Kimura of Hiroshima University and Professor Zoltan A. Schelly and Dr. Kiyoshi Tamura of the University of Texas for their discussions.

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Triligating 11-Membered Rings Containing *tert*-Phosphino Sites. Synthesis and Structure

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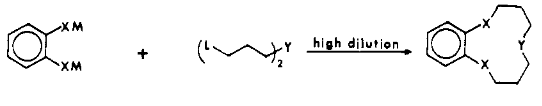
Abstract: The synthesis and characterization of seven 11-membered triheteromacrocycles, of the type 2,6,10-triheterobicyclo[9.4.0]pentadeca-11(1),12,14-triene, are described. The compounds include **3** [2,6,10-$(PPh)_3$], **4** [2,10-$(PPh)_2$-6-S], **5** [2,10-$(PPh)_2$-6-O], **6** [2,10-$(PPh)_2$-6-NMe], **7** [2,10-$(PPh)_2$-6-NPh], **8** [2,10-$(PPh)_2$], **9** [2,10-S_2-6-PPh], and **12** [2,6,10-S_3]. These macrocycles are obtained as crystalline solids using high-dilution techniques in yields ranging from 32 to 56%. Results of crystal structure determinations of five of these are reported and conformational features of the cycloundecene-type macrocycle are described. Crystal structure data follow. **3:** $a = 10.823$ Å, $b = 17.934$ Å, $c = 13.122$ Å, $\beta = 93.15°$, $P2_1/n$, $Z = 4$, $R = 0.103$, 4175 reflections with $I > 2\sigma_I$. **9:** $a = 15.805$ Å, $b = 8.862$ Å, $c = 13.083$ Å, $\beta = 113.79°$, $P2_1/c$, $Z = 4$, $R = 0.048$, 2754 reflections with $I > 2\sigma_I$. **7** · acetone: $a = 9.243$ Å, $b = 16.441$ Å, $c = 18.963$ Å, $\beta = 93.13°$, $P2_1/c$, $Z = 4$, $R = 0.058$, 3879 reflections with $I > 2\sigma_I$. **6:** $a = 9.690$ Å, $b = 15.576$ Å, $c = 16.436$ Å, $\beta = 117.60°$, $P2_1/c$, $Z = 4$, $R = 0.079$, 3782 reflections with $I > 2\sigma_I$. **12:** $a = 5.419$ Å, $b = 16.090$ Å, $c = 13.664$ Å, $\beta = 98.03°$, $P2_1/c$, $Z = 4$, $R = 0.028$, 2430 reflections with $I > 2.5\sigma_I$. X-ray data were collected on a Syntex $P2_1$ autodiffractometer with monochromated Mo Kα radiation at −35 °C, except for **9**, which was studied at room temperature with monochromated Cu Kα radiation. The three macrocycles bearing phenyl rings at the 6 position, **3**, **9**, and **7**, all display the same conformation of approximate $m(C_s)$ symmetry. In all five structures, the ring system adopts an L-shaped arrangement, with angles between the plane of the benzo ring and that of the three heteroatoms ranging from 97.2° in **12** to 113.9° in **6**. In all cases, the phenyl substituents on the *o*-phenylenediphospha unit are cis, and occupy pseudoequatorial positions in the conformations observed in the crystalline state.

Interest in macrocyclic polyhetero ligand systems has been and continues to be quite intense.[1] Thus far the majority of such systems have been used for the ligation of the relatively hard[2] alkali and alkaline earth metal cations, although some nitrogen- and sulfur-containing cyclic ligands have been used for transition metals.[1a] We,[3] along with others,[4,5] recently communicated the synthesis and properties of several *tert*-phosphino-containing macrocyles which are much more appropriate for ligation of the softer[2] transition metals. We now describe our efforts concerning the synthesis of a number of 11-membered multiheteromacrocycles which, with one exception, contain at least one *tert*-phosphino site.

Results and Discussion

Synthesis. The macrocyclizations described here involve the reaction of a bis(nucleophile) (**1**) and a bis(electrophile) (**2**), with the formation of two bonds, under high-dilution conditions, to give **3–9** and **12** in yields of 30–60% (eq 1). The



(1)

1a, X = PPh, M = H
b, X = PPh, M = Li
c, X = S, M = H
d, X = S, M = Li

2a, Y = PPh, L = Cl, Br
b, Y = S, L = Br
c, Y = O, L = Cl
d, Y = NMe, L = Cl
e, Y = NPh, L = Cl
f, Y = CH_2, L = Br

3, X = Y = PPh
4, X = PPh, Y = S
5, X = PPh, Y = O
6, X = PPh, Y = NMe
7, X = PPh, Y = NPh
8, X = PPh, Y = CH_2
9, X = S, Y = PPh
[**10**, X = O, Y = PPh]
[**11**, X = NMe, Y = PPh]
12, X = Y = S

high-dilution reaction involves the dropwise (8–12 drops/min) addition of separate THF solutions (ca. 0.1 M) of **1** and **2** to separate dilution chambers continuously charged with hot THF by distillation. The diluted solutions of **1** and **2** then add

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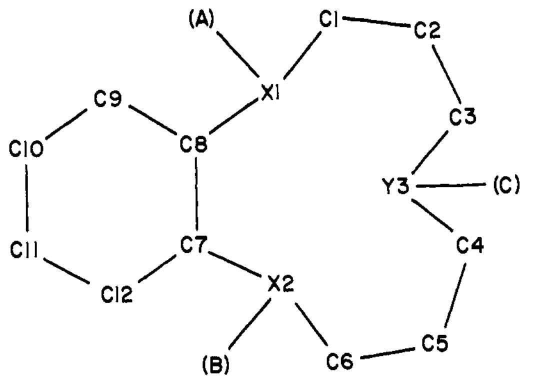
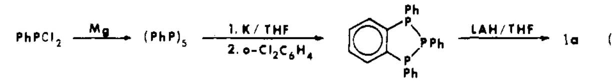


Figure 1. Numbering system used in presentation and discussion of crystallographic results.

to the reaction reservoir via an overflow method in a modified apparatus described previously.[6] In one case (3), the macrocyclization was attempted by reacting 0.1 M THF solutions of **1a** and **2a** directly, which gave rise to polymeric material and a negligible yield of the macrocycle.

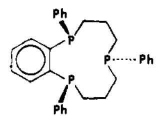
The lithium salts **1b** and **1d** were generated from the corresponding protonated species **1a** and **1c** using *n*-butyllithium. The diphosphine **1a** was obtained via the route outlined in eq 2, a minor modification of a procedure by Mann.[7] The bis(electrophile) **2a** was synthesized in 36% yield by the addition of *n*-butyllithium to a THF solution of phenylphosphine and 1-bromo-3-chloropropane (1:10 mole ratio) at −78 °C. The reaction gave mainly the dichloride but some bromochloro and dibromo derivatives were also formed. Considerably higher yields (~80%) can be realized if distillation of the product is eschewed, since even under the mildest conditions (Kugelrohr distillation 95 °C, 10 μ) considerable quaternization of the phosphine occurs. Dibromide **2b** was produced in 46% yield by the reaction of 1,3-dibromopropane with sodium sulfide (10:1 mole ratio) in boiling acetone. Species **1a** and **2c–e** were prepared by known literature methods.



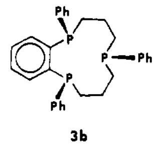
(2)

Attempts to synthesize **10** and **11** have thus far resulted in failure. Apparently the dilithium salt of catechol is not reactive enough to effect nucleophilic substitution rapidly enough to avoid a buildup of reactants in the reaction reservoir. The disodium salt of catechol is insoluble in THF, and, when the high-dilution reaction of this salt and **2a** was run in absolute ethanol, in which both reagents are soluble, only polymeric materials were obtained. A single attempt to synthesize **11** from the dilithio salt of *o*-bis(methylamino)benzene in THF also resulted only in polymeric products.

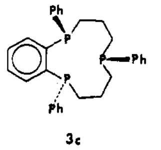
Structure. Since the barrier to inversion at phosphorus in *tert*-phosphines is about 35 kcal/mol,[8] a priori it might be expected that more than one isomer of macrocycles containing more than one phosphine might be isolated. For example, **3** might give rise to three isomers: meso-trans (**3a**), meso-cis (**3b**), and *dl* (**3c**). In fact, in all cases, including **3**, only one isomer was isolated by crystallizaton,[9] as evidenced by sharp melting points, uncomplicated ^{31}P NMR spectra, and in four of the seven macrocycles, single-crystal X-ray structure determinations.



3a



3b



3c

There are two principal points of stereochemical interest in these compounds. The first is the relative configurations of the *o*-phosphino groups (where pertinent), and the second is the comparison of the macrocycle conformations, about which there is a paucity of information. Thus, a connectivity search carried out of the 19 574 reported crystal structures contained in the Cambridge Crystallographic Data Centre Structural Database[10] for 11-membered rings composed only of C, N, O, S, or P atoms, with only one planar constraint in the form of a cis C–C double or aromatic bond, revealed no structures of this type. To our knowledge, the five structures described herein represent the only reported structural data on *cis*-cycloundecene-type species.

Inspection of ORTEP plots of **3**, **6**, **7**, and **9** (Figures 2 and 3) reveals that, where there exists a stereochemical question concerning the orientation of the phenyl groups about the *o*-bis(*tert*-phosphino)benzo unit, only the cis configuration is obtained. In all of these cases, the substituents of the heteroatoms occupy pseudoequatorial positions, and it appears from inspection of CPK and Drieding models that the trans configurations on the benzo linkage have associated with them considerably more nonbonded steric interactions, thus apparently making the unobserved isomers thermodynamically less stable. Since it was possible that the macrocyclization would give isomer distributions which did not reflect thermodynamic stabilities, **4**, **6**, and **7** were heated under conditions (xylene, 135 °C, 1 h) sufficient to cause inversion at tertiary phosphines.[3b,8] There was no evidence in any of these cases that the isomer with the trans configuration across the benzo fusion was populated, as evidenced by identical melting points and ^{31}P NMR spectra before and after heating.

In considering the macrocycle conformations, inspection of the bond lengths (Table V) and bond angles (Table VI) reveals no unusual values. One gross feature which is consistently observed in these structures is the roughly L-shaped arrangement of the two principal planes of the ring. Thus the dihedral angle between the plane of the six carbons of the benzo ring and the plane of the three heteroatoms is determined to be as follows: **3**, 100.3°; **9**, 108.9°; **7**, 108.9°; **6**, 113.9°; **12**, 97.2°. This general feature is maintained in the metal complexes of the 11-cycles whose structures have been studied in these laboratories,[11] as well as in the structures of related 14-membered macrocycles, both free[3b] and complexed, which we have studied.

The conformations of these 11-membered rings may be discussed in more detail by consideration of the torsion angles and the distances between heteroatoms (i.e., potential metal-complexing sites) which are presented in Figure 4. Inspection of the torsion angles about X–C, C–C, or Y–C bonds in the $X1-(CH_2)_3-Y3-(CH_2)_3-X2$ portion (see Figure 1) of these molecules reveals that these angles fall into two groups—one group ranging in magnitude from 53.7 to 94.8° (approximately gauche) and another ranging in magnitude from 148.0 to 168.8° (approximately anti). In Figure 4 and in the discussion which follows, each torsion angle, including sign, can be classified by one of four descriptors (where the limits of the ranges are arbitrary but consistent with common usage): −g (gauche, range −50 to −100°), −a (anti, range −145 to −180°), a (anti, range 145 to 180°), and g (gauche, range 50 to 100°)—though, of course, signs become less significant for torsion angles with magnitudes near 180°. The patterns of torsion angles shown in Figure 4 then clearly fall into three groups.

(1) The three macrocycles bearing phenyl rings on Y3—**3**, **7**, and **9**—all display the same conformation in the crystal. In this conformation, the pattern of torsion angles about bonds in the two $X(CH_2)_3Y$ strands is [−g, −g, a, −g] on one side (X1 to Y3) and the enantiotopic pattern [g, g, −a, g] on the other side (X2 to Y3). Thus, this ring conformation has approximate $m(C_s)$ symmetry. The stereoscopic drawing of **3** in

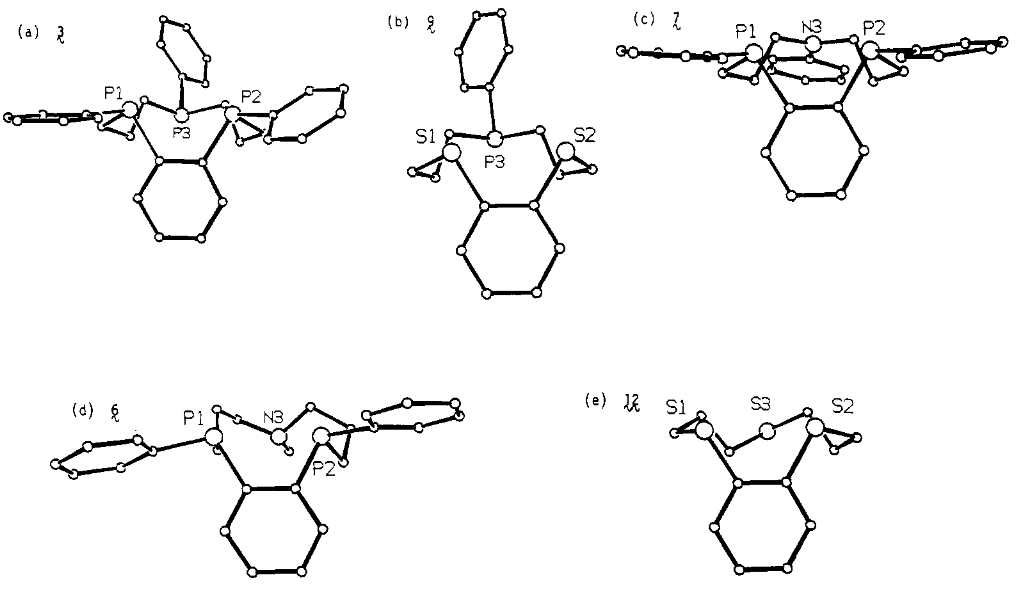


Figure 2. Molecular geometry, emphasizing comparison of ring conformations.

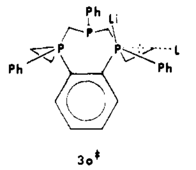
Figure 3 illustrates the conformation common to these three macrocycles (see Figure 2). As evidenced both by the magnitudes of the torsion angles in the two methylene strands of each molecule and by the X1 ··· Y3 and X2 ··· Y3 distances, this idealized $m(C_s)$ symmetry is more closely approximated in **7** than in **3** or **9**. This may be accounted for in terms of the planarity of N3 in **7** as contrasted with the pyramidality of P3 in **3** and **9** (see ORTEP plots, Figures 2 and 3, and bond angles, Table VI). The resulting nonbonded contacts between H atoms on the phenyl ring and those on C3 and C4 are less severe in **7** than they would be in **3** or **9** were these not somewhat distorted from idealized symmetry. Further, in **3** and **9**, these H ··· H contacts are alleviated by a combination of twist of the phenyl ring and skewing of the macrocyclic ring from idealized symmetry; both these distortions are opposed in **7** by the tendency of the $PhNR_2$ grouping to remain coplanar. Such details of differences among **3**, **7**, and **9** notwithstanding, the occurrence of the same conformation in the different environments of three different crystal structures suggests that this conformer is surely among the more stable for this ring system.

(2) In the structure of **6**, which differs from **3**, **9**, and **7** in having the much smaller methyl group at Y3, a much less symmetrical conformation is observed (see Figures 2d, 3b, and 4). In **6** we observe the most marked difference, 0.6 Å, between X1 ··· Y3 and X2 ··· Y3 in any of the five compounds investigated. Further, the patterns of torsion angles along the two strands are unrelated—[a, a, g, g] from X1 to Y3 vs. [−a, g, g, −a] from X2 to Y3. It is to be noted, however, that we have observed this same conformation for one of the two crystallographically independent molecules in the structure of **4**; in this latter X-ray study, however, marked disorder in the other independent molecule has so far precluded the satisfactory refinement of the crystal structure. Nevertheless, the unsymmetrical conformation described here for the 11-ring in **6** has now been observed in two different packing environments, for 11-cycles with small (**6**) or no (**4**) substituents on Y3.

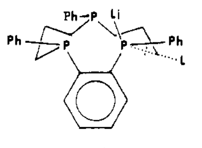
(3) A still different conformation is seen for **12**, a ring system with no substituents at any heteroatom (see Figures 2e, 3c, and 4). It seems possible that the absence of substituents on the ring would render the conformation of **12** more flexible than the other cycles, and hence more dependent on its surroundings either in solution or in the crystal. It is noteworthy, though, that the torsion angle pattern [−g, −g, a, −g] from X2 to Y3 in **12** is the same as that seen repeatedly in the two strands of **3**, **7**, and **9**.

Preliminary low-temperature ^{1}H NMR studies of **5** and **6** reveal that only minor spectral changes occur down to −90 °C. This is indicative either of the population of a single conformer or of the population of more than one conformer with low barriers to interconversion. In light of our observation that several conformations are observed in the crystalline state for the cycles described herein, along with the work of the Dale and Anet groups[12] on cycloundecane, the latter seems to be more likely.

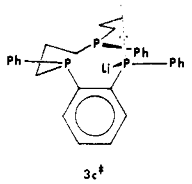
Stereochemistry of the Ring-Closing Step. With the knowledge gained from these X-ray structural studies concerning the conformations available to such 11-membered rings, a comment concerning the exclusive formation of the *cis-o*-benzodiphosphino moiety within the cycle is appropriate. Using the most complicated case (**3**) as an example, an examination of Drieding and CPK space-filling models indicates reasonable transition states to be $\mathbf{3a}^{\ddagger}$, $\mathbf{3b}^{\ddagger}$, and $\mathbf{3c}^{\ddagger}$ leading to the corresponding three isomers of **3**. There are, of course, so many degrees of freedom in the 11-membered chain that it is very difficult to identify a particular conformer as that leading to the transition states indicated. Nonetheless, $\mathbf{3a}^{\ddagger}$–$\mathbf{3c}^{\ddagger}$ seem to be reasonable models for the ring-closing intramolecular substitution reaction. It seems apparent that both $\mathbf{3a}^{\ddagger}$ and $\mathbf{3b}^{\ddagger}$ are conformationally relatively comfortable, with the three large phenyl groups occupying pseudoequatorial positions and with the absence of any severe nonbonded repulsions. On the other hand, $\mathbf{3c}^{\ddagger}$ appears to be much more sterically congested and presumably much higher in energy than $\mathbf{3a}^{\ddagger}$ and $\mathbf{3b}^{\ddagger}$. This is particularly true if one considers that the P–Li group would require solvation which is relatively easy in $\mathbf{3a}^{\ddagger}$ and $\mathbf{3b}^{\ddagger}$, but *very* difficult in $\mathbf{3c}^{\ddagger}$, which would lead to very little **3c** being formed.



$3a^{\ddagger}$



$3b^{\ddagger}$



$3c^{\ddagger}$

Experimental Section

General. Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental

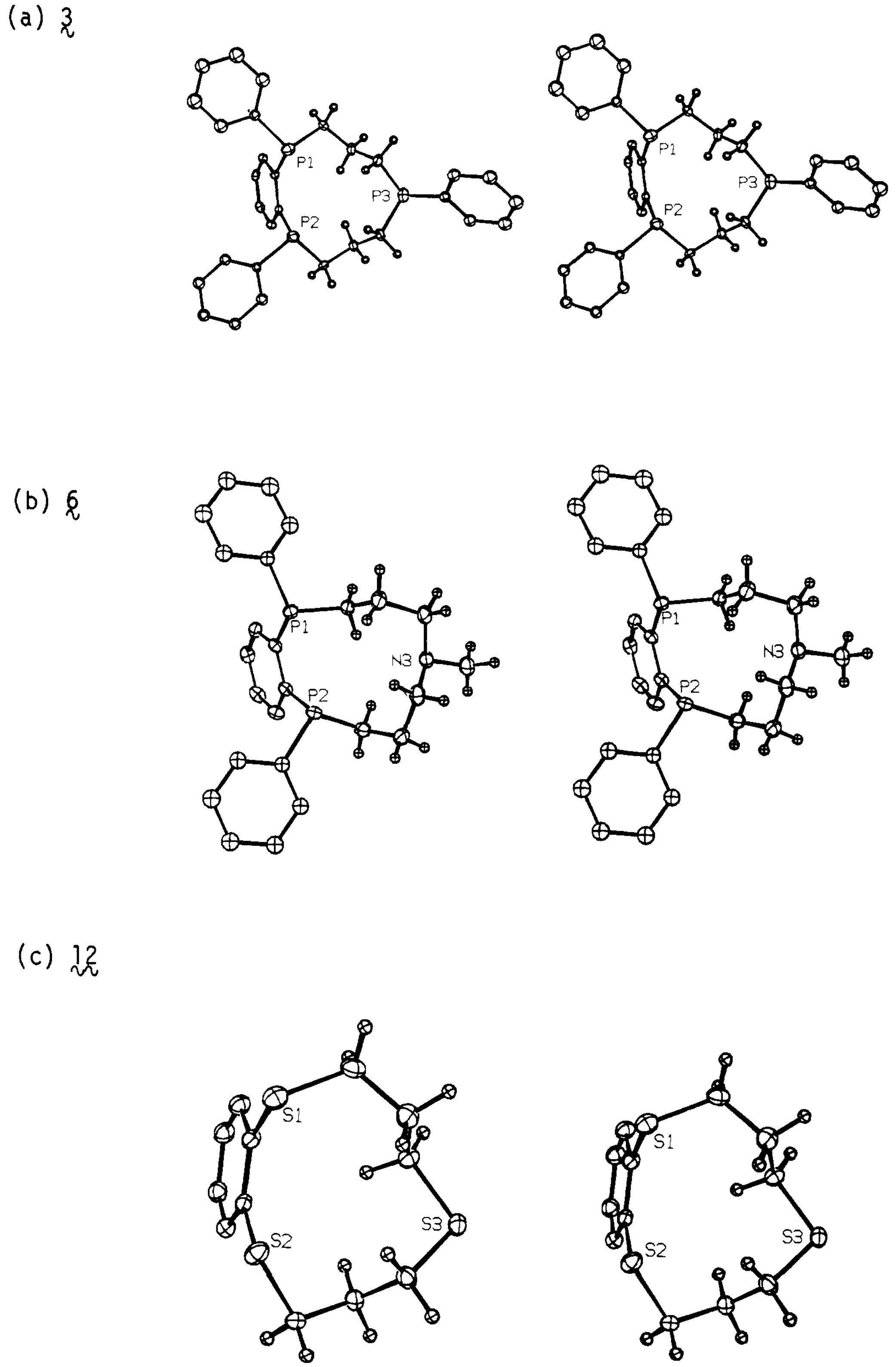


Figure 3. Stereoscopic representations of molecular geometry: (a) **3**, macrocycles **7** and **9** have similar conformations (see text and Figure 2); (b) **6**; (c) **12**.

analyses were performed by Chemalytics, Inc., Tempe, Ariz.

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

Proton magnetic resonance spectra (^{1}H NMR) were obtained on Perkin-Elmer R-12, Varian A-60, or Varian HA-100 instruments. 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. ^{13}C and ^{31}P 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 Du Pont 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 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 Vidar 6300 digital integrator.

X-ray structure determinations 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 using nitrogen pressure, or by syringe.

The following compounds were prepared according to literature procedures or only minor modifications thereof: *o*-bis(phenylphosphino)benzene (**1a**);[7] dithiocatechol (**1c**);[13] bis(3-chloropropyl) ether (**2c**);[14] *N,N*-bis(3-chloropropyl)methylamine (**2d**);[15] *N,N*-bis(3-chloropropyl)aniline (**2e**).[16]

Bis(3-chloropropyl)phenylphosphine (2a). A 2.1 M hexane solution of *n*-butyllithium (141 mL, 296 mmol) was added dropwise to a solution of phenylphosphine (16.1 g, 146 mmol) and 1-bromo-3-chloropropane (205 g, 1300 mmol) in THF (250 mL) at −78 °C. The resulting mixture was allowed to warm to room temperature and concentrated on a rotary evaporator. The residue was evacuated at 40 °C to 20 μ (dry ice cooled receiver). The resulting mixture was partitioned between ether (200 mL) and water (2 × 50 mL), followed by 1 N hydrochloric acid (50 mL) and brine (100 mL), and dried (MgSO$_4$). The solution was concentrated to give a pale yellow oil (30 g) which was distilled [Kugelrohr, 95 °C (20 μ)] to give **2a** as a clear, colorless oil (13.7 g, 36%); ^{1}H NMR (CDCl$_3$) δ 7.43 (m, 5 H), 3.56 (m, 4 H), 1.87 (m, 8 H); ^{31}P NMR (CDCl$_3$) δ −25.99 (s); mass spectrum *m/e* 306 (M$^+$ of ^{79}Br^{35}Cl derivative), 262 (M$^+$ of ^{35}Cl$_2$ derivative), intensity ratio *m/e* 262/306 $\gtrsim$ 20.[17]

Bis(3-bromopropyl) Sulfide (2b). A solution of 1,3-dibromopropane (83.6 g, 416 mmol) and sodium sulfide nonahydrate (10 g, 41.7 mmol) in acetone (100 mL) was boiled under reflux for 48 h. The cooled reaction mixture was extracted with water (80 mL), 10% aqueous sodium hydroxide (50 mL), and brine (50 mL) and dried (MgSO$_4$). The solvent was evaporated and the residue was distilled to give **2b** as a colorless liquid (5.3 g, 46%): bp 109–111 °C (250 μ); ^{1}H NMR (CDCl$_3$) δ 3.50 (t, J = 6 Hz, 4 H), 2.65 (t, J = 6 Hz, 4 H), 2.10 (quintet, J = 6 Hz, 4H); mass spectrum *m/e* 274 (M$^+$ for ^{79}Br^{79}Br).

Anal. Calcd for C$_6$H$_{12}$Br$_2$S: C, 26.11; H, 4.38. Found: C, 26.36; H, 4.10.

2,6,10-Triphenyl-2,6,10-triphosphabicyclo[9.4.0]pentadeca-11(1),12,14-triene (3). The following description is typical of all the macrocyclizations carried out in this work. The dianion **1b** [from 4.55 g (15.5 mmol) of **1a** and 2.1 M *n*-BuLi in hexane (14.8 mL, 31.0 mmol)] in THF (240 mL) and **2a** (4.07 g, 15.5 mmol) in THF (250 mL) were added dropwise (8–12 drops/min) simultaneously from separate constant addition funnels via overflow dilution chambers[6] to a round-bottom flask initially charged with 1 L of boiling THF. After the addition was complete the slightly cloudy reaction mixture was concentrated on a rotary evaporator. The glassy residue was dissolved in ether (750 mL), washed with saturated aqueous ammonium chloride (200 mL), water (100 mL), and brine (100 mL), and dried (MgSO$_4$). Upon concentration under vacuum a pale yellow glass (5.1 g) was obtained which was dissolved in hot benzene-cyclohexane (1:6 v/v, 175 mL). This solution upon cooling to 5 °C gave white crystals (2.86 g), mp 103–120 °C, which contained benzene and cyclohexane (by ^{1}H NMR). The solvent was removed by heating under vacuum [80 °C (20 μ), 3 h] to give the crude **3** as a white solid (2.52 g, 34%), mp 158–160 °C. An analytical sample was prepared by recrystallization from acetone: mp 163–166 °C; ^{1}H NMR (CDCl$_3$) δ 7.4 (m, 19 H), 2.37 (br m, 12 H); ^{13}C NMR (CDCl$_3$) δ 148–126 (aromatic), 31.0 (complex m), 23.35 (d of t, $^1J_{\text{P-C}}$ = 20.6 Hz, $^3J_{\text{P-C}}$ = 7.4 Hz); ^{31}P NMR (CDCl$_3$) δ −30.56 (2 P), −25.99 (1 P); mass spectrum *m/e* 484 (M$^+$).

Anal. Calcd for C$_{30}$H$_{31}$P$_3$: C, 74.37; H, 6.45. Found: C, 74.21; H, 6.32

2,10-Diphenyl-2,10-diphospha-6-thiabicyclo[9.4.0]pentadeca-11(1),12,14-triene (4). The dianion **1b** [from **1a** (9.3 g, 31.6 mmol) and a 3.53 M hexane solution of *n*-butyllithium (18 mL, 635 mmol)] in THF (250 mL) was reacted with dibromide **2b** (8.75 g, 31.7 mmol) in THF (250 mL) under the high-dilution conditions described for **3**. The cooled reaction mixture was concentrated and the residue was partitioned between ether (500 mL) and water (500 mL). The ethereal solution was dried (MgSO$_4$) and concentrated to give a pale yellow glass (10.4 g). This was crystallized and recrystallized from acetone to give **4** as a white, crystalline solid (5.32 g, 51%): mp 112–112.5 °C; ^{1}H NMR (CDCl$_3$) δ 7.4 (m, 14 H), 2.94 (m, 4 H), 2.34 (m, 4 H), 1.70 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 133–127 (aromatic carbon atoms, complex), 32.39 (t, J = 5 Hz), 27.44 (t, J = 5 Hz), 27.05 (t, J = 9 Hz); ^{31}P NMR (CDCl$_3$) δ −29.35 (s); mass spectrum *m/e* 408 (M$^+$).

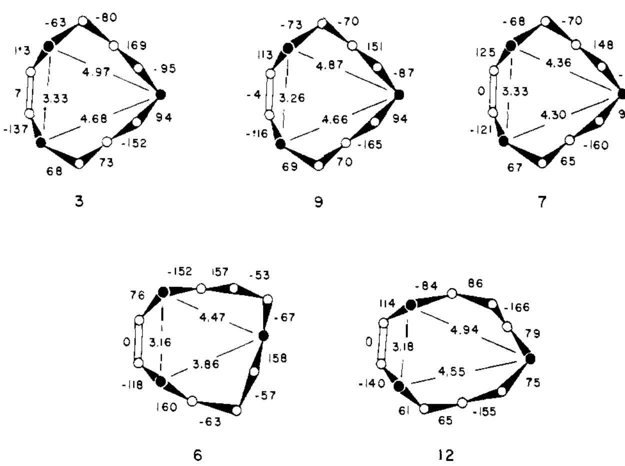


Figure 4. Ring torsion angles (deg) and wedge representations of 11-membered ring conformations.

Anal. Calcd for C$_{24}$H$_{26}$P$_2$S: C, 70.56; H, 6.43. Found: C, 70.82; H, 6.37.

2,10-Diphenyl-6-oxa-2,10-diphosphabicyclo[9.4.0]pentadeca-11(1),12,14-triene (5). Reaction of **1b** (33.2 mmol) and **2c** (33.2 mmol) as described for **3** above gave, after the extractive and evaporative workup, a colorless oil (13 g). This was distilled [Kugelrohr, 150 °C (50 μ)] to give **5** as a colorless glass (4.1 g, 32%); ^{1}H NMR (CDCl$_3$) δ 7.4 (m, 14 H), 3.77 (m, 2 H), 3.30 (m, 2 H), 2.44 (m, 4 H), 2.15 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 133–127 (aromatic), 63.33 (t, J = 5 Hz), 27.18 (t, J = 4 Hz), 26.08 (5, J = 6 Hz); ^{31}P NMR (CDCl$_3$) δ −28.94 (s); mass spectrum *m/e* 392 (M$^+$).

Anal. Calcd for C$_{24}$H$_{26}$OP$_2$: C, 73.45; H, 6.69. Found: C, 73.32; H, 6.49.

2,10-Diphenyl-6-methyl-6-aza-2,10-diphosphabicyclo[9.4.0]pentadeca-11(1),12,14-triene (6). Reaction of **1b** (17.7 mmol) and **2d** (17.7 mmol) as described for **3** above gave, after the extractive and evaporative workup, a colorless glass. This was recrystallized from acetone to give **6** as colorless crystals (3.01 g, 42%): mp 145–147 °C; ^{1}H NMR (CDCl$_3$) δ 7.4 (m, 14 H), 31.5 (m, 2 H), 2.34 (m, 6 H), 2.19 (s, 3 H), 1.96 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 139–127 (aromatic), 54.75 (t, J = 5 Hz), 40.79 (s), 25.61 (t, J = 5 Hz), 24.64 (t, J = 9 Hz); ^{31}P NMR (CDCl$_3$) δ −27.2 (s); mass spectrum *m/e* 405 (M$^+$).

Anal. Calcd for C$_{25}$H$_{29}$NP$_2$: C, 74.06; H, 7.21; N, 3.45. Found: C, 74.16; H, 7.60; N, 3.42.

2,6,10-Triphenyl-6-aza-2,10-diphosphabicyclo[9.4.0]pentadeca-11(1),12,14-triene (7). Reaction of **1b** (18.1 mmol) and **2e** (18.1 mmol) as described for **3** above gave, after the extractive and evaporative workup, a colorless glass. This was recrystallized from acetone to give **7** as an acetone solvate (ca. 1:1 molar ratio, 5.24 g, 56%), mp 71–73 °C, resolidify 75–78 °C, remelt 145–147 °C. An analytical sample was prepared by sublimation, mp 147–149 °C: ^{1}H NMR (CDCl$_3$) δ 7.6–6.6 (m, 19 H), 3.78 (m, 4 H), 2.23 (m, 6 H), 1.74 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 149–128 (aromatic), 53.2 (t, J = 5 Hz), 27.2 (t, J = 6 Hz), 25.6 (t, J = 8 Hz); ^{31}P NMR (CDCl$_3$) δ −30.1 (s); mass spectrum *m/e* 467 (M$^+$).

Anal. Calcd for C$_{30}$H$_{31}$NP$_2$: C, 77.07; H, 6.68; N, 3.00. Found: C, 77.04; H, 6.99; N, 2.70.

2,10-Diphenyl-2,10-diphosphabicyclo[9.4.0]pentadeca-11(1),12,14-triene (8). Reaction of **1b** (31.8 mmol) and **2b** (31.8 mmol) as described for **3** above gave, after the extractive and evaporative workup, a colorless oil (12 g) which upon crystallization from acetone yielded **8** as white crystals (4.1 g, 33%): mp 120–121 °C; ^{1}H NMR (CDCl$_3$) δ 7.3 (m, 14 H), 2.2 (m, 4 H), 1.35 (br m, 10 H); ^{13}C NMR (CDCl$_3$) δ 134–127 (aromatic), 28.64 (t, J = 6 Hz), 26.99 (s), 25.56 (s), 24.06 (t, J = 7 Hz); ^{31}P NMR (CDCl$_3$) δ −25.4 (s); mass spectrum *m/e* 390 (M$^+$).

Anal. Calcd for C$_{25}$H$_{28}$P$_2$: C, 76.91; H, 7.23. Found: C, 76.74; H, 7.11.

Table I. Crystal Data at −35 °C

	3	**9**	**7**	**6**	**12**
crystn solvent	acetone	cyclohexane	acetone	acetone	ether/pentane
unit cell data[a]					
a, Å	10.823(1)	15.805(1)[b]	9.243(2)	9.690(2)	5.419(1)
b, Å	17.934(1)	8.862(1)	16.441(3)	15.576(2)	16.090(2)
c, Å	13.122(1)	13.083(1)	18.963(3)	16.436(4)	13.664(1)
α, deg	90	90	90	90	90
β, deg	93.15(1)	113.79(1)	93.13(2)	117.60(2)	98.03(1)
γ, deg	90	90	90	90	90
no. reflections for detn of cell data	44	42	44	45	45
range of 2θ for detn of cell data, deg	23–25	40–45	18–22	24–27	26–28
d_{calcd}, g/cm^3 (−35 °C)	1.266	1.317	1.214[c]	1.225	1.444
d_{measd}, g/cm^3 (21 °C)	1.24	1.28	1.19	1.23	1.34
liquid for d_{measd}	aq $ZnCl_2$	aq $ZnCl_2$	aq $ZnCl_2$	aq $ZnCl_2$	aq $ZnCl_2$
systematic absences	$0k0$: $k = 2n + 1$ $h0l$: $h + l = 2n + 1$	$0k0$: $k = 2n + 1$ $h0l$: $l = 2n + 1$	$0k0$: $k = 2n + 1$ $h0l$: $l = 2n + 1$	$0k0$: $k = 2n + 1$ $h0l$: $l = 2n + 1$	$0k0$: $k = 2n + 1$ $h0l$: $l = 2n + 1$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	4	4	4	4
$F(000)$, electrons	1024	704	1120[c]	864	544
formula of asymmetric unit	$C_{30}H_{31}P_3$	$C_{18}H_{21}PS_2$	$C_{30}H_{31}NP_2 \cdot C_3H_6O$[c]	$C_{25}H_{29}NP_2$	$C_{12}H_{16}S_3$
formula weight	484.5	332.5	525.6[c]	405.4	256.4

[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] All measurements for **9** were made at room temperature (~21 °C) with Cu Kα radiation. [c] Includes one molecule of acetone per asymmetric unit. Omitting acetone gives a value of 1.08 g/cm^3 for d_{calcd}.

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

	3	**9**	**7**	**6**	**12**
check reflections (every 96 reflections)	(211), $(2\bar{2}\bar{1})$, (0,10,0), $(\bar{2}21)$	$(1\bar{4}2)$, (512), $(\bar{4}06)$, (025)	$(\bar{3}\bar{1}4)$, $(\bar{1}\bar{3}\bar{1})$, $(20\bar{4})$, (200)	$(31\bar{3})$, $(12\bar{1})$, $(04\bar{1})$, $(\bar{1}13)$	$(\bar{2}\bar{2}3)$, (060), $(10\bar{4})$, $(21\bar{1})$
hours of data collection	101	58	104	91	46
quadratic coefficients, s, t, $\times 10^6$, in decay analysis[b] (with esd)	−15(53) −1(1)	1361(231) −27(4)	−45(56) 0(1)	−33(50) 1(1)	−51(93) 0(2)
decay correction	no	yes	no	no	no
2θ range, deg	4–55	4–150	4–55	4–55	4–55
total reflections measured	5836	3110	5639	5064	2821
absorption coefficient, μ(Mo Kα), cm^{-1}	2.54	35.7	2.12	1.81	5.17
approx dimensions of data crystal, mm	0.55 × 0.25 × 0.3	0.5 × 0.2 × 0.2	0.35 × 0.25 × 0.25	0.4 × 0.3 × 0.3	0.5 × 0.4 × 0.3
p factor	0.04	0.06	0.02	0.05	0.02

[a] Syntex P2$_1$ autodiffractometer equipped with a graphite monochromator and a Syntex LT-1 inert-gas low-temperature delivery system. X-ray data for **9** were collected at room temperature (21 °C) using Cu Kα radiation (λ = 1.541 78 Å). X-ray measurements for other compounds were performed with Mo Kα radiation (λ = 0.719 69 Å). [b] Reference 19.

6-Phenyl-6-phospha-2,10-dithiabicyclo[9.4.0]pentadeca-11(1),12,14-triene (9). Reaction of **1d** [from **1c** (2.72 g, 19.2 mmol) and a 3.11 M hexane solution of *n*-butyllithium (12.3 mL, 38.3 mmol)] in THF (250 mL) and **2a** (19.2 mmol) in THF (250 mL) as described for **3** above gave, after the usual workup, pale yellow crystals (4.42 g). These were recrystallized from benzene-hexane (1:4 v/v) to give pale yellow crystals (3.1 g), mp 106–109 °C. This material was anaerobically chromatographed on alumina using 1,2-dichloroethane-hexane (1:2 v/v) as eluent. Recrystallization of purified material from cyclohexane gave **9** as white rods (2.70 g, 42%): mp 109.5–110 °C; ^{1}H NMR (CDCl$_3$) δ 7.4 (m, 9 H), 3.05 (m, 4 H), 1.85 (br m, 8 H); ^{13}C NMR (CDCl$_3$) δ 140–127 (aromatic), 38.9 (d, J = 10 Hz), 26.3 (d, J = 15 Hz), 24.6 (d, J = 12 Hz); ^{31}P NMR (CDCl$_3$) δ −23.05 (s); mass spectrum *m/e* 332 (M$^+$).

Anal. Calcd for $C_{18}H_{21}PS_2$: C, 65.03; H, 6.37. Found: C, 65.08; H, 6.17.

2,6,10-Trithiabicyclo[9.4.0]pentadeca-11(1),12,14-triene (12). Reaction of **1d** [from **1c** (2.93 g, 206 mmol) and a 2.02 M hexane solution of *n*-butyllithium (20.4 mL, 41.3 mmol)] in THF (250 mL) and **2b** (5.36 g, 19.4 mmol) in THF (250 mL) as described for **3** above gave, after workup, a yellowish solid (4.89 g). This was recrystallized from acetone-hexane (1:9 v/v) to give **12** as a white crystalline solid (2.25 g, 43%): mp 61–62 °C; ^{1}H NMR (CDCl$_3$) δ 7.5 (m, 2 H), 7.25 (m, 2 H), 3.00 (m, 4 H), 2.58 (m, 4 H), 1.95 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 140.0, 133.6, 128.1 (aromatic), 37.2, 31.7, 29.6 (methylenes); mass spectrum *m/e* 256 (M$^+$).

Anal. Calcd for $C_{12}H_{16}S_3$: C, 56.20; H, 6.29. Found: C, 56.37; H, 6.34.

Crystallographic Analysis. Crystals were grown by cooling from the solvents indicated in Table I. In each case the crystals were clear, colorless prisms, elongated to rods in the case of **9**. 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, except for **9**, it was maintained in a stream of cold (−35 °C), dry nitrogen during the course of all diffraction experiments. In the case of **9**, the refrigeration unit used to cool the heat exchange bath in the Syntex LT-1 low-temperature system was not operational, so that crystal was investigated at room temperature. Crystal data and details of intensity data collection and processing are summarized in Table 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 from 2 to 5 deg min^{-1}. The measured intensities were reduced and assigned standard deviations as described elsewhere.[18] No absorption corrections were applied, and in only one case, **9**, was a time-dependent correction for crystal decay (maximum value 2%) deemed necessary.

Table III. Fractional Crystallographic Coordinates $\times 10^4$ [a]

atom		**3**	**9**	**7**	**6**	**12**
X1[b]	*x*	58 374(17)	6624(5)	24 828(12)	−38 980(8)	6447(7)
	y	11 051(11)	32 142(8)	14 991(7)	−10 064(4)	−71 742(3)
	z	61 587(15)	−269(7)	−7664(6)	−22 117(5)	−20 272(3)
X2[b]	*x*	34 370(17)	13 789(4)	46 036(12)	−15 097(8)	9595(7)
	y	323(11)	2928(8)	29 317(8)	−14 661(4)	−55 732(2)
	z	68 848(14)	16 106(6)	−132(6)	−1633(4)	−33 662(3)
Y3[b]	*x*	21 081(18)	37 192(4)	877(4)	1204(3)	−39 351(8)
	y	14 208(11)	42 083(8)	2463(2)	−1306(2)	−46 999(2)
	z	38 122(14)	23 612(6)	1188(2)	−1291(2)	−11 173(3)
C1	*x*	5491(7)	1286(2)	530(5)	−2211(3)	−1208(3)
	y	1937(4)	4539(3)	1423(3)	−1262(2)	−7088(1)
	z	5340(6)	−512(3)	−613(3)	−2399(2)	−1034(1)
C2	*x*	4120(7)	2322(2)	109(6)	−1191(4)	−1611(3)
	y	1971(5)	4470(4)	2006(3)	−492(2)	−6214(1)
	z	4948(6)	139(3)	−34(2)	−2324(3)	−692(1)
C3	*x*	3794(7)	2642(2)	823(6)	458(4)	−3803(3)
	y	1470(5)	5068(4)	1799(3)	−760(2)	−5799(1)
	z	4037(6)	1333(2)	688(3)	−2105(2)	−1289(1)
C4	*x*	1773(7)	3232(2)	2221(5)	1524(4)	−1698(3)
	y	556(4)	2560(3)	2911(4)	−869(2)	−4400(1)
	z	4530(5)	2798(2)	1256(3)	−430(2)	−1893(1)
C5	*x*	1428(7)	3217(2)	2387(5)	1696(4)	−2654(3)
	y	738(4)	1131(3)	3628(3)	−1488(2)	−4463(1)
	z	5627(5)	2126(2)	747(3)	330(2)	−2978(1)
C6	*x*	1723(6)	2609(2)	3958(5)	281(3)	−626(3)
	y	118(4)	−112(3)	3755(3)	−2063(2)	−4598(1)
	z	6382(6)	2260(2)	554(3)	69(2)	−3604(1)
C7	*x*	3764(6)	1195(2)	3466(4)	−3019(3)	−1432(3)
	y	911(4)	216(3)	3132(3)	−2258(2)	−6299(1)
	z	7388(5)	180(2)	−829(2)	−846(2)	−3669(1)
C8	*x*	4814(6)	917(2)	2584(4)	−4092(3)	−1548(3)
	y	1344(4)	1482(3)	2536(2)	−2056(2)	−6997(1)
	z	7211(5)	−520(2)	−1142(2)	−1758(2)	−3078(1)
C9	*x*	5068(7)	786(2)	1777(5)	−5223(3)	−3393(3)
	y	1971(4)	1327(3)	2716(3)	−2666(2)	−7577(1)
	z	7809(5)	−1640(2)	−1770(2)	−2274(2)	−3335(1)
C10	*x*	4282(7)	933(2)	1847(5)	−5269(4)	−5168(3)
	y	2184(4)	−29(4)	3470(3)	−3457(2)	−7461(1)
	z	8555(5)	−2051(2)	−2080(3)	−1907(2)	−4134(1)
C11	*x*	3246(7)	1200(2)	2719(5)	−4201(4)	−5068(3)
	y	1778(4)	−1276(3)	4062(3)	−3658(2)	−6771(1)
	z	8713(5)	−1360(3)	−1768(2)	−1015(2)	−4707(1)
C12	*x*	2987(6)	1313(2)	3509(5)	−3092(4)	−3210(3)
	y	1150(4)	−1152(3)	3896(3)	−3061(2)	−6203(1)
	z	8140(5)	−267(2)	−1150(2)	−487(2)	−4486(1)
C13	*x*				2630(4)	
	y				−1658(3)	
	z				−1243(3)	

[a] See Figure 1 for identity of the atoms. Numbers in parentheses are the estimated standard deviations in the units of the last digit shown. [b] For all P and S atoms, coordinates are given $\times 10^5$.

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.[19] 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,[20] and H[21] were used in these calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections[20] 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, 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 III, and their anisotropic temperature parameters are given in Supplementary Table II.[22] The rigid group

Table IV. Rigid Group Parameters for Phenyl Rings.[a]

compd	ring	x_0	y_0	z_0	ϕ	θ	ρ
3	A	0.7353(4)	0.1389(3)	0.6758(4)	1.817(4)	2.744(3)	−0.917(4)
	B	0.3409(4)	−0.0639(2)	0.7769(3)	−0.039(4)	2.326(2)	1.062(4)
	C	0.1870(4)	0.1096(3)	0.2487(3)	−0.673(8)	−1.932(3)	2.552(8)
9	C	0.3940(1)	0.5571(2)	0.3512(1)	2.866(1)	2.391(1)	−1.939(1)
7	A	0.2629(3)	0.0886(2)	−0.1572(1)	0.278(2)	−2.220(2)	2.798(3)
	B	0.6349(2)	0.3342(2)	−0.0283(1)	1.926(2)	−2.792(1)	1.090(2)
	C	−0.0352(3)	0.2716(2)	0.1510(2)	−1.899(2)	2.555(2)	−0.384(2)
6	A	−0.1625(2)	−0.1516(1)	−0.0925(1)	−1.987(3)	1.676(1)	−1.448(3)
	B	−0.5586(2)	−0.0994(1)	−0.3370(1)	−1.692(1)	−2.547(1)	−1.378(2)

[a] A description of these group parameters is provided elsewhere.[26] Angular coordinates are in radians. The internal coordinate system of a phenyl ring has been defined previously.[27]

Table V. Bond Lengths (Å) Not Involving Hydrogens or within Phenyl Rings

bond	**3**	**9**	**7**	**6**	**12**
X1-C1	1.865	1.806	1.848	1.847	1.803
X1-C8	1.867	1.774	1.853	1.844	1.755
X1-C(exo)	1.851		1.842	1.846	
X2-C6	1.882	1.818	1.849	1.842	1.796
X2-C7	1.851	1.777	1.852	1.818	1.752
X2-C(exo)	1.866		1.847	1.848	
Y3-C3	1.834	1.855	1.445	1.469	1.787
Y3-C4	1.862	1.846	1.446	1.464	1.785
Y3-C(exo)	1.839	1.851	1.383	1.454	
C1-C2	1.545	1.512	1.523	1.523	1.508
C2-C3	1.522	1.530	1.525	1.526	1.502
C4-C5	1.542	1.537	1.537	1.526	1.505
C5-C6	1.513	1.518	1.532	1.523	1.500
C7-C8	1.407	1.403	1.388	1.409	1.389
C8-C9	1.391	1.400	1.402	1.381	1.378
C9-C10	1.385	1.376	1.375	1.382	1.364
C10-C11	1.362	1.382	1.376	1.384	1.364
C11-C12	1.376	1.373	1.374	1.383	1.363
C12-C7	1.399	1.392	1.398	1.401	1.378
			Range of Esd		
P-C, S-C	0.004-0.008	0.002-0.003	0.003-0.005	0.002-0.003	0.001-0.002
C-C, N-C	0.010-0.011	0.003-0.005	0.004-0.008	0.003-0.005	0.002

Table VI. Bond Angles (deg) Not Involving Hydrogens or within Phenyl Rings

angle	**3**	**9**	**7**	**6**	**12**
C1-X1-C8	97.7	101.5	101.1	101.2	102.7
C1-X1-C(exo)	99.8		102.1	104.6	
C8-X1-C(exo)	99.8		100.2	100.0	
C6-X2-C7	101.3	100.1	99.7	98.1	102.7
C6-X2-C(exo)	99.0		102.1	−105.1	
C7-X1-C(exo)	100.4		99.7	102.6	
C3-Y3-C4	100.3	100.0	116.3	113.9	98.5
C3-Y3-C(exo)	104.7	97.9	121.2	110.6	
C4-Y3-C(exo)	101.2	103.3	122.1	108.9	
X1-C1-C2	112.5	113.3	111.2	113.6	115.1
C1-C2-C3	114.6	113.5	113.1	113.5	112.6
C2-C3-Y3	109.5	115.3	114.8	112.9	114.4
Y3-C4-C5	111.1	112.8	116.7	113.3	113.5
C4-C5-C6	113.7	113.4	112.4	111.9	113.1
C5-C6-X2	111.6	114.2	112.3	114.2	113.2
X2-C7-C8	121.5	122.2	121.7	117.8	119.6
X2-C7-C12	120.4	118.9	119.8	123.7	118.6
C8-C7-C12	118.0	118.8	118.6	118.5	121.8
X1-C8-C7	120.8	120.8	121.8	119.0	121.8
X1-C8-C9	119.5	120.4	119.0	121.6	118.9
C7-C8-C9	119.3	118.7	119.2	119.5	119.3
C8-C9-C10	120.8	121.2	121.2	120.9	121.1
C9-C10-C11	120.2	119.9	119.6	119.7	119.4
C10-C11-C12	120.0	119.6	119.8	120.3	120.5
C11-C12-C7	121.7	121.7	121.6	121.0	121.0
			Range of Esd		
at P, S	0.3-0.4	0.1	0.2	0.1	0.1
at C, N	0.5-0.7	0.2-0.3	0.3-0.5	0.2-0.3	0.1

parameters used to describe phenyl rings are presented in Table IV, and the fractional crystallographic coordinates of the C atoms of these groups appear in Supplementary Table III.[22]

Structure of 3. The 4175 reflections with $I > 2.0\sigma_I$ were used in the solution and refinement. The structure was solved by direct methods[23] and refined to final R and wR values of 0.103 and 0.128, respectively. Hydrogen atom positions did not refine satisfactorily, so these atoms were placed at idealized positions[24] with B values equal to those of the carbon atom to which they are attached, and held fixed. Rigid group hydrogen B values were not refined from their initial value of 2.5 Å^2. In spite of the relatively high R and wR values for this structure, a final difference density map contained only peaks 0.5-0.7 e Å^{-3} in height, in the vicinity of the phenyl rings.

Structure of 9. Those 2754 reflections having $I > 2.0\sigma_I$ were used in the analysis. The structure which had been obtained by heavy-atom methods was refined to final R and wR values of 0.048 and 0.071, respectively. All hydrogen atoms were satisfactorily refined, both in position and temperature factor. Refinement for the effects of secondary extinction by Zachariasen's method[25] led to a final value of 1.1 (2) × 10^{-5} for this isotropic parameter. A final difference density map contained only peaks less than 0.5 e Å^{-3} in height.

Structure of 6. The structure was solved by the heavy-atom method and refined to final R and wR values of 0.079 and 0.070, respectively, using the 3782 reflections with $I > 2.0\sigma_I$. Positions of hydrogen atoms were refined, and these atoms were assigned B values equal to those of the atom to which they were attached. A final difference map showed only peaks 0.5-0.8 e Å^{-3}, associated with rigid phenyl groups.

Structure of 7. The 3879 reflections with $I > 2.0\sigma_I$ were used in the heavy-atom method solution of the structure and in the refinement to final R and wR values of 0.058 and 0.072, respectively. Both the comparison of observed and calculated crystal density and the ^{1}H NMR spectrum of the sample from which the crystal used for structure studies was chosen suggested the presence of acetone in a 1:1 mole ratio with **7**. The nonhydrogen atoms of the acetone molecule were located in the initial heavy-atom map, phased with two phosphorus atoms, and have been refined isotropically; the final crystallographic parameters describing the acetone molecule appear in Supplementary Table IV.[22] Positional and thermal parameters for all hydrogens, including those of acetone, were satisfactorily refined. Peaks in a final difference density map ranging from 0.5 to 1.2 e Å^{-3} were located near either a rigid phenyl group or the oxygen atom of acetone.

Structure of 12. The structure was solved by the heavy-atom method and refined to final R and wR values of 0.028 and 0.034, respectively, using the 2430 reflections with $I > 2.5\sigma_I$. All hydrogen parameters, positional and thermal, were refined. A final difference density map contained no peaks larger than 0.3 e Å^{-3}.

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Supplementary Material Available: Tables of observed and calculated structure factor amplitudes (Supplementary Tables Ia–Ie), anisotropic thermal parameters (Supplementary Table II), coordinates of the acetone molecule in the crystal structure of **7** (Supplementary Table III), and the crystallographic coordinates of the rigid group atoms (Supplementary Table IV) (111 pages). Ordering information is given on any current masthead page.

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(10) 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 Oct 1978 issue of the database, using programs originating at the Data Centre.

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Studies of Solution Character by Molecular Spectroscopy. 8. Ion Sites in Solutions of NaCo(CO)$_4$ in Several Solvents Doped with Cryptand C221

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Abstract: NaCo(CO)$_4$ was dissolved in THF, 1,2-DME, THP, and MTHF and the Na$^+$ complexed with the cryptand C221. In each case, the normal mix of ion sites in the solution was converted into a single ion site. This site was the previously reported solvent-separated ion site of T_d symmetry in the THF and 1,2-DME cases. The new ion site formed in the THP and MTHF solutions shows C_{2v} symmetry. Thus, the anion in THP and MTHF is not isolated from the perturbing influence of the Na$^+$ by complexing the latter with the cryptand, in contrast to the situation in THF and 1,2-DME. Solution structures are proposed for these two kinds of ion sites in the cryptand-complexed salt solutions. Comparison of the infrared spectra of the salt in THF and 1,2-DME solutions doped with C221 with the complex, overlapped spectra of the salt in these neat solvents provides an independent confirmation of the previous report of a computer-aided analysis of the latter spectra and supports its interpretation in terms of ion structures. Altering the normal ion site mix of a solution by adding cryptands provides a very useful tool for the interpretation of its complex vibrational spectrum.

The knowledge of structure at ion sites in solution is fundamental to understanding the physical and chemical properties of ionic solutions. The CO stretching vibrations of the Co(CO)$_4^-$ ion are sensitive to its environment and hence can serve as a probe of solution structure.[1,2] A study has been made of these vibrations in the infrared spectra of several alkali metal salts of the Co(CO)$_4^-$ anion dissolved in several common aprotic solvents.[1-3] The results were interpreted in terms of two kinds of ion-site structures, which were shown to be solvent-separated and contact ion pairs. In the contact site, the cation was found to be associated with the anion in the structure Na$^+$- - -O≡CCo. Further, the mix of ion sites was seen to vary with solvent, being solvent-separated ion pairs in strong bases (H$_2$O, DMF, Me$_2$SO) and showing an increasing percent of contact pairs as the solvent base strength falls (1,2-DME, THF). Adding a strong donor solvent (DMF, H$_2$O) to salts of this anion in a weaker donor solvent (THF) shifts the ion-site mix to form solvent-separated pairs at the expense of contact pairs.

Similar infrared studies by Brown,[4a] Darensbourg,[4b,5] Pannell,[6a] Rosenblum,[6b] and their co-workers have shown that solvent-separated and contact ion pairs also exist in some nonaqueous solutions containing the metal carbonylate anions Mn(CO)$_5^-$,[4] Mn(CO)$_4$L$^-$,[4b] HFe(CO)$_4^-$,[5] (C$_5$H$_5$)Fe(CO)$_2^-$,[6] and (C$_5$H$_5$)Mo(CO)$_2^-$.[6a] Contact ion pairs in each of these solutions were found with the Na$^+$- - -O≡CM structure and a dependence of ion site mix on solvent basicity was also seen insofar as it was investigated.

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