Tetradentate 14-Membered *tert*-Phosphino-Containing Macrocycles[1]

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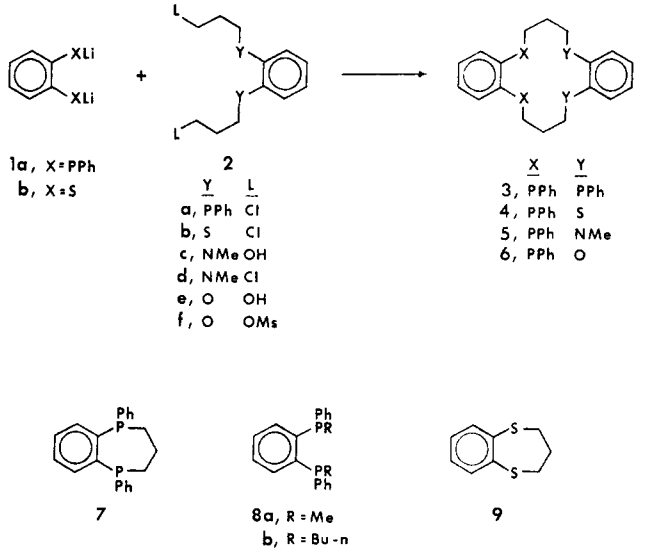
Abstract: Five 14-membered rings of the type 2,6,13,17-tetraheteratricyclo[16.4.0.0^{7,12}]docosa-7(12),8,10,1(18),19,21-hexaene have been synthesized, where the heteroatoms are **3A** and **3B**, [2,6,13,17-$(PPh)_4$], **4**, [2,17-S_2-6,13-$(PPh)_2$], **5**, [2,17-$(PPh)_2$-6,13-$(NMe)_2$], and **6**, [2,17-$(PPh)_2$-6,13-O_2]. High-dilution macrocyclization techniques gave these species as colorless crystalline materials in yields ranging from 18 to 45%. Two side products in these syntheses, 2,6-diheterabicyclo[5.4.0]-undeca-1(7),8,10-triene, where the heteroatoms are S and PPh, were also characterized. The *cis,trans,cis*-**3A** and *cis,cis,cis*-**3B** can be equilibrated thermally either in xylene solution at 135 °C or in the melt at 240 °C. The results of crystal structure determination of **3–6** are reported, and conformational features of the cyclotetradeca-1,8-diene-type macrocycle are outlined. Crystal structure data follow. **3A**: $a = 9.634$ Å, $b = 11.586$ Å, $c = 8.746$ Å, $\alpha = 100.86°$, $\beta = 104.70°$, $\gamma = 107.31°$, $P\bar{1}$, $Z = 1$ (molecular site symmetry C_i), $R = 0.058$, 3417 reflections with $I > 2\sigma_I$. **3B**·2THF: $a = 25.504$ Å, $c = 13.796$ Å, $I4_1/a$, $Z = 8$ (molecular site symmetry C_2), $R = 0.092$, 2390 reflections with $I > 2\sigma_I$. **4**: $a = 8.636$ Å, $b = 15.277$ Å, $c = 24.206$ Å, $\beta = 107.17°$, $P2_1/c$, $Z = 4$, $R = 0.066$, 3985 reflections with $I > 2\sigma_I$. **5**: $a = 37.396$ Å, $b = 7.728$ Å, $c = 19.594$ Å, $\beta = 101.51°$, $C2/c$, $Z = 8$, $R = 0.058$, 3520 reflections with $I > 3\sigma_I$. **6**·0.5 ethyl acetate: $a = 17.626$ Å, $b = 9.105$ Å, $c = 18.977$ Å, $\beta = 107.42°$, $P2_1/c$, $Z = 4$, $R = 0.084$, 4280 reflections with $I > 3\sigma_I$. X-ray data were collected on a Syntex $P2_1$ autodiffractometer with monochromated Mo Kα radiation at −35 °C. The *o*-bis(trimethylenephospha)benzene moiety exhibits a greater variability of conformations than had been observed in the analogous 11-membered ring compounds but again with recurring patterns of torsion angles. In all cases, the phenyl substituents on the *o*-phenylenediphospha unit are cis, as with the 11-ring macrocycles, and are pseudoequatorial in the conformations observed in the crystalline state. All benzo bridges except the one joining oxygen atoms in **6** are pseudoaxial.

We have described recently the synthesis and structural characterization of a number of 11-membered cycles containing *tert*-phosphino sites.[2] As part of our continuing effort in the area of macrocyclic ligands for transition metals, we now report the synthesis and detailed structural characterization of a number of 14-membered tetradentate cycles (**3–6**). These are of interest since, on the basis of the study of molecular models, they are capable of ligating a transition metal in a square-planar fashion (metal in the cavity). This is in contrast to our 11-membered cycles whose cavities are far too small to house a metal and thus allow only pyramidal coordination (pseudotetrahedral with 4-coordinate complexes[3] and the *fac* isomer with octahedral complexes[4]).

Results and Discussion

Synthesis. Scheme I outlines the synthesis of the macrocycles to be described below. The preparations of **1a,b** have been described,[2] and species **2a–c,e** were prepared by alkylation of **1a,b** as well as *N,N'*-dimethyl-*o*-phenylenediamine and the disodium salt of catechol with the appropriate 1,3-disubstituted propane. Material **2a** was too sensitive to decomposition, particularly polymerization via intermolecular phosphonium salt formation, to be purified adequately for combustion analysis. Nonetheless, the spectroscopic properties were in reasonable accord with structure **2a**. Particularly informative was the ^{31}P NMR spectrum which featured only three singlets at δ −28.1, −27.5 and −16.1 in an area ratio of 3:5:2, respectively. Since we were unable to purify **2a** without excessive losses, we used this material directly in the macrocyclization (vide infra). The material giving rise to the ^{31}P NMR absorption at δ −16.1 ppm survived the reaction and was isolated by chromatography on silica gel. It was identified as cycle

Scheme I



7 on the basis of spectroscopic and combustion analytical data. In order to show that the above ^{31}P absorptions at δ −28.1 and −27.5 were due to diastereomers (meso and *dl*) of **2a**, we alkylated species **1a** with methyl iodide to give **8a**, which exhibited ^{31}P NMR singlets at δ −35.8 and −35.0 (area ratio 2:3). The meso isomer of **8a**, isolated as described by Roberts and Wild,[5] gave the lower field absorption. A similar alkylation by *n*-butyl mesylate gave **8b**, with ^{31}P absorptions at δ −27.0 and −26.4 (area ratio 3:7). When one extrapolates from the data of **8a**, it seems reasonable that the *meso*-**2a** is the major isomer formed upon alkylation of **1a** with 1-bromo-3-chloropropane and represents about 50% of the crude mixture of **2a**.

The synthesis of **2b** was also accompanied by a side reaction which gave **9** in about 10% yield. This material was carried through the macrocyclization which gave **4** and was isolated by

(1) (a) Part 9 of the series "Phosphino Macrocycles". For part 8 see: Kyba, E. P.; Chou, S.-S. P. *J. Org. Chem.* **1981**, *46*, 860. (b) A preliminary report of this work has appeared: Davis, R. E.; Hudson, C. W.; Kyba, E. P. *J. Am. Chem. Soc.* **1978**, *100*, 3642.

(2) Kyba, E. P.; John, A. M.; Brown, S. B.; Hudson, C. W.; McPhaul, M. J.; Harding, A.; Larsen, K.; Niedzwiecki, S.; Davis, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 139.

(3) Davis, R. E.; Kyba, E. P.; John, A. M.; Yep, J. M. *Inorg. Chem.* **1980**, *19*, 2540.

(4) Kyba, E. P.; Brown, S. B. *Inorg. Chem.* **1980**, *19*, 2159.

(5) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254.

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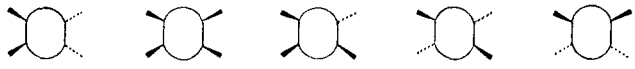
chromatographic resolution of the crude **4** product mixture. Combustion analysis of **2b** was consistent with ca. 10% of **9** being present.

The problem of cyclization to give products analogous to **7** and **9** was avoided with the *o*-phenylenediamine derivative and catechol by using 1-chloro-3-hydroxypropane as the alkylating agent to give **2c** and **e**, respectively. The bis(electrophiles) **2d** and **f** were then generated by using thionyl chloride and mesyl chloride, respectively. All attempts to use this approach to synthesize **2a** (i.e. $SOCl_2$ and the corresponding diol) or the corresponding dimesylate failed because of the preferential attack of thionyl chloride and mesyl chloride at the *tert*-phosphine site, resulting in the ultimate generation of the corresponding phosphine oxides after aqueous workup.

The reaction of the bis(nucleophile) **1** with bis(electrophile) **2** in boiling THF under high dilution conditions[2] gave macrocycles **3–6** in isolated yields of 18–45%. With the exception of **3**, only a single isomer was isolated from each macrocyclization, as evidenced by sharp melting point behavior, thin-layer chromatographic homogeneity and especially ^{31}P NMR evidence. The crude reaction mixtures were examined by ^{31}P NMR spectroscopy prior to any chromatographic workup and revealed no evidence for isomers other than those isolated. In some cases the macrocycles were obtained with solvent of crystallization, which we have found to be rather typical of these types of molecules.

With **3**, two isomers were obtained by using solubility differences in ether as the basis for the separation. The more soluble isomer, designated **3B**, mp 160–164 °C, exhibited a ^{31}P NMR singlet at δ −26.1, whereas the less soluble **3A**, mp 227–229 °C, gave a ^{31}P NMR singlet at δ −28.9. Isomer **3B** was found to convert completely to **3A** in the melt at ca. 185 °C (by ^{31}P NMR spectroscopy).[1a] On the other hand, when **3B** was heated in xylene at 135 °C for 40 min, a mixture of 3B/3A was obtained in a ratio of 43:57 (by integration of ^{31}P NMR singlets) which did not change with further heating. Heating isomer **3A** above its melting point (240 °C) for 10 min gave rise to a mixture of **3B**/**3A** in a ratio of 40:60.[6] Apparently the complete conversion of **3B** → **3A** at 185 °C is due to the insoluble **3A** crystallizing out of the melt and removing itself from equilibration with **3B**.

Structures. All the macrorings reported here have stereochemical questions associated with them, viz., the relative orientation of the phenyl substituents on phosphorus.[7] We have established with 11-membered rings that the *P,P'*-diphenyl-1,2-diphospha moiety is always cis,[2] and we now present evidence that the same situation obtains with 14-membered cycles. The stereochemically most complicated species in this work is **3**, which is capable of exhibiting five isomers, **3A–E**, shown schematically



3A 3B 3C 3D 3E

below, where the straight lines represent benzo fusions, the curved lines represent trimethylene chains, and the orientation of the phenyl groups is indicated by wedges and dashed lines. Of course **3C** would be a racemate, whereas the others are all meso forms. As mentioned above, only two isomers of **3** are isolated and we have determined them to be the *cis,trans,cis*-**3A** (high-melting) and the *cis,cis,cis*-**3B** (low-melting) species.

Before the details of the structures determined in this work are described, it should be mentioned that a connectivity search in the Cambridge Crystallographic Data Centre Structural Database[8] for 14-membered rings containing only C, N, O, S, or P atoms,

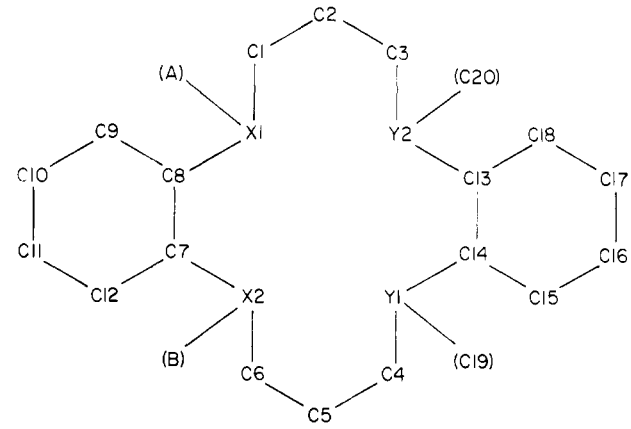


Figure 1. Numbering system used in presentation and discussion of crystallographic results. All structures were numbered so that the distance X1···Y1 is greater than the distance X2···Y2. Coordinates have been presented so that the torsion angle C2–C1–X1–C8 is negative (see Figures 2 and 4). Identity of heteroatoms: **3A** and **3B**, X1 = X2 = Y1 = Y2 = P(Ph); **4**, X1 = X2 = P(Ph), Y1 = Y2 = S; **5**, X1 = X2 = P(Ph), Y1 = Y2 = N(Me); **6**, X1 = X2 = P(Ph), Y1 = Y2 = O.

with two planar constraints in the form of *cis,cis*-1,8-diene revealed no such structures. Thus, to our knowledge, the five structures described below are the only reported structural data on *cis,cis*-cyclotetradeca-1,8-diene-type species. A number of structures of tetraazacyclotetradeca-1,8-diene have been determined, but the unsaturations are, in fact, of the trans-imine type.[9]

It is clear from the ORTEP plots of **3–6** shown in Figures 2–4 that as in the case of the analogous 11-membered compounds[2] only the cis configuration of phenyl groups about the *o*-bis(*tert*-phosphino)benzo unit is observed in any of these macrocycles. In all of the present cases, the substituents of the heteroatoms occupy pseudoequatorial positions, including the methyl groups on nitrogen of **5**.

Inspection of bond lengths (Table III) and bond angles (Table IV) reveals no unusual values, with the exception of those involving O1 of **6** where, as is suggested by the large thermal ellipsoids of Figure 2e, some disorder may be present. In all five structures, the four heteroatoms are nearly coplanar, though less so in **6**; the range of deviations of heteroatoms from the least-squares plane of all four heteroatoms are 0 Å in **3A**, ±0.08 Å in **3B**, ±0.03 Å in **4**, ±0.01 Å in **5**, and ±0.21 Å in **6**. In **3B** and **4**, the methylene carbons are all less than 0.28 Å out of the best heteroatoms plane; corresponding maximum out-of-plane distances for the methylene carbons of the other, less planar, macrocycles are 0.55 Å in **5**, 0.65 Å in **6**, and 0.92 Å in **3A**.

A general structural feature noted in the analogous 11-membered rings[2] which persists in the 14-membered rings reported here is the tendency for the benzo bridge to be approximately perpendicular to the plane of the heteroatoms (i.e., bridging pseudoaxial positions). Angles between the benzo plane and the heteroatom plane are 102.6° in **3A**, 91.8° in **3B**, 95.7° at P in **4**, 89.2° at S in **4**, 116° at P in **5**, 101.5° at N in **5**, 126.3° at P in **6**, and 161.2° at O in **6**. Thus, the only benzo ring which is not in a pseudoaxial position is the one which bridges the oxygens in **6**, this one adopting a position commonly seen in benzo-fused crown ethers.[10]

The 14-membered rings reported here exhibit a larger variety of conformations than was observed in similar 11-membered rings, but again recurring patterns can be seen. For example, compounds **3B** and **4** adopt almost identical conformations (except, of course, for the fusion of the benzo bridges with different stereochemistry), fully extended along each polymethylene chain. It should be noted that the resulting arrangement of heteroatoms is not rectangular but is in the shape of a parallelogram with diagonals approximately

(6) There was no evidence in any of the thermal equilibration studies for the formation of isomers other than **3A,B** in amounts that would be observable by ^{31}P NMR spectroscopy.

(7) The inversion barrier for diarylalkylphosphines is in the range of 29–31 kcal/mol: Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 3090.

(8) The Structural Database is maintained by the Cambridge Crystallographic Data Centre, Department of Chemistry, Cambridge CB2 1EW, England. Our searches were carried out on a local copy of the July 1979 issue of the database, using programs originating at the Data Centre.

(9) Curtis, N. F. In "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; Chapter 4.

(10) See, for example: Hughes, D. L.; Nowell, I. W. *J. Chem. Res., (Synop.)* **1978**, 112.

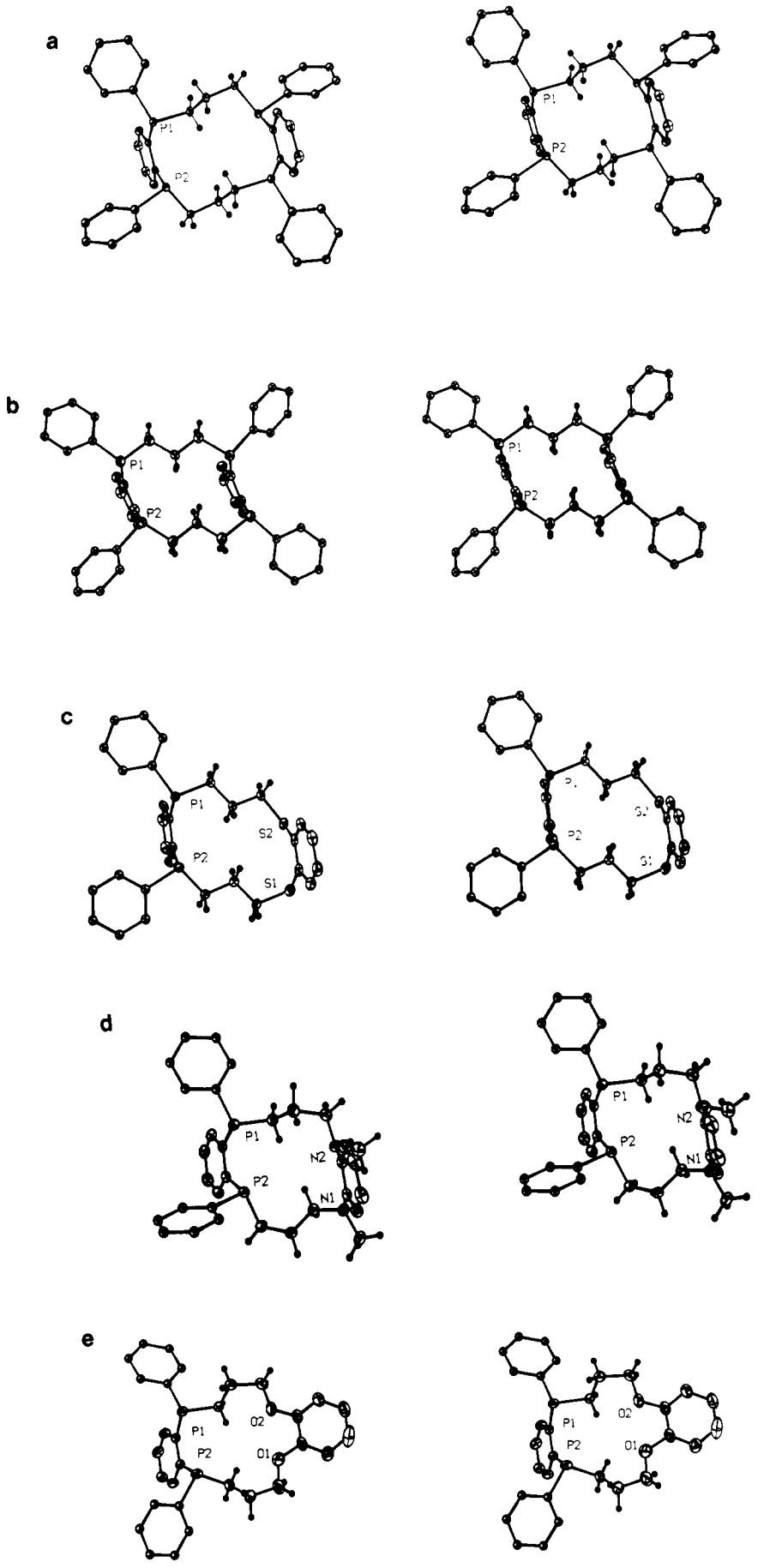


Figure 2. Stereoscopic representations of molecular geometry: (a) **3A**; (b) **3B**; (c) **4**; (d) **5**; (e) **6**.

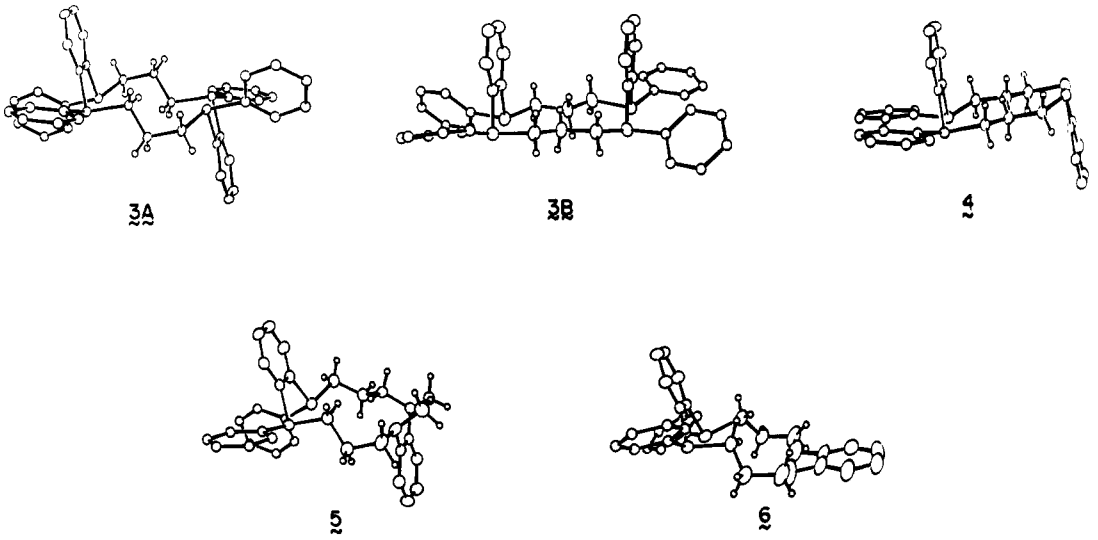


Figure 3. Molecular geometry, emphasizing comparisons of benzo bridge geometry.

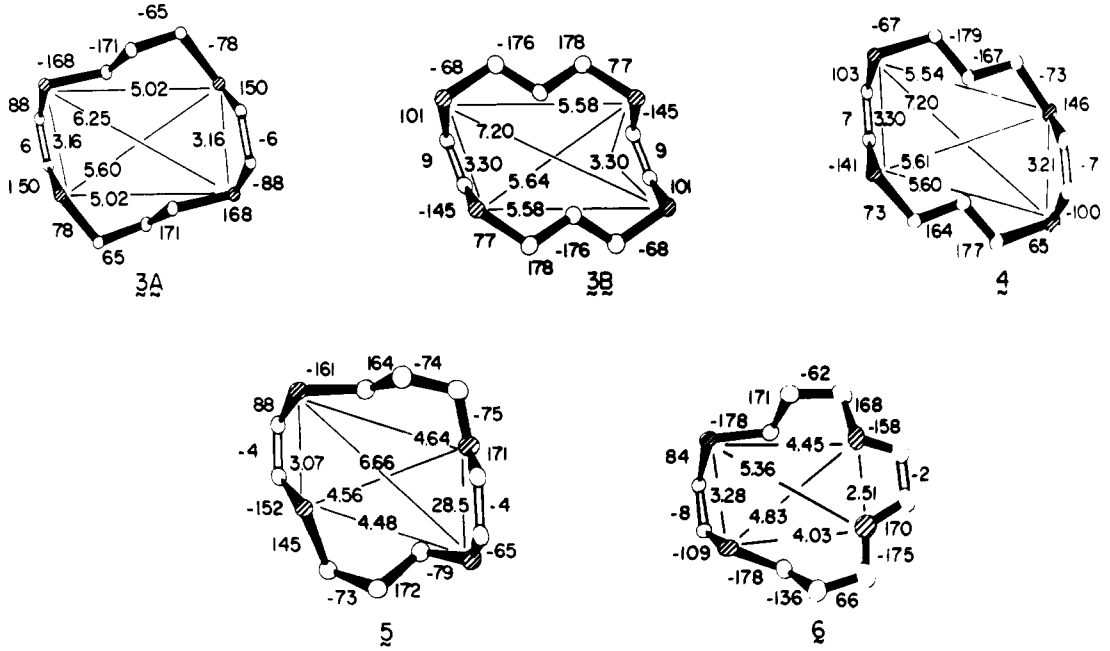


Figure 4. Wedge representations of 14-membered ring conformations, with ring torsion angles (deg). Heteroatoms are shaded. Distances between pairs of heteroatoms (Å) are shown.

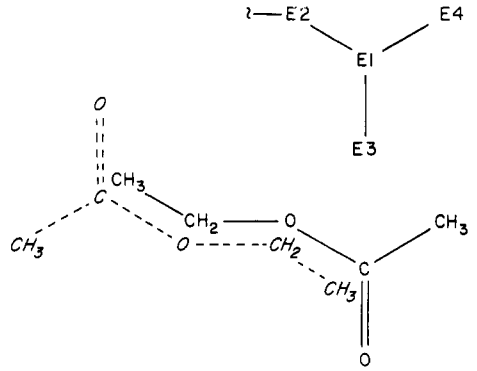


Figure 5. The disorder in the ethyl acetate solvent of crystallization in the crystal structure of **6**. The inversion center at (0, 0, $^1/_2$) is midway between the methylene carbon and the alkoxy oxygen.

7.2 and 5.6 Å. Again (since the difference between torsion angles of −171 and +164 is actually only 25°), the conformational pattern of one polymethylene strand of **5** matches that seen (twice) in centrosymmetric **3A**.

If we describe the torsion angles ±(50–100°) as gauche (±g) and ±(145–180°) as anti (±a), then the conformation of each strand of atoms bridging the benzo moieties can be referred to in terms of four descriptors, running from phosphorus to the other heteroatom in the bridge. There are six conformations which appear in the ten bridging strands (ignoring the direction of the rotation):[11] [g,a,a,g], **4**; [g,a,a,−g], **3A**; [g,g,a,a], **3B**; [a,a,g,a], **6**; [a,a,g,g] and [a,g,a,g], **5**. The first three of the four descriptors account for the conformation of the *o*-bis(trimethylenephospha)benzene moiety, an element common to these 14-membered rings as well as the 11-membered rings that we have reported previously. It is apparent that there is reasonable flexibility of this unit within the macrocycles, since four different arrangements are observed: [g,a,a] (four strands); [a,a,g] (three strands); [g,g,a] (two strands); [a,g,a] (one strand). In contrast, in the 11-membered rings, the [g,g,a] conformation appears in seven of ten strands observed, presumably as a consequence of the smaller ring requiring a more coiled conformation per bond in the ring.

(11) It is assumed that +a ≃ −a and the direction of the gauche torsion angle is important only when measured against another gauche torsion angle in the same strand.

Stereochemistry in the Macrocyclization. We have noted earlier, and suggested an explanation for, the exclusive formation of the *cis*-Ph_2 across the benzo fusion in 11-membered rings.[2] The rationale in essence is that in the key macrocyclization step the substituent phenyl groups on the *o*-phosphine atoms on the benzo group must be *cis* in order that both occupy pseudoequatorial positions in the 11-membered ring being formed. A similar situation apparently obtains with the 14-membered rings now being described, since only *cis*-Ph_2 species have been found. An added stereochemical complication is present in the formation of **3A** and **3B**, in which the transition state for macrocyclization apparently will not tolerate the *trans*-Ph_2 across the benzo moiety not involved in the crucial intramolecular nucleophilic substitution. In this context it is interesting to note in an analogous reaction the macrocyclization transition state is tolerant of a *trans*-Me_2 across a 1,2-diarsenobenzene moiety.[1]

Experimental Section

General Information. Melting points were obtained by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Chemalytics, Inc., Tempe, AZ.

Infrared spectra (IR) were recorded on a Perkin-Elmer 237B grating spectrophotometer.

Proton magnetic resonance spectra (^1H NMR) were obtained on Perkin-Elmer R-12, Varian A-60, or Varian HA-100 instrument. Chemical shifts are given as parts per million (ppm) downfield from tetramethylsilane in δ units, and coupling constants are reported in hertz. Multiplicities are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Carbon-13 and phosphorus-31 NMR spectra were determined on a Bruker instrument at 22.6 and 36.4 MHz, respectively. Chemical shifts are given as parts per million (ppm) relative to Me_4Si for ^{13}C NMR and relative to 85% H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield from 85% H_3PO_4 are defined as negative for the ^{31}P spectra. The ^{13}C and ^{31}P NMR spectra are proton decoupled.

Mass spectra were determined on a CEC-21-100 high-resolution instrument or a DuPont 21-491 instrument, at 70 eV.

Gas chromatographic analyses were performed on either a Varian-Aerograph 2720 (thermal conductivity detector) or 2740 (flame ionization detector) instrument by using either 5% or 20% SE-30 on Gas Chrom Q, packed in stainless-steel columns (6 ft by 0.188 in. or 6 ft by 0.125 in.). Peak area measurements were obtained with the aid of a Vidar 6300 ditital integrator.

All X-ray measurements were performed on a Syntex $P2_1$ autodiffractometer.

Unless noted, all of the reactions, manipulations, and purification steps involving phosphines were performed under a dry nitrogen or argon atmosphere. Air-sensitive liquids were transferred by Teflon flexneedles by using nitrogen pressure or by syringe. All concentrations of solutions were carried out on a rotary evaporator under water aspirator pressures unless otherwise noted. Solutions were dried with anhydrous magnesium sulfate.

The following compounds have been described elsewhere: *o*-bis(phenylphosphino)benzene (**1a**),[12] dithiocatechol (**1b**);[13] *o*-bis(methylamino)benzene (**1d**).[14]

***o*-Bis((3-chloropropyl)phenylphosphino)benzene (2a).** Diphosphide **1a** (20.9 mmol) was generated from the corresponding diphosphine (6.15 g, 20.9 mmol) in THF (200 mL) at −78 °C and *n*-BuLi (42.1 mmol). This was added dropwise to a vigorously stirred solution of 1-bromo-3-chloropropane (64 g, 400 mmol) in THF (250 mL) at 0 °C. The resulting mixture was stirred for 1 h at 25 °C and then concentrated, first by rotary evaporation and then under vacuum (20 μm) at 40 °C with a dry ice–acetone trap. Ether (500 mL) was added to the residue, which was then washed with water (100 mL) and brine (100 mL), dried, and concentrated to give a pale yellow oil (11.9 g). This was passed through a column of alumina (40 g, anaerobic) by using 1,2-dichloroethane–hexane as eluant. Following rotary evaporation, last traces of solvent and of 1-bromo-3-chloropropane were removed by warming under vacuum (40 °C (20 μm), 3 h) to give **2a** (4.9 g, ~50%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.3 (7, 14 H), 3.8–3.3 (m, 4 H), 2.4–1.6 (br m, 8 H); ^{31}P NMR ($CDCl_3$) δ −28.13 (s), −27.52 (s) (area ratio 4:6), −16.14 (s) (vide infra). The area ratio of the first two peaks to the −16.14 peak was 4:1. Mass spectrum: *m/e* 446 (M^+ for ^{35}Cl–^{35}Cl, 3% of base peak), 334 (base peak, −2 Cl, $-C_3H_6$). Attempts at further purification for combustion analyses led to partial polymerization via quaternizations at phosphorus.

***o*-Bis((3-chloropropyl)thio)benzene (2b).** A 1.77 M hexane solution of *n*-BuLi (20 mL) was added (10 min) to a solution of dithiocatechol (2.5 g, 17.6 mmol) and 1-bromo-3-chloropropane (27.7 g, 176 mmol) in THF at −77 °C, and the resulting solution was allowed to warm to room temperature. The reaction mixture was concentrated (rotary evaporator), and the excess bromochloropropane was removed under high vacuum (40 °C, 40 μm, dry ice–acetone trap). The residue was partitioned between ether and water (100 mL/100 mL), and the ether solution was dried. Concentration gave a clear yellow oil which was Kugelrohr distilled (20 μm, oven temperature 140 °C) to give **2b** as a slightly yellow oil (3.6 g, 69%): ^1H NMR ($CDCl_3$) δ 7.3 (m, 4 H), 3.65 (t, 4 H), 3.05 (t, 4 H), 2.05 (q, 4 H); mass spectrum, *m/e* 294 (M^+ for ^{35}Cl–^{35}Cl, 46% of base peak), 218 (base peak, −Cl, $-C_3H_5$).

Anal. Calcd for $C_{12}H_{16}Cl_2S_2$: C, 48.81; H, 5.46. Found: C, 49.96, H, 5.33. Calcd for $C_{12}H_{16}Cl_2S_2 \cdot 0.1(C_9H_{10}S_2)$: C, 49.92; H, 5.47.

***o*-Bis((3-hydroxypropyl)methylamino)benzene (2c).** A mixture of *N,N'*-dimethyl-1,2-diaminobenzene (5.0 g, 37 mmol), 1-chloro-3-hydroxypropane (10.4 g, 110 mmol) and calcium carbonate (3.7 g, 37 mmol) in water (40 mL) was heated at reflux (bath temperature 115 °C) for 48 h under a nitrogen atmosphere. The cooled reaction mixture was poured into 10% aqueous potassium carbonate (50 mL) and extracted with chloroform (3 × 100 mL). The chloroform extracts were combined, dried, and concentrated, and the residue was distilled to give **2c** as a colorless viscous oil (7.2 g, 78%): bp 153–155 °C (40 μm); ^1H NMR ($CDCl_3$) δ 7.1 (narrow m, 4 H), 4.5 (br s, 2 H, exchanges with D_2O), 3.70 (t, J = 6.0 Hz, 4 H), 3.04 (t, J = 7.0 Hz, 4 H), 2.70 (s, 6 H), 1.71 (quint, $J \simeq$ 6.5 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 148.1, 124.4, 121.5, 60.2, 53.5, 41.5, 29.5 (all singlets); mass spectrum, *m/e* 252 (M^+).

Anal. Calcd for $C_{14}H_{24}N_2O_2$: C, 66.61; H, 9.60; N, 11.10. Found: C, 66.84; H, 9.82; N, 11.44.

***o*-Bis((3-chloropropyl)methylamino)benzene (2d).** The above diol **2c** (15.6 g, 61.7 mmol) in chloroform (75 mL) was treated with gaseous hydrogen chloride until precipitation ceased. Thionyl chloride (16.2 g, 136 mmol) was added, and the mixture was boiled under reflux for 5 h. The cooled reaction mixture was diluted with chloroform (75 mL), extracted with aqueous sodium carbonate, dried, and concentrated. The residue was dissolved in benzene (400 mL) and passed through a short column of alumina (60 g). The filtrate was concentrated on a rotary evaporator and then on a vacuum line (room temperature, 20 μm) for 1 h, to give **2d** as a light yellow oil (15.6 g, 87%), which decomposed slowly at room temperature and rapidly upon attempted distillation at elevated temperatures: ^1H NMR ($CDCl_3$) δ 6.96 (narrow m, 4 H), 3.54 (t, J = 6.5 Hz, 4 H), 3.28 (t, J = 7.0 Hz, 4 H), 2.78 (s, 6 H), 1.96 (quint, $J \simeq$ 7 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 145.3, 128.4, 122.6, 51.0, 43.4, 40.0, 30.1 (all singlets); mass spectrum, *m/e* 288 (M^+ for ^{35}Cl–^{35}Cl). This material was stored in a freezer and used directly in the macrocyclization described below.

***o*-Bis((3-hydroxypropyl)oxy)benzene (2e).** Catechol (15.1 g, 137 mmol) and 1-chloro-3-hydroxypropane (65.9 g, 697 mmol) were boiled under reflux for 48 h in a solution sodium hydroxide (13.6 g, 340 mmol) in 95% ethanol (120 mL) under a nitrogen atmosphere. The resulting mixture was concentrated, and the residue was partitioned between ether and 10% sodium hydroxide. The ether layer was dried and concentrated to give a yellow oil which was crystallized and recrystallized from hexane–acetone (9:1, v/v) to give **2e** as a white crystalline solid (20.1 g, 65%): mp 51–53 °C; lit.[15] mp 56–57 °C.

***o*-Bis((3-(methanesulfonyloxy)propyl)oxy)benzene (2f).** Methanesulfonyl chloride (45 g, 393 mmol) was added dropwise to a solution of diol **2e** (20.1 g, 88.9 mmol) and triethylamine (100 g, 100 mmol) in dichloromethane (450 mL) at 0 °C. The reaction mixture was stirred for 2 h and then extracted with ice water, cold 10% aqueous hydrochloric acid, saturated sodium bicarbonate, and brine. The organic layer was dried and concentrated to give a dark oil which was crystallized and recrystallized from hexane–ethyl acetate (4:1, v/v) to give **2f** as white crystals (19.6 g, 58%): mp 43–45 °C; ^1H NMR ($CDCl_3$) δ 6.95 (narrow m, 4 H), 4.47 (t, J = 6.3 Hz, 4 H), 4.13 (t, J = 6.0 Hz, 4 H), 3.00 (s, 6 H), 2.25 (quint, $J \approx$ 6 Hz, 4 H); mass spectrum, *m/e* 382 (M^+).

Anal. Calcd for $C_{14}H_{22}O_8S_2$: C, 43.96; H, 5.80. Found C, 44.12; H, 5.88.

Alkylation of the Dilithio *o*-Bis(phenylphosphido)benzene (1a). A 2.27 M hexane solution of *n*-BuLi (4.8 mL, 10.9 mmol) was added to **1a** (1.57 g, 5.34 mmol) in THF (50 mL) at −78 °C. To this was added methyl iodide (1.55 g, 10.9 mmol), and the reaction mixture was allowed to warm to room temperature. The mixture was concentrated, and the residue was partitioned between ether (50 mL) and brine (50 mL). The dried ether solution was concentrated on a rotary evaporator and then

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Table I. Crystal Data at −35 °C

	3A	3B	4	5	6
crystallizatn solvent	acetone/THF	acetone/THF	acetone/THF	acetone/EtOH	ethyl acetate
unit cell data[a]					
a, A	9.634 (1)	25.504 (15)	7.636 (1)	37.396 (16)	17.626 (2)
b, A	11.586 (2)	25.504 (15)	15.277 (3)	7.728 (3)	9.105 (1)
c, A	8.746 (1)	13.796 (2)	24.206 (5)	19.594 (7)	18.977 (2)
α, deg	100.86 (1)	90	90	90	90
β, deg	104.70 (1)	90	107.17 (2)	101.51 (4)	107.42 (1)
γ, deg	107.31 (1)	90	90	90	90
no. reflctns for detn of cell data	58	30	45	45	45
range of 2θ for detn of cell data, deg	24.1–28.0	20.1–23.3	26.1–28.0	20.0–22.9	28.2–29.9
d_{calcd}, g/cm^3 (−35 °C)	1.286	1.204[c]	1.272	1.165	1.153[d]
d_{measd}, g/cm^3 (21 °C)		1.15			1.18
liquid for d_{measd}		aq NaCl			aq $CaCl_2$
systematic absences	none	*hkl*, $h + k + l = 2n + 1$; *hk0*, $h(k) = 2n + 1$; *00l*, $l = 4n$	*h0l*, $l = 2n + 1$; *0k0*, $k = 2n + 1$	*hkl*, $h + k = 2n + 1$; *h0l*, $l = 2n + 1$	*h0l*, $l = 2n + 1$; *0k0*, $k = 2n + 1$
cryst system	triclinic	tetragonal	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$I4_1/a$ (No. 88)[b]	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
Z	1	8	4	8	4
cryst symmetry of molecule	C_i	C_2	C_1	C_1	C_1
F(000), electrons	352	1728[c]	1088	2080	1072
formula of asymmetric unit	$0.5(C_{42}H_{40}P_4)$	$0.5(C_{42}H_{40}P_4)\cdot C_4H_8O$[c]	$C_{30}H_{30}P_2S_2$	$C_{30}H_{36}N_2P_2$	$C_{28}H_{30}O_2P_2\cdot 0.5(C_4H_8O_2)$
fw	668.7	406.4[c]	516.6	486.6	504.5[d]

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles (2θ) of a number of reflections collected within the high 2θ range shown. [b] Origin taken at $\bar{1}$ at 0, $^1/_4$, $^1/_8$ from $\bar{4}$. [c] Includes one molecule of THF per asymmetric unit. [d] Includes half of a molecule of ethyl acetate per asymmetric unit.

on a vacuum line (25 °C (20 μm) to give **8** (R = Me) as a colorless oil (1.6 g, 93%): ^{31}P NMR ($CDCl_3$) δ −35.8 (s), −35.0 (s) (area ratio 4:6). The meso isomer of **7** was isolated according to the procedure of Roberts and Wild[5] and exhibited a singlet of δ −35.0 in the ^{31}P NMR ($CDCl_3$).

With use of a procedure similar to that above, the dilithio salt **1a** was alkylated with *n*-butyl mesylate to give a material which exhibited two singlets in the ^{31}P NMR spectrum at δ −27.0 and −26.4 (area ratio 3:7).

***cis,cis,cis*- and *cis,trans,cis*-2,6,13,17-Tetraphenyl-2,6,13,17-tetraphosphatricyclo[16.4.0.0^{7,12}]docosa-7(12),8,10,1(18),19,21-hexane (3A and 3B).** A THF solution (240 mL) of diphosphide **1a** (15.6 mmol) at −78 °C was obtained from the diphosphine precursor (4.58 g, 15.6 mmol) and a 2.9 M hexane solution of *n*-BuLi (10.6 mL). The resulting solution and a solution of dichloride **2a** (7.0 g, 16 mmol) in THF (250-mL total volume) were reacted under high dilution conditions[1,2] (addition time 24 h). The reaction mixture was concentrated, and the residue was partitioned between ether (500 mL) and water (100 mL) to give a yellow ether solution and an insoluble white solid. The dried ether solution was filtered through Celite and concentrated to give a yellow glass (6.1 g). The glass was dissolved in hot THF–acetone (1:1, 200 mL) which upon cooling to room temperature gave **3B** (630 mg). The mother liquor was concentrated to 100 mL and cooled to −20 °C to give a further batch of **3B** (750 mg). The combined solids were recrystallized from acetone to give **3B** as colorless prisms (1.13 g, 11%): mp 158–163 °C; ^{1}H NMR ($CDCl_3$) δ 7.4–6.9 (m, 28 H), 2.50–1.18 (br m, 12 H), 2.18 (s, 6 H, acetone solvent of crystallization); ^{31}P NMR ($CDCl_3$) δ −26.1 (s); mass spectrum, *m/e* 668 (M^+). The solvent was removed by heating in a vacuum (80 °C, 20 μm, 4 h) to give an analytical sample of **3B**, mp 160–164 °C.

Anal. Calcd for $C_{42}H_{40}P_4$: C, 75.44; H, 6.03. Found: C, 75.15; H, 6.12.

The above ether-insoluble white solid was extracted with 1,2-dichloroethane (250 mL), and the resulting solution was dried ($MgSO_4$), filtered though Celite, and concentrated under vacuum to give a yellow solid (4.9 g). This was recrystallized from THF–ether (70–40 mL) to give a white solid (3 g) which was recrystallized from THF–hexane (80–10 mL) to give **3A** as colorless prisms (2.65 g, 25%): mp 227–229 °C; ^{1}H NMR ($CDCl_3$) δ 7.4–6.9 (m, 28 H), 2.7–1.3 (br m, 12 H), 3.75 and 1.85 (m due to THF solvent of crystallization, ca. 4 H and 4 H); ^{31}P NMR ($CDCl_3$) δ −28.9 (s); mass spectrum, *m/e* 668 (M^+). The solvent was removed by heating under vacuum (80 °C, 20 μm, 4 H) to give an analytical sample of **3A** as a white solid, mp 214–216 °C.

Anal. Calcd for $C_{42}H_{40}P_4$: C, 75.44; H, 6.03. Found: C, 75.34; H, 5.88.

***cis*-2,6-Diphenyl-2,6-diphosphabicyclo[5.4.0]undeca-1(7),8,10-triene (7).** A 0.5-g portion of the above-described ether-soluble residue from the workup of the reaction mixture from the preparation of **3A** and **B** was chromatographed on silica gel by using hexane-1,2-dichloroethane (96:4, v/v) as eluant to give **7** as white crystals (50 mg): mp 144–145 °C; ^{1}H NMR ($CDCl_3$) δ 7.4–6.4 (complex m, 14 H), 2.92–1.75 (complex m, 6 H); ^{31}P NMR ($CDCl_3$) δ −16.14 (s); mass spectrum, *m/e* 334 (M^+).

Anal. Calcd for $C_{21}H_{20}P_2$: C, 75.44; H, 6.03. Found: C, 75.22; H, 6.08.

Thermal Equilibration of 3A and 3B. Macrocycle **3B** (50 mg) was heated in an evacuated flask in an oil bath at 185 °C for 0.5 h. The sample melted and then resolidified. The ^{31}P NMR spectrum ($CDCl_3$) showed a peak of δ −28.9 and no trace of absorption at δ −26.1, and no other peaks were evident.

Isomer **3A** (50 mg) was heated in an evacuated flask at 240 °C for 10 min and then immersed in an ice bath. The ^{31}P NMR spectrum ($CDCl_3$) exhibited only two singlets at δ −28.9 and −26.1 in an area ratio of 6:4.

Isomer **3B** (50 mg) was heated in degassed *p*-xylene at 135 °C for 40 min. The xylene was removed under high vacuum, and the ^{31}P NMR spectrum showed two singlets at δ −28.9 and −26.1 in an area ratio of 57:43. Further heating at 135 °C resulted in no further spectral changes.

***cis*-6,13-Diphenyl-6,13-diphospha-2,17-dithiatricyclo[16.4.0.0^{7,12}]docosa-7(12),8,10,1(18),19,21-hexaene (4) and 2,6-Dithiabicyclo[5.4.0]undeca-1(7),8,10-triene (9).** Diphosphide **1a** (20.8 mmol) was generated from the diphosphine precursor (6.11 g, 20.8 mmol) in THF (240 mL) and *n*-BuLi (41.6 mmol). The resulting red solution was warmed to room temperature and reacted under high dilution conditions[2] (20 h) with dichloride **2b** (6.22 g, 21.1 mmol) in THF (250 mL). The cooled reaction mixture was concentrated, and the residue was digested with boiling ether (500 mL). The resulting ether solution was washed with water (100 mL), 10% aqueous sodium carbonate (2 × 100 mL), and brine (100 mL). It was then dried, filtered through Celite, and concentrated to give a white glass (5.7 g), which was chromatographted on alumina (50 g) by using hexane–1,2-dichloroethane (3:1, v/v) to give two crystalline materials. The chromatographically more mobile material was recrystallized from ethanol to give **9** (350 mg, ca. 10% of starting **2b**): mp 59.5–60.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.37 (m, 4 H), 2.85 (m, 4 H), 2.27 (br m, 2 H); mass spectrum, *m/e* 182 (M^+).

Anal. Calcd for $C_9H_{10}S_2$: C, 59.30; H, 5.53. Found: C, 59.33; H, 5.69.

The less chromatographically mobile solid was recrystallized from acetone to give **4** as white needles (2.80 g, 26%): mp 111–112 °C; ^{1}H NMR ($CDCl_3$) 7.4–6.9 (m, 18 H), 3.15 (br m, 4 H), 2.05 (br m, 8 H); ^{31}P NMR ($CDCl_3$) δ −27.0 (s); mass spectrum, *m/e* 516 (M^+).

Anal. Calcd for $C_{30}H_{30}P_2S_2$: C, 69.74; H, 5.86. Found: C, 69.79; H, 5.84.

Table II. Collection[a] and Processing of Intensity Data

	3A	3B	4	5	6
check reflctns (every 96 reflctns)	(012), (2̄12), (3̄10), (022̄)	(10,2,0), (62̄0), (114), (060)	(1̄13), (302̄), (041̄), (10̄8)	(5̄13), (008̄), (020), (827)	(402̄), (24̄0), (023), (313̄)
hours of data collectn	65	121	113	84	123
quadratic coeff s and t, $\times 10^6$, in decay analysis[b] (with esd)	−392 (128), 5(2)	87 (49), −1(0)	−188(35), −1(0)	37(79), −2(1)	−127(28), 1(0)
decay correctn	no	no	yes	no	yes
2θ range, deg	4–55	4–52	4–55	4–50	4–55
total reflctns measd	3968	4392	6186	4868	6695
abs coeff μ(Mo Kα), cm^{-1}	2.52	2.10	3.29	1.81	1.81
p factor	0.03	0.02	0.04	0.03	0.02

[a] Syntex P2$_1$ autodiffractometer equipped with a graphite monochromator and a Syntex LT-1 inert-gas low-temperature delivery system. All X-ray measurements were performed with Mo Kα radiation (λ = 0.71069 Å). [b] Reference 18.

In a duplicate run of the above reaction the yield of **4** was 45%.

6,13-Dimethyl-*cis*-2,17-diphenyl-2,17-diphospha-6,13-diazatricyclo-[16.4.0.0^{7,12}]docosa-7(12),8,10,1(18),19,21-hexaene (5). The dilithio salt **1a** (5.71 g, 19.4 mmol) in THF (250 mL) was generated as described for **3** and **4** and then reacted under high dilution conditions with dichloride **2d** (5.61 g, 19.4 mmol) in THF (250 mL). The workup was as described for **4**, and the ether-soluble material was crystallized from ethanol and then recrystallized from acetone to give **5** as fine white crystals (1.8 g, 18%): mp 116–118 °C; ^{1}H NMR ($CDCl_3$) δ 7.4–6.9 (complex m, 18 H), 3.40 (m, 4 H), 2.74 (s, 6 H), 2.1 (m, 4 H), 1.9 (m, 4 H); ^{31}P NMR ($CDCl_3$) δ −24.9 (s); mass spectrum, m/e 510 (M^+).

Anal. Calcd for $C_{32}H_{36}N_2P_2$: C, 75.25; H, 7.12. Found: C, 75.00, H, 7.26.

***cis*-2,17-Diphenyl-2,17-diphospha-6,13-dioxatricyclo[16.4.0.0^{7,12}]docosa-7(12),8,10,1(18),19,21-hexaene (6).**[16] The dilithio salt **1a** (5.2 g, 17.7 mmol), in THF (250 mL) was generated as for **3** and **4** and then reacted under high dilution conditions with dimesylate **2f** (6.76 g, 17.7 mmol) in THF (250 mL). With use of a workup as described for **4** a colorless glass (3.6 g, 42%) was obtained after filtration through silica gel by using hexane–ethyl acetate (7:3, v/v). This was crystallized and recrystallized from ethyl acetate to give **6** as colorless crystals containing ethyl acetate of crystallization (3.3 g, 38%): mp 69–70 °C; ^{1}H NMR ($CDCl_3$) δ 7.7–6.9 (complex m, 18 H), 4.44 (m, 2 H), 3.98 (m, 2 H), 2.42 (m, 4 H), 2.10 (m, 4 H), with ethyl acetate signals at δ 4.15 (q, J = 7.5 Hz), 2.04 (s), and 1.25 (t, J = 7.5 Hz), giving an integration consistent with 0.5 mol of EtOAc to 1.0 mol **6**; ^{31}P NMR ($CDCl_3$) δ −26.4 (s); mass spectrum, m/e 484 (M^+).

Anal. Calcd for $C_{30}H_{30}O_2P_2$: C, 74.37; H, 6.24. Calcd for $C_{30}H_{30}O_2P_2 \cdot 0.5(C_3H_8O_2)$: C, 72.71; H, 6.48. Found: C, 72.73; H, 6.59.

Crystallographic Analysis. Crystals were grown by cooling from the solvents indicated in Table I. In each case, the crystals were clear, colorless prisms. For each compound a suitable single crystal was affixed to a glass fiber attached to a goniometer head and then transferred to a Syntex P2$_1$ autodiffractometer where it was maintained in a stream of cold (−35 °C) dry nitrogen during the course of all diffraction experiments. Crystal data and details of intensity data collection and processing are summarized in Tables I and II. Intensity data were collected by the variable-speed ω-scan technique, with scan width of 1° centered at the position of the K$\bar{\alpha}$ maximum. Background measurements were obtained at settings of ±1° in ω from this setting. Scan speeds for each crystal ranged 2–5 deg min^{-1}. The measured intensities were reduced and assigned standard deviations as described elsewhere.[17] No absorption corrections were applied, and only for **4** and **6** were time-dependent corrections for crystal decay applied (maximum values for correction factor to intensity were 3.5% for **4** and 1.4% for **6**).

Solution and Refinement of the Structures. The structures were solved either by standard heavy-atom procedures or by direct methods, as indicated below, and were refined by full-matrix least-squares methods.[18] The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight is $1/\sigma^2(|F_o|)$, the reciprocal square of the standard deviation of each observation, $|F_o|$. The conventional (R) and weighted (wR) crystallographic agreement factors used to assess the structures are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ respectively. Neutral atom scattering factors for S, P, O, C,[19] and H[20] were used in these calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections[19] for anomalous dispersion were applied to the S and P scattering curves. In each structure, phenyl rings were treated as rigid groups, constrained with C–C = 1.392 Å, C–H = 1.00 Å, and C–C–C = C–C–H = 120°, with carbon and, usually, hydrogen temperature factors individually varied isotropically. For each structure, refinement was continued until shifts in all parameters were less than one estimated standard deviation in the respective parameter. Further details of refinement of the individual structures are given below. Final fractional crystallographic coordinates for the nonhydrogen, nongroup atoms appear in Table SII, and their anisotropic temperature parameters are given in Table SIII.[21] The rigid-group parameters used to describe phenyl rings

Table III. Bond Lengths (Å) Not Involving Hydrogens or within Phenyl Rings[a]

bond	3A[b]	3B[b]	4	5	6
X1–C1	1.851	1.857	1.860	1.831	1.843
X1–C8	1.856	1.850	1.855	1.847	1.852
X1–C(exo)	1.852	1.851	1.846	1.836	1.846
X2–C6	1.853	1.852	1.853	1.861	1.834
X2–C7	1.845	1.843	1.858	1.842	1.847
X2–C(exo)	1.851	1.850	1.850	1.840	1.840
Y1–C4			1.828	1.460	1.426
Y1–C14			1.781	1.439	1.360
Y1–C(exo)				1.469	
Y2–C3			1.817	1.459	1.384
Y2–C13			1.774	1.404	1.419
Y2–C(exo)				1.462	
C1–C2	1.528	1.510	1.521	1.550	1.534
C2–C3	1.535	1.530	1.521	1.506	1.512
C4–C5			1.524	1.520	1.482
C5–C6			1.526	1.522	1.530
C7–C8	1.404	1.413	1.396	1.408	1.413
C8–C9	1.396	1.374	1.396	1.387	1.382
C9–C10	1.378	1.389	1.378	1.376	1.376
C10–C11	1.387	1.399	1.384	1.368	1.383
C11–C12	1.387	1.377	1.373	1.382	1.371
C12–C7	1.398	1.399	1.399	1.387	1.396
C13–C14			1.409	1.421	1.379
C14–C15			1.386	1.397	1.373
C15–C16			1.365	1.383	1.374
C16–C17			1.381	1.368	1.375
C17–C18			1.382	1.385	1.380
C18–C13			1.389	1.383	1.370
P–C, S–C[c]	0.002–0.003	0.007–0.008	0.003–0.005	0.002–0.004	0.003–0.005
C–C, N–C, O–C[c]	0.003–0.005	0.010–0.012	0.004–0.008	0.005–0.006	0.006–0.010

[a] See Figure 1 for identity of atoms. [b] Y1 = X1′, Y2 = X2′, C4 = C1′, C5 = C2′, C6 = C3′, C13 = C7′, C14 = C8′, C15 = C9′, C16 = C10′, C17 = C11′, C18 = C12′. For **3a**, prime denotes the transformation $-x, -y, -z$ applied to the crystallographic coordinates. For **3B**, prime denotes the transformation $1 - x, {}^1/_2 - y, z$ applied to the crystallographic coordinates. [c] Range of esd.

(16) We warmly thank Mr. Ryan C. Holcomb for this preparation.
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Table IV. Bond Angles (Deg) Not Involving Hydrogens or within Phenyl Rings[a]

angle	3A[b]	3B[b]	4	5	6
C1-X1-C8	97.8	97.8	97.7	98.5	101.7
C1-X1-C(exo)	103.2	102.7	101.7	105.8	102.9
C8-X1-C(exo)	102.2	102.2	102.0	102.1	101.5
C6-X2-C7	102.8	103.3	103.3	103.5	100.0
C6-X2-C(exo)	101.4	101.0	100.9	101.6	102.8
C7-X2-C(exo)	102.5	100.7	98.8	103.4	101.1
C4-Y1-C14			99.0	116.5	119.7
C4-Y1-C(exo)				113.2	
C14-Y1-C(exo)				118.2	
C3-Y1-C13			103.8	117.9	119.7
C3-Y1-C(exo)				109.9	
C13-Y1-C(exo)				113.7	
X1-C1-C2	114.8	111.5	111.3	112.1	112.4
C1-C2-C3	112.3	112.5	112.7	110.6	112.0
C2-C3-Y2	111.2	111.8	111.8	113.7	105.1
Y1-C4-C5			112.9	115.8	105.8
C4-C5-C6			111.8	109.4	114.0
C5-C6-X2			112.7	109.8	114.2
X2-C7-C8	118.2	120.6	120.9	117.2	121.0
X2-C7-C12	122.6	121.7	119.9	124.6	120.7
C8-C7-C12	119.2	117.6	119.1	118.1	118.3
X1-C8-C7	118.1	119.6	120.8	116.3	119.6
X1-C8-C9	122.8	120.6	120.7	124.3	122.0
C7-C8-C9	119.0	119.7	118.4	119.5	118.2
C8-C9-C10	121.0	122.4	122.0	121.0	122.5
C9-C10-C11	120.1	118.1	119.1	120.1	119.5
C10-C11-C12	119.8	120.1	120.1	119.7	119.2
C11-C12-C7	120.9	122.0	121.2	121.7	122.2
Y2-C13-C14			119.0	119.9	
Y2-C13-C18			121.9	122.0	
C14-C13-C18			118.9	118.0	
Y1-C14-C13			121.8	120.6	
Y1-C14-C15			119.5	120.8	
C13-C14-C15			118.6	118.6	
C14-C15-C16			122.1	121.7	
C15-C16-C17			119.3	119.3	
C16-C17-C18			120.3	120.1	
C17-C18-C13			120.7	122.0	
at P, S[c]	0.1	0.3-0.4	0.2	0.1-0.2	0.2
at C, N, O[c]	0.2-0.3	0.5-0.8	0.3-0.5	0.3-0.5	0.3-0.6

[a] See Figure 1 for identity of atoms. [b] See footnote *b*, Table III. [c] Range of esd.

are presented in Table SIV, and the fractional crystallographic coordinates of the C atoms of these groups appear in Table SV.[21]

The Structure of 3A. The 3417 reflections with $I > 2.0\sigma_I$ were used in the solution and refinement. The structure was solved by heavy-atom methods and refined to final R and wR values of 0.058 and 0.089, respectively. Hydrogen atoms refined satisfactorily, including the B values for the rigid group H atoms.

The Structure of 3B. The structure was solved by direct methods[22] and refined to final R and wR values of 0.092 and 0.080, respectively, by using the 2390 reflections with $I > 2.0\sigma_I$. Nongroup hydrogen atoms refined satisfactorily, but those in the rigid groups were assigned fixed B values of 4.0 Å^2. As was suggested by comparison of the observed and calculated crystal densities and also by the ^{1}H NMR spectrum of the crystallization sample, the crystal contains THF of solvation. Peaks which were interpreted as representing this molecule were discernible only after the refinement had progressed for some time. Thermal motion in this molecule of solvation was so high that it was not possible to distinguish which atom was the oxygen, perhaps due to rotational disorder within this group. Attempted refinement of group occupancy indicated near unit occupancy; final temperature factors for these atoms ranged from 13 to 21 Å^2.

The Structure of 4. Those 3985 reflections with $I > 2.0\sigma_I$ were used in the analysis. The structure which had been obtained by direct methods was refined to final R and wR values of 0.066 and 0.077, respectively. Nongroup hydrogen atoms were refined satisfactorily in position but not in thermal parameters, so in the final cycles these were held fixed at values equal to the final isotropic B value of the C atom to which each H was attached. Phenyl group H atoms were assigned fixed B values of 3.5 Å^2.

The Structure of 5. The 3520 reflections with $I > 3.0\sigma_I$ were used in the direct methods solution of the structure and in the refinement to final R and wR values of 0.058 and 0.068, respectively. All hydrogen atom parameters refined satisfactorily.

The Structure of 6. The structure was solved by the heavy-atom method and refined to final R and wR values of 0.084 and 0.092, respectively, by using the 4280 reflections with $I > 3.0\sigma_I$. Non-group hydrogen atom positions and temperature factors refined well; phenyl group hydrogen atoms were assigned fixed B values equal to those of the carbon atom to which each was attached. The appearance in difference density maps of a branched zig-zag chain of peaks in the vicinity of an inversion center indicated the presence of solvent of crystallization. This could be interpreted as two molecules of ethyl acetate (the solvent from which the crystals were grown), each at half-occupancy, disordered across the inversion center as shown in Figure 5. The refinement of this solvent was carried out by treating E1 as occupied by a full carbon, E2 by a half-carbon and a half-oxygen (simulated with the nitrogen scattering factor curve), E3 by a half-oxygen and E4 by a half-carbon.

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Supplementary Material Available: Tables of observed and calculated structure factor amplitudes (Tables SIa–e), fractional crystallographic coordinates for the nonhydrogen, nongroup atoms (Table SII), anisotropic thermal parameters (Table SIII), rigid-group parameters used to describe phenyl rings (Table SIV), derived fractional coordinates for carbon atoms of rigid phenyl groups (Table SV), fractional coordinates of the tetrahydrofuran molecule in the crystal structure of **3B** (Table SVI) and fractional coordinates for disordered ethyl acetate in the crystal structure of **6** (Table SVII) (137 pages). Ordering information is given on any current masthead.

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