Calixarenes: Structure of an Acetonitrile Inclusion Complex and Some Transition Metal Rimmed Derivatives*

WEI XU and RICHARD J. PUDDEPHATT**
Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

and

LJUBICA MANOJLOVIC-MUIR, KENNETH W. MUIR** and
CHRISTOPHER S. FRAMPTON
Department of Chemistry, University of Glasgow, Glasgow, Scotland G12 8QQ

Abstract. The host *t*-butylcalix[4]arene, **1a**, forms a 1 : 1 inclusion compound with acetonitrile as guest. The inclusion compound has been isolated and characterised by X-ray analysis of a twinned crystal at 123 K. The acetonitrile guest lies on a crystallographic four-fold symmetry axis passing through the centre of the bowl of **1a** which adopts a regular cone conformation. A known tetradentate and a new tridentate phosphinitocalix[4]arene derivative, **2a** and **2c** respectively, have been synthesized from **1a** and Ph₂Cl. Both **2a** and **2c** show a strong ability to coordinate with late transition metals and new complexes of gold(I), palladium(II) and platinum(II) are reported.

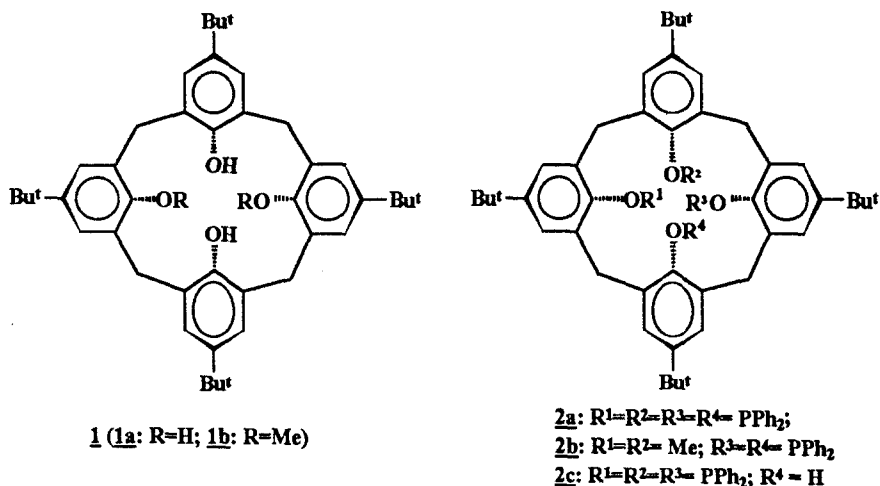**Key words:** Calix[4]arene, phosphinite, coordination, transition metal.

1. Introduction

The calixarenes are a group of phenolic macrocyclic compounds that have become significant in supramolecular chemistry during the past decade [1]. The most useful property of calixarenes is their ability to function as molecular baskets which can engulf small neutral or ionic guests [2–3]. The calixarene **1**, which contains hydroxyl groups at the bottom rim, has been extensively studied and its transition metal complexes are attracting attention [4–8]. Both fully hydroxylated **1a** and partially hydroxylated *tert*-butylcalixarene **1b** have been reacted with chlorodiphenylphosphine to give the fully substituted [9] and partially substituted [10] diphenylphosphinocalix[4]arenes, **2a** and **2b**. The compound **2a** was used as a phosphorus donor ligand in forming copper(I) [9] and iron(0) carbonyl [11] complexes. This paper

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** Author for correspondence.

reports the synthesis of the tridentate phosphinitocalix[4]arene derivative **2c** and a study of the coordination chemistry of **2a** and **2c** with late transition metals. The conformations of the calixarenes with transition metal substituents on the lower rim will be discussed, and the structure of a host–guest complex of **1a** with acetonitrile will be described.

1 (1a: R=H; 1b: R=Me)

2a: $R^1=R^2=R^3=R^4=$ PPh$_2$;
2b: $R^1=R^2=$ Me; $R^3=R^4=$ PPh$_2$
2c: $R^1=R^2=R^3=$ PPh$_2$; $R^4=$ H

2. Experimental

[AuCl(SMe$_2$)] [12], [PtCl$_2$(SMe$_2$)$_2$] [13], [PdCl$_2$(PhCN)$_2$] [14], and *p-tert*-butyl-calix[4]arene [15] were prepared by literature methods. NMR spectra were recorded by using a Varian Gemini 300 MHz spectrometer. ^{1}H- and ^{13}C-NMR chemical shifts were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane. ^{31}P-NMR chemical shifts were determined relative to 85% H$_3$PO$_4$ as an external standard. IR spectra were recorded on a Bruker IFS32 FTIR spectrometer with Nujol mulls. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, U.S.A.

p-tert-Butylcalix[4]arene(OPPh$_2$)$_4$, **2a**, was prepared as described in the literature [9, 11]. The ^{1}H-NMR spectrum is in good agreement with the literature [11]. The ^{31}P-NMR spectrum gives a singlet at $\delta = 123$ (Lit. $\delta = 29.27$, note the large discrepancy [11]) in CD$_2$Cl$_2$.

p-tert-Butylcalix[4]arene(OPPh$_2$)$_3$(OH), **2c**: Bu^{n}Li (2.5 M, 2 mL) was added at room temperature to a THF (15 mL) suspension of *p-tert*-butylcalix[4]arene **1** (1 g, 1.54 mmol). An orange solution was formed. Then the mixture was cooled to 0° and ClPPh$_2$ (1.14 mL, 6.25 mmol) was added slowly. The mixture was kept at 0°C for 2 h and then warmed to room temperature and stirred for 12 h. The resulting brown solution was heated to 60°C and kept at this temperature for another 48 h.

Most of the solvent was then evaporated under vacuum. MeCN (20 mL) was added and the mixture was cooled to 0°C for 4 h, when **2c** (1.15 g, 62.1%) was precipitated as a white solid, which was washed with MeCN and dried under vacuum. *Anal. Calc.* for **2c** $C_{80}H_{83}O_4P_3$·MeCN: C, 79.3; H, 7.0; *Found*: C, 79.1; H, 6.8%. Spectroscopic data of **2c**: NMR in CD_2Cl_2: $\delta(^{31}P) = 121.8$ [s, 2P] and 112.9 [s, 1P]. $\delta(^1H) = 1.11$ [s, 18H, t-Bu], 1.21 [s, 9H, t-Bu], 1.15 [s, 9H, t-Bu], 2.78 [d, $^2J_{HH} = 13.2$ Hz, 2H, CH_2], 3.78 [d, $^2J_{HH} = 15.6$ Hz, 2H, CH_2], 4.25 [d, $^2J_{HH} = 14.9$ Hz, 2H, CH_2], 4.20 [d, $^2J_{HH} = 13.4$ Hz, 2H, CH_2], 6.6–7.84, [PC_6H_5, and CC_6H_5], 1.97 [s, 3H, CH_3CN]. IR: $\nu_{OH} = 3351$ cm^{-1}.

p-tert-Butylcalix[4]arene(OPPh$_2$·AuCl)$_3$(OH), **3**. A mixture of [AuCl(SMe$_2$)]$^-$ (0.147 g, 0.50 mmol) and *p-tert*-butylcalix[4]arene(OPPh$_2$)$_3$(OH), **2c**, (0.20 g, 0.167 mmol) in CH_2Cl_2 was stirred at room temperature for 15 h. The CH_2Cl_2 and SMe$_2$ were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 (4 mL) and crystallized by diffusion with MeCN (10 mL). A white solid (0.17 g, yield 53.6%) was obtained, washed with MeCN and dried under vacuum. *Anal. Calc.* for **3** $C_{80}H_{83}Au_3Cl_3O_4P_3$·$CH_2Cl_2$: C, 49.1; H, 4.3; *Found*: C, 48.7; H, 4.0%. Spectroscopic data of **3**: NMR in CD_2Cl_2: $\delta(^{31}P) = 117.8$ [s, 2P], 114.8 [s, 1P]. $\delta(^1H) = 0.93$ [s, 18H, t-Bu], 0.99 [s, 9H, t-Bu], 1.25 [s, 9H, t-Bu], 2.91 [d, $^2J_{HH} = 12$ Hz, 2H, CH_2], 3.16 [d, $^2J_{HH} = 14.8$ Hz, 2H], 3.38 [d, $^2J_{HH} = 14.8$ Hz, 2H], 3.51 [s, 1H, OH], 3.66 [d, $^2J_{HH} = 13.6$ Hz, 2H, CH_2], 6.59 [t, $J_{HH} = 4.6$ Hz, 4H, ArH], 6.95 [d, $J_{HH} = 8.4$H, 4H, ArH], 7.3–7.9 [m, 30H, PC_6H_5], 5.33 [s, 2H, CH_2Cl_2]. IR: $\nu_{OH} = 3366$ cm^{-1}.

p-tert-Butylcalix[4]arene(OPPh$_2$AuCl)$_4$, **4a**. A mixture of [AuCl(SMe$_2$)] (0.17 g, 0.58 mmol) and *p-tert*-butylcalix[4]arene(OPPh$_2$)$_4$, **2a**, (0.20 g, 0.145 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 15 h. The CH_2Cl_2 and SMe$_2$ were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 and crystallized by diffusion with MeCN. Platelike colourless crystals (0.25 g, yield 74.5%) were obtained, washed with MeCN and dried under vacuum. Spectroscopic data of **4a**: *Anal. Calc.* for **4a** $C_{92}H_{92}Au_4Cl_4O_4P_4$·MeCN: C, 47.9; H, 4.1; *Found*: C, 48.1; H, 4.2%. NMR in CD_2Cl_2: $\delta(^{31}P) = 115.9$ [s]. $\delta(^1H) = 1.03$ [s, 36H, t-Bu], 1.97 [s, 3H, CH_3CN], 2.61 [d, $^2J_{HH} = 13.2$ Hz, 4H, CH_2], 4.44 [d, $^2J_{HH} = 13.2$ Hz, 4H, CH_2], 6.69 [s, 8H, ArH], 7.15–7.20 [m, 16H, PC_6H_5, meta to P], 7.42–7.48 [m, 8H, PC_6H_5, para to P], 7.62–7.70 [m, 16H, PC_6H_5, ortho to P].

p-tert-Butylcalix[4]arene(OPPh$_2$AuCCPh)$_4$, **4b**. A mixture of [(AuCCPh)$_n$] (0.17 g, 0.58 mmol) and *p-tert*-butylcalix[4]arene(OPPh$_2$)$_4$, **2a**, (0.20 g, 0.145 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 15 h. The same procedure as above was used and a white solid (0.19 g, yield 49.9%) was obtained and washed with MeCN and dried under vacuum. Spectroscopic data of **4b**: *Anal. Calc.* for **4b** $C_{124}H_{112}Au_4O_4P_4$·MeCN: C, 56.4; H, 4.4; *Found*: C, 56.5; H, 4.2%.

NMR in CD_2Cl_2: $\delta(^{31}P) = 132.3$ [2]. $\delta(^1H) = 1.04$ [s, 36H, t-Bu], 1.97 [s, 3H, CH_3CN], 2.69 [d, $^2J_{HH} = 13.4$ Hz, 4H, CH_2], 4.57 [d, $^2J_{HH} = 13.4$ Hz, 4H, CH_2], 5.30 [s, 4H, CH_2Cl_2], 6.70 [s, 8H, ArH], 7.07–7.84 [m, 68H, PC_6H_5, and CC_6H_5].

p-tert-Butylcalix[4]arene(OPPh₂)₄(PtCl₂)₂, **5a**. A mixture of [$PtCl_2(SMe_2)_2$] (0.12 g, 0.30 mmol) and *p-tert*-butylcalix[4]arene(OPPh₂)₄, **2a**, (0.20 g, 0.145 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 15 h. The CH_2Cl_2 and SMe_2 were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 and crystallized by diffusion with MeCN. A white solid (0.18 g, yield 67.1%) was obtained, washed with MeCN and dried under vacuum. *Anal. Calc.* for **5a** $C_{92}H_{92}Cl_4P_4Pt_2O_4\cdot MeCN$: C, 57.6; H, 4.9; *Found*: C, 57.9; H, 5.1%. Spectroscopic data of **5a**: NMR in CD_2Cl_2: $\delta(^{31}P) = 83.5$ [s, $^1J_{Pt-P} = 4364.5$ Hz]. $\delta(^1H) = 0.90$ [s, 36H, t-Bu], 2.01 [s, 3H, CH_3CN], 2.88 [d, 2H, $^2J_{HH} = 14$ Hz, CH_2, exo], 2.91 [d, 2H, $^2J_{HH} = 14$ Hz, CH_2, exo to P—Pt—P ten-membered ring], 4.49 [d, 2H, $^2J_{HH}$ = 14 Hz, CH_2, endo], 5.85 [dt, 2H, $^2J_{HH} = 14$ Hz, $^5J_{PH} = 3.4$ Hz, CH_2, endo to P—Pt—P ten-membered ring], 6.30 [s, 4H, ArH, endo to P—Pt—P ten-membered ring], 6.47 [s, 4H, ArH, exo to P—Pt—P ten-membered ring], 7.33–7.46 [m, 16H, PC_6H_5, para to P], 7.60–7.70 [m, 8H, PC_6H_5, meto to P], 8.12–8.22 [m, 16H, PC_6H_5, ortho to P].

p-tert-Butylcalix[4]arene(OPPh₂)₄(PdCl₂)₂, **5b**. A mixture of [$PdCl_2(PhCN)_2$] (0.08 g, 0.29 mmol) and *p-tert*-butylcalix[4]arene(OPPh₂)₄ **2a** (0.20 g, 145 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 15 h. The CH_2Cl_2 and SMe_2 were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 and crystallized by diffusion with MeCN. A white solid (0.11 g, yield 43.7%) was obtained, washed with MeCN and dried under vacuum. *Anal. Calc.* for **5b** $C_{92}H_{92}Cl_4P_4Pd_2O_4\cdot MeCN$: C, 63.4; H, 5.4; *Found*: C, 63.8; H, 5.4%. Spectroscopic data of **5b**: NMR in $CDCl_3$: $\delta(^{31}P) = 115.7$ [s]. $\delta(^1H) = 0.89$ [s, 36H, t-Bu], 2.07 [s, 3H, CH_3CN], 2.78 [d, 2H, $^2J_{HH} = 13.6$ Hz, CH_2, exo], 2.81 [d, 2H, $^2J_{HH} = 13.6$ Hz, CH_2, exo to P—Pt—P ten-membered ring], 4.38 [d, 2H, $^2J_{HH}$ = 14 Hz, CH_2, endo], 5.90 [dt, 2H, $^2J_{HH} = 14$ Hz, $^5J_{PH} = 3.4$ Hz, CH_2, endo to P—Pt—P ten-membered ring], 6.28 [s, 4H, ArH, endo to P—Pt—P ten-membered ring], 6.48 [s, 4H, ArH, exo to P—Pt—P ten-membered ring], 7.33–7.47 [m, 16H, PC_6H_5, para to P], 7.55–7.70 [m, 8H, PC_6H_5, ortho to P].

CRYSTAL STRUCTURE ANALYSIS OF **1a·**MeCN

Crystal data. $C_{44}H_{56}O_4\cdot CH_3CN$, M = 689.98, T = 123 K, tetragonal, space group $P4/n$ (origin at $\bar{1}$ a = 12.7194(4), c = 12.7668(3) Å, V = 2065.5(1)) Å³, Z = 2, $D_{calc} = 1.109$ g cm⁻³, F(000) = 748, MoK$_\alpha$ X-rays, $\lambda = 0.71073$ Å, $\mu = 0.65$ cm⁻¹.

Measurements. The unit cell dimensions were obtained by a least-squares treatment of the setting angles of 25 reflections with $11° < \theta(MoK_\alpha) < 13°$. The

TABLE I. Fractional coordinates and equivalent isotropic displacement parameters (Å^2) of nonhydrogen atoms.

	x/a	y/b	z/c	U^*
O(1)	0.1147(1)	0.1861(1)	-0.0561(1)	0.019
C(2)	0.0655(1)	0.1573(1)	0.0363(1)	0.015
C(4)	-0.0038(1)	0.2298(1)	0.0814(1)	0.01
C(5)	0.1607(1)	-0.0190(1)	0.0362(1)	0.015
C(6)	0.0828(1)	0.0593(1)	0.0819(1)	0.014
C(7)	0.0282(1)	0.0344(1)	0.1740(1)	0.016
C(8)	-0.0422(1)	0.1035(1)	0.2207(1)	0.016
C(9)	-0.0563(1)	0.2012(1)	0.1726(1)	0.015
C(11)	-0.1059(2)	0.0762(2)	0.3189(1)	0.021
C(12)	-0.2233(2)	0.0757(2)	0.2911(2)	0.029
C(16)	-0.0861(2)	0.1598(2)	0.4039(2)	0.031
C(20)	-0.0773(2)	-0.0361(2)	0.3632(2)	0.034
C(28)	1/4	1/4	0.3688(7)	0.080
C(29)	1/4	1/4	0.2488(4)	0.038
N(27)	1/4	1/4	0.4677(7)	0.124

$^*U$ is one third of the trace of the orthogonalised anisotropic displacement tensor.

intensities of 4860 reflections with $1° < \theta\text{Mo}K_\alpha < 27°$, h 0–16, k 0–16, l 6–16, were determined from $\omega/2\theta$ scans. Those of two standard reflections, remeasured every 2 h, showed random fluctuations of $< 3.2\%$ about their mean values. All measurements were made at 123 K on an Enraf–Nonius diffractometer. Averaging, assuming $4/m$ Laue symmetry, gave $R_{\text{int}} = 0.037$ for 2155 unique intensities measured more than once and yielded 2257 independent structure amplitudes of which 1846 with $I > 3\sigma(I)$ were used in the subsequent analysis.

Structure Analysis. The positions of the nonhydrogen atoms were obtained by direct methods [16]. Further progress was only possible after it was realised that the specimen crystal was twinned. Using the program CRYSTALS [17] the function $\sum \omega(|F_{\text{obs}}| - |F_{\text{calc}}|)^2$ was minimised with $|F_{\text{calc}}| = [pF^2(hkl) + (1 - p)F^2(khl)]^{1/2}$; p defines the relative amounts of the two twin components and $F(hkl)$ is the calculated structure factor for an untwinned crystal (with $p = 0$). Refinement of 176 parameters converged at $R = 0.052$ and $R_\omega = 0.059$, with $p = 0.715(2)$ and a maximum shifted/esd ratio < 0.001. Anisotropic displacement parameters were refined for nonhydrogen atoms. The hydrogen atoms of the calixarene host were observed in difference syntheses and their positional and isotropic displacement parameters were included in the refinement. The acetonitrile H-atoms were not located and are presumed to be disordered. Final parameters for nonhydrogen atoms are presented in Tables I and II.

TABLE II. Selected interatomic distances (Å) and angles(°).

(a) *Bond lengths:*			
C(2)—C(4)	1.400(2)	C(2)—C(6)	1.393(2)
C(4)—C(5′)	1.520(2)	C(4)—C(9)	1.391(2)
C(5)—C(6)	1.521(2)	C(6)—C(7)	1.402(2)
C(7)—C(8)	1.389(2)	C(8)—C(9)	1.398(2)
C(8)—C(11)	1.533(3)	C(11)—C(12)	1.535(4)
C(11)—C(16)	1.540(4)	C(11)—C(20)	1.527(4)
C(28)—C(29)	1.532(11)	O(1)—C(2)	1.385(2)
C(28)—N(27)	1.263(13)		

(b) *Bond angles:*			
C(29)—C(28)—N(27)	180.0	O(1)—C(2)—C(4)	117.4(2)
O(1)—C(2)—C(6)	121.4(2)	C(4)—C(2)—C(6)	121.1(2)
C(2)—C(4)—C(5′)	121.8(2)	C(2)—C(4)—C(9)	118.3(2)
C(5′)—C(4)—C(9)	119.8(2)	C(4″)—C(5)—C(6)	111.6(2)
C(2)—C(6)—C(5)	121.9(2)	C(2)—C(6)—C(7)	118.3(2)
C(5)—C(6)—C(7)	119.8(2)	C(6)—C(7)—C(8)	122.4(2)
C(7)—C(8)—C(9)	117.2(2)	C(7)—C(8)—C(11)	123.3(2)
C(9)—C(8)—C(11)	119.5(2)	C(4)—C(9)—C(8)	122.6(2)
C(8)—C(11)—C(12)	109.0(2)	C(8)—C(11)—C(16)	109.5(2)
C(8)—C(11)—C(20)	112.4(2)	C(12)—C(11)—C(16)	109.0(2)
C(12)—C(11)—C(20)	108.3(3)	C(16)—C(11)—C(20)	108.7(2)

(c) *Torsion angles:*			
O(1)—C(2)—C(6)—C(5)	3.3(2)	C(9″)—C(4″)—C(5)—C(6)	88.6(2)
C(4″)—C(5)—C(6)—C(2)	89.6(2)	C(4″)—C(5)—C(6)—C(7)	-88.7(2)
C(7)—C(8)—C(11)—C(12)	-116.0(3)	C(7)—C(8)—C(11)—C(16)	124.9(3)
C(7)—C(8)—C(11)—C(20)	4.1(2)		

3. Results and Discussion

The calixarene system is known to be a clathrating agent for organic molecules [2, 18]. The determination of the crystal structure of **1a·MeCN** affords yet another illustration of this property. The calixarene host is centred around a crystallographic C_4 axis in the expected symmetrical cone conformation. The linear guest molecule occupies the resulting bowl-shaped cavity; its C and N atoms lie on the central C_4 axis of the calix with the methyl group directed towards the lower rim formed by the four hydroxyl groups (see Figure 1). The acetonitrile C—C and C—N bond lengths [1.53(1) and 1.26(l) Å] are sufficiently different from accepted values [1.47 and 1.14 Å, see Ref. 19] to suggest that the positions of atoms C(29), C(28) and N(27) are subject to systematic error which may arise from the complications caused by twinning (*vide supra*) or from the failure to include the disordered methyl
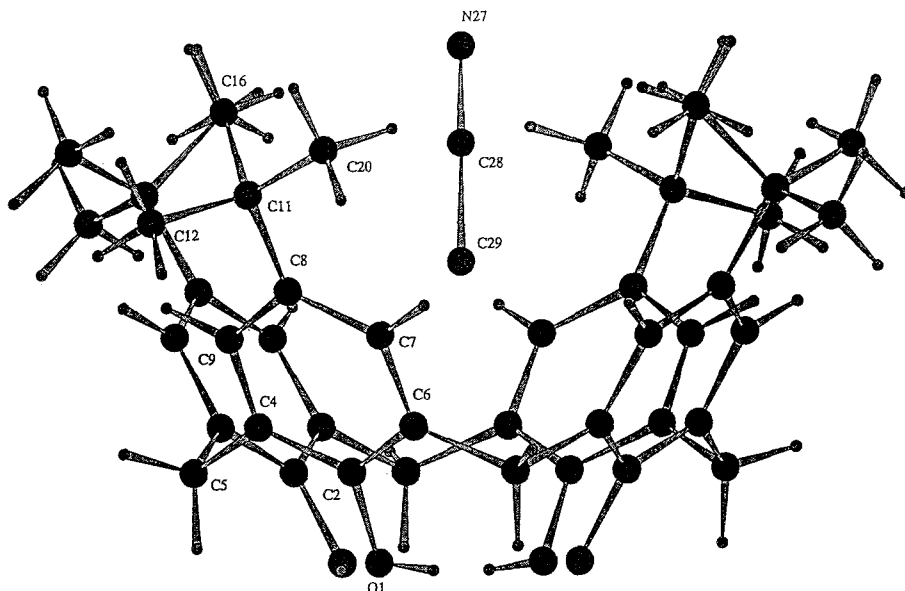
Fig. 1.   A view of the *t*-butylcalix[4]arene host and its acetonitrile guest.

group hydrogen atoms attached to C(29) in the structure analysis. Some caution is therefore necessary in the interpretation of the shortest contacts between the host and the guest atoms C(29), C(28) and N(27), namely C(29)$\cdots$C(2) 3.776(4) and C(28)$\cdots$C(16) 4.449(3) Å; N(27) is more than 5.0 Å from any C or O atom of its host calixarene. These distances suggest that the acetonitrile methyl group is wedged into the bowl of **1a**, whereas the environments of C(28) and N(27) are more open. The progressive increase in the mean displacement parameters, U, along the sequence C(29)—C(28)—N(27) (see Table I) is consistent with this view.

   The symmetrical cone conformation of **1a** found here may be characterised by the dihedral angle of 123.1° between the phenyl ring plane and that of the four hydroxyl oxygen atoms; similar values of 122.6°–125.8° have been found for the corresponding angles in **1a**·toluene [20], **1a**·dimethyl sulphoxide [21], (**1a**)$_2$·anisole [22] and (**1a**-H)·Cs(MeCN) [23]. In all of these complexes the **1a** host has exact C_4 symmetry and the disordered guest straddles the central C_4 symmetry axis of the calix cavity. Alternatively, the conformation of **1a** may be specified, as recently suggested by Ugozzoli and Andreetti [23], in terms of the point symmetry of the calixarene and of the torsion angles, ϕ and χ, about each of the independent C(aromatic)—CH$_2$ bonds [in Table II ϕ = C(9″)—C(4″)—C(5)—C(6) and χ = C(4″)—C(5)—C(6)—C(7)]; for **1a**·MeCN the conformation is specified as C4 +88.6(2) -88.7(2)°; for comparison, the **1a**·toluene complex is described by Ugozzoli and Andreetti as C4 +88.9 -89.4° and the similarity of the conformations of the **1a** hosts in the MeCN and toluene complexes is thereby strikingly revealed. As has been found in the structures of other calixarene
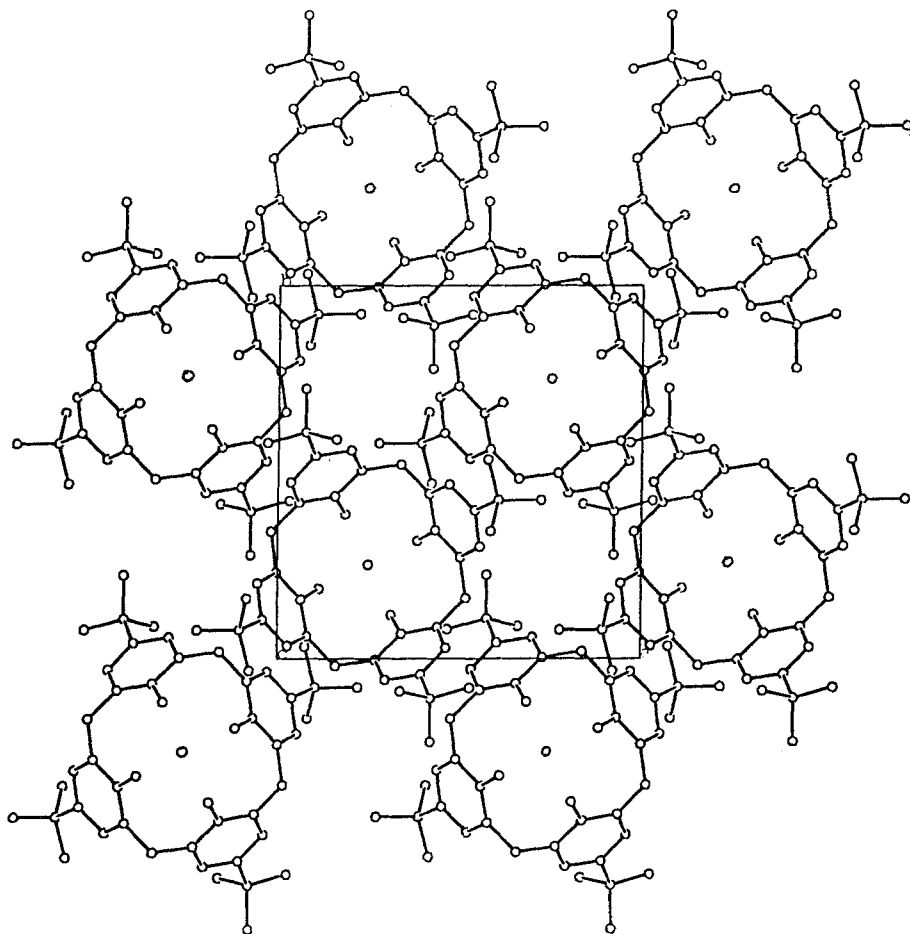
Fig. 2.   The unit cell contents of **1a**·MeCN crystals viewed in projection down c. The cell origin is at the lower left corner, a is horizontal and b is vertical.

complexes the hydroxyl rim of the calix cavity in **1a**·MeCN is supported by O—H···O hydrogen bonds, although the O(1)···O(1) separation of 2.692(2) Å is slightly greater than corresponding values in related complexes [e.g. 2.670(9) Å in **1a**·toluene and 2.652(4) and 2.654(5) Å in (**1a**)$_2$·anisole].

Bond lengths and angles within **1a** (Table II) are unexceptional. The phenyl carbon atoms are coplanar to within 0.005(2) Å and the internal ring angles at C-substituted C(4), C(6) and C(8) are all ca. 2° less than 120°. O(1) and C(11) are displaced by 0.04–0.06 Å from the phenyl ring away from the C_4 axis and C(5) is displaced towards the axis by 0.04 Å. The t-butyl group has staggered conformations across its C—CH$_3$ bonds and its orientation brings C(20) close to the plane of the phenyl ring.

The crystal packing in **1a**·MeCN (Figure 2) contains two types of channel running parallel to the c-axis: the wider channels are centred on the four-fold

symmetry axes and contain the guest MeCN molecules; in addition, there are channels centred on the bar-4 axes at $(3/4, 1/4, z)$ and $(1/4, 3/4, z)$ which are evidently too narrow to accommodate even small guest molecules. There are only three $\mathbf{1} \cdots \mathbf{1a}$ contacts involving nonhydrogen atoms which are 0.1 Å less than the sum of the appropriate van der Waals radii: $C(2) \cdots C(5i)$, 3.497(2), $C(5) \cdots C(6i)$ 3.483(2) and $C(12) \cdots C(20ii)$ 3.789(4) Å (i: $-x$, $-y$, $-z$; ii: $-1/2 - y$, x, z). The arrangement shown in Figure 2 closely resembles that found in $\mathbf{1a}$·toluene [20], $\mathbf{1a}$·dimethyl sulphoxide [21] and $(\mathbf{1a}\text{-H})\cdot\text{Cs(MeCN)}$ [23]. These compounds are approximately isomorphous: they all crystallize in the tetragonal space group $P4/n$ with unit cells containing two $\mathbf{1a}$ residues and of similar dimensions (a = 12.7–13.1, c = 12.5–13.8 Å). For tetragonal crystals a condition for twinning is that the square of the $c : a$ axial ratio must approach a rational number [24]; this condition is nearly satisfied for most of the structurally characterised $\mathbf{1a}$ complexes (e.g. $\mathbf{1a}$·MeCN $c : a = 1.0037$; $\mathbf{1a}$·dimethyl sulphoxide $c : a = 1.02$ [21]) and it may well be that twinning is a general feature of the crystal structures of the complexes of $\mathbf{1a}$ and related calix[4]arenes with small organic molecules.

In solution, the ^{1}H-NMR spectra of $\mathbf{1a}$·MeCN and $\mathbf{1a}$·2MeCN did not give separate resonances for included MeCN and free MeCN. Therefore, a rapid equilibrium between included MeCN and free MeCN in solution is expected. Even in the solid state, the included MeCN is only loosely bound in the calixarene cavity and it can be completely removed *in vacuo* (0.1 mm Hg) in one day. However, the structure is important as a model for the calixarene part of the more complex molecules described below which, though they were often obtained in crystalline form, always failed to diffract sufficiently to allow X-ray structure determination. Instead it is necessary to rely on spectroscopic techniques, comparing the NMR spectra with that of the parent calixarene whose structure is known (Figure 1).

Since polydentate ligands play an important role in coordination chemistry, the preparation of new polydentate ligands with unusual geometry, which may then coordinate to transition metals in unusual ways, is highly desirable. Although the ligand $\mathbf{2a}$ has been reported previously [9, 11], this ligand is unstable to hydrolysis by traces of water. It also decomposes quickly when dissolved in the NMR solvent CDCl$_3$. However, by changing reaction conditions, the ligand $\mathbf{2c}$ with three PPh$_2$ donors at the bottom rim of the calixarene can be obtained in high yield. Its ^{1}H-NMR spectrum shows three Bu^t groups at δ 1.2, 1.1 and 1.15 in 1 : 1 : 2 ratio, corresponding to three different Bu^t environments. The methylene groups also show four sets of doublet resonances [2]. The ^{31}P{^{1}H}-NMR spectrum contained only two singlet resonances in a 2 : 1 ratio, as expected for $\mathbf{2c}$ in the cone conformation. Less symmetrical conformations can be discounted on this basis. The presence of the hydroxy group also was confirmed by the IR spectrum, which gives ν(OH) at 3351 cm^{-1}. The higher stability of $\mathbf{2c}$ than $\mathbf{2a}$ is attributed to steric relief when there is one less bulky PPh$_2$ group present.

It is expected that $\mathbf{2c}$ and $\mathbf{2a}$ will show different coordination to transition metals. Thus, treatment of $\mathbf{2c}$ with [AuCl(SMe$_2$)] gave a conformer of $\mathbf{3}$. The three PAuX
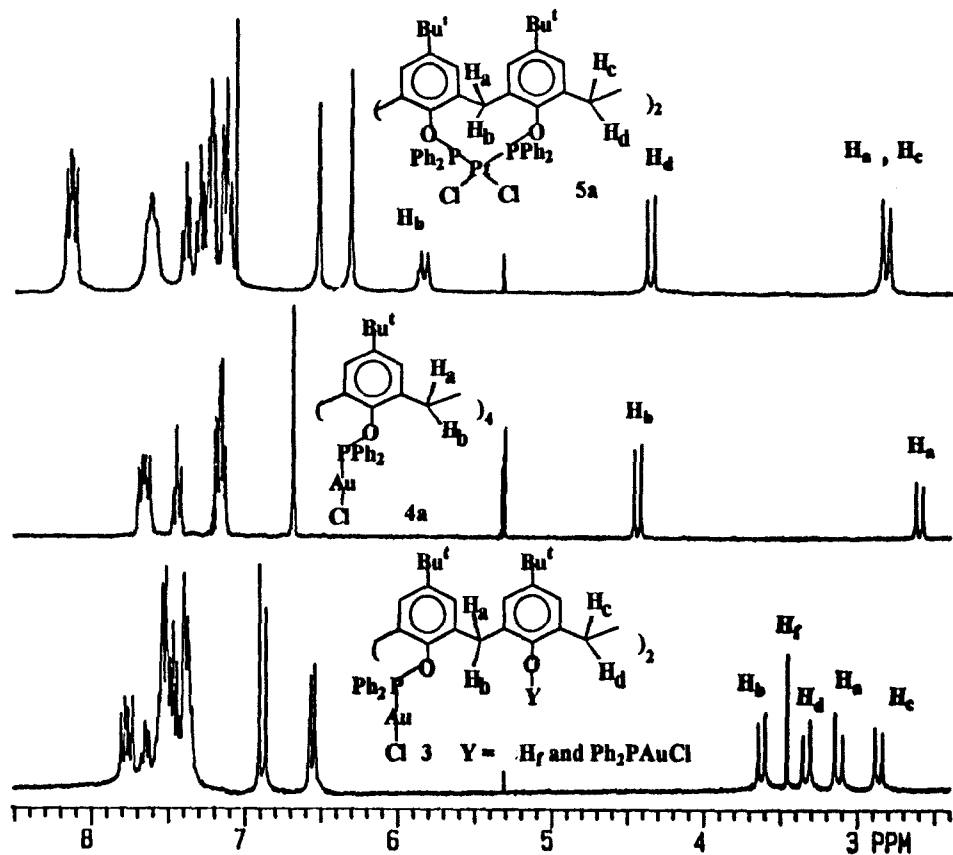
Fig. 3.   The ^{1}H-NMR spectra of **3**, **4a** and **5a** (the *t*-butyl groups are omitted for clarity).

units are not identical. The ^{31}P$\{^1$H$\}$-NMR spectrum shows two singlets at δ = 114.8 (s) and δ = 117.8 (s). The observation of four pairs of methylene resonances and three singlet Bu^t resonances clearly supports the proposed structure with three PPh$_2$ substituents (see Figure 3a). The FTIR spectrum also confirmed that the ArOH group was still present from the absorption band at ν(OH) = 3366 cm^{-1}.

In order to compare the behavioral difference between the tridentate phosphintocalix[4]arene **2c** and the tetradentate **2a**, compound **2a** has also been coordinated with some later transition metals. Thus, treatment of **2a** with [AuCl(SMe$_2$)] or [(AuCCPh)$_n$] gave the air and moisture stable tetrametal complexes, **4** (**4a**, X = Cl, **4b**, X = CCPh), containing one gold(I) per phosphorus atom. The four PAuX units are now identical as shown by the ^{31}P-NMR spectra [δ = 105 (s), X = Cl; δ = 135 (s), X = CCPh]. The complexes are highly symmetric and contain a golden rim at the bottom of the calix[4]arene. Since the bridging CH$_2$ groups may serve as spectroscopic probes [2], the structures and conformations of **4** are clearly indicated by their ^{1}H-NMR spectra (see Figure 3b). There is only one pair of methylene signals,

indicating that the calixarene bowls are still in the cone conformation. The inclusion behaviour of **4** is not as obvious as with other calixarenes [2]. Nevertheless, the complexes **4** crystallize with MeCN, which may be present inside the bowl, as in the precursor **1** (Figure 1) or outside the cavity forming a clathrate-like compound. The experimental data do not distinguish between these possible structures.

3   **4a**
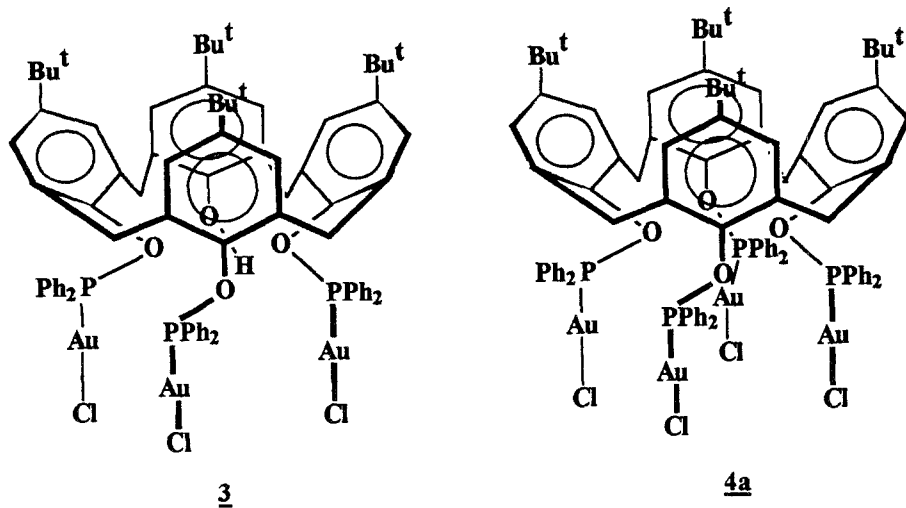
As expected, **2a** can either act as a monodentate ligand or as a chelating ligand. Reaction of [PtCl$_2$(SMe$_2$)$_2$] or [PdCl$_2$(PhCN)$_2$], with **2a** occurred with displacement of SMe$_2$ or PhCN to give the dimetal complexes, **5** (**5a**, M = Pt; **5b**, M = Pd) in which each metal is chelated by two phosphorus atoms. Though the four phosphorus atoms are still identical, as indicated by their ^{31}P-NMR spectra, there are two different pairs of methylene (ArCH_2Ar) resonances in the ^{1}H-NMR spectrum, indicating that the molecules no longer have four-fold symmetry (see Figure 3c). One of these pairs of resonances appears as two doublets at δ = 2.9 and 4.45, while the second pair appears as a doublet at δ = 2.9 and a doublet of triplets at δ = 5.9. The resonance with the extra triplet coupling is assigned to the protons on the CH$_2$ groups located between the chelating phosphorus atoms, and particularly to the two protons which are directed towards the metal atoms. These protons, embraced by the P—Pt—P ten-membered ring, couple not only to the geminal hydrogen but also to the two adjacent phosphorus atoms through space. This unusual [1]H—[31]P through space coupling was confirmed by excluding all other proton couplings by the homonuclear decoupling technique and by recording the COSY spectrum (see Figure 4). Molecular mechanics calculations [25] also indicate that the distance between H$_\alpha$ and the near ^{31}P atom is only 2.79 Å, and so it is reasonable to expect this through space coupling.

5 (5a: M=Pt; 5b: M=Pd)
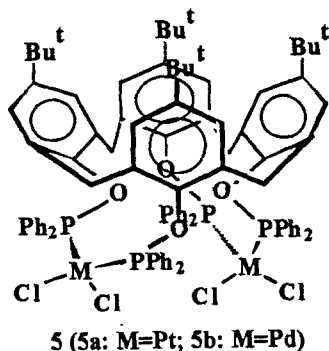
Although most of these transition metal complexes are crystalline compounds, none was suitable for X-ray analysis. Hence the question of the ability of the complexes to act as hosts for small molecules such as MeCN could not be answered with certainty.

4. Conclusions

When phosphinite groups are introduced into the lower rim of the calix[4]arene, the trisubstituted derivatives are more stable to hydrolysis than the tetrasubstituted derivatives. This is proposed to be due to lower steric strain in the trisubstituted compound. The introduction of bulky substituents, such as the Ph_2P groups described here, on the lower rim of the calixarene is also expected to affect the geometry of the bowl such that the bulky Bu^t groups on the upper rim will be forced closer together and so reduce the size of the entrance to the bowl. The introduction of additional metal substituents accentuates this effect. Such relatively minor conformational changes may, of course, have a considerable effect on subsequent host–guest chemistry.
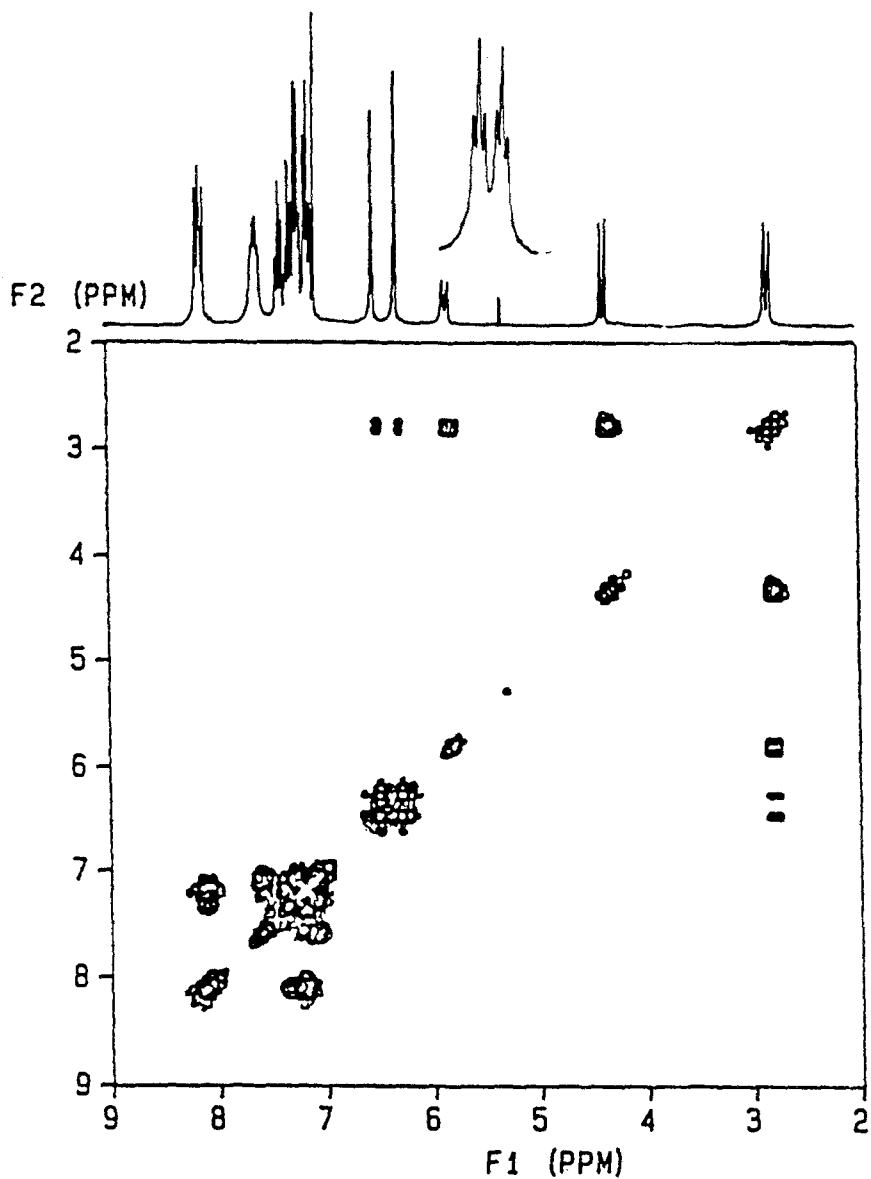
Acknowledgements

Fig. 4.   The two-dimensional ^{1}H—^{1}H correlated NMR spectrum (COSY) of complex **5a**. The triplet coupling in the resonance at $\delta = 5.9$ is shown in the expansion. Note that two resonances overlap accidentally at $\delta = 2.9$ and the correlations with resonances at $\delta = 5.9$ and 4.45 are clear.

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