Articles

Stereoselective Formation of the *R,S* Isomer of a Methylene-Bridged Diphosphine Derivative of *p-tert*-Butylcalix[4]arene and Subsequent Reactivity[†]

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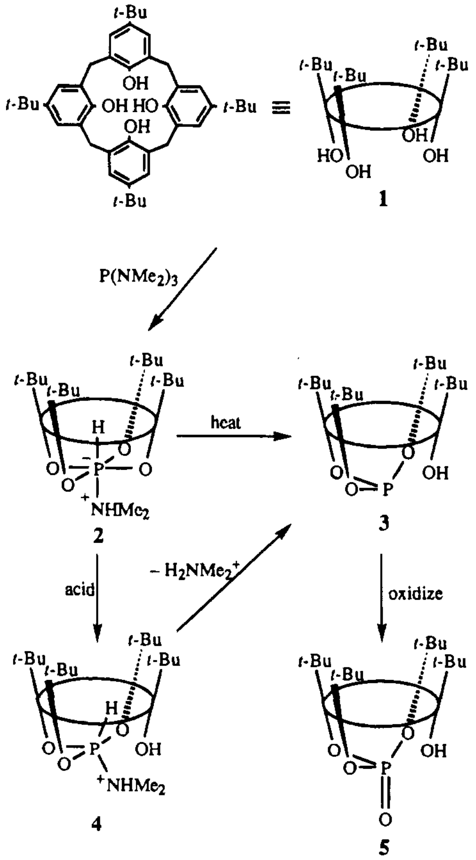
Treatment of *p-tert*-butylcalix[4]arene, **1**, with $(Me_2N)_2PCH_2P(NMe_2)_2$ yields the half-substituted product *p-tert*-butylcalix[4]arene$[(Me_2N)PCH_2P(NMe_2)]$, **6**, in which only 2 mol of dimethylamine have been lost and the PCH_2P unit bridges adjacent oxygens of the calix[4]arene. This reaction is both regiospecific and stereoselective, giving the *R,S* isomer. Subsequent heating of this species leads to loss of the remaining dimethylamine and yields the full-substituted derivative *p-tert*-butylcalix[4]arene(PCH_2P), **7**. This product undergoes reactions typical of trivalent phosphorus: treatment with oxygen or sulfur gives the diphosphoryl and dithiophosphoryl compounds *p-tert*-butylcalix[4]arene$[P(X)CH_2P(X)]$, **8** and **9**, respectively (X = O, S). In general, attempts to derivatize the phosphorus atoms of **6** led to reaction at only one phosphorus. Thus, treatment of **6** with phenyl azide, iodomethane, and tetrachloro-1,2-bezoquinone led to the monoimino, monophosphonium, and monophosphorane products *p-tert*-butylcalix[4]arene$[P(X)CH_2P]$, **10**, **11**, and **12**, respectively (X = =NPh, Me^+, 1,2-$O_2C_6Cl_4$). Unexpectedly, the reaction of **6** with tris(dimethylamino)phosphine led to $(Me_2N)_2PCH_2P(NMe_2)_2$ and the zwitterionic six-coordinate phosphorus species *p-tert*-butylcalix[4]arene$[P(H)NHMe_2]$, **2**, which had previously been synthesized by another route. Crystal data for **6**: $P2_1/c$, $a = 16.480(5)$ Å, $b = 14.740(3)$ Å, $c = 23.830(6)$ Å, $\beta = 97.53(2)°$, $Z = 4$. Crystal data for **8**: $P\bar{1}$, $a = 10.481(4)$ Å, $b = 12.869(4)$ Å, $c = 19.809(6)$ Å, $\alpha = 102.97(2)°$, $\beta = 93.59(3)°$, $\gamma = 95.34(3)°$, $Z = 2$.

Our recent investigations[1] of the insertion of phosphorus into calix[4]arenes demonstrated that the calix[4]arene framework is able to accommodate phosphorus in six- and five-coordinate hypervalent geometries, as well as the more usual three- and four-coordinate structures. Scheme 1 illustrates this for derivatives of *p-tert*-butylcalix[4]arene, **1**. We are currently studying the insertion of more than one phosphorus atom into calix[4]arenes via the reagent $(Me_2N)_2PCH_2P(NMe_2)_2$ in an effort to compare and contrast the two systems, and we herein report our initial findings. A previous report of a P(O)OP(O)-bridged calix[4]arene has appeared.[2]

Scheme 1



Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen, unless otherwise indicated. Solvents were dried using standard procedures and distilled under a nitrogen atmosphere and either used immediately or stored in the drybox prior to use. Glassware was oven-dried at 140 °C overnight prior to use. The reagents iodomethane and tetrachloro-1,2-benzoquinone were purchased commercially and used without further purification. The reagents $(Me_2N)_2PCH_2P(NMe_2)_2$,[3] tris(dimethylamino)phosphine,[4] and phenyl azide[5] were synthesized by literature methods. The starting material *p-tert*-butylcalix[4]arene·toluene[6] was synthesized according to the literature method and oven-dried at 120 °C overnight prior to use to remove

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[†] Dedicated to Reinhard Schmutzler on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.

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moisture and most of the toluene of crystallization. Stoichiometric calculations for *p-tert*-butylcalix[4]arene (**1**) omit toluene. All NMR spectra were recorded on an IBM/Bruker WP200SY multinuclear NMR spectrometer (equipped with a Tecmag computer system) resonating at 200.132 (^{1}H) and 81.026 (^{31}P) MHz. ^{1}H resonances were measured relative to residual proton solvent peaks and referenced to Me_4Si. ^{31}P resonances were measured relative to external 85% H_3PO_4. ^{31}P NMR spectra are proton-decoupled, unless otherwise indicated. Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were obtained from E & R Microanalytical Laboratories, Inc., Corona, NY.

Synthesis of 6. A stirred suspension of **1** (1.00 g, 1.54 mmol) in dichloromethane (6 mL) was treated dropwise with $(Me_2N)_2PCH_2P(NMe_2)_2$ (0.43 g, 1.7 mmol). Stirring was continued for 40 min after addition was complete. The volatiles were then pumped off from the resulting homogeneous solution, and the crystalline residue was dissolved in dichloromethane (2.5 mL). Ether (3 mL) was added and the solution cooled to −20 °C for 3 d. The resulting precipitate was separated from the mixture and pumped dry to yield **6** as a colorless, crystalline solid (0.66 g, 53%). Mp: 200 °C. Anal. Calcd for $C_{49}H_{68}N_2O_4P_2$: C, 72.57; H, 8.45; N, 3.45. Found: C, 72.59; H, 8.40; N, 3.64. NMR ($CDCl_3$): ^{1}H, δ 1.21 (s, 18H, *t*-Bu), 1.23 (s, 18H, *t*-Bu), 1.69 (dt, $^{2}J_{PH} = 4.4$ Hz, $^{2}J_{HH} = 12.6$ Hz, 1H, P−CH$_2$−P), 3.03 (t, $^{3}J_{PH} = 10.0$ Hz, 12H, N−CH$_3$), 3.29−3.50 (m, not resolved, 1H, P−CH$_2$−P), 3.36 (d, $^{2}J_{HH} = 12.9$ Hz, 2H, Ar−CH$_2$−Ar), 3.40 (d, $^{2}J_{HH} = 13.5$ Hz, 1H, Ar−CH$_2$−Ar), 3.44 (d, $^{2}J_{HH} = 13.5$ Hz, 1H, Ar−CH$_2$−Ar), 4.35 (d, $^{2}J_{HH} = 13.5$ Hz, 1H, Ar−CH$_2$−Ar), 4.43 (d, $^{2}J_{HH} = 12.6$ Hz, 2H, Ar−CH$_2$−Ar), 4.81 (dt, $J_{PH} = 8.2$ Hz, $^{2}J_{HH} = 13.5$ Hz, 1H, Ar−CH$_2$−Ar), 6.99−7.08 (m, 8H, Ar), 9.23 (s, 2H, OH); ^{31}P, δ 135.

Synthesis of 7. A suspension of **6** (1.12 g, 1.38 mmol) in toluene (10 mL) was heated in a 100 °C oil bath for 14 h. After the first 2 h of heating, all the solid had dissolved. The solution was then cooled to − 20 °C and allowed to stand for 3 weeks. The resulting precipitate was isolated and pumped dry to yield **7** as a colorless, crystalline solid (0.46 g, 46%). Mp: 298−300 °C. Anal. Calcd for $C_{45}H_{54}O_4P_2$: C, 74.98; H, 7.55. Found: C, 74.42; H, 7.53. NMR ($CDCl_3$): ^{1}H, δ 1.19 (s, 36H, *t*-Bu), 2.63 (t, $^{2}J_{PH} = 14.4$ Hz, 2H, P−CH$_2$−P), 3.29 (d, $^{2}J_{HH} = 13.0$ Hz, 2H, Ar−CH$_2$−Ar), 3.56 (d, $^{2}J_{HH} = 15.4$ Hz, 2H, Ar−CH$_2$−Ar), 4.45 (d, $^{2}J_{HH} = 13.0$ Hz, 2H, Ar−CH$_2$−Ar), 4.59 (dt, $J_{PH} = 2.6$ Hz, $^{2}J_{HH} = 15.4$ Hz, 2H, Ar−CH$_2$−Ar), 6.92 (s, 2H, Ar), 6.93 (s, 2H, Ar), 7.03 (s, 2H, Ar), 7.04 (s, 2H, Ar); ^{31}P, δ 196.

Synthesis of 8. The crude reaction mixture of **7** (see above) was exposed to the atmosphere through a needle via a $CaCl_2$-filled tube for about 1 month. The precipitate that formed was washed with toluene and pumped dry to yield **8** as a colorless, crystalline product (43%). Mp: 388−390 °C. Anal. Calcd for $C_{45}H_{54}O_6P_2$: C, 71.79; H, 7.23. Found: C, 71.75; H, 7.23. NMR ($CDCl_3$): ^{1}H, δ 1.15 (s, 36H, *t*-Bu), 3.40 (d, $^{2}J_{HH} = 13.4$ Hz, 2H, Ar−CH$_2$−Ar), 3.52 (t, $^{2}J_{PH} = 20.4$ Hz, 2H, P−CH$_2$−P), 3.58 (d, $^{2}J_{HH} = 15.3$ Hz, 2H, Ar−CH$_2$−Ar), 4.44 (d, $^{2}J_{HH} = 13.4$ Hz, 2H, Ar−CH$_2$−Ar), 4.75 (d, $^{2}J_{HH} = 15.3$ Hz, 2H, Ar−CH$_2$−Ar), 6.96 (s, 2H, Ar), 6.97 (s, 2H, Ar), 7.03 (s, 2H, Ar), 7.04 (s, 2H, Ar); ^{31}P, δ 11.

Synthesis of 9. Sulfur (0.060 g, 1.88 mmol) was added to a solution of **7** (0.52 g, 0.72 mmol) in dichloromethane (4 mL). This mixture was stirred for 24 h. The volatiles were then pumped off. The residue was purified by column chromatography (silica gel, $R_f = 0.77$, 1/1 dichloromethane/hexane) to yield **9** as a colorless solid (0.46 g, 82%). Mp: 337−338 °C. Anal. Calcd for $C_{45}H_{54}O_4P_2S_2$: C, 68.85; H, 6.93. Found: C, 68.75; H, 6.79. NMR ($CDCl_3$): ^{1}H, δ 1.14 (s, 36H, *t*-Bu), 3.39 (d, $^{2}J_{HH} = 13.7$ Hz, 2H, Ar−CH$_2$−Ar), 3.53 (d, $^{2}J_{HH} = 15.3$ Hz, 2H, Ar−CH$_2$−Ar), 4.23 (t, $^{2}J_{PH} = 13.9$ Hz, 2H, P−CH$_2$−P), 4.39 (d, $^{2}J_{HH} = 13.7$ Hz, 2H, Ar−CH$_2$−Ar), 5.00 (d, $^{2}J_{HH} = 15.3$ Hz, 2H, Ar−CH$_2$−Ar), 6.90−7.10 (m, 8H, Ar); ^{31}P, 76.

Reaction of 6 with Tris(dimethylamino)phosphine. A solution of **6** (0.20 g, 0.25 mmol) in dichloromethane (2 mL) was treated dropwise with tris(dimethylamino)phosphine (0.082 g, 0.50 mmol). The solution was allowed to stand for 24 h. The solid that precipitated was isolated and pumped dry. This product was identified as **2** (0.11 g, 61%) by spectral comparison with a sample synthesized according to the usual literature procedure.[1a]

Synthesis of 10. A solution of **6** (0.25 g, 0.31 mmol) in dichloromethane (2 mL) was treated with phenyl azide (0.040 g, 0.34 mmol). The mixture was allowed to stand for 45 min. The volatiles were then quickly pumped off (5 min), and the crystalline solid residue was dissolved in hexane (3 mL). The product **10** precipitates from solution over a period of 2 h as colorless crystals (0.17 g, 61%). This compound is unstable in both solution and the solid state, and we were unable to obtain satisfactory elemental analyses. NMR ($CDCl_3$): ^{1}H, δ 1.12 (s, 9H, *t*-Bu), 1.17 (s, 9H, *t*-Bu), 1.21 (s, 9H, *t*-Bu), 1.25 (s, 9H, *t*-Bu), 2.18 (dt, $^{2}J_{PH} = 14.5$ Hz, $^{2}J_{HH} = 6.73$ Hz, 1H, PCH$_2$P), 2.99 (d, $^{3}J_{PH} = 9.2$ Hz, 6H, N−CH$_3$), 3.15 (d, $^{3}J_{PH} = 10.4$ Hz, 6H, N−CH$_3$), 3.2−3.5 (unresolved m, 1H, PCH$_2$P), 3.35−3.54 (m, 4H, Ar−CH$_2$−Ar), 4.10 (d, $^{2}J_{HH} = 13.4$ Hz, 1H, Ar−CH$_2$−Ar), 4.29 (d, $^{2}J_{HH} = 13.4$ Hz, 1H, Ar−CH$_2$−Ar), 4.80 (d, $^{2}J_{HH} = 12.2$ Hz, 1H, Ar−CH$_2$−Ar), 5.65 (dd, $^{2}J_{HH} = 14.3$ Hz, $J_{PH} = 7.3$ Hz, 1H, Ar−CH$_2$−Ar), 6.45−7.17 (m, 13H, Ar), 9.30 (s, 1H, OH), 9.74 (s, 1H, OH), ^{31}P, 16 (P=NPh), 135 ($^{2}J_{PP} = 44$ Hz).

Synthesis of 11. A solution of **6** (0.50 g, 0.62 mmol) in dichloromethane (4 mL) was treated dropwise with iodomethane (0.35 g, 2.47 mmol). After 24 h, the ^{31}P NMR spectrum of the reaction mixture showed the presence of two products (see Results and Discussion) with the following parameters (3:1 ratio), δ:67, 125 ($^{2}J_{PP} = 68$ Hz); 76, 125 ($^{2}J_{PP} = 21$ Hz). The volatiles were then pumped off, and the white crystalline residue was dissolved in dichloromethane (1.5 mL). Ether (2 mL) was added and the solution cooled to −20 °C for 24 h. The major product precipitated and was isolated and pumped dry to yield **11** as colorless crystals (0.21 g, 36%). This compound is unstable in both solution and the solid state; however, satisfactory elemental analyses were obtained. ^{1}H NMR spectra showed the product to contain about $^{1}/_{2}$ mol of dichloromethane. Anal. Calcd for $C_{50}H_{71}IN_2O_4P_2\cdot{}^{1}/_{2}CH_2Cl_2$: C, 60.93; H, 7.29; N, 2.81. Found: C, 61.02; H, 7.49; N, 2.97. NMR ($CDCl_3$): ^{1}H, δ 1.21 (s, 9H, *t*-Bu), 1.23 (s, 9H, *t*-Bu), 1.24 (s, 9H, *t*-Bu), 1.26 (s, 9H, *t*-Bu), 2.75 (d, $^{2}J_{PH} = 12.86$ Hz, 3H, P−CH$_3$), 3.09 (d, $^{3}J_{PH} = 9.9$ Hz, 6H, N−CH$_3$), 3.29 (d, $^{3}J_{PH} = 11.0$ Hz, 6H, N−CH$_3$), 3.40−3.60, 4.05−4.54 (m, 2H, P−CH$_2$−P, 8H, Ar−CH$_2$−Ar), 6.97−7.25 (m, 8H, Ar), 9.16 (s, 1H, OH), 9.24 (s, 1H, OH); ^{31}P, 67 (P−Me), 125 ($^{2}J_{PP} = 68$ Hz).

Synthesis of 12. A suspension of **6** (0.17 g, 0.21 mmol) in toluene (3 mL) was cooled to −20 °C and the cooling bath removed. A solution of tetrachloro-1,2-benzoquinone (0.054 g, 0.218 mmol) in toluene (3 mL) was quickly added. After 1 h, the mixture turned colorless and was clear except for a small amount of very fine precipitate. The solution was separated from the precipitate. The ^{31}P NMR spectrum of the solution showed only two doublets at δ −26 and 145 ($^{2}J_{PP} = 44$ Hz). The solution was concentrated to about three-fourths of its original volume, and a colorless, crystalline precipitate formed after 10 h. These crystals were found to be pure **1**. The ^{31}P NMR spectrum of the resulting supernatant solution showed several small-intensity peaks.

X-ray Structure Determination and Refinement. A colorless, prismatic crystal of **6** and a plate-shaped crystal of **8**, coated with dried mineral oil, were mounted on a Siemens R3m/V diffractometer under a low-temperature nitrogen stream. Final unit cell parameters, given in Table 1, were obtained by a least-squares fit of the angles of 25 accurately centered reflections (15° < 2θ < 25° for **6** and 16° < 2θ < 27° for **8**, respectively). Relevant data-collection conditions are listed in Table 1. Three standard reflections monitored after every 150 reflections did not show any significant change in intensity during the data collection. The data were corrected for Lorentz and polarization effects. An absorption study was not applied because of the low absorption coefficient. Both structures were solved by direct methods and subsequent difference Fourier syntheses using the SHELXTL-Plus package.[7] Scattering factors were taken from common sources.[8] Full-matrix least-square refinements were performed in each case. The weight had the form $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ where $g = 0.001$ for

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Table 1. Crystallographic Data

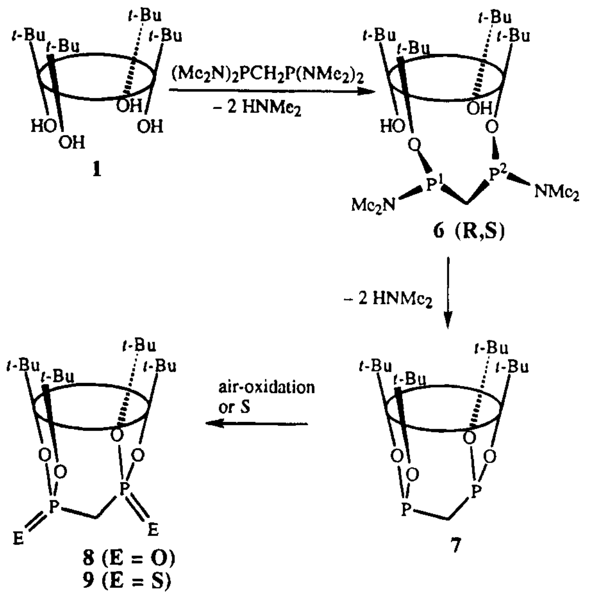
	6	8
formula	$C_{49}H_{68}O_4N_2P_2\cdot 3CH_2Cl_2$	$C_{45}H_{54}O_4P_2\cdot 2C_7H_8$
fw	1065.8	937.1
color	colorless	colorless
habit	prisms	plates
space group	$P2_1/c$	$P\bar{1}$
a, Å	16.480(5)	10.481(4)
b, Å	14.740(3)	12.869(4)
c, Å	23.830(6)	19.809(6)
α, deg		102.97(2)
β, deg	97.53(2)	93.59(3)
γ, deg		95.34(3)
V, Å^3	5739(3)	2567(2)
Z	4	2
D_{calcd}, g cm^{-3}	1.234	1.212
μ $_{\text{calcd}}$, mm^{-1}	0.397	0.135
radiation	Mo Kα (λ = 0.710 69), graphite monochromator	
cryst dimens, mm	0.25 × 0.25 × 0.30	0.30 × 0.25 × 0.10
T, K	230	230
scan type	ω	ω
scan width, deg	1.20 + Kα separation	
2θ range, deg	3.5–40.0	3.5–42.0
std reflns	3 measured every 150 reflections	
decay, %	none	none
no. of data collcd	5600	5885
no. of obsd reflns, $F > 6.0\sigma(F)$	1882	3639
no. of params refined	470	617
GOF	1.79	1.53
R	0.080	0.049
R_w	0.092	0.064

both structures. Hydrogen atoms of the calixarene frame were placed in calculated positions.

Structure of 6. Three solvated dichloromethane molecules were included in the lattice. All were disordered. In addition, one of the *tert*-butyl groups on the calixarene molecule [C(27), C(28), C(29), and C(30)] was statically disordered. The refinement showed the s.o.f. for C(28), C(29), and C(30) to be 66%, while the occupancy factor for C(281), C(291), and C(301) was 34%. The disordered *tert*-butyl group and dichloromethane molecules were elastically restrained during the final stage of refinement. All non-hydrogen atoms, except for those of the disordered dichloromethane molecules and *tert*-butyl group, were anisotropically refined. Hydrogen atoms of the dichloromethane molecules were placed using a "riding model". No attempts were made to locate the hydroxyl hydrogen atoms. Final cycles of refinement converged at $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.080$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2} = 0.092$, and GOF = 1.79 for 1882 observed reflections [$F > 6.0\sigma(F)$]. The fairly high R factor is likely due to the disordered *tert*-butyl group and dichloromethane molecules. One molecule of dichloromethane is located within the calixarene basket. The closest contact distances between the calixarene and dichloromethane molecules are C(20)–Cl(1) ($2 - x$, $^1/_2 + y$, $^3/_2 - z$) 3.487Å and C(30)–Cl(3) ($2 - x$, $1 - y$, $1 - z$) 3.253 Å. The maximum and minimum residuals found on the final DF map were 0.58 and −0.41 e/Å^3, respectively.

Structure of 8. Two solvated toluene molecules were included in the structural lattice. One of the toluene molecules is disordered [C(71) through C(77)]. The disorder is such that 70% of the molecules lie in one orientation, while 30% are in an orientation arising from a 180° rotation about the axis containing the ortho carbons. C(72) and C(76) are fully occupied and are the ortho carbons in both orientations; C(74) and C(77) are also fully occupied but represent the para and methyl carbons, respectively, in the major orientation and the methyl and para carbons, respectively, in the minor orientation. The remaining positions are partially occupied: 70% for C(71), C(73), C(75); 30% for C(711), C(731), C(751). The disordered toluene was elastically restrained during the final stage of refinement. All non-hydrogen atoms, except for C(711), C(731), and C(751), were anisotropically refined. O(5) and O(6) are trans to the plane of P(1), P(2), and C(3), with the torsion angles O(5)–P(1)–C(3)–P(2) of 163.1° and O(6)–P(2)–C(3)–P(1) of 158.5°. The closest contact distances between the calixarene and toluene molecules are C(39)–C(66) ($-x$, $1 - y$, $1 - z$) 3.584 Å and C(51)–C(751) ($1 - x$, $1 - y$, $2 - z$) 3.639 Å. Final cycles of refinement converged at $R = 0.049$, $R_w = 0.064$, and GOF = 1.53 for 3639 observed reflections [$F > 6.0\sigma(F)$]. The maximum and minimum residuals found on the final DF map were 0.38 and −0.31 e/Å^3, respectively.

Scheme 2



Results and Discussion

Treatment of **1** with $(Me_2N)_2PCH_2P(NMe_2)_2$ in dichloromethane at ambient temperature leads exclusively to the "half-substituted" product **6** (Scheme 2). Such types of heterocycles containing two phosphorus atoms in the ring are usually formed as a mixture of isomers due to "cis" and "trans" orientations of the substituents at phosphorus.[9] Because of the calix[4]arene, more isomers are possible for **6**. However, the ^{31}P NMR spectrum of the reaction mixture shows only one signal at δ 135, which indicates that only one isomer is formed. Low-temperature NMR spectra did not reveal the appearance of any other isomer. The ^1H NMR spectrum of **6** shows equivalent dimethylamino groups and equivalent hydroxyl hydrogens. However, the two hydrogens of the PCH_2P unit are inequivalent. X-ray structural analysis of **6** (see below) shows it to be the *R,S* (P^1,P^2) isomer.

After isolation, **6** is stable in an inert atmosphere both in the solid state and in solution at ambient temperature. However, when **6** is heated in toluene at 100 °C for 14 h, the further elimination of 2 mol of dimethylamine yields the "full-substituted" derivative **7** . The ambient-temperature ^1H NMR spectrum of **7** shows only one peak for the *tert*-butyl groups. Examination of molecular models of **7** shows that there should be two different types of *tert*-butyl groups: opposite groups are equivalent whereas adjacent ones are not. This is due to the flattened cone conformation[10] of the calix[4]arene in which two opposite phenol groups are in a normal cone geometry while the other two are bent back (see X-ray structure of **8**, below).

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(9) See, for example: Gallager, M. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; p 306.

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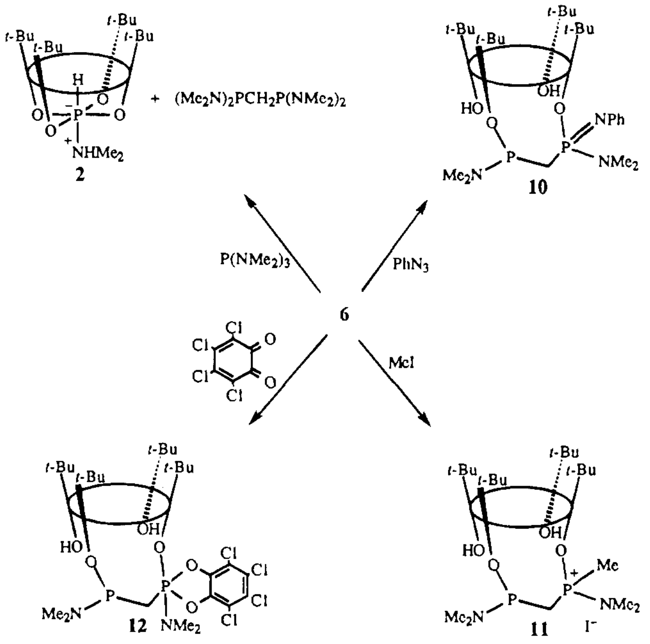
Scheme 3



The two types of phenol groups interconvert by bond rotation. In fact, cooling to −40 °C slows the interconversion rate to the point where two *tert*-butyl groups are observed. This phenomenon has been observed previously.[2]

The ^{1}H NMR spectra of **6** and **7** reveal an unusual feature. The spectrum of **6** shows the expected doublets for the calix[4]arene methylene groups, since the hydrogens on each carbon are inequivalent.[10] However, one of the doublets is additionally split to give a doublet of triplets due to phosphorus coupling ($J_{PH} = 8.2$ Hz). We have previously observed five-bond P−H coupling only in calix[4]arene derivatives with five- and six-coordinate phosphorus geometries (e.g., **2** and **4**). It is possible that the coupling in **6** (and possibly **7**) may be due to a through-space interaction between the phosphorus atoms and the "axial" hydrogen of the calix[4]arene methylene group in the 10-membered ring (see X-ray analysis below). The smaller coupling observed in **7** ($J_{PH} = 2.6$ Hz) may be a result of larger P⋯H distances.

The full-substituted species **7** can be oxidized to the diphosphoryl and dithiophosphoryl derivatives **8** and **9**, respectively (Scheme 2). In the case of **9**, the reaction occurs in two stages which can be observed by NMR spectroscopy. One phosphorus atom is oxidized rapidly to give an intermediate with two phosphorus signals, one at δ 84 and the other at δ 179, with a phosphorus coupling of 29 Hz. The formation of **9** is complete within 24 h.

We attempted to derivatize **6** with several reagents. In an effort to further substitute the two hydroxyl groups with phosphorus, **6** was treated with tris(dimethylamino)phosphine. Surprisingly, this reaction leads to formation of the zwitterionic six-coordinate species **2** and the original diphosphine $(Me_2N)_2PCH_2P(NMe_2)_2$ (Scheme 3). The initial step in this reaction most likely involves phosphorus substitution at a hydroxyl to give an intermediate which eliminates the diphosphine and forms the very stable species **2**. In support of this pathway, no reaction is observed between the full-substituted compound **7** and tris(dimethylamino)phosphine.

In general, attempts to derivatize the phosphorus atoms of **6** led to reaction at only one phosphorus. Treatment of **6** with phenyl azide yields the monosubstituted imino derivative **10**. Only one phosphorus can be derivatized, even with a large excess of phenyl azide. The ^{31}P NMR spectrum shows two signals at δ 16 and 135 with a phosphorus coupling of 44 Hz. Although **10** can be isolated as a crystalline product, it completely decomposes in solution over a period of a few days. Alkylation of **6** with iodomethane proceeds smoothly to give **11**. Again, even with an excess of iodomethane, only one phosphorus can be alkylated. The crude reaction mixture of **11** appears to contain two isomers, one **11a** having ^{31}P NMR signals at δ 67 and 125 ($^2J_{PP} = 68$ Hz) and the other **11b** with signals at δ 76 and 125 ($^2J_{PP} = 21$ Hz), in an approximate 3:1 ratio. The appearance of two isomers in this reaction is somewhat puzzling and may be due to flipping of the phenolic units of the calix[4]arene framework. Crystallization of this mixture led to isolation of an analytically pure sample of **11a** in 36% yield (based on **6**). Either in the solid state or in solution, pure **11a** partially rearranges to **11b**. Prolonged standing of **11** (either isomer) in solution leads to decomposition. Compound **6** can be oxidized easily with tetrachloro-1,2-benzoquinone to give a single product **12**. Only two doublets are observed in the ^{31}P NMR spectrum at δ −26 and 145 ($^2J_{PP}$ = 44 Hz). The upfield signal is characteristic for five-coordinate phosphorus. However, within about 10 h in solution, **12** decomposes to give free *p-tert*-butylcalix[4]arene as well as other unidentified products.

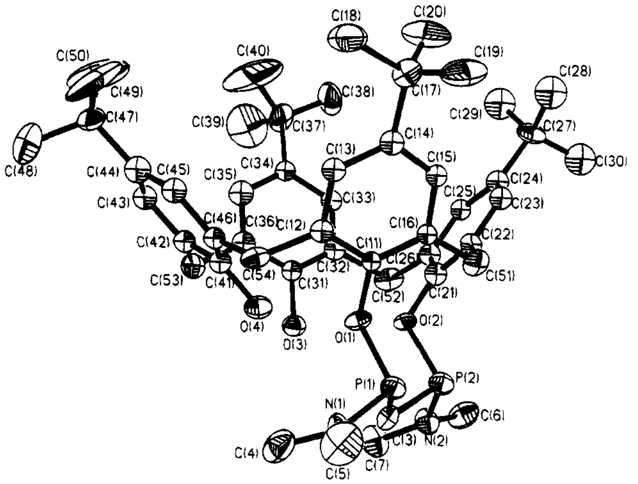


Figure 1. Perspective view of **6**. The dichloromethane molecule within the basket is not shown. All hydrogen atoms are omitted for clarity.

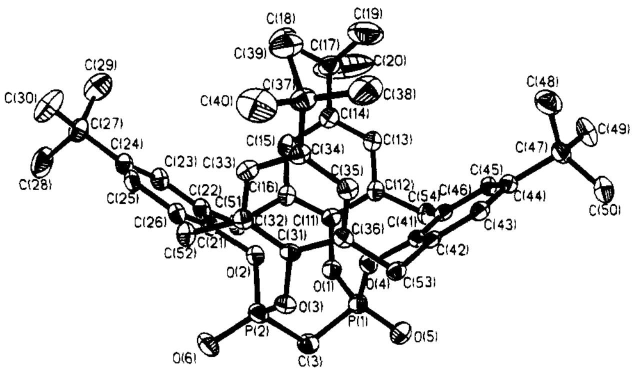


Figure 2. Perspective view of **8**. The toluene molecule within the basket is not shown. All hydrogen atoms are omitted for clarity.

The instability of **10**−**12** is most likely due to the presence of the calix[4]arene framework, since similar derivatives, such as **13**[11] and **14**,[12] with other substituents appear to be quite stable.

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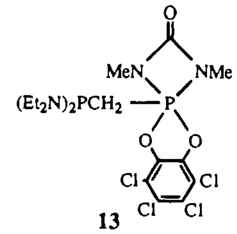
[11] Shevchenko, I. V.; Schmutzler, R. *Heteroat. Chem.* **1993**, *4*, 307.



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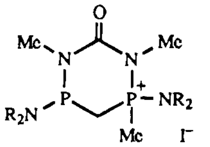

14

This may be due to steric repulsion of the calix[4]arene framework with the added substituents and/or the presence of reactive phenolic protons.

The X-ray crystal structures of **6** and **8** were obtained and are illustrated in Figures 1 and 2, respectively. Selected bond lengths and angles appear in Table 2. The calix[4]arene backbone in both molecules adopts the cone conformation, although in **8** it is best described as a flattened cone. Both phosphorus atoms in **6** are pyramidal with the sum of the bond angles about 300° for each. The solid-state structure of **6** reveals that there is no plane of symmetry. This can best be seen by the P−O−C angles of 117 and 123°, as well as the different P−C bond lengths. This asymmetry may be caused by different intramolecular hydrogen-bonding interactions: the O(4)−O(1) and O(3)−O(2) distances are 2.685 and 3.015 Å, respectively. In solution, however, the ^1H NMR spectrum is consistent with the molecule possessing a mirror plane. As expected, the nitrogen atoms are close to planar with bond angle sums of 356 and 359°. The proximity of the phosphorus atoms to C(51) is evident in Figure 1. The average P−C(51) distance is 3.40 Å and the average P−H(axial) distance is 2.67 Å (determined from the calculated H position). This may be close enough for the observed P−H coupling to be due to a through-space mechanism (see above). The solid-state structure of **8** shows it to possess an approximate C_2 axis. The phosphorus atoms are distorted tetrahedral, and the bond lengths and angles about phosphorus are within usual ranges.

Table 2. Bond Lengths (Å) and Bond Angles (deg) for **6** and **8**

Compound **6**			
P(1)−O(1)	1.699(11)	P(1)−N(1)	1.638(17)
P(1)−C(3)	1.812(14)	P(2)−O(2)	1.685(11)
P(2)−N(2)	1.679(14)	P(2)−C(3)	1.867(17)
N(1)−C(4)	1.448(26)	N(1)−C(5)	1.462(25)
N(2)−C(6)	1.426(24)	N(2)−C(7)	1.423(25)
O(1)−P(1)−N(1)	105.2(7)	O(1)−P(1)−C(3)	93.0(6)
N(1)−P(1)−C(3)	100.6(8)	O(2)−P(2)−N(2)	106.5(7)
O(2)−P(2)−C(3)	93.5(6)	N(2)−P(2)−C(3)	99.7(7)
P(1)−O(1)−C(11)	123.0(9)	P(2)−O(2)−C(21)	116.8(10)
P(1)−N(1)−C(4)	126.2(14)	P(1)−N(1)−C(5)	119.1(13)
C(4)−N(1)−C(5)	113.3(16)	P(2)−N(2)−C(6)	115.9(12)
P(2)−N(2)−C(7)	127.0(13)	C(6)−N(2)−C(7)	112.9(14)
P(1)−C(3)−P(2)	112.7(8)		
Compound **8**			
P(1)−C(3)	1.770(5)	P(1)−O(5)	1.445(4)
P(1)−O(1)	1.578(4)	P(1)−O(4)	1.576(3)
P(2)−C(3)	1.784(5)	P(2)−O(6)	1.456(3)
P(2)−O(2)	1.573(3)	P(2)−O(3)	1.576(4)
C(3)−P(1)−O(5)	113.0(2)	C(3)−P(1)−O(1)	105.5(2)
O(5)−P(1)−O(1)	114.4(2)	C(3)−P(1)−O(4)	101.4(2)
O(5)−P(1)−O(4)	117.4(2)	O(1)−P(1)−O(4)	103.6(2)
C(3)−P(2)−O(6)	113.1(2)	C(3)−P(2)−O(2)	103.2(2)
O(6)−P(2)−O(2)	116.2(2)	C(3)−P(2)−O(3)	104.7(2)
O(6)−P(2)−O(3)	114.7(2)	O(2)−P(2)−O(3)	103.6(2)
P(1)−C(3)−P(2)	118.0(2)	P(1)−O(1)−C(11)	127.8(3)
P(2)−O(2)−C(21)	125.7(3)	P(2)−O(3)−C(31)	126.5(3)
P(1)−O(4)−C(41)	128.6(3)		

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Supporting Information Available: Packing diagrams and tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates (17 pages). Ordering information is given on any current masthead page.

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(12) Shevchenko, I. V.; Furmanova, M. V.; Kukhar, V. P.; Schmutzler, R. *Z. Naturforsch.* **1992**, *47B*, 258.