Complexation of Cobalt(II) at the Upper Rim of Two New Calix[4]arene/Bipyridine-Based Podands

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Keywords: Calix[4]arenes / Bipyridines / Podands / Cobalt complexes

Introduction of one or two 2,2′-bipyridine units at the upper rim of the calix[4]arene platform was performed by means of the Wittig reaction. The resulting alkenes were hydrogenated to give two new bipyridyl-based calixarene podands, which were studied as ligands for Co^{II} cation. The mono-bipyridyldichlorocobalt complex was notably fully characterised by ^{1}H-NMR and X-ray crystal structure analyses, which confirmed the tetrahedral coordination mode involving the bipyridyl subunit and the two chlorine atoms around the cobalt centre.

Introduction

As recently reviewed by Matt et al.,[1] the calixarenes display interesting properties for transition metal chemistry, via their own binding sites (oxygens, aryl rings), or by their ability to act as carriers and spatial organisers of various types of chelating agents, such as esters, phosphanes, or heterocycles. In this domain, our contribution resulted in the synthesis and study of the complexation properties of various podands incorporating 2,2'-bipyridine and 2,2'-bithiazole chelating units at the lower rim of the tetra-*p*-*tert*-butylcalix[4]arene platform.

In order to develop a similar approach at the upper rim, but in a different way than through the potentially coordinating amide links developed by Beer and coll.,[3] we found that the Wittig reaction could be an interesting synthetic tool for building a new family of lipophilic ligands in which the chelating units would be attached by a stable and non-coordinating ethylenic linkage to the calixarene platform.

As a first step, this reaction was applied on the mono[*p*-(formyl)]tris[*p*-(*tert*-butyl)]calix[4]arene model, leading to the conjugated phenol-bipyridyl system **1**.[4] The relative instability of this ligand and its copper(I) complex ([**1**/Cu/**1**]PF_6),[5] especially on chromatographic supports, limited the interest of this family of unsaturated ligand in our field of investigations, and led us to develop the complexation studies of the corresponding saturated podands.

We thus present here the syntheses and some complexation properties towards Cobalt(II) of two new calixarene-based bipyridine ligands, in which the chelating units are bound by an ethylenic linkage to the upper rim of the calixarene platform.

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Results and Discussion

Syntheses of ligands (Scheme 1 *and Scheme* 2*)*. Ligand **2** was obtained quantitatively by catalytic hydrogenation of **1**, but we found it better to reduce the raw Wittig material directly, in order to eliminate the loss of **1** during chromatography. In this way, **2** was obtained in a yield of 40% *vs* the formylcalixarene platform, instead of 27% with isolation of **1**.

The synthetic strategy developed for the disubstituted podand **3** was similar to **1** and **2**, and involved a selective double deterbutylation of the tetra-*p*-*tert*-butylcalix[4]arene **4**, followed by a double Gross formylation[6] applied on the unprotected calixarene platform. The resulting aldehyde was then treated in alcoholic basic conditions with the monophosphonium salt of bipyridine **5** to give the corresponding diene which was directly catalytically hydrogenated into the desired armed calixarene.

The selective introduction of two chelates at the 5th and 17th positions of the calix[4]arene platform **4** involved a preliminary retro-Friedel and Crafts di-deterbutylation step developed by Gutsche and coll.[7] *via* a selective protective dinitrobenzoylation of two hydroxyl groups in diametrical positions. The resulting diester was obtained in three different acylation media, namely dichlorophenylphosphate/dinitrobenzoic acid/DMF/ pyridine, $AlCl_3$/dinitrobenzoyl chloride/DMF, or dinitrobenzoyl chloride/pyridine systems, with yields of 75, 67, and 95%, respectively. More recently, Huang and coll.[8] described the formation of the dibenzoyl analogue **6** in a benzoyl chloride/$CHCl_3$/NEt_3 medium with a yield of 68%. We found that **6** could easily be synthesised from **4** and benzoyl chloride using MeCN as solvent and K_2CO_3 as base, with a good yield of 91%.

The subsequent retro-Friedel and Crafts deterbutylation step was carried out in toluene using only five equivalents

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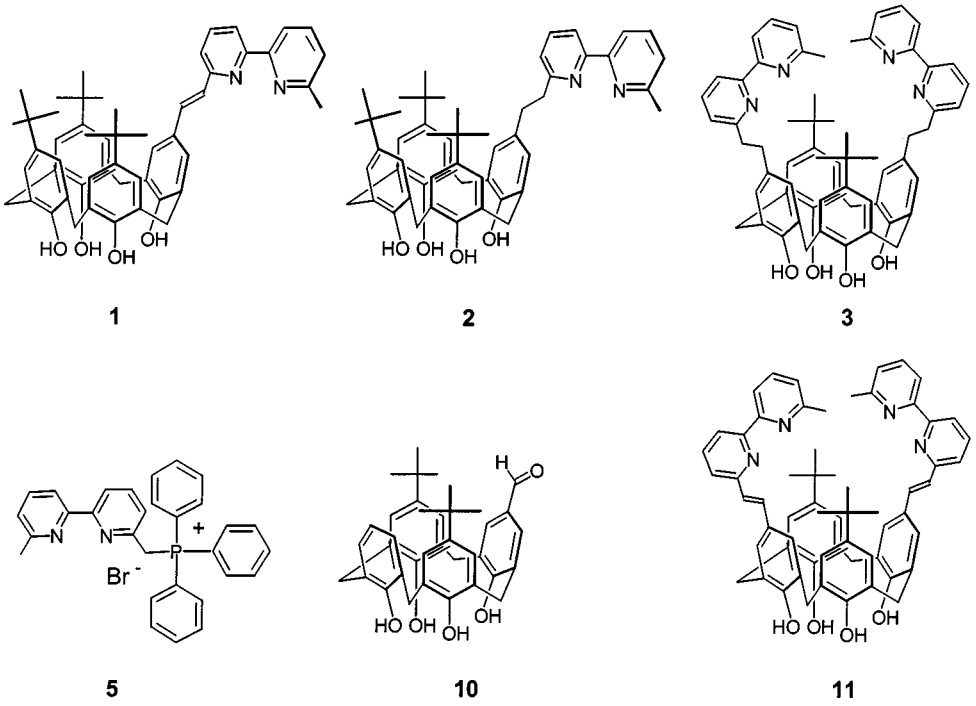
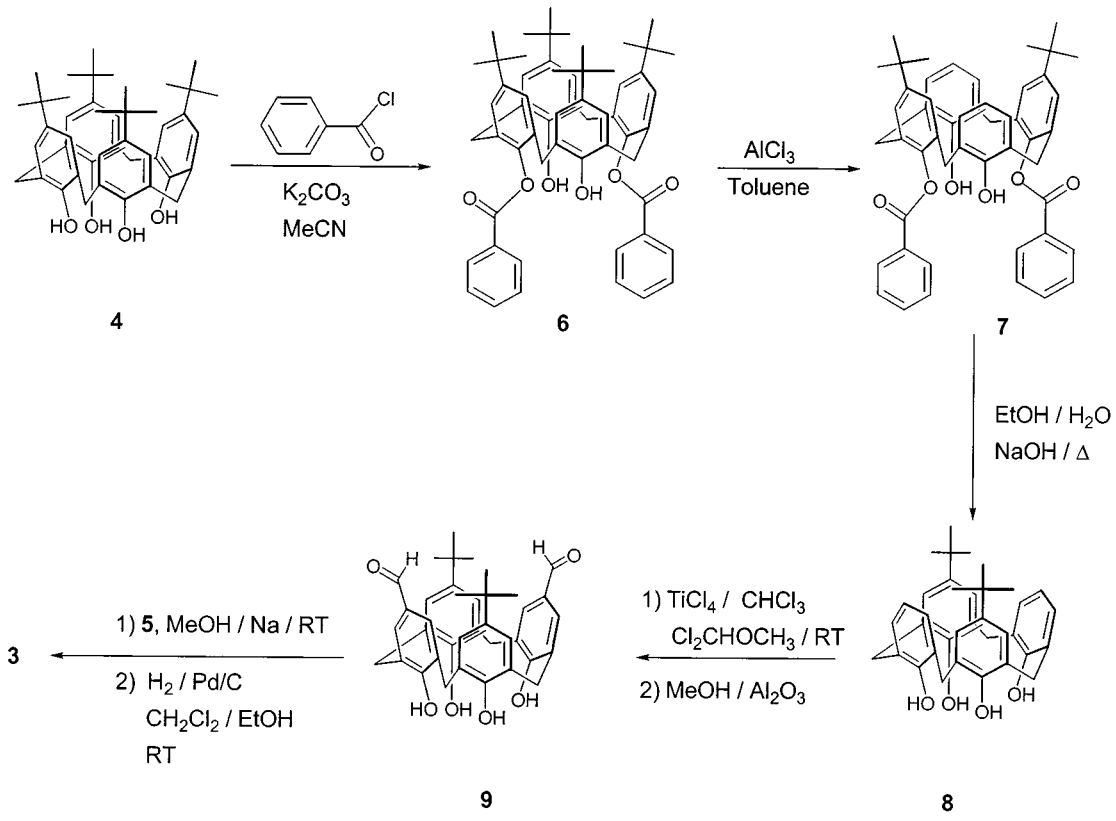


Scheme 1



Scheme 2

of $AlCl_3$ relative to **6**. The reaction was initiated by a gentle warming and was completed in ca. 1–2 hours, giving **7** with a yield of 80%. Based on the recent work of Magrans and coll., dedicated to the conformational study of 1,3-di-*O*-benzoylated calix[4]arenes,[9] the ^{13}C-NMR analyses of compounds **6** and **7** show that they should not be in a pure cone conformation. The resonance signals of the Ar–CH_2-Ar groups appear at δ = 33.39 and 33.84, respectively, between the standard δ = 31 and 37 values observed for the pure *syn* and *anti* conformations. This suggests that a rapid exchange between the conic and the 1,3-alternate conformations takes

place in solution. Nevertheless, for legibility, **6** and **7** are drawn in the conic conformation in Scheme 2.

The benzoate groups were then removed in alcoholic NaOH at reflux. The 11,23-di-*p*-*tert*-butylcalix[4]arene **8** was thus obtained in an almost quantitative yield.

Introduction of the two formyl groups at the upper rim of **8** failed when the previously described conditions were employed. The use of $TiCl_4$ instead of $SnCl_4$ was successful, affording the bis-aldehyde **9** and some mono-aldehyde **10,** in yields of 65 and 19%, respectively. It is interesting to note that, as previously mentioned,[4] a treatment of the raw electrophilic substitution material over Al_2O_3 was mandatory to liberate the formylated species.

Reaction of **9** with two equivalents of **5**[4] in the presence of an excess of NaOMe in MeOH afforded a mixture of compounds from which only low amounts of pure bis(alkene) **11** were isolated. For this reason, we preferred to hydrogenate the raw Wittig material directly. From the resulting mixture, the bisalkane **3** was isolated after chromatography in a yield of 22%.

Complexation Studies

Cobalt(II) Complex of 2

The reactivity of 6,6'-dimethyl-2,2'-bipyridine (dmbpy) towards Co^{II} cation has notably been studied by Newkome and coll., who prepared, based on UV/Vis spectroscopy and elemental analysis, the neutral tetrahedral $Co(dmbpy)Cl_2$ complex **12**.[10] The same approach applied to an octobipyridylcalix[4]resorcinarene ligand allowed us to prepare, based on UV/Vis spectroscopy, elemental and ES-MS analyses, the corresponding octodichlorocobalt species,[2b] which demonstrated that the presence of a bulky substituent close to the chelating site was not limiting the complexation process.

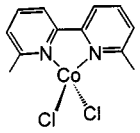
In **2** or **3**, the presence of the ethylenic linkage should give a more pronounced (dimethyl)bipyridine character to the chelating site than in the above-mentioned example, and therefore facilitate the coordination process of Co^{II}.

Thus, reacting **2** with one equivalent of anhydrous $CoCl_2$ in a $MeOH/CH_2Cl_2$ mixture at room temperature gave the light-blue complex **13** (Scheme 3), which was purified by chromatography on Sephadex LH20, and then crystallised as fine needles from a hexane/CH_2Cl_2 mixture. Unfortunately these were unsuitable for X-ray analysis. Elemental analysis was consistent with the presence of 0.2 equivalent of CH_2Cl_2.

The latter was found in the standard ^{1}H-NMR spectrum of **13**, which also did not display the resonance pattern of the bipyridyl group, thereby confirming the paramagnetic nature of the complex subunit. The remaining part of the molecule, out of the sphere of direct influence of Co^{II}, displayed resonance signals in the expected regions. In $CDCl_3$, at 300 MHz, two singlets assigned to *tert*-butyl groups were found at δ = 1.24 (9 H) and δ = 2.15 (18 H); four broad singlets located at δ = 2.50, 2.95, 3.34, and 3.94 (2 H each) were assigned to the Ar–CH_2-Ar groups, considering that the ethylenic bridge, which supports the effect of the cobalt cation, did not give resonance signals. Changing $CDCl_3$ for CD_2Cl_2 resulted in the transformation of these four singlets into two well-separated broad AB systems, confirming our previous assignment and suggesting a probable rigidification due to a specific interaction between this solvent and the macrocycle.

In the aromatic part, two sharp singlets at δ = 6.92 and 7.06, and a broad one at δ = 7.82, each integrating 2H, were assigned to the aromatic protons of the unsubstituted phenol rings. Finally, a broad singlet located at δ = 9.32 was assigned to the four hydroxyl groups.

The fact that the resonance signals of protons close to the metallic centre, with regards to the supposed structure of complex **13**, are absent in these classical analytical conditions led us to seek them in a larger frequency domain. Recording data over 65000 Hz (216 ppm at 300 MHz) allowed the exhibition of ten new signals: six relatively sharp singlets ($\Delta\nu_{1/2}$ = 30–38 Hz) integrating for 1 H each, at δ = 70.71, 69.92, 49.10, 46.67, –14.77, and –15.72 that we suspect correspond to the bipyridine protons; a larger singlet



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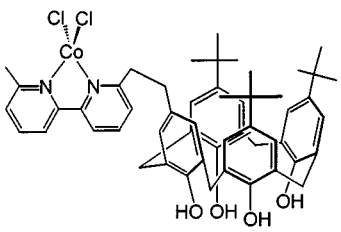

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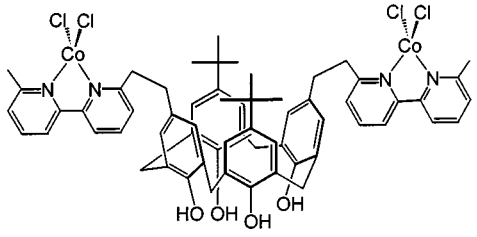

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Scheme 3

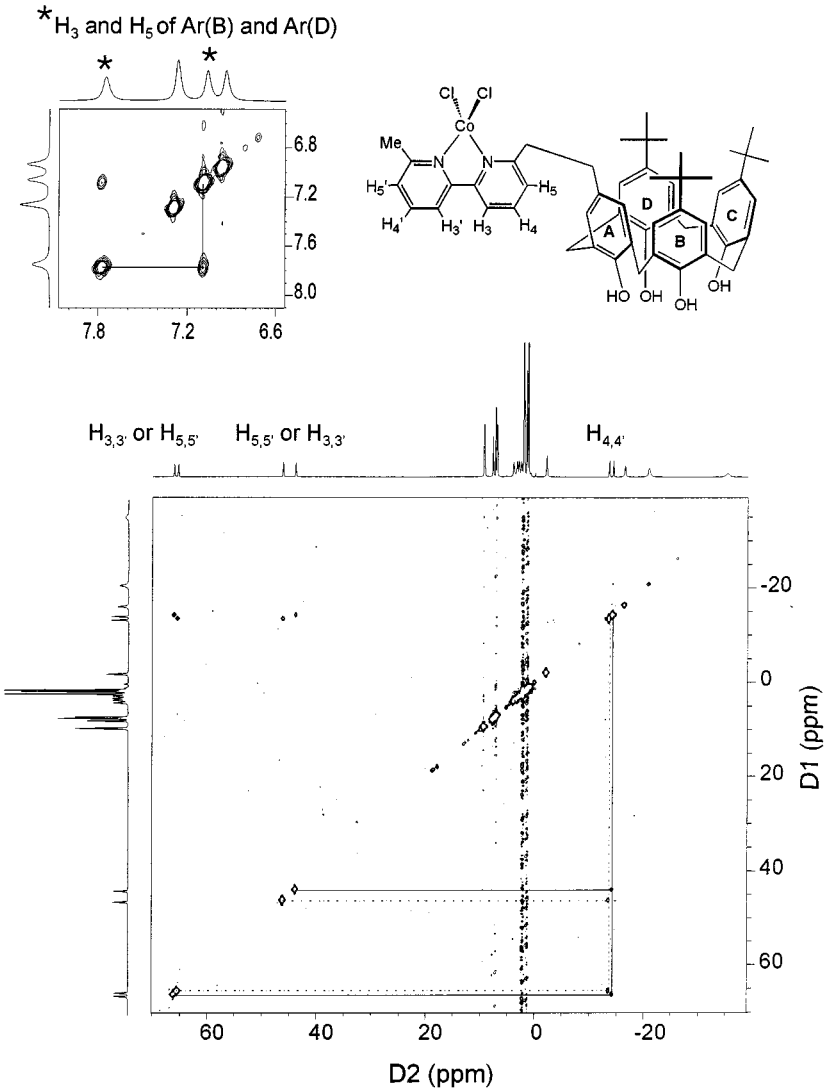


Figure 1. COSY correlations between protons of complex **13** ($CDCl_3$, 500 MHz, 293 K) (main spectrum: bipyridine resonance pattern; offset: aryl resonance pattern)

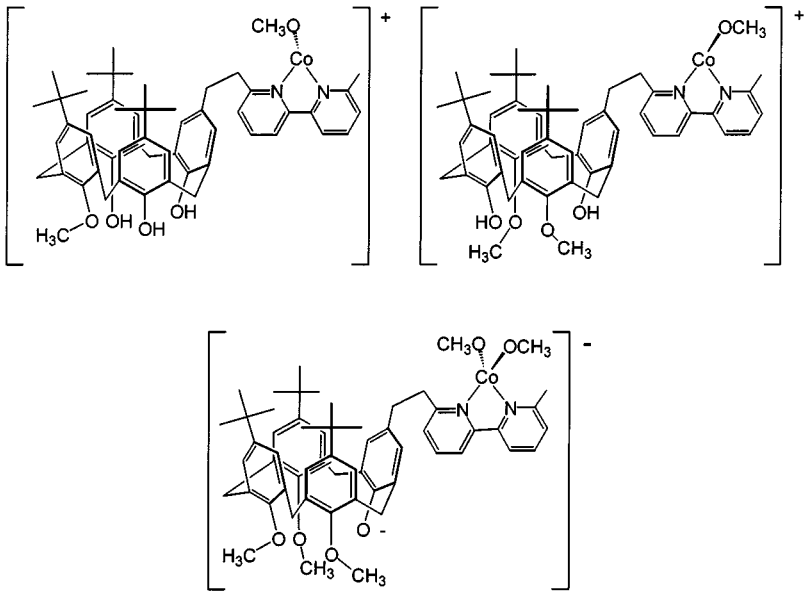
at δ = –2.63 ($\Delta\nu_{1/2}$ = 48 Hz) integrating for 2 H, which was assigned to the substituted phenol ring protons, and three large singlets, one integrating for 2 H ($\Delta\nu_{1/2}$ = 92 Hz) at δ = –17.21, another one integrating for 3 H ($\Delta\nu_{1/2}$ = 169 Hz) at δ = –21.68, and the last singlet integrating for 2 H ($\Delta\nu_{1/2}$ = 300 Hz) at δ = –37.73, which were assigned to the CH_2-phenol, the CH_3-bpy and the CH_2-bpy groups, respectively.

Working at 500 MHz resulted in slight changes in chemical shifts (see Experimental Section). 500-MHz COSY experiment (58000 Hz, 116 ppm) (Figure 1) confirmed the attribution of the bipyridine protons, with two groups of signals at δ = 66.06, 43.87, –14.30, and δ = 65.35, 46.17, –13.52, the negative signals corresponding to the H(4) and H(4') spin systems. Another scalar correlation was found in the calixarene aromatic region between the singlets at δ = 7.75 and δ = 7.07, which were thus assigned to the two lateral phenol rings.

UV/Vis spectroscopy of **13** in CH_2Cl_2 showed a complex ligand-centred absorption pattern associated with a metal-centred transition at 655.5 nm with a molar extinction coefficient of ca. 530 $dm^3.mol^{-1}.cm^{-1}$, identical to the values reported for **12** and corresponding to a tetrahedral coordination mode.[10]

ES-MS analysis confirmed the formation of **13**. The preliminary measurements were performed in CH_2Cl_2 containing some MeOH as proton source. In the positive mode, three peaks corresponding to species containing the native ligand **13** were observed at 846.5, 811.6 and 789.7 a.m.u. and were attributed to the mono-charged cations [**13** – $2Cl^-$ – H^+]$^+$, [**13** – $CoCl_2$ + Na^+]$^+$, and [**13** – $CoCl_2$ + H^+]$^+$, respectively. They were accompanied by compounds of higher molecular weights which were analysed as complex **13** in which one or two phenol groups were *O*-methylated and one chlorine was exchanged with a methoxy anion: 906.6 a.m.u. [$(CH_3O)_2$ **13**–$2Cl^-$ + CH_3O^-]$^+$ and 892.6 a.m.u. [(CH_3O) **13**–$2Cl^-$ + CH_3O^-]$^+$ (Scheme 4).

In the negative mode, which usually gives, in the calixarene family, the mono- or polyphenate anions, the same phenomenon was observed at –50 V, but with a much lower



Scheme 4

intensity, the base peak at 787.6 a.m.u. corresponding to the deprotonated ligand **2**. The molecular peak was observed at 916.6 a.m.u. [**13** – H^+]$^-$, accompanied by the mono- and the bis-dehalogenated species at 880.5 a.m.u. [**13** – Cl^- – $2H^+$]$^-$ and 844.5 a.m.u. [**13** –$2Cl^-$ – $3H^+$]$^-$, respectively. Three peaks at 950.6, 940.6, and 926.6 a.m.u. were attributed to complexes containing one tris-, one bis-, and one monomethylated ligand with a double or single anion metathesis, i.e. [$(CH_3O)_3$**13** –$2Cl^-$ + $2CH_3O^-$ – H^+]$^-$ (Scheme 4), [$(CH_3O)_2$**13** – Cl^- + CH_3O^- – H^+]$^-$, and [(CH_3O) **13** – Cl^- + CH_3O^- – H^+]$^-$. We found in fact, that these methylation reactions and anion metatheses occurred during the analysis: changing the solvent for alcohol-free CH_2Cl_2 (stabilised with 2-methyl-2-butene), gave, in the positive mode (+ 80 V), peaks at 882.5, 846.6, and 789.9 5 a.m.u. which were attributed to [**13** – Cl^-]$^+$, [**13** –$2Cl^-$ – H^+]$^+$, and [**13** – $CoCl_2$ + H^+]$^+$, respectively.

Blue single crystals of complex **13**, suitable for X-ray diffraction analysis, were obtained in a closed tube by liquid diffusion of Et_2O into a solution of **13** in CH_2Cl_2. This study confirmed the presence of the expected dichlorocobalt-bipyridine complex subunit attached by an ethylene link to the upper rim of the tri-*tert*-butylcalix[4]arene platform (Figure 2). The cobalt cation is coordinated in a distorted tetrahedral mode to the two bipyridyl nitrogen atoms and to the two chlorine anions (Table 1), confirming the hypothesis of Newkome et al.[10] The bipyridyl group is parallel to the supporting phenol ring **A**, making with it an angle of only 4.25°.

The cyclic tetramer is in a boat-shaped cone conformation, with the expected usual hydrogen bonds between the hydroxyl groups (2.608–2.731 Ä). The angles between the phenol rings **A**, **B**, **C**, and **D**, and the mean plane defined by the methylene bridges amount to 122.7(2), 118.0(2), 132.7(1), and 117.1(2)°, respectively. Surprisingly, the presence of the bulky complex substituent do not result in the leaning of the supporting phenol ring **A**, while **C**, in the alternate position, is strongly inclined. The *tert*-butyl group of the latter occupies two positions, differing by a rotation of about 60°, with occupancies of 51% and 49%.

Each complex unit is associated with a molecule of Et_2O and one of CH_2Cl_2. The former, which is not shown in Figure 2, is located between the macrocycles, while the latter is trapped into the calixarene cavity, on the level of the *tert*-butyl groups (Figure 3).[11] This molecule of CH_2Cl_2 is found in disordered positions called Cl20–C100–Cl10 (73%) (Figure 2), and Cl30–C200–Cl40 (27%); Cl20 and C200 on one part, Cl40 and C100 on the other part, are positioned on the same sites. The interactions between dichloromethane and calixarene are found between C100 and ring **C** (3.46 Å) and C200 and ring **A** (3.34 Å).

This specific complexation found in the solid state can be correlated with the modifications of the ^{1}H-NMR spectrum of complex **13**, which were previously observed between its $CDCl_3$ and CD_2Cl_2 solutions.

According to the proposal for classification and nomenclature of host-guest type compounds given by Weber and Josel,[12] compound **13** can be defined as a cryptato-tubulato clathrate.

Cobalt(II) Complex of 3

In a similar way, ligand **3** was reacted with two equiv. of $CoCl_2$ to give the dinuclear grey-blue complex **14**. The expected M_2L stoichiometry was verified by UV/Vis spectroscopy in CH_2Cl_2, with an ε value of 1030 dm^3 mol^{-1} cm^{-1} at 656.5 nm, twice the value of **13**, and by C, H, and N elemental analyses. Positive- or negative mode ES-MS analysis of **14** showed methylation reactions and anion metatheses similar to those observed with **13** when methanolic CH_2Cl_2 was used as the solvent (*see Experimental Section*). In the negative mode (–50 V), in alcohol-free CH_2Cl_2, the complex exhibited a single mass of peaks at 1185.5–1189.3

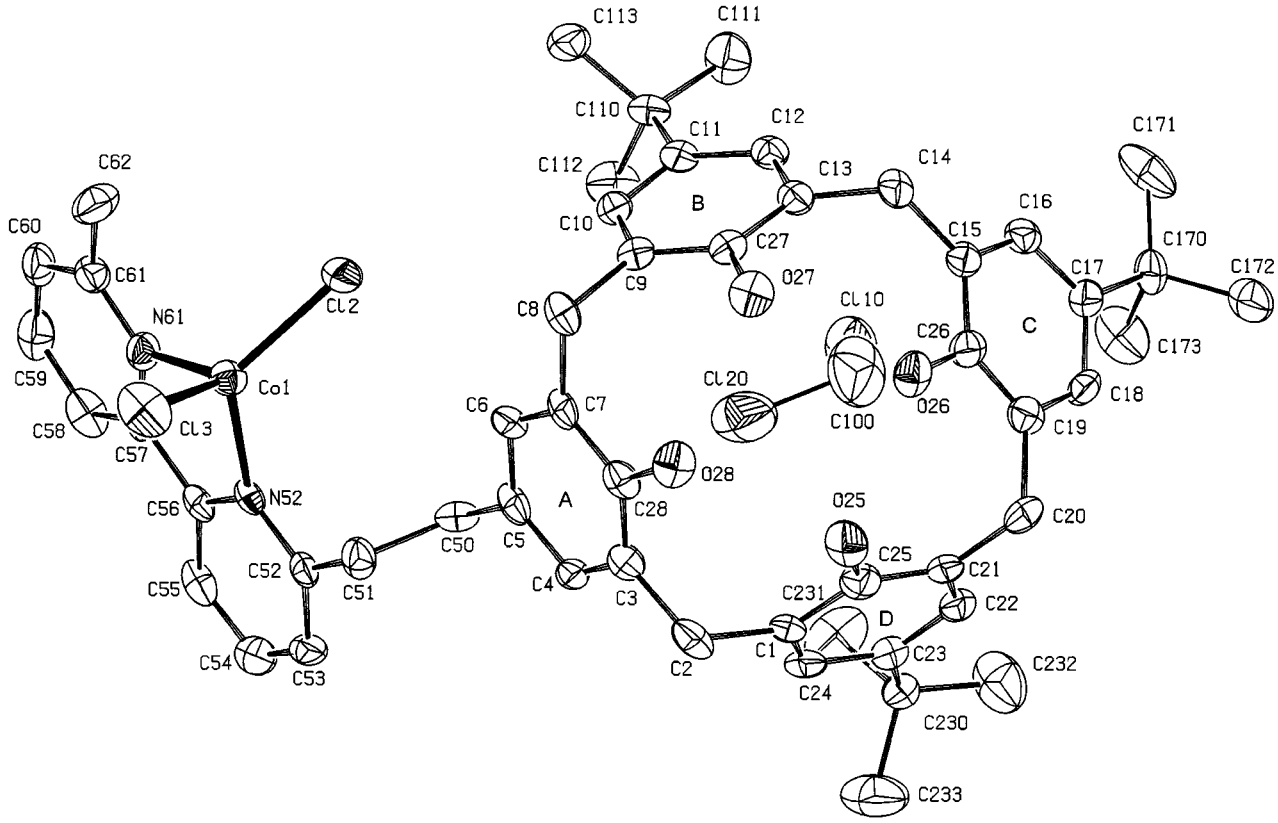


Figure 2. Numbering scheme and ORTEP underside-view of complex **13**

Table 1. Selected geometric parameters around the cobalt centre

Bond lengths [Å]			
Co–N52	2.021(5)	Co–N61	2.027(6)
Co–Cl2	2.213(2)	Co–Cl3	2.222(2)
Bond angles [°]			
Cl2–Co–Cl3	118.4(9)°	N52–Co–N61	82.3(2)
Cl2–Co–N52	119.6(2)°	Cl3–Co–N61	110.1(2)
N52–Co–Cl3	108.7(2)°	N61–Co–Cl2	112.0(2)

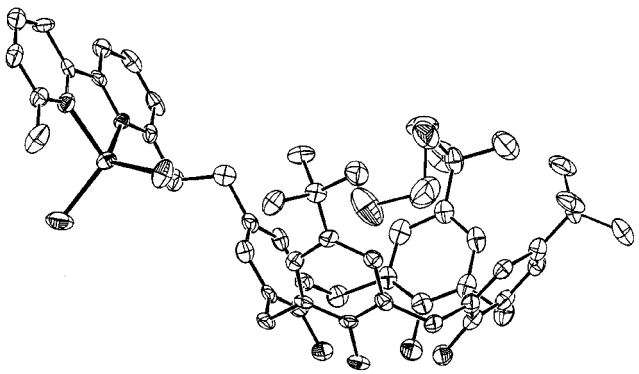


Figure 3. ORTEP side-view of complex **13**

a.m.u. which was attributed to the monophenate species [**14** – H^+]$^-$, confirming the results of UV/Vis and elemental analyses.

Unfortunately, the lack of solubility of **14** did not allow us to verify the ^{1}H-NMR results obtained with **13**.

Conclusion

By a Wittig reaction *plus* hydrogenation process, we have selectively incorporated one and two bipyridine units at the upper rim of *p*-(*tert*-butyl)calix[4]arene platforms. The two new ligands thus obtained displayed coordinating behaviour towards cobalt(II), and the resulting mono- and dinuclear complexes were fully characterised. With the monometallic species, ^{1}H-NMR COSY experiment performed on a large frequency domain allowed us to recover and to assign the bipyridine resonance signals, and X-ray analysis confirmed the tetrahedral coordination of the bipyridine and the two chlorine atoms around the cobalt centre. The complexation studies of other transition metal cations and the building of the tris- and tetra-substituted analogues are now under investigation.

Experimental Section

General: Melting points (°C, uncorrected) were determined on an Electrothermal 9100 in Capillary apparatus. – ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 300 or DRX 300 and DRX 500 ($CDCl_3$, TMS as internal standard, chemical shifts in ppm). – Mass spectra (electrospray, ES) were recorded on a Platform Mic-

romass apparatus at the Service Central d'Analyse du CNRS, Solaize. – Infrared spectroscopy was performed on a Mattson 5000 FT apparatus (KBr, $\tilde{\nu}$ in cm^{-1}). – UV spectra were recorded on a Shimadzu UV 2401 PC or a SAFAS UV mc^2 apparatus, λ_{max} in nm, ε in $dm^3\ mol^{-1}\ cm^{-1}$. – Elemental analyses were performed at the Service Central de Microanalyse, Ecole Supérieure de Chimie, Montpellier. – Macherey–Nagel TLC plates were used for chromatography analysis (SiO_2, Polygram SIL G/UV254, ref.805021). All commercially available products were used without further purification unless otherwise specified.

Calix[4]arene-25,26,27,28-tetrol 2. – Indirect Method: To a solution of 0.05 g of **1**[3] ($0.063 \cdot 10^{-3}$ mol) in 5 mL of EtOH/CH_2Cl_2, was added 0.01 g of 5% Pd/C, and H_2 was bubbled through the solution for 1 min. The mixture was stirred at room temp. overnight under H_2 and then filtered over Celite. Evaporation of the filtrate to dryness afforded 0.045 g of pure **2** (90%).

Direct Method: The raw Wittig material obtained from 0.5 g (0.8 mmol) of monoformylcalixarene was neutralised with 1 M HCl and evaporated to dryness. The resulting glassy material was dissolved in 50 mL of CH_2Cl_2, dried over Na_2SO_4 and concentrated to ca. 20 mL. EtOH (30 mL) and 0.2 g of 5% Pd/C were added, and the resulting mixture was stirred under H_2 overnight. The suspension was filtered over Celite and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and addition of MeOH resulted in the precipitation of a raw material which was purified by chromatography (Al_2O_3, CH_2Cl_2/hexane, then CH_2Cl_2/MeOH 99:1) to give 0.25 g of **2** (40%). –UV/Vis (CH_2Cl_2): λ (ε) = 281.0 (23390), 289.0 (24180), 304.0 (10400). – ^{1}H NMR ($CDCl_3$): δ = 1.198 (s, 9 H, *Me*$_3$C); 1.205 (s, 18 H, *Me*$_3$C); 2.62 (s, 3 H, *Me*bpy); 2.80–3.20 (*ABm*, 4 H, C*H*$_2$–C*H*$_2$); 3.45, 4.22 ("q", *AB*, *JAB* = 13 Hz, 4 H, Ar–C*H*$_2$-Ar); 3.45, 4.22 ("q", *AB*, *JAB* = 13 Hz, 4 H, Ar–C*H*$_2$-Ar); 6.93 (s, 2 H, Ar); 7.01–7.07 (m, 7H, 6 H of Ar, 1 H of bpy); 7.02 (d, *J* = 7.6 Hz, 1 H, bpy); 7.64 (t, *J* = 7.6 Hz, 1 H, bpy); 8.19 (*d*, *J* = 7.7 Hz, 1 H, bpy); 8.20 (d, *J* = 7.7 Hz, 1 H, bpy); 10.28 (s, 4H, O*H*). – ^{13}C NMR ($CDCl_3$): δ = 24.67 (*Me*bpy); 31.40, 31.46 (*Me*$_3$C); 32.34, 32.51 (Ar–CH$_2$-Ar); 33.98, 34.03 (Me$_3$*C*); 34.95, 40.07 (*C*H$_2$–CH$_2$); 118.19, 118.53, 122.69, 123.05, 136.97 (C-3, C-4, C-5, C-3', C-4', C-5' of bpy); 125.71, 125.86, 126.03, 129.00 (CH of Ar); 127.41, 127.71, 127.90, 128.31, 135.36, 144.44, 146.37, 146.70, 147.10 (C_o, C_p, C_{ipso} of Ar); 155.90, 155.98, 157.78, 160.67 (C-2, C-2', C-6, C-6', bpy). – ES-MS (neg. mode; –50V); *m*/*z*: 787.7–788.7 [**2** – H$^+$]$^-$. – $C_{53}H_{60}N_2O_4 \cdot 0.25\ CH_2Cl_2$ (810.31): calcd. C 78.93, H 7.53, N 3.46, O 7.90; found C 79.09, H 7.58, N 3.31, O 7.98.

Calix[4]arene-26,28-diol 6: A mixture of finely powdered K_2CO_3 (2.33 g, 17 10^{-3} mol) and 5 g of *p-tert*-butylcalix[4]arene **4** (7.7 10^{-3} mol) in 250 mL of acetonitrile was stirred at 80 °C for 30 min. Benzoyl chloride (1.8 mL, 15.4 10^{-3} mol) was then added by syring, and heating was maintained for 4 h. After cooling, the solvent was evaporated to dryness and the residue dissolved in 100 mL of CH_2Cl_2. The resulting solution was washed with water (3×50 mL), dried over Na_2SO_4, then concentrated to 40 mL on a Rotavapor. The residue was then mixed with 300 mL of EtOH and the resulting cloudy solution was concentrated in vacuo to give 6 g of **6** (91%), white precipitate, m.p. 320–330 °C (dec.). – UV/Vis (CH_2Cl_2): λ (ε) = 278.5 (6100). – IR: $\tilde{\nu}$ = 1735 (C=O). – ^{1}H NMR ($CDCl_3$): δ = 1.01 (s, 18 H, *Me*$_3$C); 1.15 (s, 18 H, *Me*$_3$C); 3.49, 3.97 ("q", *AB*, *JAB* = 14.1 Hz, 8 H, Ar–C*H*$_2$-Ar); 6.91 (s, 4 H, Ar); 7.02 (s, 4 H, Ar); 7.52 (t, *J* = 7.4 Hz, 4 H of C_6H_5); 7.70 (t, *J* = 7.4 Hz, 2 H of C_6H_5); 8.33 (d, *J* = 7.1 Hz, 4 H of C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 31.53, 31.09 (*Me*$_3$C); 33.39 (Ar–CH$_2$-Ar); 33.86, 34.06 (Me$_3$*C*); 133.71, 130.50, 128.99, 126.12, 125.64 (CH of Ar and C_6H_5); 150.43, 148.87, 143.34, 142.61, 131.92, 127.78, 129.38 (C_o, C_p, C_{ipso} of Ar; C_{ipso} C_6H_5); 165.01 (*C*=O). – ES-MS (neg. mode); *m*/*z*: 855.7 [**6** – H]$^-$; (pos. mode): 857.6 [**6** + H]$^+$. – $C_{58}H_{64}O_6$ (857.15): calcd. C 81.27, H 7.53, O 11.20; found C 81.08, H 7.90, O 11.16.

Calix[4]arene-26,28-diol 7: A mixture of **6** (6 g, $7 \cdot 10^{-3}$ mol) and $AlCl_3$ (4.7 g, 35 10^{-3} mol) in 300 mL of toluene was heated until a red colouration persisted, and then stirred at room temp. for 2 h. H_2O (100 mL) was added, and the resulting emulsion was stirred for 30 min. The toluene phase was washed with water (3×100 mL), the latter extracted with CH_2Cl_2, and the combined organic phases evaporated to dryness. The yellow residue was dissolved in a mixture of CH_2Cl_2 (50 mL) and MeOH (250 mL) and then concentrated in vacuo to ca. 100 mL to give 4.2 g of **7** (80%) as a white precipitate; m.p. 320 °C(dec). – UV/Vis (CH_2Cl_2): λ (ε) = 275.0 (9480), 282.0 (sh, 8330). – IR: $\tilde{\nu}$ = 1735 (C=O). – ^{1}H NMR ($CDCl_3$): δ = 1.08 (s, 18 H, *Me*$_3$C); 3.87, 3.57 ("q", *AB*, *JAB* = 14.1 Hz, 8 H, Ar–C*H*$_2$-Ar); 6.59 (t, *J* = 7.4 Hz, 2 H, Ar); 6.93 (d, *J* = 7.4 Hz, 4 H, Ar); 7.00 (s, 4 H, Ar); 7.52 (t, *J* = 7.7 Hz, 4 H, C_6H_5); 7.72 (t, *J* = 7.4 Hz, 2 H, C_6H_5); 8.22 (d, *J* = 7.0 Hz, 4 H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 31.19 (*Me*$_3$C); 33.84 (Ar–CH$_2$-Ar); 34.15 (Me$_3$*C*); 119.62, 130.70, 129.27, 128.68, 126.31, 133.75 (CH of Ar and C_6H_5); 128.05, 131.95, 144.05, 149.04, 152.91 (C_o, C_p, C_{ipso} of Ar, C_{ipso} of C_6H_5); 164.76 (*C*=O). – ES-MS (neg. mode); *m*/*z*: 535.5 [**7**– H]$^-$. – $C_{50}H_{48}O_6$ (744.94): calcd. C 80.62, H 6.50, O 12.88; found C 80.57, H 6.73, O 12.81.

Calix[4]arene-25,26,27,28-tetrol (8): A mixture of **7** (4.2 g, 5.6 10^{-3} mol) and NaOH (8 g, 200 10^{-3} mol) in a mixture of EtOH (120 mL) and H_2O (40 mL) was heated under reflux for 12 h. After cooling, the solution was acidified to pH 5–6 with HCl to give a white precipitate which was collected by filtration, and then dissolved in CH_2Cl_2. Addition of MeOH resulted in the precipitation of 3 g of **8** (99%), m.p. 300 °C. – UV/Vis (CH_2Cl_2): λ (ε) = 277.5 (10000), 282.5 (sh, 8600). – ^{1}H NMR ($CDCl_3$): δ = 1.25 (s, 18 H, *Me*$_3$C); 4.26, 3.56 ("q", 8 H, Ar–C*H*$_2$-Ar); 6.73 (t, *J* = 7.7 Hz, 2 H, Ar); 7.08 (d, *J* = 7.7 Hz, 4 H, Ar); 7.09 (s, 4 H, Ar); 10.29 (s, 4 H, O*H*). – ^{13}C NMR ($CDCl_3$): δ = 31.52 (*Me*$_3$C); 32.22 (Ar–CH$_2$-Ar); 34.12 (Me$_3$*C*); 129.02, 125.91, 122.37 (CH of Ar); 148.72, 146.77, 144.66, 128.5, 127.56 (C_o, C_p, C_{ipso} of Ar). – ES-MS (neg. mode); *m*/*z*: 535.5 [**8** – H]$^-$. – $C_{36}H_{40}O_4 \cdot 0.9\ CH_2Cl_2$ (613.15): calcd. C 72.28, H 6.87, O 10.44; found C 72.35, H 6.97, O 10.58.

Calix[4]arene-25,26,27,28-tetrol (9) and Calix[4]arene-25,26,27,28-tetrol (10): $TiCl_4$ (1.25 mL, 11.2 10^{-3} mol) was syringed into a soln. of **8** (0.4 g, 0.65 10^{-3} mol) in 10 mL of $CHCl_3$. The resulting red solution was stirred under N_2 during 30 min. Dichloromethylmethyl ether (1 mL, 11.2 10^{-3} mol) was then added dropwise. After 2 h, 25 mL of water was added and stirring was continued for 1 h. After separation, the aqueous phase was washed with CH_2Cl_2 (3×20 mL). The combined organic phases were dried over Na_2SO_4, then concentrated to dryness. The residue was dissolved in 1:1 MeOH/CH_2Cl_2 and 2 g of aluminium oxide were added to give, after ca. 12 h, the raw aldehyde which was purified by chromatography (SiO_2, CH_2Cl_2) to give 0.08 g of the mono aldehyde **10** (19%) and 0.25 g of **9** (64%). – **Compound 9:** m.p. >350 °C. – UV/Vis (CH_2Cl_2): λ (ε) = 281.0 (18300). – IR: $\tilde{\nu}$ = 1680 (C=O). – ^{1}H NMR ($CDCl_3$): δ = 1.24 (s, 18 H, *Me*$_3$C); 4.27,3.69 (br. *AB*, 8 H, Ar–C*H*$_2$-Ar); 7.15 (s, 4 H, Ar); 7.61 (s, 4 H, Ar); 9.74 (s, 2 H, C*H*O); 10.30 (s, 4 H, O*H*). – ^{13}C NMR ($CDCl_3$): δ = 31.50 (*Me*$_3$C), 31.99 (Ar–CH$_2$-Ar); 34.28 (Me$_3$*C*); 126.41, 131.16 (CH of Ar), 126.83, 129.15, 131.30, 145.87, 146.14, 154.70 (C_o, C_p, C_{ipso} of Ar); 190.56 (*C*HO). – ES-MS (pos. mode); *m*/*z*: 615.4 [**9** + Na]$^+$. – $C_{38}H_{40}O_6 \cdot 0.1\ CH_2Cl_2$ (601.23): calcd. C 76.11, H 6.74, O 15.97;

found C 76.20, H 7.18, O 15.58. – **Compound 10:** m.p. > 350 °C. – UV/Vis (CH_2Cl_2): λ (ε) = 280.0 (13500). – IR: ν̃ = 1685 (C=O). – ^{1}H NMR ($CDCl_3$): δ = 1.27 (s, 18 H, *Me*$_3$C); 3.60, 4.29 (br. *AB*, 8 H, Ar–C*H*$_2$-Ar); 6.74 (t, *J* = 7.5 Hz, 1 H, Ar); 7.06 (d, *J* = 7.5 Hz, 2 H, Ar); 7.13 (s, 4 H, Ar); 7.64 (s, 2 H, of Ar); 9.77 (s, 1 H, ArC*H*O); 10.30 (br. s, 4 H, O*H*). – ^{13}C NMR ($CDCl_3$): δ = 31.47 (*Me*$_3$C), 32.06 (Ar–CH_2-Ar); 34.16 (Me$_3$*C*); 122.55, 125.93, 126.29, 129.00, 131.15 (CH of Ar), 125.81, 126.53, 127.82, 128.17, 129.35, 131.12, 145.21, 146.41, 148.53, 154.92 (C$_{o,}$ C$_{p,}$ C$_{ipso}$ of Ar); 190.67 (*C*=O). – ES-MS (pos. mode); *m*/*z*: 587.5 [**10** + Na]$^+$. – $C_{37}H_{40}O_5$·0.8 CH_2Cl_2 (632.67): calcd. C 71.76, H 6.63, O 12.64; found C 71.82, H 6.89, O 12.51.

Calix[4]arene-25,26,27,28-tetrol (3): The bipyridinephosphonium salt **5** (0.585 g, 0.5 10^{-3} mol) was dissolved in a solution of NaOMe in MeOH [10 ml; from 0.097 g of Na (4.05 10^{-3} mol)]. To the resulting yellow solution was added 0.3 g of **9** (0.5 10^{-3} mol). The solution was stirred at room temp. for 6 h and then evaporated to dryness. The raw material was dissolved in CH_2Cl_2 and then washed with 1 M HCl and H_2O. Evaporation of CH_2Cl_2 afforded a glassy material which was dissolved in 10 mL of EtOH and 10 mL of CH_2Cl_2. 30 mg of 5% Pd/C was added and the solution was stirred under a blanket of H_2 overnight. Solid material was filtered over Celite and rinsed with CH_2Cl_2 followed by acetone. The filtrate was evaporated to dryness and the residue was dissolved in 1 mL of CH_2Cl_2. Addition of 10 mL of MeOH resulted in the formation of a white precipitate which was recovered and purified by chromatography (Al_2O_3, CH_2Cl_2/MeOH 97/3) to give 0.105 g of **3** (22%); m.p: 274 °C. – UV/Vis (CH_2Cl_2): λ (ε) = 289.5 (43200). – ^{1}H NMR ($CDCl_3$): δ = 1.21 (s, 18 H, *Me*$_3$C); 2.62 (s, 6 H, *Me*-bpy); 3.06, 2.90 (*ABm*, 8 H, C*H*$_2$C*H*$_2$); 4.24, 3.46 ("q", *AB*, J_{AB} = 13.0 Hz, 8 H, Ar–C*H*$_2$-Ar); 6.91 (s, 4 H, Ar); 7.04 (s, 4 H, Ar); 7.05 (d, *J* = 7.0 Hz, 2 H, bpy); 7.13 (d, *J* = 7.4 Hz, 2 H, bpy); 7.65 (t, *J* = 7.0 Hz, 4 H, bpy); 8.19 (t, *J* = 5.7 Hz, 4 H, bpy); 10.3 (br. s, 4 H, OH). – ^{13}C NMR ($CDCl_3$): δ = 24.68 (*Me*–bpy); 31.47 (*Me*$_3$C); 32.26 (Ar–CH_2–Ar); 34.04 (Me$_3$*C*); 34.95, 40.07 (*C*H$_2$*C*H$_2$); 125.83, 128.98 (CH of Ar); 118.18, 118.49, 122.67, 123.06, 136.98 (CH of bpy); 127.56 128.24, 135.43, 144.48, 146.76 (C$_{o,}$ C$_{p,}$ C$_{ipso}$ of Ar); 155.90, 155.99, 157.80, 160.74 (C(2), C(2'), C(6), C(6') of bpy). – ES-MS (pos. mode); *m*/*z*: 929.5 [**3** + H]$^+$. – $C_{62}H_{64}N_4O_4$·0.1 CH_2Cl_2 (937.72): calcd. C 79.54, H 6.90, N 5.97, O 6.82; found C 79.27, H 6.92, N 5.99, O 6.60.

Calix[4]arene-25,26,27,28-tetrol Cobalt(II) (13): A solution of anhydrous $CoCl_2$ (0.0145 g, 0.111 × 10^{-3} mol) in 3 mL of MeOH was added to a solution of **2** (0.09 g, 0.111 × 10^{-3} mol) in 15 mL of CH_2Cl_2. The resulting blue solution was stirred at room temp. for 3 h and then evaporated to dryness. The blue residue was dissolved in 3 mL of CH_2Cl_2 and purified by chromatography over Sephadex LH20 (CH_2Cl_2). The middle fractions were collected and concentrated; precipitation by hexane gave 0.096 g of **13** (92%), light-blue solid. – UV/Vis (CH_2Cl_2): λ (ε) = 254.5 (12300), 280.0 (16500), 287.5 (14960), 308.0 (10420), 317.0 (11440), 341.0 (6208), 570.5 (284), 655.5 (530). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = –35.24 (br. s, Δν$_{1/2}$ = 300 Hz, 2 H, CH_2–C*H*$_2$-bpy); –20.85 (br. s, Δν$_{1/2}$ = 169 Hz, 3 H, *Me*-bpy); –16.39 (br. s, Δν$_{1/2}$ = 92 Hz, 2 H, C*H*$_2$–CH_2-bpy); –14.30 [s, Δν$_{1/2}$ = 30.50 Hz, 1 H, H(4) or H(4') of bpy]; –13.53 [s, Δν$_{1/2}$ = 30.12 Hz, 1 H, H(4) or H(4') of bpy]; –2.08 [br. s, Δν$_{1/2}$ = 48 Hz, 2 H, Ar(**A**)]; 1.27 (s, Δν$_{1/2}$ = 21.14 Hz, 9 H, *Me*$_3$C); 2.10 (s, Δν$_{1/2}$ = 21.93 Hz, 18 H, *Me*$_3$C); 2.54 (br. s, Δν$_{1/2}$ = 109 Hz, 2 H, Ar–C*H*$_2$–Ar); 3.03 (br. s, Δν$_{1/2}$ = 104.50 Hz, 2H, Ar–C*H*$_2$-Ar); 3.34 (br. s, Δν$_{1/2}$ = 98.70 Hz, 2 H, Ar–C*H*$_2$–Ar); 3.95 (br. s, Δν$_{1/2}$ = 85.25 Hz, 2 H, Ar–C*H*$_2$-Ar); 6.94 [s, Δν$_{1/2}$ = 22.00 Hz, 2 H, Ar(**C**)]; 7.07 [s, Δν$_{1/2}$ = 22.86 Hz, 2 H, H(3) or H(5) of Ar(**B**) and Ar(**D**)]; 7.75 [s, Δν$_{1/2}$ = 26.24 Hz, 2 H, H(5) or H(3) of Ar(**B**) and Ar(**D**)]; 9.33 (s, Δν$_{1/2}$ = 39.60 Hz, 4H, O*H*); 43.87 [s, Δν$_{1/2}$ = 36.50 Hz, 1 H, H(5 or 5') or H(3 or 3') of bpy]; 46.17 [s, Δν$_{1/2}$ = 35.20 Hz, 1 H, H(5' or 5) or H(3' or 3) of bpy]; 65.35 [s, Δν$_{1/2}$ = 36.80 Hz, 1 H, H(3 or 3') or H(5 or 5') of bpy]; 66.06 [s, Δν$_{1/2}$ = 38.62 Hz, 1 H, H(3' or 3) or H(5' or 5) of bpy]. – ES-MS, for $C_{53}H_{60}CoCl_2N_2O_4$ (918.91; 918): *CH_2Cl_2 + amylene, positive mode:* 882.6, 883.6, 884.6, 885.6 [**2** + $CoCl_2$ – Cl^-]$^+$; 846.6, 847.7 [**2** + $CoCl_2$ – 2 Cl^- – H^+]$^+$; 789.7, 790.7, 791.8 [**2** + H^+]$^+$. *CH_2Cl_2 + amylene + MeOH as ionising agent, positive mode*: 906.6, 907.7, 908.8, 909.9 [**2**·(OCH$_3$)$_2$ + $CoCl_2$ – 2 Cl^- + CH_3O^-]$^+$; 892.6, 893.6, 894.6, 895.5 [**2**·(OCH$_3$) + $CoCl_2$ – 2 Cl^- + CH_3O^-]$^+$; 846.5, 847.6, 848.6 [**2** + $CoCl_2$ – 2 Cl^- – H^+]$^+$; 811.6, 812.6, 813.6 [**2** + Na^+]$^+$; 789.7, 790.7, 791.7 [**2** + H^+]$^+$; *negative mode*: major peaks 787.6, 788.6, 789.7 [**2** – H^+]$^-$; minor peaks 950.6, 951.6, 952.6 [**2**·(OCH$_3$)$_3$ + $CoCl_2$ – 2 Cl^- + 2 (CH_3O^-) – H^+]$^-$; 940.6, 941.6, 942.6 [**2**·(OCH$_3$)$_2$ + $CoCl_2$ – Cl^- + CH_3O^- – H^+]$^-$; 926.6, 927.6, 928.6, 929.5 [**2**(OCH$_3$) + $CoCl_2$ – Cl^- + CH_3O^- – H^+]$^-$; 916.6, 917.6, 918.6, 919.6 [**2** + $CoCl_2$ – H^+]$^-$; 880.5, 881.6, 882.6 [**2** + $CoCl_2$ – Cl^- – 2 H^+]$^-$; 844.5, 845.5, 846.6 [**2** + $CoCl_2$ – 2 Cl^- – 3 H^+]$^-$. – $C_{53}H_{60}CoCl_2N_2O_4$·0.2 CH_2Cl_2 (935.90): calcd. C 68.27, H 6.50, N 2.99; found C 68.23, H 6.74, N 2.79.

Calix[4]arene-25,26,27,28-tetrol Cobalt(II) (14): A solution of anhydrous $CoCl_2$ (0.018 g, 0.072·10^{-3} mol) in MeOH (6 mL) and CH_2Cl_2 (6 mL) was added to a solution **3** (0.06 g, 0.065·10^{-3} mol) in 30 mL of CH_2Cl_2. The resulting light blue solution was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and then purified by chromatography over Sephadex LH20 (CH_2Cl_2) to give 0.072 g of **14** (92%). Blue-grey powder. – UV/Vis (CH_2Cl_2): λ (ε) = 280.0 (20300); 287.0 (19700), 306.0 (16600); 316.5 (17200); 572.0 (700); 656.5 (1030). – ES-MS: 1) *negative mode, alcohol-free CH_2Cl_2,* –50V: 1185.5, 1187.6, 1188.4, 1189.3 [**3** + 2 $CoCl_2$ – H]; 2) *positive mode, alcohol-free CH_2Cl_2*, +120V: 851.7, 853.6, 854.7 [**3** + $CoCl_2$ – ($C_{11}H_9N_2$) – Cl]$^+$; 989.5, 990.6, 991.6, 992.6, 994.7 [**3** + $CoCl_2$ –2Cl – H]$^+$; 3) *positive mode, CH_2Cl_2 + MeOH,* +50V: 929.7, 930.6 [**3** + H]$^+$; 951.7, 952.7, 953.7 [**3**·(OCH$_3$) + Na]$^+$; 1032.7, 1033.6, 1034.6 [**3**·(OCH$_3$) + $CoCl_2$ – 2Cl^- + CH_3O^-]$^+$; 1047.6 [**3**·(OCH$_3$)$_2$ + $CoCl_2$ – 2Cl^- + CH_3O^-]$^+$; 4) *negative mode, CH_2Cl_2 + MeOH*, –50V: 731.6, 732.6, 733.5 [**3** – CH_2CH_2bpy]$^-$; 927.7, 928.8, 929.7 [**3** – H]$^-$; 1056.6, 1057.6, 1058.7, 1059.7 [**3** + $CoCl_2$ – H]$^-$; 1065.5, 1067.5, 1068.5 [**3**·(OCH$_3$) + $CoCl_2$ – H]$^-$; 1187.4 [**3** + 2 $CoCl_2$ – H]$^-$. – $C_{62}H_{64}Co_2Cl_4N_4O_4$·$H_2O$ (1206.91): calcd. C 61.70, H 5.51, N 4.64; found C 61.99, H 5.83, N 5.18.

X-ray Crystallographic Study of Complex 13: $C_{53}H_{60}Cl_2Co_1N_2O_4$, CH_2Cl_2, $C_4H_{10}O$, crystal system monoclinic, space group *P*2(1)/*c* with *a* = 24.747(5) Å, *b* = 9.1648(18) Å, *c* = 24.231(5) Å, β = 93.12(3)°, *V* = 5487.5(19) Å^3, $D_{calcd.}$ = 1.305 g/cm^3 and *Z* = 4. The data were collected at 173 K by X-ray diffraction on an Enraf–Nonius Kappa-CCD diffractometer. Full sphere of data was collected by axis rotation with 1°.0 increments over 180°, with 30 s exposures per frame. The crystal to detector distance was 30 mm. Data were analyzed using Kappa-CCD Software.[13] Cell dimensions were refined with HKL Scalepack.[14] The structure was solved with direct methods using the SHELXS programme.[15] Refinement by SHELXL [16] leads to an *R* factor of 0.077 for 3345 F_o > 4 (F_o) and a goodness of fit of 0.947. All nonhydrogen atoms were given anisotropic displacement parameters. All hydrogen atoms were located at their theoretical position and refined as a riding model. EXYZ and EADP instructions were used for the study of the CH_2Cl_2 disorder. The final electron density difference map showed a maximum of 1.23 e.Å^{-3} and a minimum of –0.51 eÅ^{-3}. Molecular graphics were drawn with ORTEP.[17]

Table 2. Crystal data and structure refinement of **13**

Empirical formula	$C_{53}H_{60}Cl_2Co_1N_2O_4{\cdot}CH_2Cl_2{\cdot}C_4H_{10}O$
Mr	1078.23
Crystal system, space group	Monoclinic, *P*2(1)/*c*
Cell dimensions	
a [Å]	24.747(5)
b [Å]	9.1648(18)
c [Å]	24.231(5)
β [°]	93.12(3)
V [Å^3]	5487.5(19)
Z	4
D_x [Mg·m^{-3}]	1.305
D_m	not measured
T [K]	173
Crystal size [mm]	0.36 × 0.18 × 0.04
Color	blue
Enraf–Nonius Kappa-CCD diffractometer	
Wavelength [Å]	0.71073
Absorption correction	none
R_{int}	0
φ limits [°]	2.37 to 27.83
Limiting indices	$-28 \le h \le 28$, $-11 \le k \le 0$, $0 \le l \le 31$
Measured reflections	11633
Independent reflections	10917
Parameters	637
H atoms riding	
S	0.947
R	*R*1 = 0.0767, *wR*2 = 0.1429
Densities (max),(min)[eÅ^{-3}]	1.227 and –0.507

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication n° 120557. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk]. For other details see Table 2.

Acknowledgments

We are grateful to the MRES for financial support, especially J.-O. D. for a PhD fellowship; to SAFAS (Monaco) and BRUKER S.A. for UV spectroscopy and WINNMR facilities, respectively. We are indebted to Mrs Nicole Marshall for correcting the manuscript.

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Received May 31, 1999
[I99192]