2CH_2CH_3$ and $CO_2CH_2CH_3$), 0.91 (t, ^3J = 7.0 Hz, 12 H, $CH_2CH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.60 (s, CO_2), 155.09, 154.69, 151.28, 150.95, 139.01, 138.53, 138.08, 137.76,123.59 (9 × s, arom. C_{quat}), 121.60, 120.31, 116.94 (3 × arom. CH), 99.79 (s, OCH_2O), 99.53 (s, OCH_2O), 99.23 (s, OCH_2O), 61.76 (s, $CO_2CH_2CH_3$), 36.35 (s, $CHCH_2$), 36.30 (s, $CHCH_2$), 36.28 (s, $CHCH_2$), 32.00 (s, $CH_2CH_2CH_3$), 31.96 (s, $CH_2CH_2CH_3$), 31.92 (s, $CH_2CH_2CH_3$), 29.92 (s, $CHCH_2$), 29.78 (s, $CHCH_2$), 29.73 (s, $CHCH_2$), 27.52 (s, $CHCH_2CH_2$), 22.67 (s,

CH_2CH_3, ×2], 22.64 (s, CH_2CH_3), 14.23 (s, $CO_2CH_2CH_3$), 14.07 (s, CH_2CH_3), 14.06 (s, CH_2CH_3) ppm. IR: $\tilde{\nu}$ = 1732 (C=O) cm^{-1}. $C_{58}H_{72}O_{12}$ (961.18): calcd. C 72.47, H 7.55; found C 72.43, H 7.50.

5,11-Bis(hydroxymethyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (7): A solution of the diester **6** (2.000 g, 2.08 mmol) in THF (70 mL) was slowly added to a suspension of $LiAlH_4$ (0.500 g, 10.40 mmol) in THF (50 mL). The reaction mixture was stirred at room temperature for 0.5 h, after which the reaction was quenched with water (4 mL). The precipitate formed was eliminated by filtration, and the mother liquor was washed with brine before being dried with Na_2SO_4. Evaporation of the solvent gave **7** (1.750 g, 96%); m.p. 183–184 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.12 (s, 2 H, arom. CH), 7.10 (s, 2 H, arom. CH), 6.51 (s, 2 H, arom. CH), 5.91 and 4.34 (AB spin system, ^2J = 7.1 Hz, 2 H, OCH_2O), 5.81 and 4.44 (AB spin system, ^2J = 7.1 Hz, 4 H, OCH_2O), 5.72 and 4.49 (AB spin system, ^2J = 7.2 Hz, 2 H, OCH_2O), 4.79 (t, ^3J = 7.9 Hz, 1 H, C*H*CH_2), 4.75 (t, ^3J = 8.1 Hz, 2 H, C*H*CH_2), 4.72 (t, ^3J = 8.0 Hz, 1 H, C*H*CH_2), 4.57 (br s, 4 H, C*H*$_2$OH), 2.27–2.18 (m, 8 H, CHC*H*$_2$CH$_2$), 1.98 (s, 2 H, OH), 1.43–1.30 (m, 24 H, *CH*$_2$*CH*$_2$*CH*$_2$CH$_3$), 0.92 (t, ^3J = 7.0 Hz, 12 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.84, 154.74, 153.62, 153.52, 138.32, 138.11 [×3], 125.98 (9×s, arom. C_{quat}), 120.44, 120.34, 116.75 (3×s, arom. CH), 99.98 (s, OCH_2O), 99.60 (s, OCH_2O), 99.32 (s, OCH_2O), 55.45 (s, CH_2OH), 36.87 (s, *C*HCH$_2$), 36.61 (s, *C*HCH$_2$), 36.35 (s, *C*HCH$_2$), 32.02 (s, *C*H$_2$CH$_2$CH$_3$), 29.98 (s, CH*C*H$_2$), 29.93 (2×s, CH*C*H$_2$), 27.59 (s, CHCH$_2$*C*H$_2$), 27.57 (s, CHCH$_2$*C*H$_2$), 22.69 (s, *C*H$_2$CH$_3$), 14.10 (s, CH_3) ppm. $C_{54}H_{68}O_{10}$ (877.11): calcd. C 73.94, H 7.81; found C 74.01, H 7.96.

5,11-Bis(bromomethyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (8): PBr_3 (0.18 mL, 1.88 mmol) was added to a solution of the diol **7** (1.500 g, 1.71 mmol) in CH_2Cl_2 (100 mL). The solution was stirred for 0.5 h at room temperature. The reaction mixture was washed with brine (3×100 mL) and then dried with Na_2SO_4, and the solvents were evaporated under vacuum to afford a pale yellow solid. The crude product was purified by column chromatography (CH_2Cl_2/petroleum ether 50:50, *v*/*v*; R_f = 0.68, CH_2Cl_2/petroleum ether 60:40, *v*/*v*); yield 1.290 g, 75%; m.p. 214–215 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.13 (s, 2 H, arom. CH), 7.12 (s, 2 H, arom. CH), 6.53 (s, 2 H, arom. CH), 6.01 and 4.62 (AB spin system, ^2J = 7.4 Hz, 2 H, OCH_2O), 5.81 and 4.63 (AB spin system, ^2J = 7.4 Hz, 4 H, OCH_2O), 5.79 and 4.73 (AB spin system, ^2J = 7.5 Hz, 2 H, OCH_2O), 4.76 (t, ^3J = 8.0 Hz, 1 H, C*H*CH_2), 4.73 (t, ^3J = 8.0 Hz, 3 H, C*H*CH_2), 4.54 (s, 4 H, CH_2Br), 2.27–2.15 (m, 8 H, CHC*H*$_2$CH$_2$), 1.45–1.29 (m, 24 H, *CH*$_2$*CH*$_2$*CH*$_2$CH$_3$), 0.91 (t, ^3J = 7.0 Hz, 12 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.92, 154.59, 153.66, 153.62, 138.53, 138.43, 137.84, 137.73, 124.51 (9×s, arom. C_{quat}), 121.01, 120.29, 117.35 (3×s, arom. CH), 99.23 (s, OCH_2O), 99.03 (s, OCH_2O), 36.83 (s, *C*HCH$_2$), 36.61 (s, *C*HCH$_2$), 36.41 (s, *C*HCH$_2$), 32.04 (s, *C*H$_2$CH$_2$CH$_3$), 32.00 (s, *C*H$_2$CH$_2$CH$_3$), 31.95 (s, *C*H$_2$CH$_2$CH$_3$), 30.00 (2×s, CH*C*H$_2$), 29.97 (s, CH*C*H$_2$), 27.59 (s, CH$_2$CH$_2$*C*H$_2$), 27.57 (s, CH$_2$CH$_2$*C*H$_2$), 23.66 (s, CH_2Br), 22.70 (s, *C*H$_2$CH$_3$), 22.68 (s, *C*H$_2$CH$_3$), 22.67 (s, *C*H$_2$CH$_3$), 14.11 (s, CH_2CH_3), 14.09 (2×s, CH_2CH_3) ppm. $C_{54}H_{66}Br_2O_8 \cdot 1/2\,H_2O$ (1002.90 + 9.01): calcd. C 64.09, H 6.67; found C 64.17, H 6.69.

5,11-Bis[(diphenylphosphoryl)methyl]-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (9): A suspension of **8** (0.960 g, 0.96 mmol) in ethyl diphenylphosphinite (4.8 mL, 22.08 mmol) was stirred for 2 h at 140 °C. After the solution had cooled to room temperature, the product was precipitated with diisopropyl ether (5 mL). Compound **9** was filtered off and washed with MeOH (2×5 mL); yield 0.970 g, 81%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.75–7.67 (m, 8 H, arom. CH of PPh_2), 7.53–7.40 (m, 12 H, arom. CH of PPh_2), 7.04 (s, 2 H, arom. CH of resorcinarene), 6.93 (d, $^6J_{P,H}$ = 1.8 Hz, 2 H, arom. CH of resorcinarene), 6.45 (s, 2 H, arom. CH of resorcinarene), 5.68 and 4.71 (AB spin system, ^2J = 7.2 Hz, 2 H, OCH_2O), 5.23 and 4.36 (AB spin system, ^2J = 7.3 Hz, 4 H, OCH_2O), 4.91 and 4.09 (AB spin system, ^2J = 7.4 Hz, 2 H, OCH_2O), 4.69 (t, ^3J = 7.9 Hz, 1 H, C*H*CH_2), 4.56 (t, ^3J = 8.0 Hz, 2 H, C*H*CH_2), 4.47 (t, ^3J = 8.2 Hz, 1 H, C*H*CH_2), 3.60 (ABX spin system, $^2J_{PA}$ = $^2J_{PB}$ = ^2J = 14.0 Hz, 4 H, CH_2P), 2.22–2.04 (m, 8 H, CHC*H*$_2$CH$_2$), 1.41–1.25 (m, 24 H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.92 (t, ^3J = 6.3 Hz, 12 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.87–132.53 (arom. C_{quat}), 131.79 (d, $^4J_{P,C}$ = 2.5 Hz, arom. CH of PPh_2), 131.75 (d, $^4J_{P,C}$ = 2.5 Hz, arom. CH of PPh_2), 131.07 (d, $^3J_{P,C}$ = 9.3 Hz, arom. CH of PPh_2), 131.04 (d, $^3J_{P,C}$ = 9.3 Hz, arom. CH of PPh_2), 128.38 (d, $^2J_{P,C}$ = 11.8 Hz, arom. CH of PPh_2), 128.36 (d, $^2J_{P,C}$ = 11.8 Hz, arom. CH of PPh_2), 120.17 (s, arom. CH of resorcinarene), 119.14 (d, $^5J_{P,C}$ = 8.7 Hz, arom. CH of resorcinarene), 116.62 (s, arom. CH of resorcinarene), 99.97 (s, OCH_2O), 99.51 (s, OCH_2O), 99.19 (s, OCH_2O), 36.88 (s, *C*HCH$_2$), 36.58 (s, *C*HCH$_2$), 36.33 (s, *C*HCH$_2$), 32.07 (s, *C*H$_2$CH$_2$CH$_3$), 32.03 (s, *C*H$_2$CH$_2$CH$_3$), 32.00 (s, *C*H$_2$CH$_2$CH$_3$), 30.24 (s, CH*C*H$_2$), 30.08 (s, CH*C*H$_2$), 29.89 (s, CH*C*H$_2$), 29.00 (d, $^1J_{P,C}$ = 67.0 Hz, CH_2PO), 27.66 (s, CHCH$_2$*C*H$_2$), 27.60 (s, CHCH$_2$*C*H$_2$), 27.53 (s, CHCH$_2$*C*H$_2$), 22.76 (s, *C*H$_2$CH$_3$), 22.71 (s, *C*H$_2$CH$_3$), 22.66 (s, *C*H$_2$CH$_3$), 14.15 (s, CH$_2$*C*H$_3$), 14.12 (s, CH$_2$*C*H$_3$), 14.09 (s, CH$_2$*C*H$_3$) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 28.4 [s, P(O)Ph$_2$] ppm. $C_{78}H_{86}O_{10}P_2$ (1245.46): calcd. C 75.22, H 6.96; found C 75.10, H 6.77.

5,11-Bis[(diphenylphosphanyl)methyl]-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (10): A suspension of the bis(phosphane oxide) **9** (0.900 g, 0.72 mmol) in $PhSiH_3$ (2.05 mL, 16.6 mmol, 23 equiv.) was stirred for 6 h at 110 °C. The reaction mixture was allowed to cool to room temperature and $PhSiH_3$ in excess was removed in vacuo. The residue was washed with MeOH (3×10 mL) to afford **10** as a white solid (0.860 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.39 (m, 8 H, arom. CH of PPh_2), 7.34–7.30 (m, 12 H, arom. CH of PPh_2), 7.10 (s, 2 H, arom. CH of resorcinarene), 6.95 (d, $^6J_{P,H}$ = 1.6 Hz, 2 H, arom. CH of resorcinarene), 6.45 (s, 2 H, arom. CH of resorcinarene), 5.72 and 4.60 (AB spin system, ^2J = 7.3 Hz, 2 H, OCH_2O), 5.37 and 4.25 (AB spin system, ^2J = 7.1 Hz, 4 H, OCH_2O), 5.06 and 3.97 (AB spin system, ^2J = 7.1 Hz, 2 H, OCH_2O), 4.72 (t, ^3J = 8.1 Hz, 1 H, C*H*CH_2), 4.65 (t, ^3J = 8.2 Hz, 2 H, C*H*CH_2), 4.58 (t, ^3J = 8.3 Hz, 1 H, C*H*CH_2), 3.28 (ABX spin system, $^2J_{PA}$ = $^2J_{PB}$ = 3.5, ^2J = 13.2 Hz, 4 H, CH_2P), 2.25–2.10 (m, 8 H, CHC*H*$_2$CH$_2$), 1.43–1.26 (m, 24 H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.92 (t, ^3J = 6.9 Hz, 6 H, CH_2CH_3), 0.93 (t, ^3J = 6.2 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.77–137.73 (arom. C_{quat}), 132.91 (d, $^2J_{P,C}$ = 19.2 Hz, arom. CH of PPh_2), 128.91 (d, $^4J_{P,C}$ = 4.3 Hz, arom. CH of PPh_2), 128.44 (d, $^3J_{P,C}$ = 6.8 Hz, arom. CH of PPh_2), 125.12 (d, $^1J_{P,C}$ = 9.9 Hz, arom. C_{quat} of PPh_2), 120.48 (s, arom. CH of resorcinarene), 118.15 (d, $^5J_{P,C}$ = 3.1 Hz, arom. CH of resorcinarene), 116.48 (s, arom. CH of resorcinarene), 99.46 (s, OCH_2O), 99.44 (s, OCH_2O), 99.35 (s, OCH_2O), 36.94 (s, *C*HCH$_2$), 36.65 (s, *C*HCH$_2$), 36.35 (s, *C*HCH$_2$), 32.04 (s, *C*H$_2$CH$_2$CH$_3$), 32.02 (2×s, *C*H$_2$CH$_2$CH$_3$), 30.20 (s, CH*C*H$_2$), 30.06 (s, CH*C*H$_2$), 29.88 (s, CH*C*H$_2$), 27.63 (s, CHCH$_2$*C*H$_2$), 27.58 (s, CHCH$_2$*C*H$_2$), 27.56 (s, CHCH$_2$*C*H$_2$), 25.53 (d, $^1J_{P,C}$ = 15.8 Hz, CH_2P), 22.73 (s, *C*H$_2$CH$_3$), 22.70 (s, *C*H$_2$CH$_3$), 22.68 (s, *C*H$_2$CH$_3$), 14.13 (s, CH$_2$*C*H$_3$), 14.11 (s, CH$_2$*C*H$_3$), 14.09

(s, CH_2CH_3) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = –9.1 (s, PPh_2) ppm. $C_{78}H_{86}O_8P_2 \cdot CH_3OH$ (1213.46 + 32.04): calcd. C 76.18, H 7.28; found C 76.02, H 7.10.

Diethyl 4(24),6(10),12(16),18(22)-Tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene-5,17-dicarboxylate (11): A solution of *t*BuLi in pentane (1.7 M, 13.27 mL, 22.56 mmol) was slowly added at –78 °C to a solution of the dibromo-resorcinarene **4** (5.500 g, 5.64 mmol) in THF (150 mL). After 2 h, ethyl chloroformate was added (2.70 mL, 28.20 mmol). The temperature was then allowed to reach room temperature and the reaction mixture was stirred for a further 16 h. The organic solution was washed with brine (3 × 100 mL) and the resulting aqueous layers were extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were then dried with Na_2SO_4, filtered and concentrated in vacuo. The crude product was recrystallised with EtOAc/EtOH to afford pure **11** (4.878 g, 90%); m.p. 161–162 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.15 (s, 2 H, arom. CH), 7.06 (s, 2 H, arom. CH), 6.47 (s, 2 H, arom. CH), 5.67 and 4.50 (AB spin system, ^2J = 7.3 Hz, 8 H, OCH_2O), 4.73 (t, ^3J = 8.0 Hz, 4 H, $CHCH_2$), 4.35 (q, ^3J = 7.1 Hz, 4 H, $CO_2CH_2CH_3$), 2.23–2.16 (m, 8 H, $CHCH_2CH_2$), 1.42–1.31 (m, 30 H, $CH_2CH_2CH_2CH_3$ and $CO_2CH_2CH_3$), 0.91 (t, ^3J = 6.8 Hz, 12 H, $CH_2CH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.92 (s, CO_2), 154.74, 150.93, 138.61, 138.15, 123.95 (5 × s, arom. C_{quat}), 121.32, 120.44, 117.12 (3 × s, arom. CH), 99.32 (s, OCH_2O), 61.81 (s, $CO_2CH_2CH_3$), 36.28 (s, $CHCH_2$), 31.95 (s, $CH_2CH_2CH_3$), 29.71 (s, $CHCH_2$), 27.50 (s, $CHCH_2CH_2$), 22.66 (s, CH_2CH_3), 14.30 (s, $CO_2CH_2CH_3$), 14.06 (s, CH_2CH_3) ppm. IR: $\tilde{\nu}$ = 1728 (C=O) cm^{-1}. $C_{58}H_{72}O_{12}$ (961.18): calcd. C 72.47, H 7.55; found C 72.59, H 7.48.

5,17-Bis(hydroxymethyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (12): A solution of the diester **11** (3.730 g, 3.88 mmol) in THF (70 mL) was added slowly to a suspension of $LiAlH_4$ (0.740 g, 19.40 mmol) in THF (50 mL). The reaction mixture was stirred at room temperature for 0.5 h, followed by dropwise addition of water (2 mL). The precipitate formed was eliminated by filtration, and the mother liquor was washed with brine before being dried with Na_2SO_4. Evaporation of the solvent gave **12** (3.250 g, 96%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.12 (s, 2 H, arom. CH), 7.10 (s, 2 H, arom. CH), 6.46 (s, 2 H, arom. CH), 5.81 and 4.48 (AB spin system, ^2J = 7.1 Hz, 8 H, OCH_2O), 4.76 (t, ^3J = 8.1 Hz, 4 H, $CHCH_2$), 4.64 (s, 4 H, CH_2OH), 2.27–2.18 (m, 8 H, $CHCH_2$), 1.43–1.31 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.91 (t, ^3J = 7.0 Hz, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.68, 153.70, 138.27, 138.20, 126.24 (5 × s, arom. C_{quat}), 120.59, 120.17, 116.91 (3 × s, arom. CH), 99.64 (s, OCH_2O), 55.29 (s, CH_2OH), 36.61 (s, $CHCH_2$), 32.02 (s, $CH_2CH_2CH_3$), 29.92 (s, $CHCH_2$), 27.59 (s, $CHCH_2CH_2$), 22.69 (s, CH_2CH_3), 14.10 (s, CH_2CH_3) ppm; m.p. 177–179 °C. $C_{54}H_{68}O_{10}$ (877.11): calcd. C 73.94, H 7.81; found C 74.10, H 7.93.

5,17-Bis(bromomethyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (13): PBr_3 (0.35 mL, 3.76 mmol) was added to a solution of the diol **12** (3.000 g, 3.42 mmol) in CH_2Cl_2 (100 mL). The solution was stirred for 0.5 h at room temperature. The reaction mixture was washed with brine (3 × 100 mL) and then dried with Na_2SO_4, and the solvents were evaporated under vacuum to afford a yellow solid. The crude product was purified by column chromatography (CH_2Cl_2/petroleum ether 50:50, *v*/*v*; R_f = 0.71, CH_2Cl_2/petroleum ether 60:40, *v*/*v*); yield 2.560 g, 75%; m.p. 211–213 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.12 (s, 2 H, arom. CH), 7.11 (s, 2 H, arom. CH), 6.49 (s, 2 H, arom. CH), 5.89 and 4.63 (AB spin system, ^2J = 7.4 Hz, 8 H, OCH_2O), 4.75 (t, ^3J = 8.2 Hz, 4 H, $CHCH_2CH_2$), 4.56 (s, 4 H, CH_2Br), 2.25–2.17 (m, 8 H, $CHCH_2CH_2$), 1.42–1.31 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.91 (t, ^3J = 7.1 Hz, 12 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.75, 153.87, 138.18, 138.01, 124.46 (5 × s, arom. C_{quat}), 121.30, 12.31, 117.26 (3 × s, arom. CH), 99.30 (s, OCH_2O), 36.66 (s, $CHCH_2$), 32.02 (s, $CH_2CH_2CH_3$), 30.01 (s, $CHCH_2$), 27.58 (s, $CHCH_2CH_2$), 23.32 (s, CH_2Br), 22.70 (s, CH_2CH_3), 14.12 (s, CH_2CH_3) ppm. $C_{54}H_{66}Br_2O_8$ (1002.90): calcd. C 64.67, H 6.63; found C 64.73, H 6.79.

5,17-Bis[(diphenylphosphoryl)methyl]-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (14): A suspension of the dibromo-resorcinarene **13** (2.000 g, 2.0 mmol) in ethyl diphenylphosphinite (10.00 mL, 45.9 mmol) was stirred for 2 h at 140 °C. After cooling to room temperature, the product was precipitated with diisopropyl ether (20 mL). Compound **14** was filtered off and washed with MeOH (2 × 5 mL); yield 2.009 g, 81%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.79–7.73 (m, 8 H, arom. CH of PPh_2), 7.52–7.41 (m, 12 H, arom. CH of PPh_2), 7.03 (s, 2 H, arom. CH of resorcinarene), 6.95 (s, 2 H, arom. CH of resorcinarene), 6.36 (s, 2 H, arom. CH of resorcinarene), 5.26 and 4.41 (AB spin system, ^2J = 7.3 Hz, 8 H, OCH_2O), 4.58 (t, ^3J = 8.0 Hz, 4 H, $CHCH_2CH_2$), 3.73 (d, $^2J_{P,H}$ = 14.0 Hz, 4 H, PCH_2), 2.24–2.03 (m, 8 H, $CHCH_2CH_2$), 1.35–1.26 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.91 (t, ^3J = 6.8 Hz, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.53, 153.66, 153.60, 138.01 (4 × s, arom. C_{quat} of resorcinarene), 137.45 (d, $^2J_{P,C}$ = 2.5 Hz, arom. C_{quat} of resorcinarene), 133.62 (d, $^1J_{P,C}$ = 98.6 Hz, C_{quat} of PPh_2), 131.72 (d, $^4J_{P,C}$ = 2.5 Hz, arom. CH of PPh_2), 130.95 (d, $^3J_{P,C}$ = 8.7 Hz, arom. CH of PPh_2), 128.40 (d, $^2J_{P,C}$ = 11.8 Hz, arom. CH of PPh_2), 120.18 (s, arom. CH of resorcinarene), 118.93 (d, $^5J_{P,C}$ = 2.5 Hz, arom. CH of resorcinarene), 116.67 (s, arom. CH of resorcinarene), 99.51 (s, OCH_2O), 36.60 (s, $CHCH_2$), 32.04 (s, $CH_2CH_2CH_3$), 30.07 (s, $CHCH_2$), 28.90 (d, $^1J_{P,C}$ = 67.2 Hz, PCH_2), 27.61 (s, $CHCH_2CH_2$), 22.72 (s, CH_2CH_3), 14.12 (s, CH_2CH_3) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 28.0 [s, $P(O)Ph_2$] ppm. $C_{78}H_{86}O_{10}P_2$ (1245.46): calcd. C 75.22, H 6.96; found C 75.10, H 6.77.

5,17-Bis[(diphenylphosphanyl)methyl]-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (15): A suspension of the bis(phosphane oxide) **14** (1.000 g, 0.803 mmol) in $PhSiH_3$ (2.28 mL, 18.5 mmol, 23 equiv.) was stirred for 6 h at 110 °C. The reaction mixture was allowed to cool to room temperature and excess $PhSiH_3$ was removed in vacuo. The residue was washed with MeOH (3 × 10 mL) to afford **15** as a white solid (0.955 g, 98%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.46 (m, 8 H, arom. CH of PPh_2), 7.39–7.32 (m, 12 H, arom. CH of PPh_2), 7.09 (s, 2 H, arom. CH of resorcinarene), 6.98 (s, 2 H, arom. CH of resorcinarene), 6.36 (s, 2 H, arom. CH of resorcinarene), 5.31 and 4.26 (AB spin system, ^2J = 7.2 Hz, 8 H, OCH_2O), 4.66 (t, ^3J = 7.9 Hz, 4 H, $CHCH_2CH_2$), 3.44 (d, $^2J_{P,H}$ = 3.4 Hz, 4 H, PCH_2), 2.23–2.15 (m, 8 H, $CHCH_2CH_2$), 1.42–1.29 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.92 (t, ^3J = 6.4 Hz, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.63, 153.49, 153.43 (3 × s, arom. C_{quat} of resorcinarene), 138.19 (s, arom. C_{quat} of resorcinarene), 137.86 (d, $^5J_{P,C}$ = 1.9 Hz, arom. C_{quat} of resorcinarene), 132.95 (d, $^2J_{P,C}$ = 19.2 Hz, arom. CH of PPh_2), 128.96 (s, arom. CH of PPh_2), 128.55 (d, $^3J_{P,C}$ = 6.8 Hz, arom. CH of PPh_2), 125.77 (d, $^1J_{P,C}$ = 11.8 Hz, arom. C_{quat} of PPh_2), 120.53 (s, arom. CH of resorcinarene), 118.12 (d, $^5J_{P,C}$ = 3.1 Hz, arom. CH of resorcinarene), 116.56 (s, arom. CH of resorcinarene), 99.68 (s, OCH_2O), 36.72 (s, $CHCH_2$), 32.07 (s, $CH_2CH_2CH_3$), 30.13 (s, $CHCH_2$), 27.64 (s, $CHCH_2CH_2$), 25.42 (d, $^1J_{P,C}$ = 16.7 Hz, PCH_2), 22.74 (s, CH_2CH_3), 14.15 (s, CH_2CH_3) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$,

25 °C): δ = –9.3 (s, PPh_2) ppm. $C_{78}H_{86}O_8P_2 \cdot CH_3OH$ (1213.46 + 32.04): calcd. C 76.18, H 7.28; found C 76.02, H 7.10.

Ethyl 4(24),6(10),12(16),18(22)-Tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene-5-carboxylate (16): A solution of *t*BuLi in pentane (1.7 M, 2.62 mL, 4.46 mmol) was added at –78 °C to a solution of the monobromo-resorcinarene **5** (2.000 g, 2.23 mmol) in THF (80 mL). After 2 h, ethyl chloroformate was added (0.64 mL, 6.70 mmol). The solution was then allowed to reach room temperature and stirred for a further 16 h. The organic solution was washed with brine (3 × 100 mL) and the aqueous layers were extracted with ethyl acetate (2 × 100 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography (EtOAc/petroleum ether 20:80, *v*/*v*; R_f = 0.39, EtOAc/petroleum ether 15:85, *v*/*v*) to afford pure **16** (1.78 g, 90%); m.p. 166–167 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.18 (s, 1 H, arom. CH), 7.08 (s, 3 H, arom. CH), 6.56 (s, 1 H, arom. CH), 6.46 (s, 2 H, arom. CH), 5.73 and 4.53 (AB spin system, ^2J = 7.1 Hz, 4 H, OCH_2O), 5.68 and 4.39 (AB spin system, ^2J = 7.1 Hz, 4 H, OCH_2O), 4.73 (t, ^3J = 7.7 Hz, 2 H, C*H*CH_2CH_2), 4.72 (t, ^3J = 7.9 Hz, 2 H, C*H*CH_2CH_2), 4.34 (q, ^3J = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 2.26–2.18 (m, 8 H, $CHCH_2CH_2$), 1.40–1.32 (m, 27 H, $CH_2CH_2CH_2CH_3$ and $CO_2CH_2CH_3$), 0.91 (t, ^3J = 6.7 Hz, 12 H, $CH_2CH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.45 (s, CO_2), 155.03, 154.94, 154.49, 150.70, 138.84, 138.69, 138.25, 137.79, 123.81 (9 × s, arom. C_{quat}), 121.60, 120.45, 120.33, 116.94, 116.56 (5 × s, arom. CH), 99.42 (s, OCH_2O), 99.38 (s, OCH_2O), 62.05 (s, $CO_2CH_2CH_3$), 36.34 (s, $CHCH_2$), 36.29 (s, $CHCH_2$), 32.01 (s, $CH_2CH_2CH_3$), 31.97 (s, $CH_2CH_2CH_3$), 29.88 (s, $CHCH_2$), 29.66 (s, $CHCH_2$), 27.55 (s, $CHCH_2CH_2$), 27.52 (s, $CHCH_2CH_2$), 22.68 (s, CH_2CH_3), 14.21 (s, $CO_2CH_2CH_3$), 14.08 (s, CH_2CH_3) ppm. IR: $\tilde{\nu}$ = 1726 (C=O) cm^{-1}. $C_{55}H_{68}O_{10} \cdot$EtOH (889.12 + 46.07): calcd. C 73.20, H 7.98; found C 73.31, H 7.92.

5-(Hydroxymethyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (17): A solution of the monoester **16** (1.350 g, 1.52 mmol) in THF (50 mL) was slowly added to a suspension of $LiAlH_4$ (0.180 g, 4.56 mmol) in THF (50 mL). The reaction mixture was stirred at room temperature for 0.5 h and was then quenched with water (2 mL). The precipitate formed was eliminated by filtration, and the mother liquor was washed with brine before being dried with Na_2SO_4. Evaporation of the solvent gave **17** (1.260 g, 98%); m.p. 218–219 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.14 (s, 1 H, arom. CH), 7.10 (s, 3 H, arom. CH), 6.55 (s, 1 H, arom. CH), 6.46 (s, 2 H, arom. CH), 5.82 and 4.41 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 5.72 and 4.55 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 4.76 (t, ^3J = 7.0 Hz, 2 H, C*H*CH_2), 4.72 (t, ^3J = 7.0 Hz, 2 H, C*H*CH_2), 4.67 (s, 2 H, CH_2OH), 2.26–2.19 (m, 8 H, $CHCH_2CH_2$), 1.44–1.29 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.92 (t, ^3J = 7.1 Hz, 12 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 155.03, 154.79, 154.65, 153.83, 138.41, 138.31, 138.29, 138.17, 125.69 (9 × s, arom. C_{quat}), 120.55 (× 2), 120.39, 116.91, 116.55 (arom. CH), 99.91 (s, OCH_2O), 99.36 (s, OCH_2O), 55.15 (s, CH_2OH), 36.67 (s, $CHCH_2$), 36.37 (s, $CHCH_2$), 32.05 (s, $CH_2CH_2CH_3$), 29.90 (s, $CHCH_2$), 27.62 (s, $CHCH_2CH_2$), 27.60 (s, $CHCH_2CH_2$), 22.71 (s, CH_2CH_3), 14.12 (s, CH_2CH_3) ppm. $C_{53}H_{66}O_9$ (847.08): calcd. C 75.15, H 7.85; found C 75.11, H 7.92.

5-(Bromomethyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (18): PBr_3 (0.07 mL, 0.75 mmol) was added to a solution of **17** (1.150 g, 1.36 mmol) in CH_2Cl_2 (100 mL). The solution was stirred for 0.5 h at room temperature. The reaction mixture was washed with brine (3 × 100 mL) and dried with Na_2SO_4, and the solvents were evaporated under vacuum to afford a yellow solid. The crude product was purified by column chromatography (CH_2Cl_2/petroleum ether 50:50, *v*/*v*; R_f = 0.85, CH_2Cl_2/MeOH, 95:5, *v*/*v*); yield 0.930 g, 75%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.13 (s, 1 H, arom. CH), 7.12 (s, 1 H, arom. CH), 7.11 (s, 2 H, arom. CH), 6.54 (s, 1 H, arom. CH), 6.48 (s, 2 H, arom. CH), 5.87 and 4.52 (AB spin system, ^2J = 7.3 Hz, 4 H, OCH_2O), 5.73 and 4.58 (AB spin system, ^2J = 7.1 Hz, 4 H, OCH_2O), 4.74 (t, ^3J = 8.0 Hz, 2 H, C*H*CH_2CH_2), 4.73 (t, ^3J = 8.0 Hz, 2 H, C*H*CH_2CH_2), 4.57 (s, 2 H, CH_2Br), 2.26–2.17 (m, 8 H, $CHCH_2CH_2$), 1.44–1.32 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.92 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 0.91 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.95, 154.84, 154.65, 153.72, 138.57, 138.39, 138.24, 137.83, 124.32 (9 × s, arom. C_{quat}), 121.36, 120.51, 120.38, 116.94, 116.55 (5 × s, arom. CH), 99.34 (s, OCH_2O), 36.61 (s, $CHCH_2$), 36.38 (s, $CHCH_2$), 32.03 (s, $CH_2CH_2CH_3$), 31.99 (s, $CH_2CH_2CH_3$), 29.95 (s, $CHCH_2$), 29.88 (s, $CHCH_2$), 27.57 (s, $CHCH_2CH_2$), 23.96 (s, CH_2Br), 22.69 (s, CH_2CH_3), 22.68 (s, CH_2CH_3), 14.10 (s, CH_2CH_3), 14.08 (s, CH_2CH_3) ppm. $C_{53}H_{65}BrO_8 \cdot H_2O$ (909.98 + 18.01): calcd. C 68.60, H 7.28; found C 68.62, H 7.20.

5-[(Diphenylphosphoryl)methyl]-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (19): A suspension of resorcinarene **18** (0.700 g, 0.77 mmol) in ethyl diphenylphosphinite (2.0 mL, 9.24 mmol) was stirred for 2 h at 140 °C. The solution was allowed to cool to room temperature, and the product was precipitated with diisopropyl ether (5 mL). Compound **19** was filtered off and washed with MeOH (2 × 5 mL); yield 0.670 g, 85%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.81–7.75 (m, 4 H, arom. CH of PPh_2), 7.56–7.47 (m, 6 H, arom. CH of PPh_2), 7.09 (s, 3 H, arom. CH of resorcinarene), 7.04 (d, $^6J_{P,H}$ = 1.8 Hz, 1 H, arom. CH of resorcinarene), 6.58 (s, 1 H, arom. CH of resorcinarene), 6.40 (s, 2 H, arom. CH of resorcinarene), 5.71 and 4.72 (AB spin system, ^2J = 7.1 Hz, 4 H, OCH_2O), 5.86 and 4.24 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 4.73 (t, ^3J = 8.0 Hz, 2 H, C*H*CH_2CH_2), 4.62 (t, ^3J = 8.0 Hz, 2 H, C*H*CH_2CH_2), 3.86 (d, $^2J_{P,H}$ = 12.5 Hz, 2 H, PCH_2), 2.24–2.16 (m, 8 H, $CHCH_2CH_2$), 1.39–1.32 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.91 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 0.90 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 155.08, 154.72, 154.56, 154.14, 138.32, 138.21, 137.60, 137.49, 137.49 (9 × s, arom. C_{quat}), 134.03 (d, ^1J = 98.3 Hz, arom. C_{quat} of PPh_2), 132.11 (s, arom. CH of PPh_2), 130.85 (d, $^3J_{P,C}$ = 9.3 Hz, arom. CH of PPh_2), 128.80 (d, $^2J_{P,C}$ = 11.8 Hz, arom. CH of PPh_2), 120.29, 120.14 (2 × s, arom. CH of resorcinarene), 118.94 (d, $^5J_{P,C}$ = 8.6 Hz, arom. CH of resorcinarene), 116.84, 116.69 (2 × s, arom. CH of resorcinarene), 100.57 (s, OCH_2O), 99.24 (s, OCH_2O), 36.65 (s, $CHCH_2$), 36.36 (s, $CHCH_2$), 32.04 (s, $CH_2CH_2CH_3$), 32.00 (s, $CH_2CH_2CH_3$), 30.18 (s, $CHCH_2$), 29.96 (s, $CHCH_2$), 27.59 (d, $^1J_{P,C}$ = 65.8 Hz, PCH_2), 27.58 (s, $CHCH_2CH_2$), 22.68 (s, CH_2CH_3), 14.10 (s, CH_2CH_3) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 26.0 [s, $P(O)Ph_2$] ppm. $C_{65}H_{75}O_9P$ (1031.26): calcd. C 75.70, H 7.33; found C 75.82, H 7.49.

5-[(Diphenylphosphanyl)methyl]-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (20): A suspension of the phosphane oxide **19** (0.690 g, 0.67 mmol) in $PhSiH_3$ (1.00 mL, 8.04 mmol, 12 equiv.) was stirred for 6 h at 110 °C. The reaction mixture was allowed to reach room temperature and excess $PhSiH_3$ was removed in vacuo. The residue was washed with MeOH (3 × 10 mL) to afford **20** as a white solid (0.670 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.47 (m, 4 H, arom. CH of PPh_2), 7.36–7.34 (m, 6 H, arom. CH of PPh_2), 7.12 (s, 1 H, arom. CH of resorcinarene), 7.11 (s, 2 H, arom. CH of resorcinarene), 6.99 (d, $^6J_{P,H} \approx 1$ Hz, 1 H, arom. CH of resorcinarene), 6.55 (s, 1

H, arom. CH of resorcinarene), 6.41 (s, 2 H, arom. CH of resorcinarene), 5.73 and 4.57 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 5.25 and 4.15 (AB spin system, ^2J = 7.3 Hz, 4 H, OCH_2O), 4.73 (t, ^3J = 8.1 Hz, 2 H, C*H*CH_2), 4.67 (t, ^3J = 8.1 Hz, 2 H, C*H*CH_2), 3.48 (d, $^2J_{P,H}$ = 4.5 Hz, 2 H, PCH_2), 2.27–2.16 (m, 8 H, CHC*H*$_2$CH$_2$), 1.39–1.32 (m, 24 H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.92 (t, ^3J = 6.8 Hz, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 155.01, 154.69, 154.67, 153.44, 153.39, 138.41, 138.38, 138.20, 137.93 (9 × s, arom. C_{quat} of resorcinarene), 132.88 (d, $^2J_{P,C}$ = 19.2 Hz, arom. CH of PPh_2), 129.12 (s, arom. CH of PPh_2), 128.64 (d, $^3J_{P,C}$ = 6.8 Hz, arom. CH of PPh_2), 126.02 (d, $^1J_{P,C}$ = 11.8 Hz, arom. C_{quat} of PPh_2), 120.51 (s, arom. CH of resorcinarene), 118.27 (d, $^5J_{P,C}$ = 3.1 Hz, arom. CH of resorcinarene), 116.62 (s, arom. CH of resorcinarene), 116.49 (s, arom. CH of resorcinarene), 99.79 (s, OCH_2O), 99.43 (s, OCH_2O), 36.72 (s, *C*HCH$_2$), 36.40 (s, *C*HCH$_2$), 32.06 (s, *C*H$_2$CH$_2$CH$_3$), 30.09 (s, CH*C*H$_2$), 29.91 (s, CH*C*H$_2$), 27.63 (s, CHCH$_2$*C*H$_2$), 27.60 (s, CHCH$_2$*C*H$_2$), 25.05 (d, $^1J_{P,C}$ = 13.6 Hz, P*C*H$_2$), 22.73 (s, *C*H$_2$CH$_3$), 14.13 (s, CH$_2$*C*H$_3$) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = –8.7 (s, PPh_2) ppm. $C_{65}H_{75}O_8P{\cdot}CH_3OH$ (1015.26 + 32.04): calcd. C 75.69, H 7.60; found C 75.84, H 7.76.

***P,P′*-{5,11-Bis[(diphenylphosphanyl)methyl]-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene}-bis[dichloro(*p*-cymene)]ruthenium(II) (21):** A solution of [$RuCl_2$(*p*-cymene)]$_2$ (0.027 g, 0.044 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution (CH_2Cl_2, 10 mL) of **10** (0.053 g, 0.044 mmol). After stirring for 0.5 h, the reaction mixture was concentrated to ca. 2 mL, after which *n*-hexane (50 mL) was added. The red precipitate was separated by filtration and dried under vacuum (0.065 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81–7.14 (20 H, arom. CH of PPh_2), 6.82 (s, 2 H, arom. CH of resorcinarene), 6.52 (s, 2 H, arom. CH of resorcinarene), 6.31 (s, 2 H, arom. CH of resorcinarene), 5.74 and 3.97 (AB spin system, ^2J = 7.1 Hz, 4 H, OCH_2O), 5.61 and 4.29 (AB spin system, ^2J = 7.0 Hz, 2 H, OCH_2O), 5.59 and 3.90 (AB spin system, ^2J = 6.9 Hz, 2 H, OCH_2O), 5.47 (d, ^3J = 5.7 Hz, 2 H, arom. CH of *p*-cymene), 5.33 (d, ^3J = 5.7 Hz, 2 H, arom. CH of *p*-cymene), 5.12 (d, ^3J = 6.0 Hz, 2 H, arom. CH of *p*-cymene), 4.89 (d, ^3J = 6.0 Hz, 2 H, arom. CH of *p*-cymene), 4.56 (t, ^3J = 7.5 Hz, 1 H, C*H*CH_2), 4.13 (t, ^3J = 7.9 Hz, 2 H, C*H*CH_2), 4.00 (t, ^3J = 7.9 Hz, 1 H, C*H*CH_2CH_2), 3.60 and 3.50 (ABX spin system, $^2J_{PA}$ = $^2J_{PB}$ = 12 Hz, 4 H, PCH_2), 2.48 [hept, ^3J = 6.9 Hz, 2 H, C*H*$(CH_3)_2$], 2.16 (s, 6 H, CH_3 of *p*-cymene), 1.92–1.77 (m, 8 H, CHC*H*$_2$), 1.32–1.26 (m, 24 H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.03 [d, ^3J = 7.0 Hz, 6 H, CH(C*H*$_3$)$_2$], 0.97 (t, ^3J = 6.4 Hz, 6 H, CH$_2$C*H*$_3$), 0.89 [d, ^3J = 7.1 Hz, 6 H, CH(C*H*$_3$)$_2$], 0.88 (t, ^3J = 7.1 Hz, 6 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.65–136.99 (arom. C_{quat}), 134.75 (d, $^2J_{P,C}$ = 8.7 Hz, arom. CH of PPh_2), 132.90 (d, $^2J_{P,C}$ = 8.7 Hz, arom. CH of PPh_2), 130.23 (s, arom. CH of PPh_2), 129.81 (s, arom. CH of PPh_2), 127.29 (d, $^3J_{P,C}$ = 9.9 Hz, arom. CH of PPh_2), 126.86 (d, $^3J_{P,C}$ = 9.9 Hz, arom. CH of PPh_2), 122.25 (d, $^1J_{P,C}$ = 11.8 Hz, arom. C_{quat} of PPh_2), 120.21 (s, arom. CH of resorcinarene), 117.77 (d, $^5J_{P,C}$ = 3.1 Hz, arom. CH of resorcinarene), 116.33 (s, arom. CH of resorcinarene), 108.85 [s, *C*CH$(CH_3)_2$ of *p*-cymene], 101.21 (s, OCH_2O), 99.34 (s, OCH_2O), 96.75 (s, OCH_2O), 94.36 (s, *C*CH$_3$ of *p*-cymene), 89.89 (d, $^2J_{P,C}$ = 6.1 Hz, arom. CH of *p*-cymene), 89.00 (d, $^2J_{P,C}$ = 6.1 Hz, arom. CH of *p*-cymene), 85.72 (d, $^2J_{P,C}$ = 6.1 Hz, arom. CH of *p*-cymene), 84.54 (d, $^2J_{P,C}$ = 6.1 Hz, arom. CH of *p*-cymene), 36.24 (s, *C*HCH$_2$), 36.12 (s, *C*HCH$_2$), 32.31 (s, *C*H$_2$CH$_2$CH$_3$), 32.17 (s, *C*H$_2$CH$_2$CH$_3$), 31.92 (s, *C*H$_2$CH$_2$CH$_3$), 30.11 (s, CH*C*H$_2$), 29.96 [s, *C*H$(CH_3)_2$], 29.83 (s, CH*C*H$_2$), 29.69 (s, CH*C*H$_2$), 27.74 (2 × s, CHCH$_2$*C*H$_2$), 27.42 (s, CHCH$_2$*C*H$_2$), 22.98 (s, *C*H$_2$CH$_3$), 22.78 (s, *C*H$_2$CH$_3$), 22.74 (d, $^1J_{P,C}$ = 15.5 Hz, P*C*H$_2$), 22.59 (s, *C*H$_2$CH$_3$), 22.15 [s, CH(*C*H$_3$)$_2$], 22.11 [s, CH(*C*H$_3$)$_2$], 21.44 [s, CH(*C*H$_3$)$_2$], 17.31 (s, *C*H$_3$C$_6$H$_4$ of *p*-cymene), 14.28 (s, CH$_2$*C*H$_3$), 14.19 (s, CH$_2$*C*H$_3$), 14.05 (s, CH$_2$*C*H$_3$) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 28.3 (s, PPh_2) ppm. $C_{98}H_{114}Cl_4O_8P_2Ru_2$ (1825.85): calcd. C 64.46, H 6.29; found C 64.26, H 6.11. MS (ESI-TOF): *m/z*: 1789.56 [M – Cl]$^+$ expected isotopic profile.

***P,P′*-{5,17-Bis[(diphenylphosphanyl)methyl]-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene}-bis[dichloro(*p*-cymene)]ruthenium(II) (22):** A solution of [$RuCl_2$(*p*-cymene)]$_2$ (0.065 g, 0.105 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution (CH_2Cl_2, 10 mL) of **15** (0.128 g, 0.105 mmol). After stirring for 0.5 h, the reaction mixture was concentrated to ca. 2 mL, after which *n*-hexane (40 mL) was added. The red precipitate was separated by filtration and dried under vacuum (0.168 g, 90%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 7.69 (t, ^3J = 8.6 Hz, 8 H, arom. CH of PPh_2), 7.36–7.23 (m, 12 H, arom. CH of PPh_2), 6.76 (s, 2 H, arom. CH of resorcinarene), 6.59 (s, 2 H, arom. CH of resorcinarene), 6.27 (s, 2 H, arom. CH of resorcinarene), 5.66 and 4.02 (AB spin system, ^2J = 7.1 Hz, 8 H, OCH_2O), 5.14 and 5.03 (2 × d, C_6H_4 of *p*-cymene, ^3J = 5.6 Hz, 8 H, AA′BB′ spin system), 4.19 (t, ^3J = 7.9 Hz, 4 H, C*H*CH_2CH_2), 3.57 (d, $^2J_{P,H}$ = 10.5 Hz, 4 H, PCH_2), 2.41 [hept, ^3J = 6.9 Hz, 2 H, C*H*$(CH_3)_2$], 2.22–1.82 (m, 8 H, CHC*H*$_2$CH$_2$), 1.74 (s, 6 H, $ArCH_3$ of *p*-cymene), 1.37–1.27 (m, 16 H, C*H*$_2$C*H*$_2$CH$_2$CH$_3$), 1.17–1.09 (m, 8 H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.94 [d, ^3J = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$], 0.92 (t, ^3J = 6.8 Hz, 12 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.52–136.87 (arom. C_{quat}), 133.86 (d, $^2J_{P,C}$ = 9.3 Hz, arom. CH of PPh_2), 130.18 (s, arom. CH of PPh_2), 127.09 (d, $^3J_{P,C}$ = 9.9 Hz, arom. CH of PPh_2), 122.31 (d, $^1J_{P,C}$ = 12.4 Hz, arom. C_{quat} of PPh_2), 120.27 (s, arom. CH of resorcinarene), 117.77 (d, $^5J_{P,C}$ = 1.6 Hz, arom. CH of resorcinarene), 116.11 (s, arom. CH of resorcinarene), 108.76 [s, *C*CH$(CH_3)_2$ of *p*-cymene], 99.04 (s, OCH_2O), 94.53 (s, *C*CH$_3$ of *p*-cymene), 89.77 (d, $^2J_{P,C}$ = 4.3 Hz, arom. CH of *p*-cymene), 85.12 (d, $^2J_{P,C}$ = 5.6 Hz, arom. CH of *p*-cymene), 36.12 (s, *C*HCH$_2$), 32.12 (s, *C*H$_2$CH$_2$CH$_3$), 29.93 [s, *C*H$(CH_3)_2$], 29.85 (s, CH*C*H$_2$), 27.69 (s, CHCH$_2$*C*H$_2$), 22.81 (s, *C*H$_2$CH$_3$), 22.47 (d, $^1J_{P,C}$ = 24.2 Hz, PCH_2), 21.77 [s, CH(*C*H$_3$)$_2$], 17.28 (s, *C*H$_3$C$_6$H$_4$ of *p*-cymene), 14.19 (s, CH$_2$*C*H$_3$) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 28.6 (s, PPh_2) ppm. $C_{98}H_{114}Cl_4O_8P_2Ru_2$ (1825.85): calcd. C 64.47, H 6.29; found C 64.26, H 6.11.

***P*-{5-[(Diphenylphosphanyl)methyl]-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene}dichloro(*p*-cymene)ruthenium(II) (23):** A solution of [$RuCl_2$(*p*-cymene)]$_2$ (0.030 g, 0.050 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution (CH_2Cl_2, 10 mL) of **15** (0.100 g, 0.098 mmol). After stirring at room temperature for 0.5 h, the reaction mixture was concentrated to ca. 2 mL, after which *n*-hexane (50 mL) was added. The red precipitate was separated by filtration and dried under vacuum (0.124 g, 95%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 7.72 (t, ^3J = 8.6 Hz, 4 H, arom. CH of PPh_2), 7.40–7.23 (m, 6 H, arom. CH of PPh_2), 7.01 (s, 1 H, arom. CH of resorcinarene), 6.94 (s, 2 H, arom. CH of resorcinarene), 6.70 (d, $^6J_{P,H} \approx 1$ Hz, 1 H, arom. CH of resorcinarene), 6.43 (s, 1 H, arom. CH of resorcinarene), 6.38 (s, 2 H, arom. CH of resorcinarene), 5.73 and 4.08 (AB spin system, ^2J = 7.1 Hz, 4 H, OCH_2O), 5.68 and 4.38 (AB spin system, ^2J = 7.1 Hz, 4 H, OCH_2O), 5.18 and 5.06 (AA′BB′ spin system, ^3J = 5.1 Hz, 4 H, C_6H_4 of *p*-cymene), 4.65 (t, ^3J = 8.0 Hz, 2 H, C*H*CH_2CH_2), 4.26 (t, ^3J = 8.0 Hz, 2 H, C*H*CH_2CH_2), 3.62 (d, $^2J_{P,H}$ = 10.7 Hz, 2 H, PCH_2), 2.42 [hept, ^3J = 6.8 Hz, 1 H, C*H*$(CH_3)_2$], 2.18–2.09 (m, 8 H, CHC*H*$_2$CH$_2$), 1.77 (s, 3 H, $ArCH_3$ of *p*-cymene), 1.37–1.19 (m, 24 H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.96 [d, ^3J = 6.8 Hz,

6 H, $CH(CH_3)_2$], 0.88 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 0.87 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.64–132.40 (arom. C_{quat}), 133.90 (d, $^2J_{P,C}$ = 8.7 Hz, arom. CH of PPh_2), 130.33 (d, $^4J_{P,C}$ = 2.5 Hz, arom. CH of PPh_2), 127.16 (d, $^3J_{P,C}$ = 9.3 Hz, arom. CH of PPh_2), 122.33 (d, $^1J_{P,C}$ = 12.4 Hz, arom. C_{quat} of PPh_2), 120.43 (s, arom. CH of resorcinarene), 120.40 (s, arom. CH of resorcinarene), 118.00 (d, $^5J_{P,C}$ = 3.9 Hz, arom. CH of resorcinarene), 116.53 (s, arom. CH of resorcinarene), 116.29 (s, arom. CH of resorcinarene), 108.74 [s, *C*CH(CH_3)$_2$ of *p*-cymene], 99.52 (s, OCH_2O), 99.06 (s, OCH_2O), 94.64 (s, *C*CH_3 of *p*-cymene), 89.79 (d, $^2J_{P,C}$ = 4.3 Hz, arom. CH of *p*-cymene), 85.20 (d, $^2J_{P,C}$ = 6.2 Hz, arom. CH of *p*-cymene), 36.25 (s, *C*HCH_2), 36.22 (s, *C*HCH_2), 32.13 (s, *C*$H_2CH_2CH_3$), 31.98 (s, *C*$H_2CH_2CH_3$), 29.97 [s, *C*H(CH_3)$_2$], 29.90 (s, CH*C*H_2), 29.77 (s, CH*C*H_2), 27.74 (s, $CHCH_2CH_2$), 27.50 (s, $CHCH_2CH_2$), 22.85 (s, *C*H_2CH_3), 22.64 (s, *C*H_2CH_3), 22.34 (d, $^1J_{P,C}$ = 20.3 Hz, PCH_2), 21.77 [s, CH-(CH_3)$_2$], 17.31 (s, *C*$H_3C_6H_4$ of *p*-cymene), 14.20 (s, CH_2CH_3), 14.07 (s, CH_2CH_3) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 28.9 (s, PPh_2) ppm. $C_{75}H_{89}Cl_2O_8PRu$ (1321.45): calcd. C 68.24, H 6.90; found C 68.17, H 6.79. MS (ESI-TOF): *m*/*z*: 1285.42 $[M - Cl]^+$ expected isotopic profiles.

Crystal Structure of [10·CH_3OH]$_2$: Single crystals of **10** suitable for diffraction study were obtained by slow diffusion of methanol into a dichloromethane solution of the ligand. *M*r = 2490.90, monoclinic, space group $P2_1/a$, a = 15.2778(7), b = 25.9010(10), c = 35.0210(10) Å, β = 103.296(3)°, V = 13486.7(9) Å^3, Z = 4, D_x = 1.227 mg m^{-3}, λ(Mo$_{K\alpha}$) = 0.71069 Å, μ = 1.23 cm^{-1}, F(000) = 5328, T = 110(1) K. Data were collected with an Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite-monochromatized Mo-K_α radiation, λ = 0.71069 Å). The structure was solved with SIR-97,[29] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found by a Fourier difference analysis. The whole structure was refined with SHELX-97[30] and full-matrix, least-squares techniques (use of F^2; x, y, z, β_{ij} for P, C and O atoms, x, y, z in riding mode for H atoms); 1621 variables and 8236 observations with $I > 2.0\sigma(I)$; calcd. w = $1/[\sigma^2(F_o^2) + (0.0751P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. $R1$ = 0.068, $wR2$ = 0.117, S_w = 0.730, $\Delta\rho < 0.96$ e Å^{-3}. In the unit cell, two slightly different molecules are present.

Crystal Structure of 15·Hexane: Single crystals of **15** suitable for diffraction study were obtained by slow diffusion of hexane into a dichloromethane solution of the ligand. *M*r = 1294.54, triclinic, space group $P\bar{1}$, a = 14.2130(10), b = 15.6760(10), c = 17.7340(10) Å, α = 93.429(7)°, β = 93.516(7)°, γ = 113.742(7)°, V = 3594.5(4) Å^3, Z = 2, D_x = 1.196 mg m^{-3}, λ(Mo$_{K\alpha}$) = 0.71069 Å, μ = 1.17 cm^{-1}, F(000) = 1386, T = 110(1) K. Data were collected with an Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite-monochromatized Mo-K_α radiation, λ = 0.71069 Å). The structure was solved with SIR-97,[29] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found by a Fourier difference analysis. The whole structure was refined with SHELX-97[30] and full-matrix, least-squares techniques (use of F^2; x, y, z, β_{ij} for P, C and O atoms, x, y, z in riding mode for H atoms); 869 variables and 8858 observations with $I > 2.0\sigma(I)$; calcd. w = $1/[\sigma^2(F_o^2) + (0.0751P)^2]$ where P = $(F_o^2 + 2F_c^2)/3$. $R1$ = 0.074, $wR2$ = 0.252, S_w = 1.186, $\Delta\rho <$ 1.20 e Å^{-3}. The compound crystallises with a strongly disordered molecule of hexane sitting in the cavity.

Crystal Structure of 14·CH_2Cl_2: Single crystals of **14** suitable for diffraction study were obtained by slow diffusion of methanol into a dichloromethane solution of the ligand. *M*r = 1330.33, monoclinic, space group $P2_1/n$, a = 11.8303(6), b = 24.8540(10), c = 24.0280(10) Å, β = 99.445(4)°, V = 6969.2(5) Å^3, Z = 4, D_x = 1.268 mg m^{-3}, λ(Mo$_{K\alpha}$) = 0.71069 Å, μ = 1.99 cm^{-1}, F(000) = 2824, T = 110(1) K. Data were collected with an Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite-monochromatized Mo-K_α radiation, λ = 0.71069 Å). The structure was solved with SIR-97,[29] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found by a Fourier difference analysis. The whole structure was refined with SHELX-97[30] and full-matrix, least-squares techniques (use of F^2; x, y, z, β_{ij} for P, C and O atoms, x, y, z in riding mode for H atoms); 838 variables and 4868 observations with $I > 2.0\sigma(I)$; calcd. w = $1/[\sigma^2(F_o^2) + (0.0751P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. $R1$ = 0.058, $wR2$ = 0.138, S_w = 0.741, $\Delta\rho < 1.73$ e Å^{-3}.

Crystal Structure of 23·3CH_3OH: Single crystals of **23** suitable for diffraction study were obtained by slow diffusion of methanol into a dichloromethane solution of the complex. *M*r = 1417.53, triclinic, space group $P\bar{1}$, a = 14.1603(3), b = 16.7385(3), c = 17.2835(3) Å, α = 98.225(2), β = 99.215(2), γ = 110.885(2)°, V = 3687.98(12) Å^3, Z = 2, D_x = 1.277 mg m^{-3}, λ(Mo$_{K\alpha}$) = 0.71073 Å, μ = 3.65 cm^{-1}, F(000) = 1500, T = 150(2) K. Data were collected with an Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite-monochromatized Mo-K_α radiation, λ = 0.71073 Å). The structure was solved with SIR-97,[29] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found by a Fourier difference analysis. The whole structure was refined with SHELX-97[30] and full-matrix, least-squares techniques (use of F^2; x, y, z, β_{ij} for P, C and O atoms, x, y, z in riding mode for H atoms); 841 variables and 11868 observations with $I > 2.0\sigma(I)$; calcd. w = $1/[\sigma^2(F_o^2) + (0.0677P)^2]$ where P = $(F_o^2 + 2F_c^2)/3$. $R1$ = 0.041, $wR2$ = 0.108, S_w = 0.997, $\Delta\rho < 1.14$ e Å^{-3}. One molecule of MeOH lies near the upper cavity entrance.

CCDC-666659 (for [**10**·CH_3OH]$_2$), -719933 (for **15**·hexane), -720311 (for **14**·CH_2Cl_2) and -725748 (for **23**·3 CH_3OH) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors thank the French Agence Nationale de la Recherche for financial support (ANR project MATCALCAT). Johnson Mathey is gratefully acknowledged for a generous gift of ruthenium salts.

[1] J. R. Moran, S. Karbach, D. J. Cram, *J. Am. Chem. Soc.* **1982**, *104*, 5826–5828.
[2] S. Högberg, *J. Am. Chem. Soc.* **1980**, *102*, 6046–6050.
[3] D. J. Cram, S. Karbach, H.-E. Kim, C. B. Knobler, E. F. Maverick, J. L. Ericson, R. C. Helgeson, *J. Am. Chem. Soc.* **1988**, *110*, 2229–2237.
[4] H. El Moll, D. Sémeril, D. Matt, M.-T. Youinou, L. Toupet, *Org. Biomol. Chem.* **2009**, *7*, 495–501.
[5] M. T. Reetz, S. R. Waldvogel, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 865–867.
[6] M. T. Reetz, *Catal. Today* **1998**, *42*, 399–411.
[7] C. Wieser-Jeunesse, D. Matt, M. R. Yaftian, M. Burgard, J. Harrowfield, *C R. Acad. Sci.,. Sér. IIc: Chim.* **1998**, 479–502.
[8] C. Gibson, J. Rebek Jr., *Org. Lett.* **2002**, *4*, 1887–1890.
[9] C. Jeunesse, D. Armspach, D. Matt, *Chem. Commun.* **2005**, 5603–5614.
[10] D. Sémeril, D. Matt, L. Toupet, *Chem. Eur. J.* **2008**, 7144–7155.
[11] H. Boerrigter, W. Verboom, D. N. Reinhoudt, *J. Org. Chem.* **1997**, *62*, 7148–7155.

[12] H. Boerrigter, T. Tomasberger, W. Verboom, D. N. Reinhoudt, *Eur. J. Org. Chem.* **1999**, 665–674.
[13] M. Burgard, M. R. Yaftian, C. Jeunesse, I. Bagatin, D. Matt, *J. Inclusion Phenom. Macrocyclic Chem.* **2000**, *38*, 413–421.
[14] S. V. Fedorenko, A. R. Mustafina, E. K. Kazakova, S. N. Pod'yachev, N. I. Kharitonova, M. A. Pudovik, A. I. Konovalov, I. G. Tananaev, B. F. Myasoedov, *Russ. Chem. Bull.* **2003**, *52*, 562–566.
[15] E. Malinowska, L. Górski, D. Wojciechowska, M. M. Reinoso-Garcıá, W. Verboom, D. N. Reinhoudt, *New J. Chem.* **2003**, *27*, 1440–1445.
[16] X. Zeng, N. Hucher, O. Reinaud, I. Jabin, *J. Org. Chem.* **2004**, *69*, 6886–6889.
[17] E. Dalcanale, P. Jacopozzi, F. Ugozzoli, G. Mann, *Supramol. Chem.* **1998**, *9*, 305–316.
[18] P. Jacopozzi, E. Dalcanale, S. Spera, L. A. J. Chrisstoffels, D. N. Reinhoudt, T. Lippmann, G. Mann, *J. Chem. Soc. Perkin Trans. 2* **1998**, 671–677.
[19] P. Sakhaii, I. Neda, M. Freytag, H. Thönnessen, P. G. Jones, R. Schmutzler, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1246–1254.
[20] E. E. Nifantyev, V. I. Maslennikova, S. E. Goryukhina, M. Y. Antipin, K. A. Lyssenko, L. K. Vasyanina, *J. Organomet. Chem.* **2001**, *631*, 1–8.
[21] V. I. Maslennikova, O. S. Serkova, M. Gruner, S. Goutal, I. Bauer, W. D. Habicher, K. A. Lyssenko, M. Y. Antipin, E. E. Nifantyev, *Eur. J. Org. Chem.* **2004**, 4884–4893.
[22] R. J. Puddephatt, *Can. J. Chem.* **2006**, *84*, 1504–1514.
[23] E. S. Barrett, J. L. Irwin, P. Turner, M. S. Sherburn, *J. Org. Chem.* **2001**, *66*, 8227–8229.
[24] T. M. Altamore, E. S. Barrett, P. J. Duggan, M. S. Sherburn, M. L. Szydzik, *Org. Lett.* **2002**, *4*, 3489–3491.
[25] R. Pinalli, V. Cristini, V. Sottili, S. Geremia, M. Campagnolo, A. Caneschi, E. Dalcanale, *J. Am. Chem. Soc.* **2004**, *126*, 6516–6517.
[26] M. A. Bennett, T.-N. Huang, T. W. Matheson, A. K. Smith, in: *Inorg. Synthesis* (Ed.: J. P. Fackler Jr), John Wiley & Sons, New York, **1982**, vol. 21, p. 75.
[27] A. C. Cope, E. C. Friedrich, *J. Am. Chem. Soc.* **1968**, *90*, 909–913.
[28] J. L. Irwin, M. S. Sherburn, *J. Org. Chem.* **2000**, *65*, 602–605.
[29] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1998**, *31*, 74–77.
[30] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

Received: October 21, 2009
Published Online: January 13, 2010

