Synthesis of a resorcinarene-based tetraphosphine-cavitand and its use in Heck reactions†

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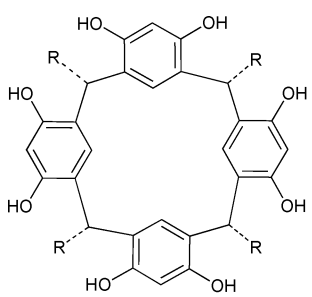
A resorcinarene cavitand substituted by four $–CH_2PPh_2$ pendant arms was synthesised starting from a generic C_5-resorcinarene. Combining this tetraphosphine with palladium acetate and Cs_2CO_3 gave an active Heck catalyst. The highest activities were observed by using a tetraphosphine/Pd ratio of *ca.* 1:1.

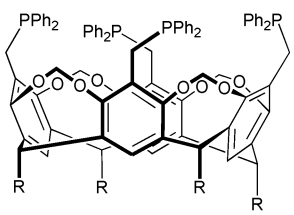
Introduction

Resorcinarene macrocycles constitute useful starting compounds for the preparation of rigid cavities that possess a bowl-shaped core.[1–4] Cavities of the latter type have led to a wide range of applications which include their utilisation as receptors and sensors for large substrates, as building blocks for the synthesis of carcerands, carceplexes and capsules, and also as simple platforms allowing the arrangement of a set of podand ligands in a circle.[5–11] Although a few phosphorus-containing resorcinarene cavitands have already been studied for their coordination and/or metal extraction properties,[12–16] there is only one catalytic study relying on such a ligand.[17] This is rather surprising considering the rich catalytic chemistry displayed by phosphorus-containing derivatives of a structurally related class of macrocyclic compounds, namely the calix[4]arenes, for which many phosphine and phosphite derivatives are known.[18–24]

In the present study, we describe the synthesis and coordinative properties of the first tetraphosphine built upon a resorcinarene cavitand (**8**). The synthesis of **8** was carried out using the tetrapentyl-substituted resorcinarene **1** (abbreviated C_5-resorcin[4]arene) as the starting compound. Ligand **8** was also assessed in Heck reactions.[25] It is worth mentioning that only three other tetraphosphines constructed on a cavity-shaped platform have been reported to date.[26–28]



1 (R = C_5H_{11})



8 (R = C_5H_{11})

Results and discussion

The full synthetic route to tetraphosphine **8**, which includes the improved syntheses of some intermediates reported earlier, is outlined in Scheme 1. The reaction sequence was begun with the bromination of **1** with N-bromosuccinimide (NBS) in ethyl methyl ketone, leading to the tetrabromo-octol **2** in 85%. The latter was then rigidified by introducing four $–CH_2–$ hinges, each linking a pair of oxygen atoms belonging to two neighbouring resorcinol units. Thus, cavitand **3** was obtained through a conventional CH_2BrCl/K_2CO_3 alkylation in DMF (yield 85%).[1] After bromine/lithium exchange with ^{n}BuLi or ^{t}BuLi, followed by reaction with ethyl chloroformate, compound **3** was converted into the tetraester **4** (90%). Reduction of the latter with $LiAlH_4$ gave tetrol **5** (96%), which was then treated with PBr_3 to yield the bromomethyl substituted compound **6** (75%). *Solvent-free* Arbusov phosphorylation with ethyl diphenylphosphinite afforded the tetra-(phosphine oxide) **7** in high yield. Note that this compound has been synthesised previously, but starting from a tetramethylated cavitand.[12] Compound **7** was then quantitatively reduced in $PhSiH_3$ (functioning as solvent and reducing agent) at 110 °C within 6 hours to the cavitand **8**. The ^{31}P NMR spectrum of **8** exhibits a single phosphorus signal at $\delta = -9.63$ ppm, a chemical shift which is in keeping with that of simple triaryl phosphines (cf. –4.5 ppm for PPh_3). The ^{1}H and ^{13}C spectra are both in accord with a C_{4v} symmetrical molecule. Thus, for example, a single AB pattern is seen for the four OCH_2O groups in the ^{1}H NMR spectrum ($\delta_A = 5.16$, $\delta_B = 4.05$; "A" corresponds to the proton turned outwards), while the corresponding methylenic carbon atoms appear at $\delta = 99.28$ in the ^{13}C NMR spectrum.

The formulation of the new tetraphosphine was further confirmed by an X-ray diffraction study (Fig. 1).† The core of the molecule adopts the typical bowl-shaped structure found in other resorcinarene cavitands, with the eight $O–CH_2$ vectors pointing "upwards".[29,30] The top rim diameters, *i.e.* the segments linking the CH_2-substituted carbon atoms of opposite resorcinol-derived rings are both 8.11 Å. Two distal phosphorus atoms lie above the inner part of the cavity and have their lone pairs pointing roughly tangentially to the cone delineated by the cavitand core. The other two phosphorus atoms lie outside this cone. A

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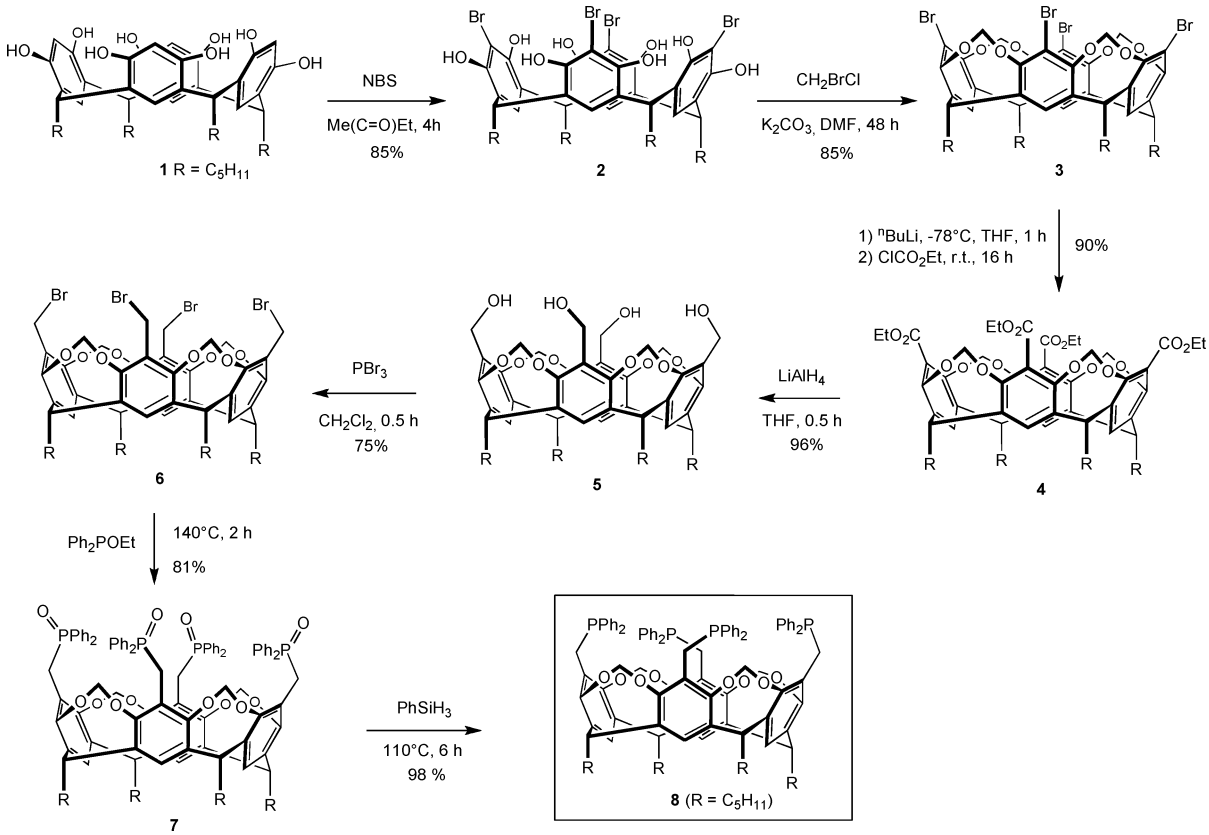
† CCDC reference number 637858. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b813373e



Scheme 1 Synthesis of the tetra-phosphinated cavitand **8**.

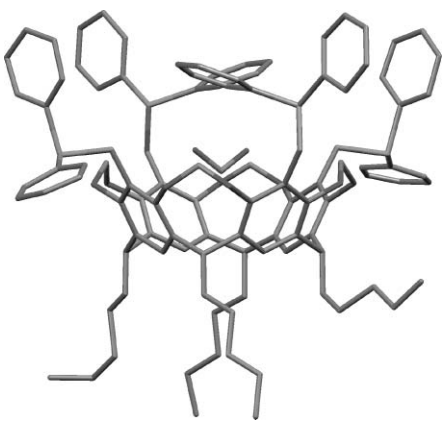
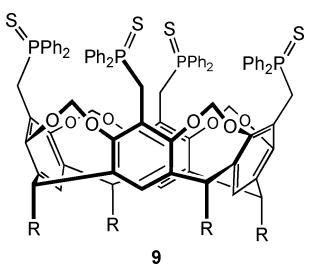


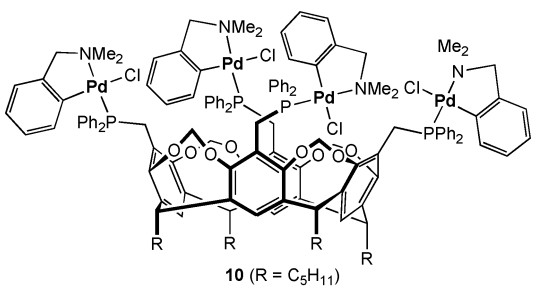
Fig. 1 X-ray structure of the tetra-phosphinated calix[4]resorcinarene **8**. The disordered methanol molecule located on the top of the cavity adopts two orientations, both being shown in the figure.

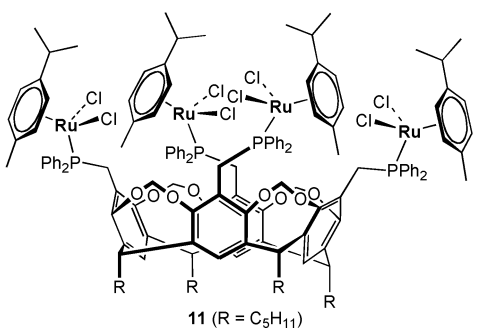


molecule of methanol, disordered over two positions, is hosted in the upper part of the hollow.

Ligand **8** readily oxidises in air, even in the solid state. Its reaction with S_8 in toluene afforded quantitatively the phosphine sulfide **9** within a few seconds.

The tetraphosphinated ligand **8** readily formed transition metal complexes in which four metal centres are connected to the upper rim and are therefore maintained in close proximity. Complexes **10** and **11** were obtained quantitatively upon reaction of **8** with





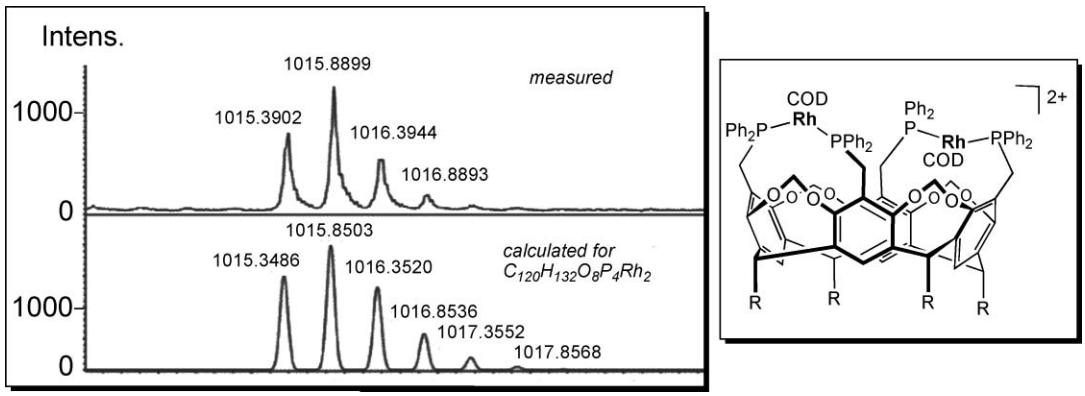
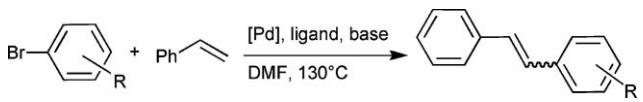


Fig. 2 MS (ESI-TOF) of the bis-chelate complex $\{\mathbf{8}\cdot[Rh(COD)]_2\}^{2+}$.

$[PdCl(o\text{-}C_6H_4CH_2NMe_2)]_2$ and $[RuCl_2(p\text{-cymene})]_2$, respectively. The NMR spectra of both complexes are in keeping with a C_{4v} symmetrical structure, but we noted that some signals of **11** were slightly broadened with respect to those of **10**. This may mean that rotation of the $-CH_2Ph_2PRuCl_2(p\text{-cymene})$ units about the corresponding $C_{Ar}-CH_2$ bonds is somewhat hindered due to the bulk of these groups.

Reaction of **8** with two equivalents of the cationic complex $[Rh(COD)_2]BF_4$ led to a mixture of rhodium complexes which could not be separated. Careful analysis of the mass spectrum of the crude reaction mixture revealed the presence of several dicationic di-rhodium species, consistent with the formation of bis-chelate complexes. In particular, a strong peak was found at $m/z =$ 1015.89 with an isotopic pattern exactly corresponding to the $\{\mathbf{8}\cdot[Rh(COD)]_2\}^{2+}$ dication (Fig. 2). These findings clearly show that the separation between two neighbouring phosphine units of **8** is compatible with the formation of chelate complexes.

The tetraphosphine cavitand **8** was assessed in the Heck reaction of aryl bromides with styrene. A literature search showed that tetraphosphines have been rarely tested in such reactions.[31–33] The reactions were carried out in DMF at 130 °C in the presence of a base (Scheme 2).



Scheme 2 Heck reaction.

We first focussed on coupling reactions with 4-bromoanisole and examined the influence of the palladium source as well as that of the palladium/tetraphosphine ratio on the catalytic outcome. Cs_2CO_3 was used as the base. Conversions were higher with $[Pd(OAc)_2]$ than with $[PdCl(\eta^3\text{-}C_3H_5)]_2$. Three **8**/Pd ratios were tested, namely, 2, 1 and 0.5, but only when a 1:1 ligand/Pd ratio was used were satisfactory results obtained (Table 1), the yields drastically dropping for higher ratios especially. Thus, applying this ratio, conversions of 67 and 100% were observed after 1 h with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and $[Pd(OAc)_2]$ (2 mol%), respectively (Table 1, entries 1–6). Interestingly, we found that the ^{31}P NMR spectrum of a 1:1 mixture of **8** and $[Pd(OAc)_2]$ in CD_2Cl_2 displayed several signals, the most intense appearing at δ 16.6 ppm, which corresponds to coordinated P(III) atoms. A signal at –8.7 ppm, corresponding to non-coordinated P(III) atoms was also seen, as well as a smaller signal in the phosphine oxide region. Addition of a further equiv. of palladium led to the decrease of the signal at 16.6 ppm with the concomitant appearance of a new signal at +6.6 ppm and complete disappearance of that at –8.7 ppm. In view of the catalysis results described above, it is likely that the signal at 16.6 ppm corresponds to the active species, but present evidence does not allow it to be said that it corresponds to a chelating moiety, although this is reasonable. Overall, it appears that the presence of free phosphine units located beside the coordinating P(III) atoms is required to keep the system catalytically active. Possibly, as frequently observed in Heck reactions, an excess of P(III) ligand helps at stabilising transient Pd(0) intermediates.

Table 1 Influence of the Pd/ligand ratio, the Pd precursor and the base[a]

Entry	Pd	Base	**8**/Pd	Conversion (%)[b]
1	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	Cs_2CO_3	2 : 1	traces
2	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	Cs_2CO_3	1 : 1	67
3	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	Cs_2CO_3	1 : 2	51
4	$[Pd(OAc)_2]$	Cs_2CO_3	2 : 1	traces
5	$[Pd(OAc)_2]$	Cs_2CO_3	1 : 1	100
6	$[Pd(OAc)_2]$	Cs_2CO_3	1 : 2	72
7	$[PdCl_2(COD)]$	Cs_2CO_3	1 : 1	traces
8	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	NEt_3	1 : 1	traces
9	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	NaH	1 : 1	traces
10	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	$NaHCO_3$	1 : 1	traces
11	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	Na_2CO_3	1 : 1	7
12	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	K_2CO_3	1 : 1	10

[a] [Pd] (20 μmol, 2 mol%), **8**, 4-bromoanisole (0.187 g, 1.0 mmol), styrene (0.208 g, 2.0 mmol), base (2.0 mmol), decane (0.10 cm^3), DMF (3 cm^3), 130 °C, 1 h. [b] Determined by GC, calibration based on decane.

Using, as above, a **8**/Pd ratio of 1 : 1, but with $[PdCl_2(COD)]$ as the source of palladium, produced only traces of coupling product (Table 1, entry 7). Substitution of Cs_2CO_3 by other bases did not increase the activity of the catalytic system $[PdCl(\eta^3\text{-}C_3H_5)]_2$/**8** (Table 1, entries 2, 8–12). Thus, while with Cs_2CO_3, 67% of 4-bromoanisole was consumed after 1 h, the conversion dropped to 10 and 7% in the same reaction period when using K_2CO_3 and Na_2CO_3, respectively. The higher conversions observed with Cs_2CO_3 possibly arise from the greater solubility of the caesium salt in DMF.[34]

We further examined the influence of the substrate on the rate of the Heck reaction. The tests were all performed under optimised conditions, namely with $[Pd(OAc)_2]$ as the palladium source and

Table 2 Influence of the aryl bromide on the Heck reaction using the Pd/**8** catalytic system[a]

Entry	ArBr	Substrate/Pd	Conversion (%)[b]	TOF (mol(ArBr) mol(Pd)$^{-1}$ h^{-1})
1	2-bromotoluene	50	traces	/
2	3-bromotoluene	50	81	40
3	4-bromotoluene	50	10	5
4	2-bromoanisole	50	traces	/
5	4-bromoanisole	50	100	50
6	4-bromoanisole	200	100	200
7	4-bromoanisole	1000	54	540
8	4-bromoanisole	10000	20	2000
9	4-bromoanisole	100000	2	2000

[a] [Pd(OAc)$_2$], **8** (1 equiv./Pd), ArBr (1.00 mmol), styrene (0.208 g, 2.00 mmol), Cs_2CO_3 (0.652 g, 2.00 mmol), decane (0.10 cm^3), DMF (3 cm^3), 130 °C, 1 h. [b] Determined by GC, calibration based on decane.

Cs_2CO_3 as the base, using a **8**/Pd ratio of 1:1 (Table 2). As expected, the steric hindrance of the aryl bromides had an important impact on the reaction rate, reagents bearing a substituent close to the Br atom giving lower conversions. For example, for an aryl bromide having an *ortho* substituent, only traces of stilbene were observed (Table 2, entries 1 and 4). The catalytic system was also sensitive to the electronic influence of the aryl substituents. Thus, with 3-bromotoluene the yield was 81%, while with 4-bromotoluene, the conversion dropped to 10%, and only traces of coupling product were observed when starting from 2-bromotoluene (Table 2, entries 1–3). The highest conversions in this study were found with 4-bromoanisole (Table 2, entry 5). These variations are in line with results reported by other authors.[35] Finally, we observed that reducing the 4-bromoanisole/palladium ratio to 1.10^5 raised the turnover number (TOF) up to 2000 mol(ArBr) mol(Pd)$^{-1}$ h^{-1} (Table 2, entries 6–9).

In summary, we have described the synthesis of the first tetraphosphine built on a resorcinarene cavitand. In the presence of [Pd(OAc)$_2$] and a base, ligand **8** is active in Heck coupling reactions. The catalytic results showed that the rate of the reaction has a maximal value when only one equivalent of cavitand is added to the palladium, any excess of **8** drastically decreasing the yield. This observation together with ^{31}P NMR investigations indicates that the presence of free phosphane units is required for stabilisation and/or generation of the catalytically active species. Further studies with related cavitands bearing only two phosphine substituents are in progress.

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 protiated solvents (7.26 ppm for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuterated solvents (77.16 ppm for $CDCl_3$), and the ^{31}P NMR data are given relative to external H_3PO_4. Chemical shifts and coupling constants are reported in ppm and in Hz, respectively. Mass spectra were recorded on a Bruker MicroTOF spectrometer (ESI) using CH_2Cl_2 as the solvent. Gas chromatographic analyses were performed on a VARIAN 3900 gas chromatograph using a WCOT fused silica column (25 m, 0.32 mm, inside diameter, 0.25 mm film thickness). The resorcinarene **1**,[36] [RuCl$_2$(*p*-cymene)]$_2$,[37] and [PdCl(*o*-C$_6$H$_4$CH$_2$NMe$_2$)]$_2$[38] were prepared according to the literature procedures. The cationic complex [Rh(COD)$_2$]BF$_4$ was obtained by reaction of [RhCl(COD)]$_2$[39] with $AgBF_4$ in CH_2Cl_2–acetone, followed by reaction with 1,5-cyclooctadiene. Synthetic routes to tetra-(phosphine oxide) **7**[2] and tetra-(phosphine sulfide) **9**[12] different from those reported herein have been described by other authors.

5,11,17,23-Tetrabromo-resorcin[4]arene (2)

To a solution of resorcinarene (**1**) (30.000 g, 36.0 mmol) in 2-butanone (180 cm^3) was added N-bromosuccinimide (38.500 g, 216.3 mmol). After stirring for 4 h at room temperature, the white product was filtered off. The residue was then placed in a Soxhlet thimble for removal of succinimide with $CHCl_3$. Compound **2** was obtained as a white solid (33.190 g, 85%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 8.29$ (s, 8H, OH), 7.62 (s, 4H, arom. CH), 4.45 (t, 4H, C*H*CH$_2$, $^3J = 7.8$ Hz), 2.34–2.27 (m, 8H, CHC*H*$_2$), 1.36–1.27 (m, 24H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.87 (t, 12H, CH$_3$, $^3J = 6.9$ Hz). ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 178.32$–99.99 (arom. C$_{quat}$), 123.58 (s, arom. CH), 35.58 (s, *C*HCH$_2$), 33.56 (s, *C*H$_2$CH$_2$CH$_3$), 31.70 (s, CH*C*H$_2$), 27.61 (s, CHCH$_2$*C*H$_2$), 22.51 (s, *C*H$_2$CH$_3$), 13.53 (s, CH$_3$). Found: C 53.10, H 5.61. $C_{48}H_{60}Br_4O_8$ (1084.60) requires C 53.15, H 5.57%.

5,11,17,23-Tetrabromo-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetra-pentyl-resorcin[4]arene (3)

To a stirred solution of 5,11,17,23-tetrabromo-resorcin[4]arene (**2**) (30.000 g, 27.80 mmol) in DMF (500 cm^3) was added K_2CO_3 (50.000 g, 510.0 mmol) and CH_2BrCl (54.150 g, *ca.* 27.0 cm^3, 418.51 mmol). The solution was heated at 65 °C for 24 h. An additional amount of CH_2BrCl (7.500 g, *ca.* 4 cm^3, 58.01 mmol) was then added, and the reaction mixture was stirred at 65 °C for a further 24 h. After cooling to room temperature, the mixture was poured into an aqueous HCl solution (2%, 600 cm^3). The solid, which contained mainly **3**, was filtered off. The aqueous layer was extracted with Et_2O (3 × 500 cm^3) and the combined organic layers were dried over Na_2SO_4. After filtration, the solvent was removed in vacuum. Both fractions of solid **3** were then submitted to column chromatography (CH_2Cl_2/petroleum ether 50:50, *v*/*v*). Yield: 26.500 g, 85%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.03$ (s, 4H, arom. CH), 5.96 and 4.39 (AB spin system, 8H, OCH$_2$O, $^2J = 7.3$ Hz), 4.85 (t, 4H, C*H*CH$_2$, $^3J = 8.1$ Hz), 2.23–2.16 (m, 8H, CHC*H*$_2$CH$_2$), 1.42–1.31 (m, 24H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.91 (t, 12H, CH$_3$, $^3J = 7.0$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 152.05$–119.03 (arom. C$_{quat}$), 113.51 (s, arom. CH), 98.47 (s, OCH$_2$O), 37.68 (s, *C*HCH$_2$), 31.86 (s, *C*H$_2$CH$_2$CH$_3$), 29.82 (s, CH*C*H$_2$), 27.42 (s, CHCH$_2$*C*H$_2$), 22.65 (s, *C*H$_2$CH$_3$), 14.06 (s, CH$_3$). Found: C 55.09, H 5.50. $C_{52}H_{60}Br_4O_8$ (1132.64) requires C 55.14, H 5.34%.

5,11,17,23-Tetra-ethoxycarbonyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetra-pentyl-resorcin[4]arene (4)

The tetrabromo-resorcinarene **3** (1.670 g, 1.47 mmol) was dissolved in dry THF (80 cm^3). The resulting solution was cooled to −78 °C, upon which a 1.5 M solution of ^{t}BuLi in pentane (7.84 cm^3, 11.76 mmol) was slowly added. After 2 h, ethyl chloroformate was added (1.40 cm^3, 14.70 mmol). The solution was then allowed to warm to room temperature and the reaction mixture was stirred for 16 h. The organic solution was washed with brine (3 × 100 cm^3) and the aqueous layers were extracted with CH_2Cl_2 (2 × 100 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and evaporated in vacuum. The crude product was recrystallised with EtOAc/EtOH to afford pure **4** (1.466 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.15 (s, 4H, arom. CH), 5.64 and 4.58 (AB spin system, 8H, OCH_2O, ^2J = 7.5 Hz), 4.75 (t, 4H, C*H*CH_2, ^3J = 8.0 Hz), 4.31 (q, 8H, $CO_2CH_2CH_3$, ^3J = 7.1 Hz), 2.23–2.16 (m, 8H, CHCH_2), 1.40–1.30 (m, 24H, $CH_2CH_2CH_2CH_3$), 1.32 (t, 12H, $CO_2CH_2CH_3$, ^3J = 7.1 Hz), 0.91 (t, 12H, $CH_2CH_2CH_3$, ^3J = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.09 (s, CO_2), 151.39–123.66 (arom. C_{quat}), 121.45 (s, arom. CH), 99.68 (s, OCH_2O), 61.65 (s, $CO_2CH_2CH_3$), 36.29 (s, *C*HCH$_2$), 31.90 (s, *C*H$_2$CH$_2$CH$_3$), 29.80 (s, CH*C*H$_2$), 27.46 (s, CHCH$_2$*C*H$_2$), 22.64 (s, *C*H$_2$CH$_3$), 14.30 (s, $CO_2CH_2CH_3$), 14.05 (s, $CH_2CH_2CH_3$). Found: C 68.78, H 7.60. $C_{64}H_{80}O_{16}$·EtOH (1105.31 + 46.07) requires C 68.85, H 7.53%.

5,11,17,23-Tetra-hydroxymethyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetra-pentylresorcin[4]arene (5)

To a suspension of $LiAlH_4$ (0.620 g, 11.76 mmol) in THF (50 cm^3) was slowly added a solution of tetra-ester **4** (1.800 g, 1.63 mmol) in THF (70 cm^3). The reaction mixture was stirred at r.t. for 0.5 h before dropwise addition of water (4 cm^3). The precipitate formed was eliminated by filtration, and the mother liquor washed with brine before being dried over $MgSO_4$. Evaporation of the solvent gave **5** (1.459 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.12 (s, 4H, arom. CH), 5.90 and 4.41 (AB spin system, 8H, OCH_2O, ^2J = 6.9 Hz), 4.78 (t, 4H, C*H*CH_2, ^3J = 8.0 Hz), 4.55 (s, 8H, CH_2OH), 2.25–2.17 (m, 8H, CHCH_2), 1.42–1.31 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.91 (t, 12H, CH_3, ^3J = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.51–126.27 (arom. C_{quat}), 120.21 (s, arom. CH), 99.74 (s, OCH_2O), 67.97 (s, CH_2OH), 36.83 (s, *C*HCH$_2$), 32.00 (s, *C*H$_2$CH$_2$CH$_3$), 30.02 (s, CH*C*H$_2$), 27.58 (s, CHCH$_2$*C*H$_2$), 22.68 (s, *C*H$_2$CH$_3$), 14.09 (s, CH_3). Found: C 71.82, H 7.80. $C_{56}H_{72}O_{12}$ (937.16) requires C 71.77, H 7.74%.

5,11,17,23-Tetrabromomethyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetra-pentylresorcin[4]arene (6)

To a solution of tetrol **5** (1.900 g, 2.03 mmol) in CH_2Cl_2 (100 cm^3) was added PBr_3 (0.42 cm^3, 4.5 mmol). The solution was stirred for 0.5 h at r.t. The reaction mixture was washed with brine (3 × 100 cm^3), dried over $MgSO_4$ and 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*). Yield: 1.800 g, 75%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.13 (s, 4H, arom. CH), 6.02 and 4.56 (AB spin system, 8H, OCH_2O, ^2J = 7.1 Hz), 4.78 (t, 4H, C*H*CH_2, ^3J = 8.0 Hz), 4.42 (s, 8H, CH_2Br) 2.23–2.16 (m, 8H, CHCH_2), 1.42–1.30 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.91 (t, 12H, CH_3, ^3J = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.56–124.54 (arom. C_{quat}), 120.98 (s, arom. CH), 99.13 (s, OCH_2O), 36.88 (s, *C*HCH$_2$), 31.98 (s, *C*H$_2$CH$_2$CH$_3$), 30.05 (s, CH*C*H$_2$), 27.55 (s, CHCH$_2$*C*H$_2$), 23.01 (s, CH_2Br), 22.67 (s, *C*H$_2$CH$_3$), 14.08 (s, CH_3). Found C 56.44, H 5.85. $C_{56}H_{68}Br_4O_8$ (1188.75) requires C 56.58, H 5.76%.

5,11,17,23-Tetrakis(diphenylphosphinoylmethyl)-4(24),6(10),12(16),18(22)-tetra-methylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (7)

A suspension of **6** (0.120 g, 0.095 mmol) in ethyl diphenylphosphinite (*ca.* 1 cm^3, 3.8 mmol) was stirred for 2 hours at 140 °C. After cooling to room temperature, the product was precipitated with diisopropyl ether (5 cm^3). Compound **7** was filtered off and washed with MeOH (2 × 5 cm^3) **7**. Yield: 0.142 g, 81%. The following NMR data usefully complement the NMR data previously published by Boerrigter *et al.*[2] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.77–7.65 (m, 16H, arom. CH of PPh_2), 7.52–7.36 (m, 24H, arom. CH of PPh_2), 6.81 (d, 4H, arom. CH of resorcinarene, $^6J_{PH}$ = 1.2 Hz), 5.23 and 4.20 (AB spin system, 8H, OCH_2O, ^2J = 7.1 Hz), 4.39 (t, 4H, C*H*CH$_2$CH$_2$, ^3J = 8.0 Hz), 3.47 (d, 8H, CH_2P, $^2J_{PH}$ = 14.7 Hz), 2.00 (q, 8H, CHCH_2CH$_2$, ^3J = 7.8 Hz), 1.34–1.31 (m, 16H, CH_2CH_2CH$_3$), 1.16–1.09 (m, 8H, CHCH$_2$CH_2), 0.93 (t, 12H, CH_3, $^3J_{HH}$ = 6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.26–119.14 (arom. C_{quat}), 118.79 (d, arom. CH of resorcinarene, $^5J_{PC}$ = 2.5 Hz), 98.83 (s, OCH_2O), 36.76 (s, *C*HCH$_2$), 32.06 (s, *C*H$_2$CH$_2$CH$_3$), 30.07 (s, CH*C*H$_2$), 29.47 (d, CH_2P, $^1J_{PC}$ = 67.0 Hz), 27.61 (s, CHCH$_2$*C*H$_2$), 22.76 (s, *C*H$_2$CH$_3$), 14.15 (s, CH$_2$*C*H$_3$). ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 29.2 (s, $P(O)Ph_2$). Found: C 73.89, H 6.93. $C_{104}H_{108}O_{12}P_4$·CH_3OH (1673.86 + 32.04) requires C 73.93, H 6.62%. *m*/*z* (ESI-TOF) 1674.69 $[M + H]^+$ requires 1674.69.

5,11,17,23-Tetrakis(diphenylphosphinylmethyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl-resorcin[4]arene (8)

A suspension of tetraphosphine oxide **7** (0.800 g, 0.478 mmol) in $PhSiH_3$ (2.42 cm^3, 19.6 mmol, 41.5 equiv.) was stirred for 6 h at 110 °C. The reaction mixture was cooled to room temperature and $PhSiH_3$ in excess was removed in vacuum. The residue was first washed with MeOH (3 × 10 cm^3), then recrystallised in CH_2Cl_2/MeOH to afford **8** as a white solid (0.753 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.38 (m, 16H, arom. CH of PPh_2), 7.33–7.28 (m, 24H, arom. CH of PPh_2), 6.92 (d, 4H, arom. CH of resorcinarene, $^6J_{PH}$ ~ 1 Hz), 5.16 and 4.05 (AB spin system, 8H, OCH_2O, ^2J = 7.2 Hz), 4.58 (t, 4H, C*H*CH$_2$CH$_2$, ^3J = 8.1 Hz), 3.19 (d, 8H, CH_2P, $^2J_{PH}$ = 2.7 Hz), 2.17–2.05 (m, 8H, CHCH_2CH$_2$), 1.40–1.22 (m, 24H, CH_2CH_2CH_2CH$_3$), 0.92 (t, 12H, CH_3, ^3J = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.23–128.17 (arom. C_{quat}), 118.13 (s, arom. CH of resorcinarene), 99.28 (s, OCH_2O), 36.92 (s, *C*HCH$_2$), 32.04 (s, *C*H$_2$CH$_2$CH$_3$), 30.22 (s, CH*C*H$_2$), 27.62 (s, CHCH$_2$*C*H$_2$), 25.89 (d CH_2P, $^1J_{PC}$ = 15.5 Hz), 22.73 (s, *C*H$_2$CH$_3$), 14.15 (s, CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = −9.63 (s, PPh_2). Found C 76.67, H 6.92. $C_{104}H_{108}O_8P_4$·CH_3OH (M_r= 1609.86 + 32.04) requires C 76.81, H 6.87%.

5,11,17,23-Tetrakis(diphenylthiophosphinoylmethyl)-4(24),6(10),12(16),18(22)-tetra-methylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (9)

To a stirred solution of **8** (1.20 g, 0.74 mmol) in toluene (30 cm^3) was added S_8 (0.095 g, 0.37 mmol). The solution was heated under reflux for 0.2 h, then evaporated to dryness under *vacuum*. Recrystallisation in CH_2Cl_2/petroleum ether afforded **9** (1.240 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.86$–7.79 (m, 16H, CH of PPh_2), 7.47–7.37 (m, 24H, CH of PPh_2), 6.80 (d, 4H, arom. CH of resorcinarene, $^6J_{PH} \sim 1$ Hz), 5.08 and 4.21 (AB spin system, 8H, OCH_2O, $^2J = 7.1$ Hz), 4.34 (t, 4H, C*H*CH_2CH_2, $^3J = 7.7$ Hz), 3.76 (d, 8H, CH_2P, $^2J_{PH} = 14.3$ Hz), 2.02–1.93 (dt, 8H, CHC*H*$_2$$CH_2$), 1.35–1.32 (m, 16H, C*H*$_2$C*H*$_2$$CH_3$), 1.14–1.09 (m, 8H, $CHCH_2$C*H*$_2$), 0.94 (t, 12H, CH_3, $^3J_{HH} = 6.7$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 153.35–119.66 (arom. C), 119.05 (d, arom. CH of resorcinarene, $^5J_{PC} = 3.7$ Hz), 98.98 (s, OCH_2O), 36.76 (s, *C*HCH_2), 33.86 (d, CH_2P, $^1J_{PC} = 52.4$ Hz), 32.09 (s, *C*$H_2CH_2CH_3$), 30.12 (s, CH*C*H_2CH_2), 27.64 (s, $CHCH_2$*C*H_2), 22.80 (s, CH_2*C*H_2CH_3), 14.19 (s, CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 41.3$ (s, P(S)Ph_2). Found: C 67.97, H 5.88. $C_{104}H_{108}O_8P_4S_4 \cdot 1.5\ CH_2Cl_2$ (1738.12 + 127.40) requires C 67.92, H 6.00%.

***P,P′,P″,P‴′*-{5,11,17,23-Tetrakis(diphenylphosphinylmethyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl-resorcin[4]arene}-tetrakis[chloro(*o*-dimethyl benzyl-aminomethylphenyl-*C*,*N*)]palladium(II) (10)**

To a stirred solution (CH_2Cl_2, 10 cm^3) of **8** (0.123 g, 0.076 mmol) was added a solution of [PdCl(*o*-$C_6H_4CH_2NMe_2$]$_2$ (0.084 g, 0.153 mmol) in CH_2Cl_2 (10 cm^3). After stirring at room temperature for 0.5 h, the reaction mixture was concentrated to *ca.* 2 cm^3, upon which *n*-hexane (50 cm^3) was added. The yellow precipitate was separated by filtration and dried under vacuum (0.155 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.66$–7.59 (m, 16H, arom. CH of PPh_2), 7.32–7.16 (m, 24H, arom. CH of PPh_2), 6.94 (d, 4H, CH ortho to CH_2N, $^3J = 7.4$ Hz), 6.76 (t, 4H, CH para to Pd, $^3J =$ 7.3 Hz), 6.58 (s, 4H, arom. CH of resorcinarene), 6.34 (dt, 4H, CH para to CH_2N, $^3J = 7.7$ Hz, $^5J_{PH} = 6.7$ Hz), 6.18 (dd, 4H, CH ortho to Pd, $^3J = 6.7$ Hz, $^4J = 6.7$ Hz), 6.01 and 3.94 (AB spin system, 8H, OCH_2O, $^2J = 7.3$ Hz), 4.18 (t, 4H, C*H*CH_2CH_2, $^3J =$ 8.0 Hz), 4.07 (s, 8H, NCH_2) 3.89 (d, 8H, CH_2P, $^2J = 12.3$ Hz), 2.88 (s, 24H, N(CH_3)$_2$), 1.91–1.83 (m, 8H, CHC*H*$_2$), 1.34–1.26 (m, 16H, C*H*$_2$C*H*$_2$$CH_3$), 1.14–1.05 (m, 8H, $CHCH_2$C*H*$_2$), 0.91 (t, 12H, CH_2C*H*$_3$, $^3J = 14.07$ Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta =$ 153.32–121.98 (arom. C), 118.08 (s, arom. CH of resorcinarene), 98.54 (s, OCH_2O), 73.18 (s, CH_2N), 50.37 (s, N(CH_3)$_2$), 36.46 (s, *C*HCH_2), 31.97 (s, *C*$H_2CH_2CH_3$), 29.91 (s, CH*C*H_2), 28.15 (d, CH_2P, $^1J_{PC} = 28$ Hz), 27.64 (s, $CHCH_2$*C*H_2), 22.74 (s, *C*H_2CH_3), 14.15 (s, CH_2*C*H_3). ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = 35.3$ (s, PPh_2). Found C 60.86, H 5.88, N 1.91. $C_{140}H_{156}Cl_4N_4O_8P_4Pd_4 \cdot CH_2Cl_2$ (2714.15 + 84.93) requires C 60.50, H 5.69, N 2.00%.

***P,P′,P″,P‴′*-{5,11,17,23-Tetrakis(diphenylphosphinylmethyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl-resorcin[4]arene}-tetrakis[dichloro(*p*-cymene)]ruthenium(II) (11)**

To a stirred solution (CH_2Cl_2, 10 cm^3) of **8** (0.125 g, 0.078 mmol) was added a solution of [$RuCl_2$(*p*-cymene)]$_2$ (0.095 g, 0.155 mmol) in CH_2Cl_2 (10 cm^3). After stirring at room temperature for 0.5 h, the reaction mixture was concentrated to *ca.* 2 cm^3, upon which *n*-hexane (50 cm^3) was added. The red precipitate was separated by filtration and dried under vacuum (0.172 g, 78%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): $\delta = 7.98$–7.12 (m, 40H, arom. CH of PPh_2), 6.33 (s br, 4H, arom. CH of resorcinarene), 5.60 and 3.62 (AB spin system br, 8H, OCH_2O), 5.21 (d of AA′BB′, 8H, *p*-cymene), 5.07 (d of AA′BB′, 8H, *p*-cymene), 3.76 (t, 4H, C*H*CH_2CH_2, $^3J = 7.7$ Hz), 3.40 (d, 8H, CH_2P, $^2J_{PH} = 10.8$ Hz), 2.45 (hept, 4H, C*H*(CH_3)$_2$), 1.85 (s, 12H, CH_3 of *p*-cymene), 1.64 (m, 8H, CHC*H*$_2$$CH_2$), 1.33 (m, 24H, C*H*$_2$C*H*$_2$C*H*$_2$$CH_3$), 0.97 (d, 24H, CH(C*H*$_3$)$_2$, $^3J = 6.9$ Hz), 0.97 (t, 12H, CH_2C*H*$_3$, $^3J = 7.1$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta =$ 153–127.03 (arom. C_{quat}), 117.68 (s, arom. CH of resorcinarene), 98.3 (s, OCH_2O), 90.8 (s, arom. CH of *p*-cymene), 85.0 (s, arom. CH of *p*-cymene), 36.02 (s, *C*HCH_2), 32.23 (s, *C*$H_2CH_2CH_3$), 30.01 (s, *C*H(CH_3)$_2$), 29.94 (s, CH*C*H_2), 27.63 (s, $CHCH_2$*C*H_2), 22.81 (s, *C*H_2CH_3), 21.80 (s, CH(*C*H_3)$_2$), 17.39 (s, CH_3 of *p*-cymene), 14.20 (s, CH_2*C*H_3). The PCH_2 signal, which is usually weak, was not detected. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = 28.0$ (s, PPh_2). Found C 59.45, H 6.03. $C_{144}H_{164}Cl_8O_8P_4Ru_4 \cdot CH_2Cl_2$ ($M_r = 2834.64 + 84.93$) requires C 59.65, H 5.73%.

Reaction of 8 with $[Rh(COD)_2]BF_4$

A solution of **8** (0.140 g, 0.087 mmol) in CH_2Cl_2 (150 cm^3) and a solution of $[Rh(COD)_2]BF_4$ (0.071 mg, 0.174 mmol) in CH_2Cl_2 (150 cm^3) were added simultaneously over a period of 2 h into a flask containing 600 cm^3 of CH_2Cl_2. The resulting solution was stirred overnight, then concentrated to *ca.* 5 cm^3. Addition of diethyl ether (100 cm^3) afforded a yellow precipitate, which turned out to contain several complexes that could not be separated. The mass spectrum of the crude reaction mixture revealed an intense peak corresponding to the dication $\{\mathbf{8}\cdot[Rh(COD)]_2\}^{2+}$. *m/z* (ESI-TOF): 1015.39 ($\{\mathbf{8}\cdot[Rh(COD)]_2\}^{2+}$ requires 1015.35).

General procedure for Heck cross-coupling reactions

$[Pd(OAc)_2]$ (0.0045 g, 0.02 mmol, 2 mol%), ligand **8** (0.02 mmol, 2 mol%) and Cs_2CO_3 (0.651 g, 2.00 mmol) were introduced into a Schlenk tube under nitrogen. DMF (3.0 cm^3), styrene (2.0 mmol, *ca.* 0.23 cm^3) and the appropriate aryl halide (1.0 mmol) were then added successively. The reaction mixture was heated at 130 °C for 1 hour. After cooling, decane (0.10 cm^3) was added acting as internal reference. A sample of 0.5 cm^3 was taken and filtered over celite before GC analysis.

Crystal structure of 8·4 CH_3OH

Single crystals of **8** suitable for diffraction study were obtained by the slow diffusion of methanol into a dichloromethane solution of the ligand. *M*r = 1769.99, monoclinic, space group *C*c, $a =$ 27.274(1), $b = 16.332(1)$, $c = 24.100(1)$ Å, $\beta = 116.999(6)°$, $V =$ 9565.0(7) Å^3, $Z = 4$, $D_x = 1.207$ mg.m^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 1.40$ cm^{-1}, $F(000) = 3712$, $T = 90(1)$ K. Data were collected on a Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite MoK_α radiation, $\lambda = 0.71073$ Å). The structure was solved with SIR-97,[40] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier difference analysis. The whole structure was refined

with SHELX-97[41] and full-matrix least-square 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; 17322 variables and 6024 observations with $I > 2.0\ \sigma(I)$; calc $w = 1/[\sigma^2(F_0^2) + (0.0988P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. $R1 = 0.060$, $wR2 = 0.146$, $S_w = 0.755$, $\Delta\rho < 2.7 e\text{Å}^{-3}$. Compound **8** crystallises with 4 molecules of MeOH, one of which is located in the cavity. The latter is disordered over two positions, while the other three display large thermal motion. Crystallographic data for this structure have been deposited with the Cambridge Crystallographic Data Centre under deposition number 637858 This data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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