Polyhedron 51 (2013) 70–74

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Tetra-hydroxy-calix[4]arene derivatives with two P(III) or P(V) units attached at the upper rim

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ARTICLE INFO

Article history:
Received 12 November 2012
Accepted 29 November 2012
Available online 14 December 2012

Keywords:
Calix[4]arene
Phosphine
Phosphine oxide
Phosphine sulfide
Binuclear complexes
Hydrogenation

ABSTRACT

5,17-Bis(diphenylphosphino)-25,26,27,28-tetra-hydroxy-calix[4]arene (**2**) and the corresponding bis-(phosphine oxide) (**3**) and bis-(phosphine sulfide) (**4**) have been synthesized. A single crystal X-ray diffraction study was carried out for bis(phosphine oxide) **3**, which revealed a pinched cone conformation for the calixarene core. In the solid state, each calixarene is linked to two other calixarenes via hydrogen bonds involving the phosphoryl groups as well as two of the four hydroxyl groups, thereby generating a supramolecular polymeric structure. Selective formation of chelate complexes from diphosphine **2** failed, probably because of rapid trans annular rotation of the phenoxyl groups that prevents appropriate ligand preorganisation. Upon reaction with appropriate Ru-, Rh-, and Ir-complexes, ligand **2** readily formed dinuclear complexes. One of them, namely the complex [**2**·{RhCl(1,5-cyclooctadiene)}$_2$] was assessed in the catalytic hydrogenation of linear and cyclic olefins.

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1. Introduction

The calix[4]arene backbone constitutes one of the most employed platforms for the preparation of highly preorganized multidentate ligands [1–4], many of which have been used in homogeneous catalysis [5]. We have recently described the coordinative properties of a series of calixarenes having two phosphino groups grafted at the distal carbon atoms 5 and 17 (upper rim) [6,7]. These so-called CALDIP ligands form straightforwardly transition metal chelate complexes in which the PMP angle undergoes a periodic variation in magnitude due to a rapid fan-like motion of the PMP plane [7–9]. The particular binding features of these ligands have been exploited in a variety of carbon carbon bond forming reactions [9–14]. To date, only CALDIPs in which the phenolic oxygen atoms are substituted by alkyl groups have been reported. We wondered whether CALDIPs devoid of substituents attached to the lower rim would display coordinative properties similar to those already reported, and in particular whether chelating behaviour is still possible. In the present work we describe the synthesis of 5,17-bis(diphenylphosphino)-25,26,27,28-tetrahydroxycalix[4]arene (**2**) together with two P(V) derivatives. The coordinative properties of **2** have been investigated towards cationic and neutral complexes. The X-ray structure of 5,17-bis(diphenylphosphinoyl)-25,26,27,28-tetrahydroxycalix[4]arene (**3**) is also reported. To date, only four other tetra-hydroxy-calixarenes bearing phosphorus-containing substituents have been reported [15–19].

2. Experimental

2.1. General data

All syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and were distilled immediately prior to use. Routine ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded by using a Bruker AVANCE 300 spectrometer. ^{1}H NMR spectra were referenced to residual protonated solvents (7.26 ppm for $CDCl_3$ or 5.32 ppm for CD_2Cl_2), ^{13}C chemical shifts are reported relative to deuterated solvents (77.16 ppm for $CDCl_3$ or 53.8 ppm for CD_2Cl_2) and the ^{31}P NMR data are given relative to external H_3PO_4. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie UMR 7177 CNRS-Université de Strasbourg. 5,17-Bis(diphenylphosphino)-25,26,27,28-tetrabenzyloxycalix[4]arene (**1**) [8] was prepared according to a method reported in the literature. In the NMR data given hereafter, the bridging methylene groups of the calix[4]arene backbone are designated by the abbreviation $ArCH_2Ar$.

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http://dx.doi.org/10.1016/j.poly.2012.11.040

2.2. Synthesis of bis-phosphine, bis-phosphine oxide/sulfide and complexes

2.2.1. General procedure for debenzylation of tetrabenzyloxycalix[4] arene derivatives

A Schlenk tube was filled with substrate (1 equiv.), $AlCl_3$ (4 equiv.) and toluene (50 mL). After stirring this suspension for 16 h, a saturated solution of NaCl (20 mL) was slowly added. The aqueous layer was extracted with CH_2Cl_2 (2×20 mL), then the combined organic layers were dried over Na_2SO_4. Evaporation under vacuum afforded a pale yellow solid, which was recrystallised from diethylether–petroleum ether. The product was collected by filtration and dried under vacuum.

2.2.2. Synthesis of 5,17-bis(diphenylphosphino)-25,26,27,28-tetrahydroxycalix[4]arene – **2**

Diphosphine **2** was obtained from **1** (0.577 g, 0.5 mmol) in 98% yield (0.386 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.13 (s, 4H, OH), 7.35–7.24 (20H, arom. CH of PPh_2), 7.04 (d, 4H, arom. CH of calix, $^3J_{H-H}$ = 7.5 Hz), 6.79 (s, 4H, arom. CH of calix), 6.66 (t, 2H, arom. CH of calix, $^3J_{H-H}$ = 7.5 Hz), 4.09 and 3.54 (AB spin system br, 8H, ArCH_2Ar). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ: 150.24 (s, arom. Cq-OH), 148.43 (s, arom. Cq-OH), 137.89–122.75 (arom. C), 31.73 (s, ArCH_2Ar). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ: −6.1 (s, PPh_2). *Anal.* Calc. for $C_{52}H_{42}O_4P_2$: C, 78.77; H, 5.34. Found: C, 78.65; H, 5.15%.

2.2.3. Synthesis of 5,17-bis(diphenylphosphinoyl)-25,26,27,28-tetrahydroxycalix[4]arene – **3**

To a solution of **2** (0.100 g, 0.12 mmol) in CH_2Cl_2 (10 mL) was added H_2O_2 (30% in water, 2 ml, 2.5 mmol). The resulting solution was stirred at room temperature for 2 h. The mixture was then treated with a mixture of CH_2Cl_2 (10 mL) and water (20 mL). After extraction of the aqueous layer with CH_2Cl_2 (2×10 mL), the organic phases were combined. The resulting solution was washed with water (2×10 mL), then dried over Na_2SO_4 and evaporated under reduced pressure to afford the bis-phosphine oxide **3** as a white solid. Yield 100% (0.104 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.15 (s, 4H, OH), 7.67–7.60 (8H, arom. CH of $P(O)Ph_2$), 7.56–7.52 (4H, arom. CH of $P(O)Ph_2$), 7.47–7.38 (12H, arom. CH of $P(O)Ph_2$ and calix), 6.87 (d, 4H, arom. CH of calix, $^3J_{H-H}$ = 7.5 Hz), 6.67 (t, 2H, arom. CH of calix, $^3J_{H-H}$ = 7.5 Hz), 4.21 and 3.54 (AB spin system br, 8H, ArCH_2Ar). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ: 152.85 (d, arom. Cq-OH, $^4J_{P-C}$ = 3.1 Hz), 147.96 (s, arom. Cq-OH), 133.43–122.90 (arom. C), 31.55 (s, ArCH_2Ar). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ: 27.9 (s, $P(O)Ph_2$). *Anal.* Calc. for $C_{52}H_{42}O_6P_2$: C, 75.72; H, 5.13. Found: C, 75.61; H, 4.98%.

2.2.4. Synthesis of 5,17-bis(diphenylthiophosphinoyl)-25,26,27,28-tetrahydroxycalix[4] arene – **4**

To a solution of **2** (0.500 g, 0.63 mmol) in toluene (15 mL) was added sulfur powder (S_8, 0.040 g, 0.16 mmol). The resulting solution was refluxed for 10 min. The solvent was further evaporated under reduced pressure to afford the bis-phosphine sulfide **4** as a white solid. Yield 100% (0.540 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.13 (s, 4H, OH), 7.89–7.41 (24H, arom. CH of $P(S)Ph_2$ and calix), 6.84 (d, 4H, arom. CH of calix, $^3J_{H-H}$ = 7.4 Hz), 6.69 (t, 2H, arom. CH of calix, $^3J_{H-H}$ = 7.4 Hz), 4.49 and 3.52 (AB spin system br, 8H, ArCH_2Ar). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ: 152.60 (s, arom. Cq-OH), 148.01 (s, arom. Cq-OH), 133.67–123.03 (arom. C), 31.60 (s, ArCH_2Ar). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ: 42.0 (s, $P(S)Ph_2$). *Anal.* Calc. for $C_{52}H_{42}O_4S_2P_2$: C, 72.88; H, 4.94. Found: C, 72.75; H, 5.11%.

2.2.5. Synthesis of 5,17-bis(diphenylphosphinoyl)-25,26,27,28-tetrabenzyloxycalix[4]arene – **5**

To a solution of **1** (0.576 g, 0.5 mmol) in CH_2Cl_2 (10 mL) was added H_2O_2 (30% in water, 4 ml, 5.0 mmol). The resulting solution was stirred at room temperature for 2 h. A mixture of CH_2Cl_2 (10 mL) and water (20 mL) was then added. After extraction of the aqueous layer with CH_2Cl_2 (2×10 mL), the organic phases were combined. The resulting solution was washed with water (2×10 mL), then dried over Na_2SO_4 and evaporated under reduced pressure to afford the bis-phosphine oxide **3** as a white solid. Yield 100% (0.511 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58–7.34 (20H, arom. CH), 7.24–6.96 (24H, arom. CH), 6.16 (t, 2H, arom. CH of calix, $^3J_{H-H}$ = 7.5 Hz), 5.90 (d, 4H, arom. CH of calix, $^3J_{H-H}$ = 7.5 Hz), 5.12 (s, 4H, CH_2Ph), 4.56 (s, 4H, CH_2Ph), 4.12 and 2.82 (AB spin system, 8H, ArCH_2Ar, $^2J_{H-H}$ = 13.8 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ: 158.97 (d, arom. Cq-OH, $^4J_{P-C}$ = 2.8 Hz), 154.29 (s, arom. Cq-OH), 137.64–122.21 (arom. C), 77.12 (s, OCH_2Ph), 75.03 (s, OCH_2Ph), 30.89 (s, ArCH_2Ar). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ: 31.0 (s, $P(O)Ph_2$). *Anal.* Calc. for $C_{80}H_{66}O_6P_2$: C, 81.06; H, 5.61. Found: C, 80.89; H, 5.72%.

2.2.6. Synthesis of 5,17-bis(diphenylthiophosphinoyl)-25,26,27,28-tetrabenzyloxycalix[4] arene – **6**

To a solution of **1** (0.500 g, 0.43 mmol) in toluene (20 mL) was added S_8 (0.028 g, 0.11 mmol). The resulting solution was refluxed for 10 min. Solvent evaporation under reduced pressure afforded the bis-phosphine sulfide **6** as a white solid. Yield 100% (0.527 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.72–7.64 (8H, arom. CH), 7.52–7.46 (8H, arom. CH), 7.35–7.24 (8H, arom. CH), 7.33 (s, 4H, arom. CH of calix), 7.15–7.09 (16H, arom. CH), 6.26 (t, 2H, arom. CH of calix, $^3J_{H-H}$ = 7.6 Hz), 5.97 (d, 4H, arom. CH of calix, $^3J_{H-H}$ = 7.6 Hz), 5.22 (s, 4H, CH_2Ph), 4.64 (s, 4H, CH_2Ph), 4.21 and 2.94 (AB spin system, 8H, ArCH_2Ar, $^2J_{H-H}$ = 13.7 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ: 159.28 (d, arom. Cq-OH, $^4J_{P-C}$ = 3.1 Hz), 154.76 (s, arom. Cq-OH), 138.04–122.63 (arom. C), 77.63 (s, OCH_2Ph), 75.48 (s, OCH_2Ph), 31.39 (s, ArCH_2Ar). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ: 42.8 (s, $P(S)Ph_2$). *Anal.* Calc. for $C_{80}H_{66}O_4S_2P_2$: C, 78.92; H, 5.46. Found: C, 79.10; H, 5.34%.

2.2.7. Synthesis of P,P′-{5,17-bis(diphenylphosphino)-25,26,27,28-tetrahydroxycalix[4] arene}-bis[dichlorido(p-cymene)]ruthenium(II) – **7**

To a solution of **2** (0.100 g, 0.12 mmol) in CH_2Cl_2 (10 mL) was added a solution of $[RuCl_2(p\text{-cymene})]_2$ (0.077 g, 0.12 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at room temperature for 0.5 h, then the reaction mixture was concentrated to *ca.* 2 mL before addition of *n*-hexane (50 mL) was added. The red product was collected by filtration and dried under vacuum. Yield (0.161 g, 92%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 10.09 (s, 4H, OH), 7.82–7.77 (8H, arom. CH of PPh_2), 7.58 (d, 4H, arom. CH of calix, $^3J_{P-H}$ = 10.0 Hz), 7.48–7.35 (12H, arom. CH of PPh_2), 6.92 (d, 4H, arom. CH of calix, $^3J_{H-H}$ = 7.6 Hz), 6.77 (t, 2H, arom. CH of calix, $^3J_{H-H}$ = 7.6 Hz), 5.15 (d, 4H, arom. CH of *p*-cymene, $^3J_{H-H}$ = 6.2 Hz), 5.05 (d, 4H, arom. CH of *p*-cymene, $^3J_{H-H}$ = 6.2 Hz), 4.23 and 3.51 (AB spin system, 8H, ArCH_2Ar, $^2J_{H-H}$ = 11.4 Hz), 2.61 (hept, 2H, CH(CH_3)$_2$, $^3J_{H-H}$ = 6.9 Hz), 1.71 (s, 6H, CH_3), 0.97 (d, 12H, CH(CH_3)$_2$, $^3J_{H-H}$ = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ: 151.33 (s, arom. Cq-OH), 148.32 (s, arom. Cq-OH), 135.56–122.39 (arom. C), 110.00 (s, arom. Cq of *p*-cymene), 95.97 (s, arom. Cq of *p*-cymene), 89.46 (s, arom. CH of *p*-cymene), 86.79 (s, arom. CH of *p*-cymene), 31.35 (s, ArCH_2Ar), 30.08 (s, CH(CH_3)$_2$), 21.40 (s, CH(CH_3)$_2$), 17.11 (s, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2) δ: 22.6 (s, PPh_2). *Anal.* Calc. for $C_{72}H_{70}O_4P_2Ru_2Cl_4$: C, 61.54; H, 5.02. Found: C, 61.32; H, 4.87%.

2.2.8. Synthesis of P,P′-{5,17-bis(diphenylphosphino)-25,26,27,28-tetrahydroxycalix[4] arene}-bis[chlorido(1,5-cyclooctadiene)]-iridium(I) – **8**

To a solution of **2** (0.100 g, 0.12 mmol) in CH_2Cl_2 (10 mL) was added a solution of $[IrCl(COD)]_2$ (0.085 g, 0.12 mmol) in CH_2Cl_2

(10 mL). The solution was stirred at room temperature for 0.5 h, then the reaction mixture was concentrated to *ca.* 2 mL before addition of *n*-hexane (50 mL) was added. The yellow product was collected by filtration and dried under vacuum. Yield (0.173 g, 97%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 10.18 (s, 4H, OH), 7.63–7.36 (24H, arom. CH of PPh_2 and calix), 6.89 (d, 4H, arom. CH of calix, $^3J_{H-H}$ = 7.4 Hz), 6.75 (t, 2H, arom. CH of calix, $^3J_{H-H}$ = 7.4 Hz), 5.13 (s br, 4H, CH of COD), 4.25 and 3.57 (AB spin system, 8H, ArCH_2Ar, $^2J_{H-H}$ = 13.1 Hz), 2.64 (s br, 4H, CH of COD), 2.64–2.11 (8H, CH_2 of COD), 1.89–1.84 (4H, CH_2 of COD), 1.58–1.54 (4H, CH_2 of COD). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2) δ: 151.64 (s, arom. Cq-OH), 148.44 (s, arom. Cq-OH), 137.05–122.42 (arom. C), 93.75 (d, CH of COD, $^2J_{P-C}$ = 14.0 Hz), 33.31 (s, CH_2 of COD), 31.38 (s, ArCH_2Ar), 29.51 (s, CH_2 of COD). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2) δ: 21.1 (s, PPh_2). *Anal.* Calc. for $C_{68}H_{66}O_4P_2Ir_2Cl_2$: C, 55.77; H, 4.54. Found: C, 55.84; H, 4.36%.

2.2.9. Synthesis of P,P′-{5,17-bis(diphenylphosphino)-25,26,27,28-tetrahydroxycalix[4] arene}-bis[chlorido(1,5-cyclooctadiene)]rhodium(I) – 9

To a solution of **2** (0.100 g, 0.12 mmol) in CH_2Cl_2 (10 mL) was added a solution of $[RhCl(COD)]_2$ (0.062 g, 0.12 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at room temperature for 0.5 h, then the reaction mixture was concentrated to *ca.* 2 before addition of *n*-hexane (50 mL) was added. The yellow product was collected by filtration and dried under vacuum. Yield (0.155 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.34 (s, 4H, OH), 7.79 (d, 4H, arom. CH of PPh_2, $^3J_{H-H}$ = 10.1 Hz), 7.75–7.7.60 (8H, arom. CH of PPh_2), 7.49–7.36 (8H, arom. CH of PPh_2 and calix), 7.26–7.02 (4H, arom. CH of PPh_2), 6.93 (d, 4H, arom. CH of calix, $^3J_{H-H}$ = 7.5 Hz), 6.77 (t, 2H, arom. CH of calix, $^3J_{H-H}$ = 7.5 Hz), 5.62 (s br, 4H, CH of COD), 4.25 and 3.54 (AB spin system, 8H, ArCH_2Ar, ^2J = 12.7 Hz), 3.07 (s br, 4H, CH of COD), 2.52–2.26 (8H, CH_2 of COD), 2.08–2.01 (4H, CH_2 of COD), 1.91–1.82 (4H, CH_2 of COD). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ: 151.69 (s, arom. Cq-OH), 148.14 (s, arom. Cq-OH), 137.10–122.88 (arom. C), 104.96 (d, CH of COD, $^2J_{P-C}$ = 12.7 Hz), 78.73 (d, CH of COD, $^2J_{P-C}$ = 12.7 Hz), 33.13 (s, CH_2 of COD), 31.65 (s, CH_2 of COD), 30.92 (s, ArCH_2Ar). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ: 30.5 (d, PPh_2, $^1J_{Rh-P}$ = 149.6 Hz). *Anal.* Calc. for $C_{68}H_{66}O_4P_2Rh_2Cl_2$: C, 63.51; H, 5.17. Found: C, 63.67; H, 5.01%.

2.3. Crystallographic analysis

Single, colourless crystals of **3** suitable for X-ray diffraction were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the bis-(phosphine oxide) at room temperature. Formula of the crystals: $C_{52}H_{42}O_6P_4$, *M*r = 824.80, orthorhombic, *Pbca*, *a* = 17.5363(7), *b* = 24.5314(9), *c* = 19.1121(8) Å, δ = 90.00, δ = 90.00, δ = 90.00°, *V* = 8221.8(6) Å^3, *Z* = 8, D_x = 1.333 Mg m^{-3}, δ (Mo Kα) = 0.71073 Å, μ = 0.159 mm^{-1}, *F*(000) = 3456, *T* = 110(2) K. The sample (0.25 × 0.20 × 0.20 mm) was mounted on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized Mo Kα radiation. The data collection ($2\theta_{max}$ = 27°, omega scan frames *via* 0.7° omega rotation and 30 s per frame, range *HKL*: *H* −22,21 *K* −31,26 *L* −18,24) gave 57600 reflections. The data led to 8957 independent reflections from which 3840 with $I > 2.0 > (I)$ were observed. The structure was solved with SIR-97 [20], which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms are found with a Fourier Difference. The whole structure was refined with SHELXL97 [21] by the fullmatrix least-square techniques (use of *F* square magnitude; *x*, *y*, *z*, βij for P, C and O atoms, *x*, *y*, *z* in riding mode for H atoms; 541 variables and 3840 observations with $I > 2.0\sigma(I)$; calc $w = 1/[\sigma^2(F_o^2) + (0.0619P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting R = 0.0493, R_W = 0.1123 and S_W = 0.822, $\Delta\rho < 0.649$ e Å^{-3}.

2.4. General procedure for the catalytic hydrogenation

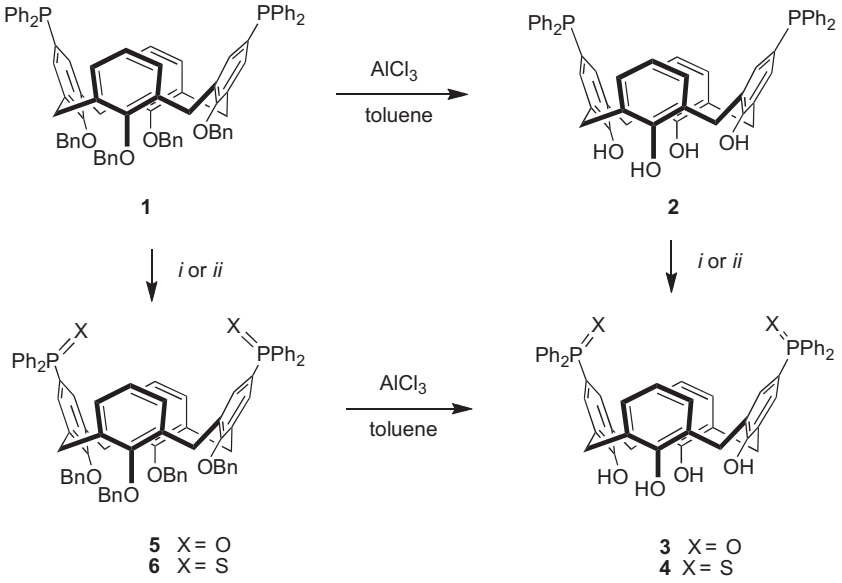
The hydrogenation experiments were carried out in a glass-lined, 100-mL stainless steel autoclave containing a magnetic stirring bar. In a typical run, the autoclave was charged successively under nitrogen with bis-rhodium complex **9** (0.006 g, 0.005 mmol, 1 mol% of Rh) dissolved in the solvent (5 mL of THF) and substrate (1.0 mmol). Once closed, the autoclave was flushed twice with hydrogen, then pressurised. At the end of the catalytic run, the autoclave was depressurized and the resulting solution was passed through a Millipore filter and analyzed by GC (Varian 3900 gas chromatograph equipped with a WCOT fused-silica column: 25 m × 0.25 mm).

3. Results and discussion

Treatment of the bis(diphenylphosphino)-tetrabenzyloxycalix[4]arene **1** with $AlCl_3$ in toluene led quantitatively to the tetrahydroxy-calixarene **2**. The oxidation of **2** with H_2O_2 gave the bis-(phosphine oxide) **3**, while reaction of **2** with S_8 in toluene resulted in the bis-(phosphine sulfide) **4**. Another route leading to **3** consisted in forming first the bis-phosphine oxide **5**, then removing the protecting benzyl groups with $AlCl_3$. A similar alternative approach was applied for the synthesis of **4** (Scheme 1). While the ^{1}H NMR ($CDCl_3$) spectra of calixarenes **1**, **5** and **6** each show a well-resolved AB pattern for the ArCH_2Ar groups (δ_A–δ_B = 1.32, 1.30 and 1.27, respectively), indicative of a calixarene fixed in the cone conformation, that of the hydroxy calixarenes **2**, **3**, and **4**, show two broad signals for the methylenic protons (δ_A–δ_B = 0.55, 0.67 and 0.97, respectively). The large methylene signals are likely to reflect rapid trans annular rotation of the phenolic rings of the tetrahydroxy-calixarenes **2**–**4**, a phenomenon that is well documented [22,23]. It is noteworthy that for all three compounds the ArCH_2Ar carbon atoms appear as a singlet at ca. 31.5 ppm in the corresponding ^{13}C NMR spectra.

Crystals of **3** suitable for X-ray diffraction formed readily upon diffusion of hexane into a dichloromethane solution of the bis-phosphine oxide. The molecule crystallises in the orthorhombic system, space group *P*bca. In the solid state (Fig. 1), the calix[4]arene cavity adopts a flattened cone conformation, with interplanar angles between opposite phenoxy rings of 28.4° and 78.6°, respectively. The separations between the aromatic carbon atoms of opposite phenolic rings are 6.54 and 9.67 Å, respectively. The P═O vectors are both pushed away from the axis of the cavity, the distance between the two phosphorus atoms being 12.691 Å. It should be mentioned here that the vast majority of tetra-hydroxy-calix[4]arenes reported in the literature adopt, in the solid state, an almost perfect cone shape owing to the formation of a stable cyclic H-bond network formed by the four hydroxyl groups [24,25]. This is not the case in **3**, possibly because of the capacity of two hydroxyl groups to form stronger hydrogen bonds with phosphoryl groups. Careful examination of the structure revealed that indeed each calixarene is linked to two other calixarenes via hydrogen bonds involving the phosphoryl groups as well as two of the four hydroxyl groups, thereby generating a polymeric chain. Thus, in the resulting supramolecular structure, each calixarene link is attached through two points to the calixarene that precedes it and also through two points to that which follows it (Fig. 2).

In order to evaluate the capacity of diphosphine **2** to form chelate complexes, this ligand was reacted with the following complexes, all suitable for coordinating two phosphine ligands: $[PtCl_2(PhCN)_2]$, $[Pd(\eta^3\text{-allyl})(acetone)_2]PF_6$, $[PdCl_2(COD)]$ (COD = 1,5-cyclooctadiene), $[RuCl(p\text{-cymene})(THF)_2]BF_4$, $[Rh(COD)(THF)_2]BF_4$, $[RhCl(CO)_2]_2$, $[Pd(SMe_2)_4](BF_4)_2$, and $[Ni(COD)(\eta^5\text{-}C_5H_5)]BF_4$. Each reaction led to a mixture of complexes, mainly



Scheme 1. Synthesis of diphosphine **2**, bis-(phosphine oxide) **3** and bis-(phosphine sulfide) **4**: i: H_2O_2 in CH_2Cl_2/H_2O; ii: S_8 in toluene.

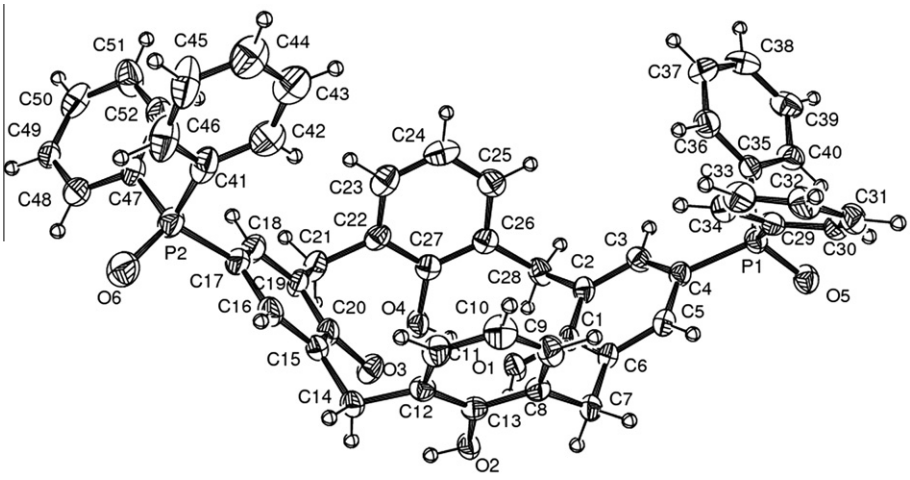


Fig. 1. ORTEP drawing of bis-(phosphine oxide) **3**. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–C(4) 1.792(3), P(1)–O(5) 1.4817(18), P(2)–C(17) 1.805(3), P(2)–O(6) 1.477(2), O(5)–P(1)–C(4) 114.87(11), O(5)–P(1)–C(35) 111.77(12), C(4)–P(1)–C(35) 106.23(13), O(5)–P(1)–C(29) 109.48(12), C(4)–P(1)–C(29) 106.29(12), C(35)–P(1)–C(29) 107.83(12), O(6)–P(2)–C(41) 114.32(14), O(6)–P(2)–C(17) 112.75(13), C(41)–P(2)–C(17) 107.61(13), O(6)–P(2)–C(47) 111.34(13), C(41)–P(2)–C(47) 103.37(14), C(17)–P(2)–C(47) 106.78(13).

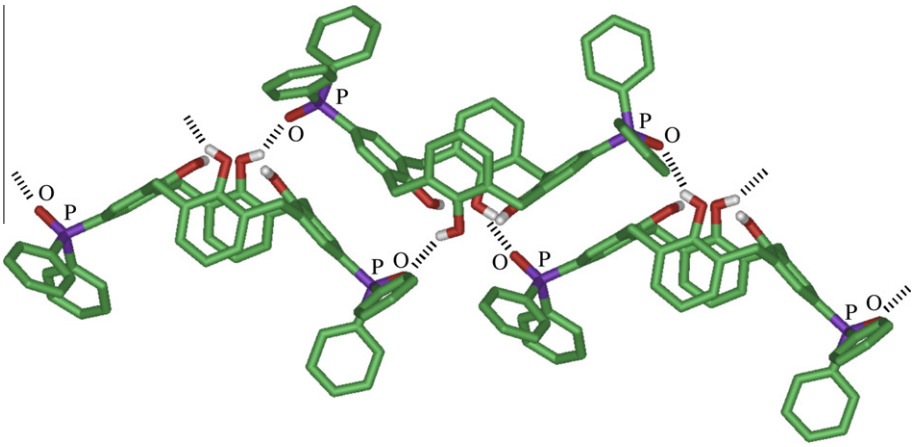
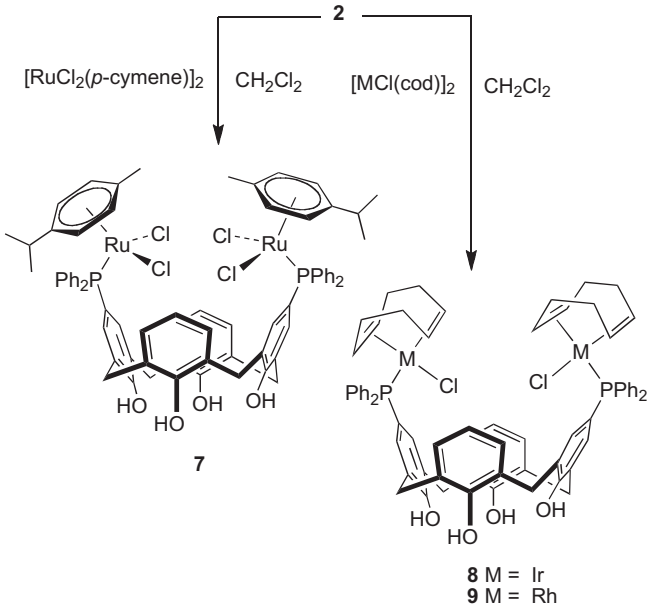
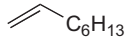
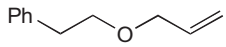
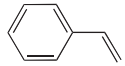
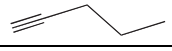


Fig. 2. Part of the polymer chain generated by **3** in the solid state.



Scheme 2. Synthesis of the dinuclear complexes **7**–**9**.

Table 1
Catalytic hydrogenation using bis-rhodium complex **9**.[a]

Entry	Substrate	Time (h)	P(H_2) (bar)	Conversion into alkane (%)
1		1	1	59.1
2		1	5	100
3		1	5	100
4		1	5	44.5
5		4	5	100
6		1	5	39.2
7		4	5	100
8		24	5	100

[a] 9 (0.006 g, 0.005 mmol, 1 mol% of Rh), substrate (1 mmol), THF (5 ml), room temperature.

oligomers, even when the reactions were carried under high dilution conditions. This behaviour markedly contrasts with that of O-alkylated CALDIPs, which selectively form chelate complexes with the above complexes [7–9,12,13]. In contrast with these reactions, quantitative formation of dinuclear complexes was observed when reacting diphosphine **2** with $[RuCl_2(p\text{-cymene})]_2$, $[IrCl(COD)]_2$ or $[RhCl(COD)]_2$, these reactions leading to complexes **7**, **8** and **9**, respectively (Scheme 2). In the corresponding ^1H NMR spectra, the chemical shifts of the methylenic $ArCH_2Ar$ protons are close to those of the free phosphine (with $\Delta\rho \approx 0.7$ ppm). The corresponding AB patterns, although being somewhat broad, thus again indicative of conformationally mobile calixarenes, were better resolved than that of **2** (J(AB) = 11.4–13.1 Hz). Overall, diphosphine **2** should be regarded as a long, flexible diphosphine suitable for forming dinuclear complexes, rather than for forming chelate complexes.

The bis-rhodium complex **9** was assessed in catalytic hydrogenation of alkenes and alkyne into alkanes (Table 1). Using 1 mol% of rhodium under a H_2 pressure of 5 bar resulted in full conversion after 1 h of alkyl substituted olefins (1-octene and allylbenzyl ether; Table 1, entries 2 and 3). Hydrogenation of styrene and cyclooctene was completed after 4 h (Table 1, entries 5 and 7), while pentyne was converted into pentane in 24 h (Table 1, entry 8). The observed activities are not unusual for rhodium-phosphine complexes.

4. Conclusion

We have described the synthesis of 5,17-bis(diphenylphosphino)-25,26,27,28-tetrahydroxycalix[4]arene (**2**), a rare example of diphosphine based on a tetra-hydroxy-calixarene skeleton, and of the corresponding bis-(phosphine oxide) **3** and bis-(phosphine sulfide) **4**. All three calixarenes display conformational mobility in solution due to easy trans-annular rotation of the phenolic rings. An X-ray structure determination revealed that in the solid state the phosphorylated compound **3** adopts a pinched rather than a "pure" cone conformation, both phosphoryl groups interacting with hydroxyl groups of neighbouring calixarenes so as to result in a polymeric chain structure. Diphosphine **2** is not suited for forming chelate complexes, but forms readily dinuclear complexes.

Acknowledgement

This work was supported by the University of Strasbourg (grant to L.M.).

Appendix A. Supplementary data

CCDC 680936 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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