Catalytic applications of keto-stabilised phosphorus ylides based on a macrocyclic scaffold: calixarenes with one or two pendant Ni(*P*,*O*)-subunits as ethylene oligomerisation and polymerisation catalysts†

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Four calix[4]arenes containing either one or two ylidic –C(O)CH=PPh_3 moieties anchored at *p*-phenolic carbon atoms were prepared starting from *cone*-25,27-dipropoxycalix[4]arene (**1**): *1,3-alternate*-5,17-bis(2-triphenylphosphoranylideneacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (**12**), *1,3-alternate*-5-(2-triphenylphosphoranylideneacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (**13**), *cone*-5-(2-triphenylphosphoranylideneacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**14**), *cone*-5,17-bis(2-triphenylphosphoranylideneacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**15**). All the ylides were shown to be suitable for the preparation of SHOP-type complexes, *i.e.* of molecules containing [NiPh{Ph_2PCH=C(O)R}(PPh_3)] subunits (R = calixarene fragment). The monometallic complexes, namely those obtained from the monophosphorus ylides **13** and **14**, proved to be efficient ethylene oligomerisation or polymerisation catalysts. At 80 °C, they displayed significantly better activities than the prototype [NiPh{Ph_2PCH=C(O)Ph}(PPh_3)], hence reflecting the beneficial role of the bulky calixarene substituent. The systems derived from the two ylides **12** and **15**, both containing two convergent ylidic moieties, resulted in lower activities, the proximity of the two catalytic centres facilitating an intramolecular deactivation pathway during the period of catalyst activation. For the first time, the solid-state structure of a complex containing *two* "NiPh(*P*,*O*)(PPh_3)" units as well as that of a SHOP-type complex having two *linked* phosphorus units were determined.

Introduction

Nickel(II) phosphanylenolates with the general formula [NiPh(*P*,*O*)L] (L = tertiary phosphine; *P*,*O* = chelating phosphanylenolato ligand) (**A**) constitute valuable precursors for highly efficient oligomerisation catalysts suitable for the selective production of linear α-olefins.[1–5] The same complexes, which are frequently referred to as SHOP-type catalysts (SHOP = Shell higher olefin process), can also be used as ethylene polymerisation catalysts if pre-treated with a phosphine sponge to remove the neutral phosphine ligand (L).[6,7] Their synthesis is usually achieved *via* oxidative addition of a keto-stabilised phosphorus ylide to a nickel(0) complex[8] in the presence of a tertiary phosphine (Scheme 1), or by reacting of a phosphanylenolate with an appropriate Ni(II) precursor.[9–11] It is noteworthy that active oligomerisation catalysts based on such complexes can directly be generated *in situ*.[12] This can also be done for forming a polymerisation catalyst (complex of type **B**), the oxidative addition being then carried out in the presence of ethylene instead of a tertiary phosphine.[13–15]

Owing to their relatively high functional group tolerance, complexes of type **B** represent interesting precatalysts for the copolymerisation of ethylene with polar monomers, which is one of the most promising fields of polyolefin industry.[16–18] Other applications include their use as ethylene polymerisation catalysts in aqueous media.[19–21] A major drawback of **B**-type polymerisation catalysts arises from their low intrinsic activity in comparison to the highly active group 4-metal catalysts. This is in part possibly due to the formation during catalysis of an inactive [Ni(*P*,*O*)$_2$] complex, which may result from the formation of a transient dimer (Scheme 2).[6,7] A logical way to prevent such a catalyst deactivation is to introduce bulky substituents in the vicinity of the oxygen atom.

In fact, only one publication using this approach has been reported to date,[14] although there is a parallel with *P*,*O*-chelates grafted to a dendrimeric unit.[22] In the present work, we describe the first syntheses of keto-stabilized phosphorus ylides and β-ketophosphines tethered to a calix[4]arene platform that may play the role of a bulky substituent. It should be recalled here that calix[4]arenes are large scaffolds, the size of which is not only easily tunable through functionalisation, but also variable due to their intrinsic conformational mobility.[23,24] The new phosphorus compounds were used for the preparation of SHOP-type complexes and assessed in ethylene oligomerisation and polymerisation. The first X-ray structure determination for a molecular catalyst containing two "Ni(*P*,*O*)" subunits forms part of this work. Assignments of the calixarene conformations were made using well-established rules based on ^{13}C and ^{1}H

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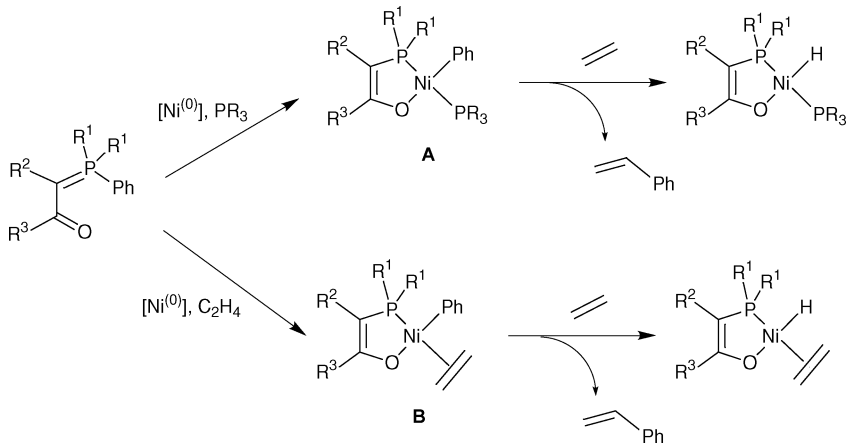
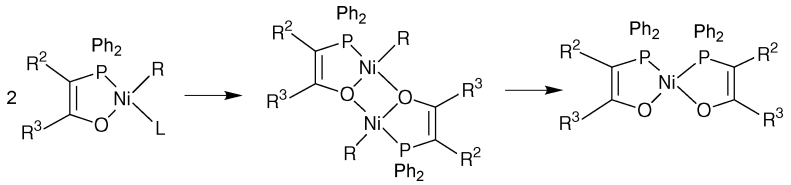
† The HTML version of this article has been enhanced with colour images.

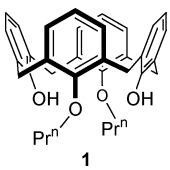


Scheme 1 Synthesis of typical SHOP-type oligomerisation (**A**) and polymerisation (**B**) catalysts.



Scheme 2 A typical deactivation pathway of SHOP catalysts.

NMR spectroscopy.[25,26] All compounds were obtained starting from 25,27-dipropoxycalix[4]arene (**1**).[27]



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Results and discussion

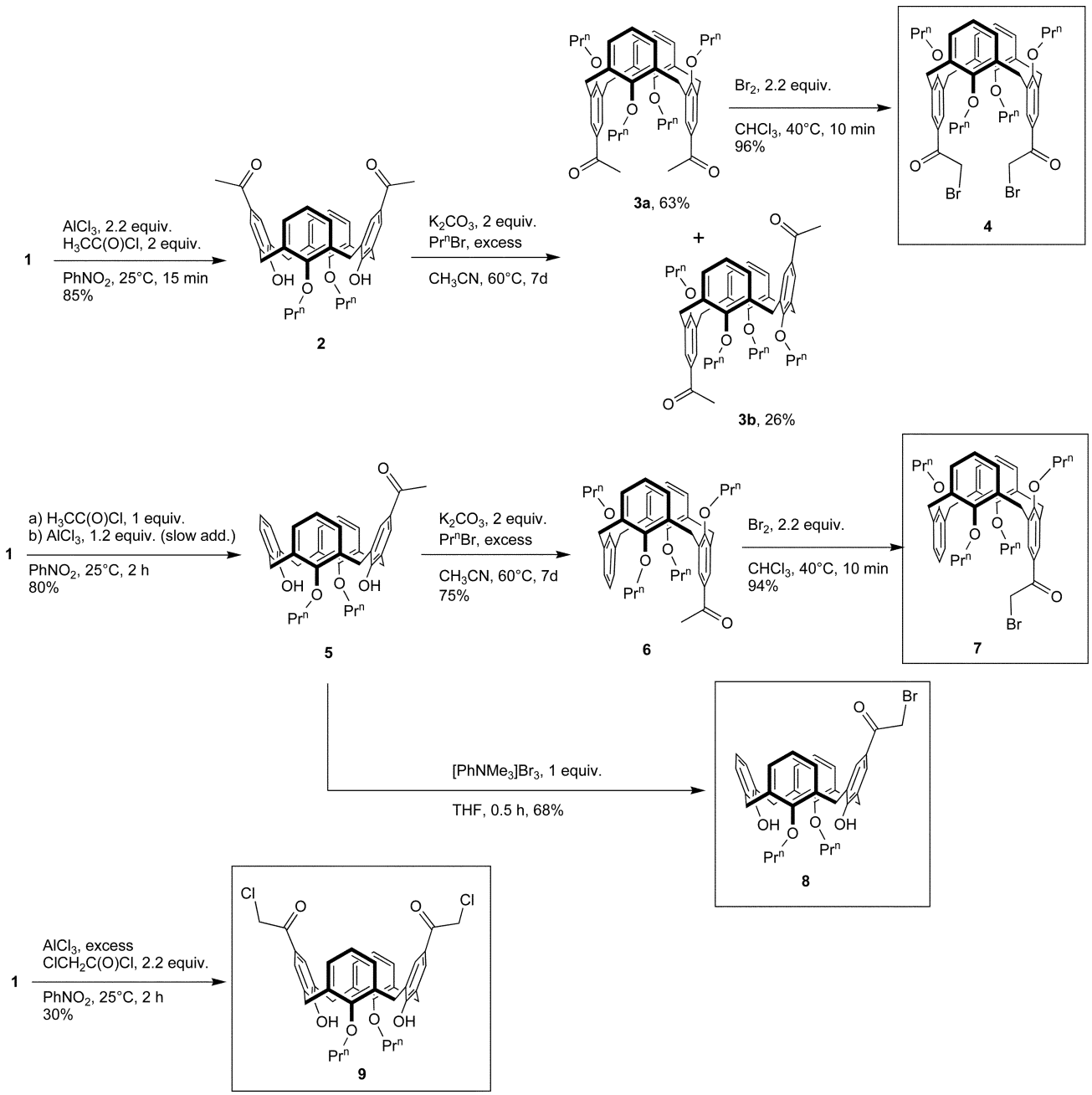
Ligand synthesis

Preparation of haloacetylated precursors. The new compounds were obtained through upper-rim functionalisation of appropriate calix[4]arene precursors. The preparation of the phosphorus ylides **12–15** required the synthesis of the haloacetylated precursors **4**, **7**, **8** and **9**, respectively. Compounds **4**, **7** and **8** were obtained *via* Friedel–Crafts acetylation of **1** in nitrobenzene at room temperature followed by a conventional bromination reaction (Scheme 3). The chloro derivative **9** was obtained in a one-step reaction using $AlCl_3/ClCH_2C(O)Cl$. It is interesting to note that the acetylation reaction leading to **2** is fast (reaction time <15 min) in comparison to the recently reported 12-h diacetylation of the 25,27-dimethoxy analogue of **1**.[28,29] To restrict the functionalisation of **1** to a selective monoacetylation, the $AlCl_3$ solution was added dropwise over 2 h to a calixarene–$CH_3C(O)Cl$ 1 : 1 mixture. Further, we observed that when the acetylations were carried out using an $CH_3C(O)Cl$: calix ratio larger than 3 : 1, acetylation of the propylated phenoxy rings also occurred, but at a slower rate (products not described in this paper). The yield of the reaction leading to **9** did not exceed 30%, unidentified side-products being formed in this case. Finally, it is worth mentioning that the Friedel–Crafts acetylation products **2**, **5** and **9** adopt a cone conformation, as unambiguously deduced from the corresponding ^{13}C NMR spectra (see Experimental section), in which the $ArCH_2$ signal appears near 31.4 ppm, that is, in a range typical for $ArCH_2Ar$ units having *syn*-oriented aryl rings.[26]

Compound **4** could be obtained from **2** in two steps: (*i*) alkylation with K_2CO_3/Pr^nBr, affording the *1,3-alternate* conformer **3a** as the major compound (yield: 63%; partial cone-**3b** was isolated in 26% yield); (*ii*) bromination of **3a** with Br_2 to yield quantitatively the bis-bromoacetylated compound **4**. Compound **7** was synthesised similarly in good yield starting from **5**. We found that direct bromination of **5** with $[PhNMe_3]Br_3$ gave **8** in 68% yield, a transformation in which the cone conformation was maintained.

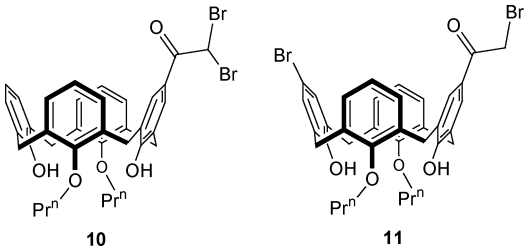
Chromatographic purification of **8** revealed that the dibrominated compound **10** was also formed (see Experimental section). When the bromination of **5** was carried out with Br_2, a mixture of compounds was formed for which chromatographic separation proved difficult. Only **11**, for which an optimised preparation is described in the Experimental section, could be isolated.

Preparation of the phosphorus ylides. The four phosphorus ylides **12–15** were eventually prepared in nearly quantitative yield according to the following sequence: (*i*) reaction of PPh_3 with the appropriate haloacetylated calixarene; (*ii*) deprotonation of the resulting phosphonium salt with NaH (Scheme 4). For each ylide, the ^{31}P NMR spectrum exhibits a singlet near 16.5 ppm. In the IR spectra, the $\nu(C{=}O)$ stretching bands appear in the range 1507–1518 cm^{-1}. The molecular structure of ylide **15** was confirmed by an X-ray diffraction study (Fig. 1). In the solid state, the calixarene core exhibits a typical flattened cone conformation, with dihedral angles between the facing phenoxy rings of 35 and



Scheme 3 Stepwise buildup of haloacetylated calixarenes suitable for the preparation of phosphorus ylides.

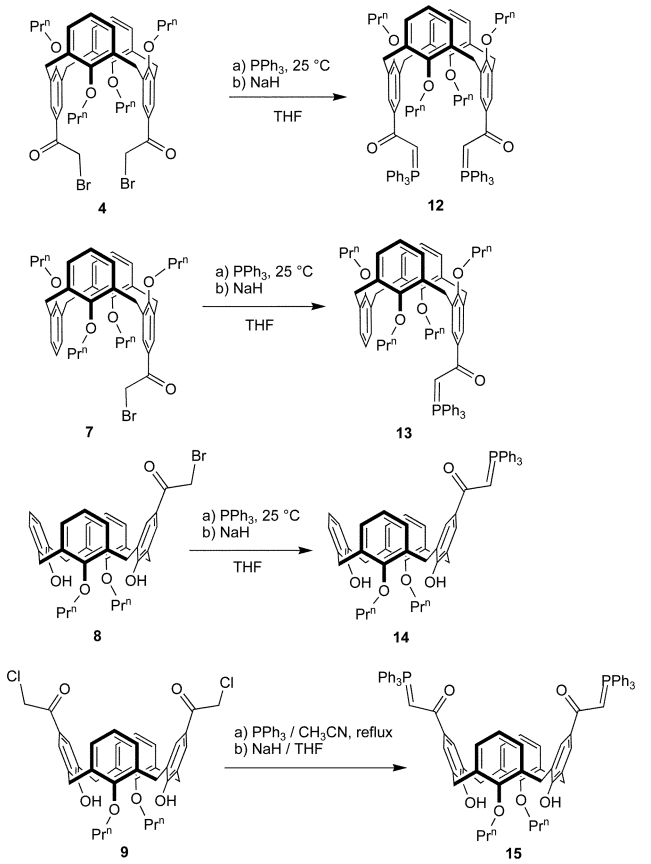
82°, respectively. The distance between the two phosphorus atoms is *ca.* 15 Å. The P=C bond lengths of the ylide moieties are 1.721(4) and 1.713(4) Å, respectively (*cf.* 1.804(5) Å for the shortest P–C(aryl) bond).



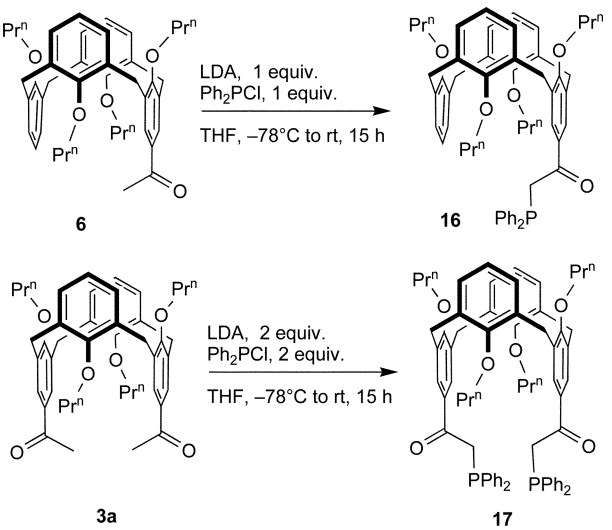
For the preparation of SHOP-type catalysts, it is sometimes of advantage to start from a β-ketophosphine instead of a phosphorus ylide.[30] We therefore also prepared the two phosphines **16** and **17**. These were obtained in high yields using a well-established procedure, namely by deprotonation of the appropriate acetyl derivative with $LiNPr^i_2$ (LDA), followed by reaction with PPh_2Cl (Scheme 5).[31] The corresponding phosphorus signals appear as singlets at −19.4 and −16.2 ppm, respectively, for **16** and **17**.

Synthesis of catalytic precursors

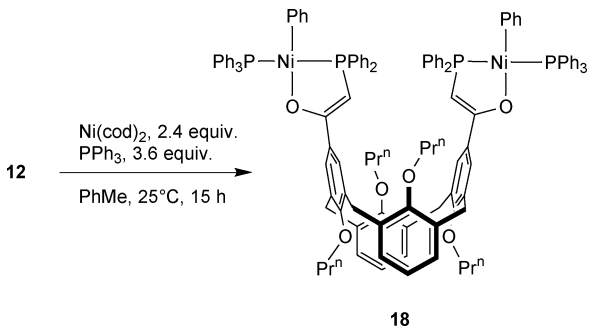
In the present study, all catalytic precursors were generated in situ from $[Ni(cod)_2]$, either in the presence of PPh_3/ethylene



Scheme 4 Synthesis of the phosphorus ylides **12–15**.



Scheme 5 Synthesis of the β-ketophosphines **16** and **17**.



Scheme 6 Synthesis of the "bis-SHOP" complex **18**.

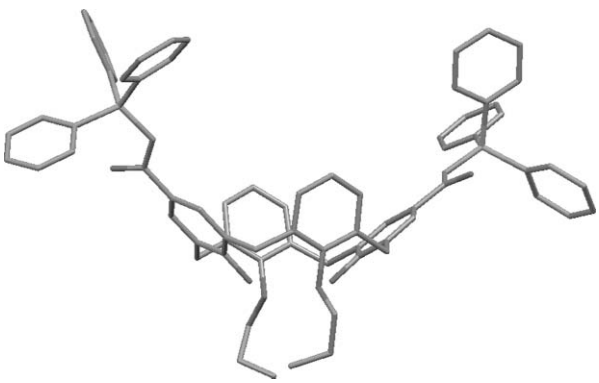


Fig. 1 X-Ray crystal structure of bis-ylide **15**. P · · · P separation: 15.14(1) Å. The compound crystallises with two molecules of MeOH and half a molecule of CH_2Cl_2 (not shown).

(for the preparation of oligomerisation catalysts) or ethylene alone (for the preparation of polymerisation catalysts). NMR studies revealed that the reaction of **12** with [Ni(cod)$_2$] in toluene at 60 °C occurs readily, affording a single product (^{31}P NMR signal at 20.5 ppm) which can be used as such for the catalytic studies. The same observation holds for the bis-ylide **15**. In order to prove that a bimetallic catalyst precursor does form, we isolated the product formed by reacting **12** with [Ni(cod)$_2$] in the presence of PPh_3. This reaction gave complex **18** (Scheme 6). We found that upon standing **18** straightforwardly undergoes reductive elimination at both nickel sites, hence reforming **12**. To avoid back formation of the ylide, it turned out to be advantageous to carry out the reaction leading to **18** in the presence of a slight excess of [Ni(cod)$_2$] and PPh_3 as well. The ^{31}P NMR spectrum of **18** shows an AB system, with a $J(PP')$ coupling constant of 283 Hz, typical of *trans*-positioned P atoms. In the ^{1}H NMR spectrum, the PCH protons appear as a broad singlet at 5.17 ppm. The solid-state structure of **18** was determined by a single-crystal X-ray diffraction study (Fig. 2). It represents the only X-ray crystal structure of a molecule with two Ni(*P*,*O*) subunits. In a strict sense, the molecule has C_1 symmetry, but it may be regarded as possessing a pseudo-plane of symmetry containing the C(29), O(3) and O(4) atoms. The two Ni–PPh_3 vectors are nearly parallel and oriented in the same direction. The calixarene adopts a 1,3-alternate conformation, each distal pair of phenol rings defining an open cavity. The interplanar angle between the rings linked to O(1) and O(2) atoms is 35°, while that between the other two distal rings is *ca.* 55°. In fact, the O(4) atom comes closer to the centre of the cavity than the O(3) atom, thereby minimising the steric interactions between the two PPh_3 ligands and the propyl chain substituting O(4). We note that the shortest C(116) · · · O(enolate) separation (3.42(1) Å) involves the O(5) atom. Both nickel atoms lie in an almost square-planar coordination environment, as usually observed in related structures.[32–34] The two metallacyclic units are structurally very similar and may be considered planar. In accord with some

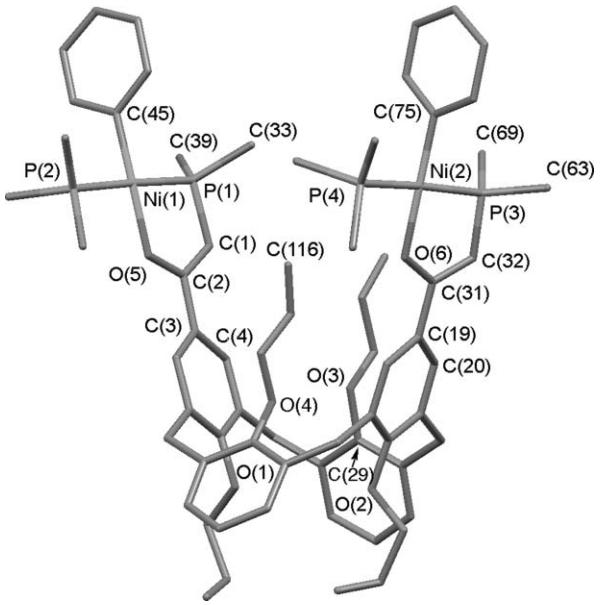


Fig. 2 X-Ray crystal structure of **18**. For clarity, only the C_{ipso} carbon atoms of the PPh units are shown.

electron delocalisation within the PCCO chelate arms, the P–CH bond lengths (both of 1.754(4) Å) are slightly shorter than those of the corresponding P–C(aryl) bonds (≥1.816(5) Å).

Both "Ni(*P*,*O*)" moieties and the phenoxy rings to which they are linked are nearly coplanar (torsion(C1C2C3C4) = −10.7(5)°; torsion(C20C19C31C32) = −18.6(5)°), thus reflecting the good conjugation between these rings (Table 1). The distance between the two nickel atoms is 8.71(1) Å. Finally, it should be mentioned that, as shown by NMR measurements, the reaction of **15** with $[Ni(cod)_2]/PPh_3$ leads also to the formation of a bimetallic complex having two SHOP-subunits (see Experimental section). The corresponding ^{1}H NMR spectrum is in keeping with a calixarene in the cone conformation.

Ethylene polymerisation

The polymerisation tests were carried out in toluene under constant ethylene pressure, the ylide $Ph_3P{=}CHC(O)Ph$ (**19**) serving as a reference compound. Temperatures higher than 60 °C were necessary to start the reaction. All four ylides catalyse, when associated to nickel(0), the polymerisation of ethylene to linear polyethylene. Surprisingly, the bis-ylides **12** and **15** showed significantly lower activities than **19** (Table 2). This contrasts with the observations made by Kurtev and Tomov on bimetallic SHOP complexes with divergent catalytic centres which were found to be remarkably active compared to related, monometallic systems.[35,36] Our findings suggest the occurrence of an intramolecular deactivation mechanism involving the two ylidic centres (*vide infra*). On the other hand, the mono-ylides **13** and **14** were more active than **19**.[37] While this is true for **13** already at 70 °C (see entries 5 and 13), the higher activity of **14** *vs.* **19** becomes really obvious when operating at temperatures near 80 °C (see entries 2 and 15). At this temperature, the activities of both complexes were roughly twice as high as those of **19**. These findings strongly suggest that the calixarene moiety behaves as a sufficiently bulky substituent for preventing a deactivation pathway according to Scheme 2 (with formation of a bis-phosphanylenolato complex). The polyethylenes obtained with the two ylides containing a phenolic function, **14** and **15**, exhibited higher molecular weights (M_w = 6000–7000 g mol^{-1}) than those obtained with the other two ylides (M_w = 3000–4000 g mol^{-1}). This observation is in line with the better donor properties of the *p*-ArOH substituents of **14** and **15**, which push some electron density into the corresponding metallacycles. Electron rich Ni(*P*,*O*) metallacycles are known to favour chain growth over β-elimination.[13,38–41] Analysis of the ^{13}C NMR spectra revealed that the polyethylene samples do not show any significant branching.

Table 1 Important bond lengths (Å) and angles (°) in complex **18**

C(2)–O(5)	1.308(4)	C(31)–O(6)	1.304(4)
C(1)–P(1)	1.754(3)	C(32)–P(3)	1.754(4)
Ni(1)–O(5)	1.919(2)	Ni(2)–O(6)	1.910(3)
Ni(1)–P(1)	2.1730(9)	Ni(2)–P(3)	2.1645(12)
Ni(1)–P(2)	2.2255(9)	Ni(2)–P(4)	2.1995(12)
Ni(1)–C(45)	1.893(3)	Ni(2)–C(75)	1.890(5)
C(1)–C(2)	1.371(5)	C(31)–C(32)	1.367(5)
P(1)–Ni(1)–O(5)	86.48(7)	P(3)–Ni(2)–O(6)	86.60(8)
P(1)–Ni(1)–P(2)	176.78(4)	P(3)–Ni(2)–P(4)	174.39(5)

Ethylene oligomerisation

In these tests a 1 : 1 Ni : PPh_3 ratio was used. The results of the oligomerisation tests are summarised in Table 3. All catalysts produce, like the system obtained from **19**, highly linear oligomers, for which the α-olefin content is 98–99% over the C_4–C_{16} range. As in the polymerisation reactions described above, the systems based on the ylides **12** and **15** displayed significantly lower activities than that of the reference compound **19**, while those obtained from the mono-ylides **13** and **14** resulted in higher activities (Table 3). For example, at 5 bar, the activity of **14** is *ca.* 30% higher than that of **19**, while that of **12** is *ca.* 35% lower. Thus, it is likely again that with the bis-ylidic systems, a deactivation mechanism takes place. The protecting effect exerted by the calixarene fragment of the monoylidic systems is logically less pronounced here than under polymerisation, because of the competing stabilising effect also exerted by PPh_3.[42] As inferred from the α values, the electronic properties of the chelates formed from **12–15** compare well with that formed with **19**. Overall, the calixarene fragment of **13** and **14** is of significant, but moderate efficiency, probably because the Ni(*P*,*O*) ring can freely rotate about the C(O)–calix axis, hence temporarily displacing the catalytic centre away from the bulky substituent and therefore limiting its protecting role.

Possible deactivation pathway of the bis-nickel complexes

The ^{31}P NMR spectra of the solutions obtained after ethylene polymerisation with **12** revealed the presence of several species. Among them, a compound, which corresponded to *ca.* 50% of the other species, exhibited a characteristic AB system (δ_A = 16.2, δ_B = 10.8 ppm), with J(AB) = 291 Hz, which is a good indication for the presence of two *trans*-arranged phosphorus atoms. This product could not be separated from the reaction mixture. We surmised that the "double-SHOP catalyst" initially formed had partially converted into a monometallic species containing *trans*-bonded phosphorus atoms. It turned out that this compound could be obtained quantitatively by reacting diphosphine **17**

Table 2 Ethylene polymerisation using ylides **12–15** and $Ph_3P{=}CHC(O)Ph$ (**19**)[a]

Entry	Ylide	Amount/μmol	*P*/bar	*T*/°C	*t*/h	PE[b]/g	TOF[c]/h^{-1}	M_w[d]/g mol^{-1}	M_n[d]/g mol^{-1}	M_w/M_n	T_m[e]/°C
1	**19**	4	5	70	0.5	1.12	20 000	6600	2600	2.5	127.0
2	**19**	4	5	80	0.5	1.87	33 300	—	—	—	126.7
3	**19**	4	5	90	0.5	2.27	40 500	3900	2200	1.8	124.0
4	**19**	2	10	70	0.5	1.06	37 800	—	—	—	—
5	**19**	2	10	70	0.25	0.58	41 400	—	—		
6	**12**	2	5	70	0.25	0.47	16 800	4100	2300	1.8	126.6
7	**12**	2	5	80	0.25	0.74	35 600	5300	2000	2.6	124.8
8	**12**	2	5	70	1	0.86	7 700	—	—	—	132.8
9	**12**	2	10	70	0.25	1.11	39 600	4000	2000	2.0	126.5
10	**13**	2	5	70	0.25	0.70	49 900	3300	2000	1.6	124.8
11	**13**	2	5	80	0.25	1.12	79 800	2700	1800	1.5	123.7
12	**13**	2	5	70	1	1.47	26 200	3300	2000	1.6	125.3
13	**13**	2	10	70	0.25	1.20	85 500	3300	2000	1.6	125.3
14	**14**	2	5	70	0.25	0.30	21 400	7000	3300	2.1	128.7
15	**14**	2	5	80	0.25	0.89	63 400	4900	2800	1.7	128.0
16	**14**	2	5	70	1	0.65	11 600	5400	3000	1.8	
17	**14**	2	10	70	0.25	0.59	42 100	5500	3000	1.8	129.0
18	**15**	2	5	70	0.25	0.18	6 400	5700	3000	1.9	
19	**15**	2	5	80	0.25	0.52	18 500	6000	2500	2.4	126.9
20	**15**	2	5	70	1	0.58	5 200	—	—	—	128.9
21	**15**	2	10	70	0.25	0.66	23 500	5700	2800	2.0	129.1

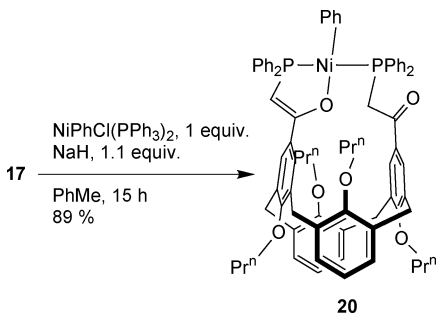
[a] General conditions: PhMe = 20 mL, 0.5 h, $[Ni(cod)_2]$/ylide unit = 10. [b] After precipitation of the reaction mixture with acidified (HCl) methanol (200 mL). [c] In (mol C_2H_4) (mol *P*,*O*-chelated Ni units)$^{-1}$ h^{-1}. [d] Determined by SEC-HT *vs.* polystyrene standard, uncorrected. [e] Measured by DSC.

Table 3 Ethylene oligomerisation using ylides **12–15** and **19**[a]

Entry	Ylide	$[Ni(cod)_2]$/μmol	PPh_3/μmol	*P*/bar	TOF/mol C_2H_4 (mol Ni)$^{-1}$ h^{-1}	α[b]	C_2H_4 consumption[c]/g
1	**19**	5	5	5	41 800	0.94	8.79
2	**19**	5	5	10	50 400	0.95	10.60
3	**12**	10	10	5	34 700	0.92	9.74
4	**12**	10	10	10	36 700	0.95	10.29
5	**13**	5	5	5	54 000	0.96	15.15
6	**13**	5	5	10	63 400	0.96	17.80
7	**14**	5	5	5	55 800	0.95	15.64
8	**14**	5	5	10	67 500	0.96	18.95
9	**15**	10	10	5	28 700	0.94	8.04
10	**15**	10	10	10	35 100	0.95	9.83

[a] General conditions: ylide 5 μmol, PhMe = 20 mL, 70 °C, 1 h, 100 mL autoclave. [b] Schulz–Flory parameter $\alpha = n(C_{n+2})/n(C_n)$. [c] Calculated value using heptane as internal standard.

with $[NiCl(Ph)(PPh_3)_2]$ in the presence of NaH (Scheme 7). It is noteworthy that the resulting complex, **20**, forms selectively even in the presence of an excess of nickel and base at 80 °C. Interestingly, we found no indication for the transient formation of complex **18** during this synthesis. Consistent with the presence of a free ketone function, the IR spectrum of **20** shows a strong absorption band at 1671 cm^{-1}. The IR spectrum further shows a strong absorption at 1495 cm^{-1} which may be assigned to the enolate system. In the ^1H NMR spectrum, the PCH proton of the enolate appears as a doublet at 4.83 ppm ($^2J(PH) = 2.2$ Hz).



Scheme 7

The crystal structure of **20** was elucidated by an X-ray diffraction study (Fig. 3). Complex **20** constitutes the first characterised example of a SHOP-type complex in which the two P(III) ligands are linked together.[43] The nickel atom adopts a slightly distorted square planar coordination geometry, the P(1)NiP(2) and C(69)NiO(1) angles being 172.7°(1) and 173.4°(1), respectively. In contrast to those of **18**, the four *p*-C atoms of the phenoxy rings are oriented towards the calixarene axis. The dihedral angles between the coordination plane and the C(15)- and the C(37)-rings are respectively 51° and 58°. It is interesting to note that the P(2), C(56), C(55) and O(6) atoms define a plane which is nearly coplanar with the C(37)-phenoxy ring. In other terms, one PCH_2 hydrogen atom lies inside the virtual tube defined by the calixarene moiety, the other points away. The inequivalence of the two PCH_2 protons was not evident in the ^1H NMR spectrum, since these

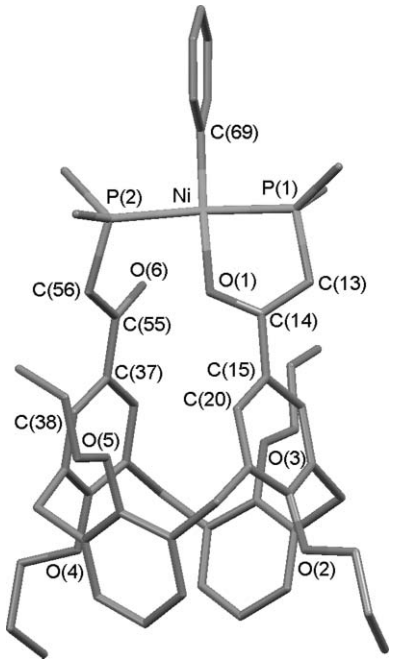
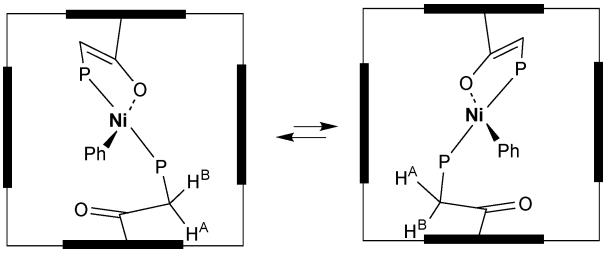


Fig. 3 X-Ray crystal structure of **20**.

protons give rise, at room temperature, to a broad signal centered at 4.22 ppm, suggesting a fast oscillation of the coordination plane about the calixarene axis as shown in Scheme 8.



Scheme 8 Postulated dynamics of complex **20** (view along the calixarene axis).

It turned out that **20** is not active, neither in oligomerisation nor polymerisation, even when operating at 30 bar and at 90 °C. Since substantial amounts of this complex were always found in the catalytic solutions after completion of the reaction, the activity of the Ni–**12** system as inferred from the data shown in Table 2 is underestimated. Careful investigations revealed that the formation of **20** requires the presence of ethylene and that **20** forms during the first minutes following addition of ethylene (1 bar) to a solution of [Ni(cod)$_2$]/**12** maintained at 70 °C. The question whether its formation can be avoided cannot be answered at this stage of our investigations.

Conclusion

In the present work we have described the first examples of calixarenes having keto-stabilized phosphorus ylides tethered to *p*-phenolic carbon atoms of the macrocyclic core. These can straightforwardly be converted into SHOP-type complexes. The monometallic complexes obtained from the corresponding monophosphorus ylides provide efficient ethylene oligomerisation or polymerisation catalysts displaying better activities than the prototype **19**, hence reflecting the protecting role of the bulky calixarene substituent against catalyst deactivation. The systems derived from the bis-ylides **12** and **15** resulted in lower activities, the proximity of the two (potential) catalytic centres facilitating an intramolecular deactivation pattern during catalyst activation. Further studies will concentrate on the way such a deactivation may be prevented.

Experimental

General procedures

Solvents were dried over suitable reagents and freshly distilled under dry nitrogen before use. $CDCl_3$ was passed through a 5 cm-thick alumina column and stored under N_2 over molecular sieves (4 Å). All reactions were carried out using Schlenk tube techniques under a dry nitrogen atmosphere. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer (KBr pellets, 4000–400 cm^{-1}) or a VERTEX 70 FT-IR spectrometer (pure, unmodified sample). Routine ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on Bruker AC-300 (^{1}H: 300.1 MHz; ^{13}C: 75.48 MHz; ^{31}P: 121.5 MHz) and ARX-500 (^{1}H: 500.1 MHz) spectrometers. Proton chemical shifts are reported relative to residual protonated solvents (C_6D_6, δ 7.16; $CDCl_3$, δ 7.26). The ^{13}C chemical shifts are referenced relative to deuterated solvents (C_6D_6, δ 128.02; $CDCl_3$, δ 77.0) and the ^{31}P NMR data are given relative to external H_3PO_4. For column chromatography Geduran SI (E. Merck, 0.040–0.063 mm) silica was used. Routine thin-layer chromatography analyses were carried out by using plates coated with Merck Kieselgel 60 GF_{254}. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus and are uncorrected. High-temperature size exclusion chromatography (HT SEC) measurements were performed at 150 °C with a "PL220" apparatus (Column set HT-MixedB-TCB-01) in 1,2,4-trichlorobenzene (with 0.2% Irganox). Calibration was made with linear polystyrene samples. DSC measurements were made using a Perkin Elmer DSC4 apparatus with a heating rate of 10 °C min^{-1}. The catalytic solutions were analysed with a Varian 3900 gas chromatograph equipped with a WCOT-fused silica column (25 m, 0.32 mm inside diameter, 0.25 mm film thickness). The calixarene **1**,[27] **19**,[44] [Ni(cod)$_2$],[44] [NiPhCl(PPh$_3$)$_2$][45] and PhNMe$_3$Br$_3$[46] were prepared according to literature procedures.

Acetylated calixarenes

5,17-Diacetyl-25,27-dipropoxy-26,28-dihydroxycalix[4]arene (*cone*) (2). To a solution of 25,27-dihydroxy-26,28-dipropoxycalix[4]arene (*cone*) (**1**) (8.100 g, 15.93 mmol) in nitrobenzene (250 mL) was added $AlCl_3$ (9.550 g, 71.66 mmol). Acetyl chloride (2.620 g, 33.45 mmol) was slowly added, and the resulting brownish solution was stirred for 0.25 h (a longer reaction time results in formation of the triacetylated compound). The reaction was quenched with 2 M HCl (150 mL). The organic phase was separated and washed with water (100 mL). The solvent was removed in *vacuo* at *ca.* 120 °C affording a brown residue. Recrystallisation from a CH_2Cl_2–MeOH mixture afforded pure **2** as a white powder. Yield: 8.020 g, 85%; mp >250 °C; IR

(KBr, cm^{-1}): ν(C=O) 1666s. ^1H NMR (300 MHz, $CDCl_3$): δ 9.04 (s, 2H, OH), 7.75, (s, 4H, *m*-ArH), 6.97 (d, 4H, *m*-ArH, ^3J = 7.6 Hz), 6.79 (t, 2H, *p*-ArH, ^3J = 7.6 Hz), 4.31 and 3.48 (AB spin system, 8H, $ArCH_2Ar$, ^2J = 12.8 Hz), 4.01 (t, 4H, OCH_2, ^3J = 6.2 Hz), 2.55 (s, 6H, $C(O)CH_3$), 2.08 (m, 4H, OCH_2CH_2), 1.33 (t, 6H, CH_2CH_3, ^3J = 7.4 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 196.90 (s, C(O)), 158.39, 151.75, 132.69, 129.58, 129.30, 128.89, 127.95 and 125.60 (8s, aryl C), 78.54 (s, OCH_2), 31.42 (s, $ArCH_2Ar$), 26.28 (s, $C(O)CH_3$), 23.51 (s, OCH_2CH_2), 10.92 (s, CH_2CH_3). Found: C, 77.05; H, 6.91. Calc. for $C_{38}H_{40}O_6$ (M_r = 592.73) C, 77.00; H, 6.80%.

5,17-Diacetyl-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate* (3a) and *partial cone* (3b)). K_2CO_3 (0.467 g, 3.38 mmol) was added to a solution of **1** (1.000 g, 1.69 mmol) in refluxing acetonitrile (100 mL). After 1 h, *n*-PrBr (0.624 g, 5.07 mmol) was added and the suspension was maintained under reflux. The reaction was monitored by TLC (R_f = 0.7 (**3b**), R_f = 0.4 (**3a**), SiO_2, AcOEt–CH_2Cl_2, 5 : 95, v/v) and heating was stopped after 7 d. After filtration the solution was evaporated to dryness and the two isomers were separated by column chromatography on silica gel using AcOEt–CH_2Cl_2 (5 : 95, v/v) as eluent.

(**3a**) Yield: 0.721 g, 63%; mp 223–226 °C; IR (KBr, cm^{-1}): ν(C=O) 1676s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.64 (s, 4H, *m*-ArH of acylated Ar), 6.99 (d, 4H, *m*-ArH, ^3J = 7.5 Hz), 6.65 (t, 2H, *p*-ArH, ^3J = 7.5 Hz), 3.71–3.65 (8H, OCH_2), 3.61 and 3.54 (AB spin system, 8H, $ArCH_2Ar$, ^2J = 13.4 Hz), 2.47 (s, 6H, $C(O)CH_3$), 1.95–1.79 (8H, CH_2CH_3), 1.09–1.01 (12H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 197.69 (s, C(O)), 160.85–121.77 (aryl and quat.-C), 74.80 (s, OCH_2), 35.37 (s, $ArCH_2Ar$), 26.40 (s, $C(O)CH_3$), 23.92 (s, CH_2CH_3), 10.64 (s, CH_2CH_3). Found: C, 77.88; H, 8.02. Calc. for $C_{44}H_{52}O_6$ (M_r = 676.89) C, 78.07; H, 7.74%.

(**3b**) Yield: 0.314 g, 26%; mp 224–226 °C; IR (KBr, cm^{-1}): ν(C=O) 1677s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.93 and 7.74 (2s, 2H each, *m*-ArH of acylated Ar), 6.94 (d, 2H, *m*-ArH, ^3J = 7.5 Hz), 6.45 (two overlapping d, 2H, *p*-ArH, $^3J = {}^3J' = 7.5$ Hz), 6.25 (d, 2H, *m*-ArH, ^3J = 7.5 Hz), 4.08 and 3.14 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 13.4 Hz), 3.85–3.80 (m, 4H, OCH_2), 3.74 and 3.67 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 12.7 Hz), 3.55 (m, 2H, OCH_2), 3.30 (m, 2H, OCH_2), 2.63 and 2.62 (2s, 3H each, $C(O)CH_3$), 2.00–1.89 (6H, CH_2CH_3), 1.35–1.27 (m, 2H, CH_2CH_3), 1.13–1.05 (9H, CH_2CH_3), 0.62 (t, 3H, CH_2CH_3 ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 197.69 and 197.27 (2s, C(O)), 162.19–121.80 (aryl and quat.-C), 76.36, 75.70 and 75.01 (3s, OCH_2), 35.82 and 30.52 (2s, $ArCH_2Ar$), 26.62 and 26.48 (2s, $CH_3C(O)$), 24.16, 23.87 and 22.12 (3s, CH_2CH_3), 10.88, 10.63 and 9.31 (3s, CH_2CH_3). Found: C, 78.03; H, 7.80. Calc. for $C_{44}H_{52}O_6$ (M_r = 676.89) C, 78.07; H, 7.74%.

5-Acetyl-25,27-dipropoxy-26,28-dihydroxycalix[4]arene (*cone*) (5). To a solution of **1** (3.000 g, 5.90 mmol) in nitrobenzene (250 mL) was added acetyl chloride (0.467 g, 5.95 mmol). A solution of $AlCl_3$ (0.790 g, 5.95 mmol) in nitrobenzene (50 mL) was then added dropwise over 2 h. The resulting brownish solution was stirred for a further 10 min and then quenched with 2 M HCl (200 mL). The organic phase was separated and washed with water (2 × 100 mL). Removal of the solvent in *vacuo* under heating at 120 °C gave a residue which was purified by column chromatography using AcOEt–CH_2Cl_2 (2 : 98, v/v) as eluant (R_f = 0.5, SiO_2, AcOEt–CH_2Cl_2, 2 : 98, v/v). Yield: 2.920 g, 90%; mp >250 °C. IR (KBr, cm^{-1}): ν(C=O) 1671s. ^1H NMR (300 MHz, $CDCl_3$): δ 9.13 (s, 1H, OH), 8.27 (s, 1H, OH), 7.76 (s, 2H, *m*-ArH of acylated ring), 7.08 (d, 2H, *m*-ArH, ^3J = 7.4 Hz), 6.96 (d, 4H, *m*-ArH, ^3J = 7.5 Hz), 6.78 (t, 2H, *p*-ArH, ^3J = 7.6 Hz), 6.67 (t, 1H, *p*-ArH, ^3J = 7.4 Hz), 4.34 and 3.48 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 13.0 Hz), 4.34 and 3.41 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 13.0 Hz), 4.01 (t, 4H, OCH_2, ^3J = 6.2 Hz), 2.56 (s, 3H, $C(O)CH_3$), 2.08 (m, 4H, OCH_2CH_2), 1.34 (t, 6H, CH_2CH_3, ^3J = 7.4 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 196.94 (s, C(O)), 158.54–119.08 (aryl and quat.-C), 78.45 (s, OCH_2), 31.48 and 31.44 (2s, $ArCH_2Ar$), 26.29 (s, $C(O)CH_3$), 23.54 (s, OCH_2CH_2), 10.96 (s, CH_2CH_3). Found: C, 78.16; H, 6.84. Calc. for $C_{36}H_{38}O_5$ (M_r = 550.69) C, 78.52; H, 6.96%.

5-Acetyl-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate*) (6). A suspension of K_2CO_3 (0.467 g, 3.38 mmol) and 5-acetyl-25,27-dipropoxy-26,28-dihydroxycalix[4]arene (*cone*) (**5**) (1.000 g, 1.69 mmol) was stirred in refluxing acetonitrile (100 mL) for 1 h. Then *n*-PrBr (0.624 g, 5.07 mmol) was added and the suspension was further stirred at 60 °C for 1 week. Product formation was monitored by TLC (R_f = 0.6, SiO_2, AcOEt–CH_2Cl_2, 2 : 98, v/v). After filtration, the solution was evaporated to dryness. The product was recrystallised from CH_2Cl_2–MeOH. Yield: 0.805 g, 75%; mp 156–158 °C; IR (KBr, cm^{-1}): ν(C=O) 1680s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (s, 2H, *m*-ArH of acylated Ar), 7.03–6.97 (6H, *m*-ArH,), 6.65 (t, 2H, *p*-ArH, ^3J = 7.5 Hz), 6.54 (pseudo-t, 1H, *p*-ArH, ^3J = 7.5 Hz), 3.69–3.56 (16H, OCH_2 and $ArCH_2Ar$), 2.58 (s, 3H, $C(O)CH_3$), 1.87–1.74 (8H, CH_2CH_3), 1.07–1.02 (12H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 197.78 (s, C(O)), 160.76–121.24 (aryl and quat.-C), 74.79, 74.59 and 74.39 (3s, OCH_2), 35.41 and 35.38 (2s, $ArCH_2Ar$), 26.52 (s, $C(O)CH_3$), 23.88 and 23.85 (2s, CH_2CH_3), 10.69 (s, CH_2CH_3). Found: C, 79.54; H, 7.93. Calc. for $C_{42}H_{50}O_5$ (M_r = 634.86) C, 79.46; H, 7.94%.

2-Haloacetylated calixarenes

5,17-Bis(2-bromoacetyl)-25,26,27,28-tetrapropoxycalix[4]arene-(*1,3-alternate*) (4). To a solution of 5,17-diacetyl-25,26,27,28-tetrapropoxycalix[4]arene (**3a**) (4.000 g, 5.91 mmol) in $CHCl_3$ (30 mL) at 40 °C was slowly added a solution of Br_2 (1.940 g, 12.11 mmol) in $CHCl_3$ (10 mL). After being stirred for 5 min the solution was washed successively with 10% Na_2SO_3 (10 mL) and 10% $NaHCO_3$ (20 mL), then dried with $MgSO_4$, and concentrated. Addition of MeOH afforded a white microcrystalline powder. Yield: 4.730 g, 96%; mp 123–126 °C; IR (KBr, cm^{-1}): ν(C=O) 1668s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (s, 4H, *m*-ArH), 6.98 (d, 4H, *m*-ArH, ^3J = 7.5 Hz), 6.63 (t, 2H, *p*-ArH, ^3J = 7.5 Hz), 4.36 (s, 4H, $C(O)CH_2Br$), 3.74 (t, 4H, OCH_2, ^3J = 7.0 Hz), 3.73 (t, 4H, OCH_2, ^3J = 7.3 Hz), 3.57 and 3.52 (AB spin system, 8H, $ArCH_2Ar$, ^2J = 13.1 Hz), 2.09–1.97 (m, 4H, CH_2CH_3), 1.97–1.83 (m, 4H, CH_2CH_3), 1.16 (t, 6H, CH_2CH_3, ^3J = 7.4 Hz), 1.10 (t, 6H, CH_2CH_3, ^3J = 7.4 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 191.04 (s, C(O)), 161.49–121.96 (aryl and quat.-C), 75.40 (s, OCH_2), 34.78 (s, $ArCH_2Ar$), 31.44 (s, $C(O)CH_2Br$), 24.15 and 24.08 (2s, CH_2CH_3), 10.79 and 10.74 (2s, CH_2CH_3). Found: C, 63.19; H, 5.89. Calc. for $C_{44}H_{50}Br_2O_6$ (M_r = 834.69): C, 63.32; H, 6.04%.

5-(2-Bromoacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate*) (7). To a stirred solution of 5-acetyl-25,26,27,28-tetrapropoxycalix[4]arene (**6**) (2.000 g, 3.15 mmol) in CH_2Cl_2 (30 mL) was added slowly a solution of Br_2 (0.500 g, 3.15 mmol) in CH_2Cl_2 (20 mL). After the addition was completed the solution was washed successively with 10% Na_2SO_3 (10 mL) and 10% $NaHCO_3$ (20 mL), dried over $MgSO_4$ and concentrated. Addition of MeOH afforded a white precipitate. Yield: 2.110 g, 94%; mp 105–109 °C; IR (KBr, cm^{-1}): ν(C=O) 1678s. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (s, 2H, *m*-ArH), 7.03 (dd, 2H, *m*-ArH, $J = 7.6$ Hz, $J' = 1.7$ Hz), 6.97 (d, 4H, *m*-ArH, $J = 7.5$ Hz), 6.64 (pseudo-t, 2H, *p*-ArH, $^3J = 7.5$ Hz), 6.52 (t, 1H, *p*-ArH, $^3J = 7.5$ Hz), 4.50 (s, 2H, C(O)CH_2Br), 3.72–3.54 (16H, OCH_2 and ArCH_2Ar), 1.93–1.82 (8H, CH_2CH_3), 1.11–1.03 (12H, CH_2CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 190.32 (s, C(O)), 161.38–121.07 (aryl and quat.-C), 75.20, 74.99 and 74.66 (3s, OCH_2), 35.12 and 35.02 (2s, ArCH_2Ar), 32.13 (s, CH_2Br), 23.99 and 23.96 (2s, CH_2CH_3), 10.76 (s, CH_2CH_3). Found: C, 70.61; H, 6.96. Calc. for $C_{42}H_{49}BrO_5$ (M_r = 713.15): C, 70.68; H, 6.92%.

5-(2-Bromoacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]-arene (*cone*) (8). To a solution of 5-acetyl-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**5**) (3.000 g, 5.45 mmol) in THF (100 mL) was added dropwise a solution of $PhNMe_3Br_3$ (2.050 g, 5.45 mmol) in THF (50 mL). The mixture was stirred until complete discolouration. After filtration the solution was evaporated to dryness. The residue was purified by column chromatography on silica gel using a cyclohexane–dichloromethane mixture (1 : 4) as eluent (R_f = 0.2, SiO_2, cyclohexane–CH_2Cl_2, 1 : 4, v/v). 5-(2,2-Dibromoacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**10**) eluted first (R_f = 0.4, SiO_2, cyclohexane–CH_2Cl_2 1:4, v/v). Yield: 2.330 g, 68%; mp 223–227 °C (decomp.); IR (KBr, cm^{-1}): ν(C=O) 1683s. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.34 (s, 1H, OH), 8.27 (s, 1H, OH), 7.80, (s, 2H, *m*-ArH), 7.08 (d, 2H, *m*-ArH, $^3J = 7.5$ Hz), 6.99–6.94 (4H, *m*-ArH), 6.78 (pseudo-t, 2H, *p*-ArH, $^3J = 7.6$ Hz), 6.67 (t, 1H, *p*-ArH, $^3J = 7.4$ Hz), 4.41 (s, 2H, C(O)CH_2Br), 4.33 and 3.49 (AB spin system, 4H, ArCH_2Ar, $^2J = 13.1$ Hz), 4.33 and 3.41 (AB spin system, 4H, ArCH_2Ar, $^2J = 13.0$ Hz), 4.04–3.98 (m, 4H, OCH_2), 2.14–2.06 (m, 4H, OCH_2CH_2), 1.34 (t, 6H, CH_2CH_3, $^3J = 7.4$ Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 190.03 (s, C(O)), 159.46–119.12 (aryl and quat.-C), 78.49 (s, OCH_2), 31.47 and 31.44 (2s, ArCH_2Ar), 30.79 (s, C(O)CH_2Br), 23.54 (s, OCH_2CH_2), 10.97 (s, CH_2CH_3). Found: C, 68.60; H, 5.85. Calc. for $C_{36}H_{37}O_5Br$ (M_r = 629.59): C, 68.68; H, 5.92%.

5,17-Bis(chloroacetyl)-25,27-dipropoxy-26,28-dihydroxycalix-[4]arene (*cone*) (9). To a solution of **1** (8.100 g, 15.93 mmol) in nitrobenzene (250 mL) was first added $AlCl_3$ (9.550 g, 71.66 mmol), then a solution of $ClCH_2C(O)Cl$ (3.780 g, 33.45 mmol) in nitrobenzene (20 mL). The resulting brownish solution was stirred for 2 h and then quenched with 2 M HCl (150 mL). The organic phase was separated and washed with water (2 × 50 mL). Removal of the solvent in *vacuo* at 120 °C gave a residue which was chromatographed on silica gel using CH_2Cl_2 as eluent (R_f = 0.2, SiO_2, CH_2Cl_2). Yield: 3.160 g, 30%; mp >250 °C; IR (KBr, cm^{-1}): ν(C=O) 1678s. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (s, 2H, OH), 7.77 (s, 4H, *m*-ArH), 6.97 (d, 4H, *m*-ArH, $^3J = 7.5$ Hz), 6.80 (t, 2H, *p*-ArH, $^3J = 7.5$ Hz), 4.66 (s, 4H, CH_2Cl), 4.31 and 3.50 (AB spin system, 8H, ArCH_2Ar, $^2J = 13.1$ Hz), 4.02 (t, 4H, OCH_2, $^3J = 6.2$ Hz), 2.15–2.03 (m, 4H, OCH_2CH_2), 1.34 (t, 6H, CH_2CH_3, $^3J = 7.4$ Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 189.74 (s, C=O), 159.25, 151.72, 132.45, 129.93, 129.43, 128.37, 125.73 and 125.71 (8s, arom. C), 78.65 (s, OCH_2), 45.70 (s, CH_2Cl), 31.39 (s, ArCH_2Ar), 23.52 (s, OCH_2CH_2), 10.95 (s, CH_2CH_3). Found: C, 68.97; H, 5.81. Calc. for $C_{38}H_{38}Cl_2O_6$ (M_r = 661.62): C, 68.98; H, 5.79%.

5-(2,2-Dibromoacetyl)-25,27-dihydroxy-26,28-dipropoxycalix-[4]arene (*cone*) (10). To a solution of 5-acetyl-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**5**) (3.000 g, 5.45 mmol) in THF (100 mL) was added dropwise a solution of $PhNMe_3Br_3$ (4.100 g, 10.90 mmol) in THF (50 mL). The mixture was stirred until complete discolouration, and was then filtered and evaporated to dryness. The residue was recrystallised from CH_2Cl_2–MeOH. Yield: 3.440 g, 89%; mp 208–212 °C (decomp.); IR (KBr, cm^{-1}): ν(C=O) 1685s. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.50 (s, 1H, OH), 8.29 (s, 1H, OH), 7.92, (s, 2H, *m*-ArH), 7.09 (d, 2H, *m*-ArH, $^3J = 7.3$ Hz), 6.99–6.94 (4H, *m*-ArH), 6.79 (pseudo-t, 2H, *p*-ArH, $^3J = 7.5$ Hz), 6.74 (s, 1H, C(O)$CHBr_2$), 6.68 (t, 1H, *p*-ArH, $^3J = 7.4$ Hz), 4.33 and 3.51 (AB spin system, 4H, ArCH_2Ar, $^2J = 13.1$ Hz), 4.33 and 3.43 (AB spin system, 4H, ArCH_2Ar, $^2J = 13.0$ Hz), 4.10–3.90 (m, 4H, OCH_2), 2.25–2.00 (m, 4H, OCH_2CH_2), 1.35 (t, 6H, CH_2CH_3, $^3J = 7.3$ Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 184.65 (s, C(O)), 160.05–119.16 (aryl and quat.-C), 78.52 (s, OCH_2), 40.38 (s, C(O)$CHBr_2$), 31.48 and 31.45 (2s, ArCH_2Ar), 23.54 (s, OCH_2CH_2), 10.98 (s, CH_2CH_3). Found: C, 60.91; H, 5.06. Calc. for $C_{36}H_{36}O_5Br_2$ (M_r = 708.49): C, 61.03; H, 5.12%.

5-(2-Bromoacetyl)-17-bromo-25,27-dihydroxy-26,28-dipropoxy-calix[4]arene (*cone*) (11). To a solution of 5-acetyl-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**5**) (4.500 g, 8.17 mmol) in $CHCl_3$ (50 mL) at 60 °C was added dropwise over 5 min a solution of Br_2 (2.600 g, 16.34 mmol) in $CHCl_3$ (20 mL). The mixture was stirred for 0.5 h and washed successively with 10% Na_2SO_3 (10 mL) and 10% $NaHCO_3$ (20 mL), dried over $MgSO_4$, filtered and concentrated to *ca.* 5 mL. Addition of hexane afforded a white precipitate. Yield: 5.990 g, 94%; mp 231–234 °C; IR (KBr, cm^{-1}): ν(C=O) 1680s. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.28 (s, 1H, OH), 8.42 (s, 1H, OH), 7.81, (s, 2H, *m*-ArH), 7.20 (s, 2H, *m*-ArH), 7.00–6.95 (4H, *m*-ArH), 6.82 (t, 2H, *p*-ArH, $^3J = 7.5$ Hz), 4.42 (s, 2H, C(O)CH_2Br), 4.32 and 3.50 (AB spin system, 4H, ArCH_2Ar, $^2J = 13.1$ Hz), 4.29 and 3.36 (AB spin system, 4H, ArCH_2Ar, $^2J = 13.1$ Hz), 4.01 (t, 4H, OCH_2, $^3J = 6.2$ Hz), 2.15–2.03 (m, 4H, CH_2CH_3), 1.34 (t, 6H, CH_2CH_3, $^3J = 7.4$ Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 190.04 (s, C(O)), 159.34–110.49 (aryl and quat.-C), 78.59 (s, OCH_2), 31.44 and 31.20 (2s, ArCH_2Ar), 30.79 (s, C(O)CH_2Br), 23.52 (s, OCH_2CH_2), 10.95 (s, CH_2CH_3). Found: C, 60.91; H, 5.23. Calc. for $C_{36}H_{36}O_5Br_2$ (M_r = 708.49): C, 61.03; H, 5.12%.

Keto-stabilized ylides

5,17-Bis(2-triphenylphosphoranylideneacetyl)-25,26,27,28-tetra-propoxycalix[4]arene (*1,3-alternate*) (12). To a solution of 5,17 - bis(2 - bromoacetyl) - 25,26,27,28 - tetrapropoxycalix[4]arene (**4**) (4.000 g, 4.79 mmol) in THF (30 mL) was added PPh_3 (2.520 g, 9.58 mmol). The solution was stirred for 15 h upon which NaH (60% in mineral oil, 0.240 g, 10 mmol) was added. After stirring for 5 h, the mixture was filtered through Celite and the resulting

solution concentrated to *ca.* 5 mL. Addition of Et_2O yielded the ylide as a white powder. Yield: 4.930 g, 86%; mp 236–240 °C (decomp.); IR (KBr, cm^{-1}): 1515s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.74–7.67 (12H, PPh_3), 7.67 (s, 4H, *m*-ArH), 7.49–7.35 (18H, PPh_3), 7.01 (d, 4H, *m*-ArH, $^3J = 7.4$ Hz), 6.78 (t, 2H, *p*-ArH, $^3J = 7.5$ Hz), 4.40–4.28 (2H, PCH), 3.89 and 3.81 (AB spin system, 8H, $ArCH_2Ar$, $^2J = 15.8$ Hz), 3.34 (t, 4H, OCH_2, $^3J = 7.3$ Hz), 3.30 (t, 4H, OCH_2, $^3J = 7.3$ Hz), 1.36–1.20 (8H, CH_2CH_3), 0.65 (t, 6H, CH_2CH_3, $^3J = 7.5$ Hz), 0.58 (t, 6H, CH_2CH_3, $^3J = 7.5$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 185.18 (d, C(O), ^2J(PC) = 3.0 Hz), 158.45–121.95 (aryl and quat.-C), 71.90 and 71.61 (2s, OCH_2), 49.12 (d, PCH, J(PC) = 114.0 Hz), 38.55 (s, $ArCH_2Ar$), 22.82 and 22.37 (2s, CH_2CH_3), 10.37 and 10.17 (2s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 16.31 (s). Found: C, 79.99; H, 6.68. Calc. for $C_{80}H_{78}O_6P_2$ ($M_r = 1197.44$): C, 80.24; H, 6.56%.

5-(2-Triphenylphosphoranylideneacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate*) (13). A mixture of 5-(2-bromoacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (**7**) (1.000 g, 1.4 mmol) and PPh_3 (0.370 g, 1.4 mmol) in THF (20 mL) was stirred at ambient temperature for 15 h. NaH (60% in mineral oil, 0.056 g, 1.4 mmol) was then added, and the suspension was stirred for 5 h. The solvent was removed *in vacuo*, and the residue was treated with toluene. After filtration through Celite, the resulting solution was concentrated to *ca.* 5 mL. Addition of hexane afforded a white microcrystalline powder. Yield: 1.040 g, 83%; mp 112–115 °C; IR (ATR sampling, cm^{-1}): 1518s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.84–7.77 (6H, PPh_3), 7.66 (s, 2H, *m*-ArH), 7.61–7.47 (9H, PPh_3), 7.05–7.01 (6H, *m*-ArH), 6.72 (pseudo-t, 2H, *p*-ArH, $^3J = 7.5$ Hz), 6.69 (t, 1H, *p*-ArH, $^3J = 7.5$ Hz), 4.31 (d, 1H, PCH, ^2J(PH) = 26.2 Hz), 3.77–3.65 (8H, $ArCH_2Ar$), 3.60–3.44 (8H, OCH_2), 1.69–1.50 (8H, CH_2CH_3), 0.91 (t, 3H, CH_2CH_3, $^3J = 7.5$ Hz), 0.90 (t, 3H, CH_2CH_3, $^3J = 7.6$ Hz), 0.82 (t, 6H, CH_2CH_3, $^3J = 7.4$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 185.90 (d, C(O), ^2J(PC) = 2.9 Hz), 158.00–121.64 (aryl and quat.-C), 73.44, 73.35 and 73.31 (3s, OCH_2), 49.28 (d, PCH, J(PC) = 112.8 Hz), 36.86 and 36.72 (2s, $ArCH_2Ar$), 23.52 and 23.35 (2s, CH_2CH_3), 10.59, 10.54 and 10.47 (3s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 16.22 (s). Found: C, 80.38; H, 6.91. Calc. for $C_{60}H_{63}O_5P$ ($M_r = 895.13$): C, 80.51; H, 7.09%.

5-(2-Triphenylphosphoranylideneacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (*cone*) (14). A mixture of 5-(2-bromoacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**8**) (2.000 g, 3.18 mmol) and PPh_3 (0.833 g, 3.18 mmol) in THF (100 mL) was stirred for 15 h. NaH (60% in mineral oil, 0.127 g, 3.18 mmol) was then added, and the white suspension was stirred for a further 5 h. The mixture was filtered through Celite upon which it was concentrated. Addition of Et_2O afforded a white powder. Yield: 2.350 g, 91%; mp >250 °C; IR (ATR sampling, cm^{-1}): 1511s. ^1H NMR (300 MHz, $CDCl_3$): δ 8.55 (s, 1H, OH), 8.30 (s, 1H, OH), 7.83 (s, 2H, *m*-ArH), 7.79–7.72 (6H, PPh_3), 7.48–7.43 (9H, PPh_3), 7.08 (d, 2H, *m*-ArH, $^3J = 7.5$ Hz), 7.03 (A part of ABX, dd, 2H, *m*-ArH, ^4J(AB) = 1.5 Hz, ^3J(AX) = 7.5 Hz), 6.92 (B part of ABX, dd, 2H, *m*-ArH, ^4J(AB) = 1.5 Hz, ^3J(BX) = 7.5 Hz), 6.71 (X part of ABX, pseudo-t, 2H, *p*-ArH, ^3J(AX) = ^3J(BX) = 7.5 Hz), 6.67 (t, 1H, *p*-ArH, $^3J = 7.5$ Hz), 4.44–4.35 (signal overlapping with $ArCH_2$, 1H, PCH), 4.37 and 3.51 (AB spin system, 4H, $ArCH_2Ar$, $^2J = 13.0$ Hz), 4.37 and 3.36 (AB spin system, 4H, $ArCH_2Ar$, $^2J = 12.9$ Hz), 4.07–3.97 (m, 4H, OCH_2), 2.17–2.06 (m, 4H, CH_2CH_3), 1.36 (t, 6H, CH_2CH_3, $^3J = 7.5$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 184.73 (s, C(O)), 155.24–119.04 (aryl and quat.-C), 78.33 (s, OCH_2), 48.95 (d, PCH, J(PC) = 115 Hz), 31.61 and 31.49 (2s, $ArCH_2Ar$), 23.59 (s, OCH_2CH_2), 11.02 (s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 16.6 (s). Found: C, 80.14; H, 6.19. Calc. for $C_{54}H_{51}O_5P$ ($M_r = 810.97$): C, 79.98; H, 6.34%.

5,17-Bis(2-triphenylphosphoranylideneacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (*cone*) (15). To a solution of 5,17-bis(2-chloroacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**9**) (2.000 g, 3.02 mmol) in acetonitrile (30 mL) was added PPh_3 (1.762 g, 6.04 mmol). The solution was stirred for 15 h under reflux, and then concentrated to *ca.* 10 mL. Addition of Et_2O afforded quantitatively the corresponding phosphonium salt as a white powder which was dried in *vacuo* for 0.5 h. The phosphonium salt was then suspended in THF (50 mL) and NaH (60% in mineral oil, 0.242 g, 6.04 mmol) was added. After 5 h the solution was filtered through Celite, then concentrated to *ca.* 20 mL. Addition of Et_2O yielded the ylide as a white powder. Yield: 2.960 g, 88%; mp > 250 °C; IR (KBr, cm^{-1}): 1666s. ^1H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 2H, OH), 7.77–7.64 (12H, PPh_3 and 4H, *m*-ArH), 7.56–7.44 (18H, PPh_3), 6.97 (d, 4H, *m*-ArH, $^3J = 7.6$ Hz), 6.69 (t, 2H, *p*-ArH, $^3J = 7.5$ Hz), 4.40–4.27 (2H, PCH), 4.30 and 3.44 (AB spin system, 8H, $ArCH_2Ar$, $^2J = 12.9$ Hz), 3.97 (t, 4H, OCH_2, $^3J = 6.2$ Hz), 2.12–2.01 (m, 4H, CH_2CH_3), 1.30 (t, 6H, CH_2CH_3, $^3J = 7.4$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 184.86 (d, C(O), ^2J(PC) = 3 Hz), 155.19–125.21 (aryl and quat.-C), 76.68 (s, OCH_2), 48.79 (d, PCH, J(PC) = 113 Hz), 31.53 (s, $ArCH_2Ar$), 23.53 (s, CH_2CH_3), 10.92 (s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 16.5. Found: C, 79.65; H, 5.83. Calc. for $C_{74}H_{66}O_6P_2$ ($M_r = 1113.28$): C, 79.84; H, 5.98%.

Calixarenes bearing β-ketophosphine units

5-Diphenylphosphinoacetyl-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate*) (16). To a solution of $HNPr^i_2$ (0.184 g, 1.82 mmol) in THF (10 mL), maintained at −78 °C, was slowly added a 1.6 M solution of *n*-BuLi in hexane (1.13 mL, 1.81 mmol). The mixture was stirred for 0.5 h, and a solution of 5-acetyl-25,26,27,28-tetrapropoxycalix[4]arene (**6**) (1.150 g, 1.81 mmol) in THF (20 mL) was subsequently added, with the temperature kept at −78 °C. After stirring the mixture for 1 h, a solution of Ph_2PCl (0.399 g, 1.81 mmol) in THF (5 mL) was slowly added. The temperature was then raised to 25 °C, and the mixture was stirred for a further 15 h. After removal of the solvent *in vacuo*, the residue was treated with toluene and the resulting suspension was filtered through Celite in order to remove LiCl. The filtered solution was evaporated to dryness. Recrystallisation from CH_2Cl_2–MeOH gave **16** as a pure white solid. Yield: 1.379 g, 93%; mp 139–141 °C; IR (KBr, cm^{-1}): ν(C=O) 1667s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (s, 2H, *m*-ArH), 7.57–7.51 (3H, ArH), 7.42–7.37 (5H, ArH), 7.03–6.95 (6H, ArH), 6.65 (pseudo-t, 2H, *p*-ArH, $^3J = 7.4$ Hz), 6.57 (t, 1H, *p*-ArH, $^3J = 7.4$ Hz), 3.80 (s, 2H, PCH_2), 3.71–3.54 (16H, OCH_2 and $ArCH_2Ar$), 1.89–1.69 (8H, CH_2CH_3), 1.06 (t, 3H, CH_2CH_3, $^3J = 7.4$ Hz), 1.03 (t, 3H, CH_2CH_3, $^3J = 7.4$ Hz), 0.91 (t, 6H, CH_2CH_3, $^3J = 7.4$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 196.20 (d, C(O), ^2J(PC) = 8.7 Hz), 160.92–121.35 (aryl and quat.-C), 74.86, 74.69 and 74.47 (3s, OCH_2), 40.68 (d, PCH_2, ^1J(PC) = 18.6 Hz), 35.31 (s, $ArCH_2Ar$), 23.92 and 23.89

(2s, CH_2CH_3), 10.71 and 10.60 (2s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ −19.4 (s). Found: C, 79.11; H, 7.51. Calc. for $C_{54}H_{59}O_5P$ (M_r = 819.04): C, 79.19; H, 7.26%.

5,17-Bis(diphenylphosphinoacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate*) (17). To a solution of $HNPr^i_2$ (0.101 g, 1.00 mmol) in THF (10 mL) at −78 °C was slowly added a 1.5 M solution of *n*-BuLi (0.67 mL, 1.00 mmol). The mixture was stirred for 0.5 h, and a solution of 5,17-diacetyl-25,26,27,28-tetrapropoxycalix[4]arene (**3a**) (0.340 g, 0.50 mmol) in THF (20 mL) was subsequently added, with the temperature kept at −78 °C. After stirring the solution for 1 h, a solution of Ph_2PCl (0.221 g, 1.00 mmol) was slowly added. The temperature was then raised to 25 °C, and the mixture was stirred for 15 h. After removal of the solvent *in vacuo*, the residue was treated with toluene and the resulting suspension was filtered through Celite in order to remove LiCl. The filtered solution was evaporated to dryness and the product was recrystallised from CH_2Cl_2–MeOH, yielding **17** as a pure white solid. Yield: 0.470 g, 90%; mp 155 °C; IR (KBr, cm^{-1}): ν(C=O) 1667s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.68 (s, 4H, *m*-ArH), 7.58–7.33 (20H, PPh_2), 6.97 (d, 4H, *m*-ArH, ^3J = 7.6 Hz), 6.63 (pseudo-t, 2H, *p*-ArH, ^3J = 7.5 Hz), 3.77 (s, 4H, PCH_2, ^2J(PH) = 0 Hz), 3.69 (t, 4H, OCH_2, ^3J = 7.1 Hz), 3.59 (t, 4H, OCH_2, ^3J = 7.6 Hz), 3.52 (s br, 8H, $ArCH_2Ar$), 1.90–1.71 (8H, CH_2CH_3), 1.06 (t, 6H, CH_2CH_3, ^3J = 7.4 Hz), 0.79 (t, 6H, CH_2CH_3, ^3J = 7.4 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 196.31 (d, C(O), ^2J(PC) = 8.3 Hz), 160.96–121.75 (aryl and quat.-C), 74.84 and 74.78 (2s, OCH_2), 40.00 (d, PCH_2, ^1J(PC) = 20.1 Hz), 35.28 (s, $ArCH_2Ar$), 24.06 and 23.98 (2s, CH_2CH_3), 10.67 and 10.40 (2s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ–16.2 (s). Found: C, 78.01; H, 6.76. Calc. for $C_{68}H_{70}O_6P_2$ (M_r = 1045.25): C, 78.14; H, 6.75%.

Nickel complexes

Complex 18. A solution of 5,17-bis(2-triphenylphosphoranylideneacetyl)-25,26,27,28-tetrapropoxycalix[4]arene **12** (1.197 g, 1.00 mmol), PPh_3 (0.944 g, 3.60 mmol) and $[Ni(cod)_2]$ (0.660 g, 2.40 mmol) in toluene (50 mL) was stirred at room temperature for 15 h. The red solution was then concentrated to *ca.* 10 mL. Slow diffusion of hexane (70 mL) into this solution afforded yellow crystals suitable for X-ray diffraction study. After removal of the supernatant the crystals were washed with hexane and dried under vacuum. Yield: 0.331 g, 18%. Note, sometimes **18** crystallises with some red crystals of $[Ni(PPh_3)_4]$. The latter can easily be removed mechanically. ^1H NMR (300 MHz, C_6D_6): δ 7.90–6.62 (70H, ArH), 5.17 (s, 2H, PCH), 3.76 (s br, 8H, $ArCH_2Ar$), 3.33 (4H, OCH_2), 3.06 (4H, OCH_2), 1.40–1.10 (8H, CH_2CH_3), 0.88 (t, 6H, CH_2CH_3, $^3J \sim 7$ Hz), 0.72 (t, 6H, CH_2CH_3, $^3J \sim 7$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 21.8 and 19.4 ppm (AB spin system, J(PP′) = 283 Hz). Found: C, 75.43; H, 5.87. Calc. for $C_{116}H_{108}Ni_2O_6P_4$ (M_r = 1839.32): C, 75.75; H, 5.92%.

Complex 20. To a solution of 5,17-diphenylphosphinoacetyl-25,26,27,28-tetrapropoxycalix[4]arene (**17**) (0.200 g, 0.19 mmol) and $[NiPhCl(PPh_3)_2]$ (0.132 g, 0.19 mmol) in THF (20 mL) was added NaH (0.010 g, 0.42 mmol). After stirring for 4 h, the suspension was filtered through Celite and the resulting yellow solution was concentrated to *ca.* 2 mL. Addition of hexane (*ca.* 20 mL) afforded **20** as a yellow powder. Yield: 0.200 g, 89%; IR (KBr, cm^{-1}): ν(C=O) 1671s. ^1H NMR (300 MHz, C_6D_6): δ 8.09–6.62 (35H, ArH), 4.83 (d, 1H, PCH, ^2J(PH) = 2.2 Hz), 4.22 (s br, 2H, PCH_2), 3.68–3.49 (16H, $ArCH_2Ar$ and OCH_2), 1.80–1.73 (8H, CH_2CH_3), 1.00 (t, 3H, CH_2CH_3, ^3J = 7.4 Hz), 0.95 (t, 3H, CH_2CH_3, ^3J = 7.4 Hz), 0.70 (s br, 6H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 193.39 (s, CH_2C=O, ^2J(PC) = 0 Hz), 160.53–120.62 (aryl and quat.-C), 79.16 (d, PCH, ^1J(PC) = 50 Hz), 75.80, 75.76 and 75.34 (3s, OCH_2), 40.13 (d, PCH_2, ^1J(PC) = 29 Hz), 34.47 and 34.41 (2s, $ArCH_2Ar$), 24.21, 24.14 and 24.04 (3s, CH_2CH_3), 10.69, 10.63 and 10.49 (3s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 16.2 and 10.8 (AB spin system, J(PP′) = 291 Hz). Found: C, 75.12; H, 6.24. Calc. for $C_{74}H_{74}NiO_6P_2$ (M_r = 1180.04): C, 75.32; H, 6.32%.

Reaction of 15 with $[Ni(cod)_2]$. To a cold (0 °C) solution of 5,17-bis(2-triphenylphosphoranylideneacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (*cone*) (1.000 g, 0.90 mmol) and PPh_3 (0.685 g, 2.6 mmol) in toluene (20 mL) was added a cold solution (0 °C) of $[Ni(cod)_2]$ (0.550 g, 2.00 mmol) in toluene (20 mL). The mixture was stirred for 15 h, then concentrated to *ca.* 5 mL. Addition of hexane precipitated a yellow powder. Yield: 2.960 g, 67%. ^1H NMR (300 MHz, C_6D_6): δ 8.48 (s, 2H, OH), 7.72–6.23 (70H, ArH), 5.32 (s, 2H, PCH), 4.35 and 3.22 (AB spin system, 8H, $ArCH_2Ar$, ^2J = 13.0 Hz), 3.64 (s br, 4H, OCH_2), 1.77 (s br, 4H, CH_2CH_3), 1.16 (s br, 6H, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 22.6 and 20.0 (AB spin system, J(AB) = 284 Hz). $C_{110}H_{96}Ni_2O_6P_4$ (M_r = 1755.217).

X-Ray crystallography

Crystal data for 15. Crystals of **15** suitable for X-ray diffraction were obtained by slow diffusion of methanol into a dichloromethane solution of the compound. $C_{74}H_{66}O_6P_2 \cdot 0.5CH_2Cl_2 \cdot 2CH_3OH$, M = 1219.75, triclinic, space group $P\bar{1}$, colourless prisms, a = 10.127(2), b = 16.167(2), c = 20.818(4) Å, α = 86.82(5), β = 83.22(5), γ = 78.40(5)°, V = 3313.6(1) Å^3, Z = 2, μ = 0.162 mm^{-1}, F(000) = 1290, D_c = 1.222 g cm^{-3}. Crystals of the compound were glued to a glass fibre and mounted on a Nonius Kappa CCD instrument. X-Ray diffraction measurements were made using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 173 K. Data collection was carried out using the Nonius collect suite[47] 19 356 Reflections collected ($1.00 < \theta < 30.03°$), 10532 data with $I > 2\sigma(I)$. The structure was solved by direct methods with SHELXS-97 and refined with SHELXL-97.[48] Hydrogen atoms were included and refined using a riding model in SHELX-97. Final results: R_1 = 0.0927, wR_2 = 0.237, goodness of fit = 0.96, 769 parameters, residual electron density: min./max. = −0.97/1.02 e Å^{-3}.

Crystal data for 18. Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a toluene solution. Data collection and structure solution were as for compound **15**. $C_{116}H_{108}Ni_2O_6P_4$, M = 1839.32, monoclinic, space group $P2_1/c$, yellow prisms, a = 18.498(2), b = 28.088(2), c = 18.725(2) Å, β = 98.181(3)°, V = 9630.0(2) Å^3, Z = 4, μ = 0.514 mm^{-1}, F(000) = 3872, D_c = 1.269 g cm^{-3}. Crystals of the compound were glued to a glass fibre and mounted on a Nonius Kappa CCD. X-Ray diffraction measurements were made using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 173 K. Data collection and structure solution was as for **18**. 28035 Reflections

collected ($1.32 < \theta < 30.05°$), 17204 data with $I > 2\sigma(I)$. Final results: $R_1 = 0.0839$, $wR_2 = 0.2572$, goodness of fit = 0.94, 1137 parameters, residual electron density: min./max. = −1.094/2.051 e Å^{-3}. Some positional disorder was found in aryl rings C(75)–C(80), C(81)–C(86) and C(87)–C(92). Several attempts to improve the structure were made using PART instructions (SHELX), which led to unstable refinements. The disorder found in a propyl group bound could not be resolved.

Crystal data for 20. Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a toluene solution of the compound. $C_{74}H_{74}NiO_6P_2$, $M = 1180.06$, monoclinic, space group $P2_1/n$, yellow prisms, $a = 17.548(7)$, $b = 19.597(6)$, $c = 18.816(8)$ Å, $\beta = 104.88(3)°$, $V = 6254(4)$ Å^3, $Z = 4$, $\mu = 0.415$ mm^{-1}, $F(000) = 2496$, $D_c = 1.253$ g cm^{-3}. Crystals of the compound were glued to a glass fibre and mounted on a STOE IPDS diffractometer. X-Ray diffraction measurements were made using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 173 K. Data collection was carried out using the STOE IPDS software. 48066 reflections were collected ($1.5 < \theta < 26.9°$), 13324 being found to be unique (merging $R = 0.069$). The structure was solved by direct methods with the program SIR92.[49] Least squares refinement was carried out using the program CRYSTALS.[50,51] Hydrogen atoms are in calculated positions. Final results: $R_1 = 0.0678$ ($I > 1.4\sigma(I)$), $wR_2 = 0.0547$ (all data), goodness of fit = 1.20, residual electron density: min./max. = −1.05/1.35 e Å^{-3}.

CCDC reference numbers 294726–294728.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603861a

Catalytic runs

The catalytic runs were carried out in a stainless steel autoclave (100 mL) equipped with a mechanical stirrer, a heating device, and an internal temperature probe. The reactor was dried under vacuum at 100 °C for 1 h before use. In a typical procedure, a solution of the ylide in toluene (10 mL) was added by injection at ambient temperature followed by a toluene solution (10 mL) either containing 1 equiv. of [Ni(cod)$_2$] and 1 equiv. of PPh_3 (for oligomerisation runs) or an excess of [Ni(cod)$_2$] (for polymerisation runs). The autoclave was then pressurised with ethylene and heated up to the desired temperature. If necessary, the evolution of heat was controlled by means of an ice-bath. After completion of the oligomerisation runs, the autoclave was cooled with an ice-bath and depressurised over 1 h. The solution was analysed by GC. Heptane (200 μL/10 mL of catalytic solution) was used as internal reference. For the polymerisation runs, the reaction was quenched by venting the autoclave, and the reaction mixture was subsequently poured into a stirred solution (200 mL) of acidified methanol (10% HCl) to precipitate the polymer. The white powder was isolated by filtration, washed with methanol, and dried in *vacuo* at 50 °C.

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