High-Dilution Syntheses of 14-Membered Tetradentate Macrocycles Incorporating the Diars Moiety[1]

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Received October 7, 1980

Six 14-membered *tert*-arsino-containing macrocycles are described. These are the 2,17-dimethyl-2,17-diarsa-6,13-diheteratricyclo[16.4.0.0^{7,12}]docosa-7(12),8,10,18(1),19,21-hexaenes, where 6,13-dihetera is dioxa, dithia, bis(methylarsa) and bis(phenylphospha). The stereochemistry of substituents on the heteroatoms is assigned unambiguously on the basis of NMR spectral evidence in some cases and in others, tentatively, on the basis of analogies with previously described macrorings. A newly developed high-dilution apparatus is described in detail.

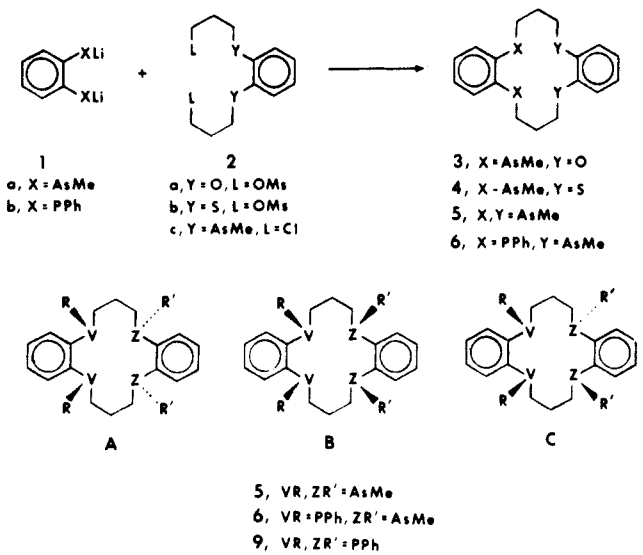
The synthesis of macrocyclic ligands and the study of guest complexation behavior of such hosts[2] have been an active area of research in recent years.[3] Our interest has been focussed on macrocycles which have soft[4] ligating sites, appropriate for coordination of transition metals. We have recently described 11-[5] and 14-membered[6] rings which contain *tert*-phosphino sites, as well as 11-membered rings which contain *tert*-arsino-ligating sites.[7] We now describe the synthesis of a series of 14-membered rings which contain the *o*-bis(methylarsino)benzene moiety.

Results and Discussion

The macrocyclizations described in this work were carried out in boiling THF in a high-dilution apparatus described in detail in the Experimental Section.[8] As shown in Scheme I, the high-dilution reaction involves the dilithium salt 1 and the bis(electrophile) 2. After a standard extractive workup, 3–6 were purified by anaerobic chromatography on silica gel, followed by crystallization and recrystallization; all were sharp-melting white solids. The yields of macrocycles generally fall in the 20–40% range and appear to be consistently lower with **1a** as the nucleophile than with **1b**, where the yields are in the 30–60% range.[5,6] The reasons for the low yields of **5** are not apparent.

Cycles **3** and **4** can exist as two isomers (meso and *dl*), and **5** and **6** could have as many as five and six isomers,[9]

Scheme I



respectively, since inversion barriers for *tert*-arsines are in excess of 40 kcal/mol[10] and those for *tert*-phosphines are in the range of 32–35 kcal/mol.[11] In fact, we isolated only one isomer of **3** and **4**, as evidenced by sharp melting points and clean ^{1}H and ^{13}C NMR spectra (see Table I). We have established that macrocyclizations involving **1b** give only the *cis*-Ph_2 species for both 11- and 14-membered rings.[5,6] Evidence has also been presented that **1a** gives only the *cis*-Me_2 11-membered cycles.[7] On this basis, the isomers isolated with **3** and **4** are assigned the cis configuration. In the case of **4** we have carried out a thermal equilibration (230 °C, 16 h) which resulted in the recovery of starting material only. There was no evidence for the formation of a new isomer (by TLC and ^{1}H and ^{13}C NMR), in contrast to our finding that an 11-membered cycle

(1) Part 8 of "Phosphino-Macrocycles". For part 7 see: Kyba, E. P.; Chou, S.-S. P. *J. Am. Chem. Soc.* **1980**, *102*, 7012.

(2) For a discussion of host–guest chemistry, see: Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8.

(3) For recent reviews, see: (a) Melson, G. A., Ed. "Coordination Chemistry of Macrocyclic Compounds"; Plenum Press: New York, 1979. (b) Bradshaw, J. S.; Stott, P. E. *Tetrahedron* **1980**, *36*, 461.

(4) Ho, T.-L. "Hard and Soft Acids and Bases Principle in Organic Chemistry"; Academic Press: New York, 1977.

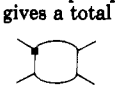
(5) Kyba, E. P.; John, A. M.; Brown, S. B.; Hudson, C. W.; McPhaul, M. J.; Harding, A.; Larsen, K.; Niedzwiecki, S.; Davis, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 139.

(6) Kyba, E. P.; Davis, R. E.; Hudson, C. W.; John, A. M.; Brown, S. B.; McPhaul, M. J.; Liu, L.-K.; Glover, A. C. *J. Am. Chem. Soc.*, in press.

(7) Kyba, E. P.; Chou, S.-S. P. *J. Chem. Soc., Chem. Commun.* **1980**, 449.

(8) The apparatus described here is a considerable improvement over that which we described previously[5] and also quite possibly over others described in the literature: (a) Newman, M. S.; et al. *J. Org. Chem.* **1975**, *40*, 2863; (b) Rastetter, W. H.; Phillion, D. P. *Tetrahedron Lett.* **1979**, 1469; (c) Frensch, K.; Vögtle, F. *J. Org. Chem.* **1979**, *44*, 884; (d) Hammerschmidt, E.; Vögtle, F. *J. Chem. Res. (S)* **1980**, 192; *J. Chem. Res. (M)* **1980**, 2776.

(9) In the 14-As_4 case, the isomers possible may be depicted by using *i* in which the straight lines represent the benzo fusion and the curved lines the trimethylene chains. The substituents may be either up (U) or down (D) with respect to the plane of the molecule. If one starts at the shaded position and proceeds counterclockwise, the following would be obtained: UUDD ≡ **5A**, UUUU ≡ **5B**, UUUD ≡ **5C**, UDDU ≡ **5D**, UDUD ≡ **5E**. In the case of 14-As_2P_2 the analysis would be similar except that the shaded site would be defined as a phosphorus atom and then UUUD ≡ **6C** ≠ UDUU ≡ **6C'**, which gives a total of six isomers.



i

(10) (a) Baechler, R. C.; Casey, J. P.; Cook, R. J.; Senkler, G. H., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1972**, *94*, 2859. (b) Horner, L.; Hofer, W. *Tetrahedron Lett.* **1965**, 4091.

(11) Baechler, R.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 3090.

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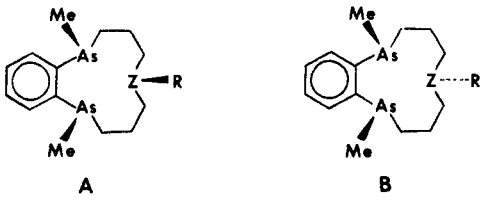
Table I. ^{13}C NMR Chemical Shifts of Methylene Carbon Atoms [As-C(1)-C(2)-C(3)-Het] and ^{1}H NMR Chemical Shifts in Macrocycles 3-6[a]

	^{13}C shift, δ				
	C(1)	C(2)	C(3)	AsMe	^{1}H AsMe shift, δ
3	26.3	25.9	70.1	7.6	1.15
4	28.2	25.7	36.1	8.3	1.05
5A	33.0	24.7	33.0	9.5	1.11
5B	30.6	23.5	30.6	8.1	1.03
5C	32.7, 32.0[b]	24.4, 23.6	31.5, 31.0[b]	8.9, 8.7, 8.2, 7.7	1.26, 1.23, 1.17
6C	31.2, 30.5	23.6, 23.4[c]	29.1[d]	8.0, 7.6	1.31, 1.27

[a] Spectra determined in ca. 0.1 M solutions in $CDCl_3$. See the Experimental Section for details. The chemical shift assignments for the ^{13}C data have not been rigorously established. [b] The assignment of the C(1) and C(3) absorptions is arbitrary. [c] Overlapping triplets, both with $J = 12$ Hz. [d] Triplet, $J = 6$ Hz.

(11-As_2S)[7] under less vigorous conditions does isomerize.

Chromatographic resolution of the crude **5** gave three isomers; the chromatographically most mobile material, **5A** (mp 206–207.5 °C), and the middle fraction, **5B** (mp 121–122 °C), were clearly symmetrical molecules as evidenced in particular by single absorptions for the three methylene carbon atoms and methyl groups in the ^{13}C NMR spectra (see Table I). Although the structures of these two isomers can only be assigned with certainty by X-ray crystallographic means, they have been tentatively designated as **5A,B** as shown in Scheme I, on the basis of two previous observations. First, we have found that in the 11-membered arsino macrocycles, the meso-trans isomers (e.g., **7B** and **8B**) are chromatographically more



7, ZR = AsMe
8, ZR = PPh

mobile than the meso-cis species (e.g., **7A** and **8A**),[1,7] suggesting that the less mobile **5B** is the all-cis isomer. Second, *cis,trans,cis*-**9A** is considerably higher melting than the *all-cis*-**9B** (mp 163 °C; cf. 229 °C, respectively), consistent with the assignment of the isomers of **5**. In contrast to **5A** and **5B**, the chromatographically least mobile **5C** (mp 117.5–118.5 °C) was not symmetrical. All ten aliphatic carbon atoms exhibited separate absorptions in the ^{13}C NMR spectrum (Table I), and the aromatic carbon region was very complex in comparison with those of isomers **5A** and **5B**. The only structure consistent with these spectral data is the *dl*-**5C** structure shown in Scheme I, since the other four isomers[9] possess some element of symmetry.

It has been our general experience that phosphine-containing macrocyclic isomers are much more difficult to separate chromatographically than the corresponding arsine-containing species. This was true also with cycle **6**, which was isolated crude as a mixture of what appeared to be two isomers (e.g., ^{31}P NMR signals at −25.7 and −29.2 ppm in an area ratio of 0.73:1). Careful fractional crystallization gave a single isomer as a sharp-melting crystalline solid which we assign as *dl*-**6C** on the basis of the ^{13}C and ^{1}H NMR data presented in Table I as well as the ^{31}P NMR spectrum which features an AB quartet, indicative of nonidentical phosphorus atoms. The assignment of **6C** rather than **6C'**[9] for this isomer follows from previous work[5,6] in which phenyl groups trans across the benzo fusion have yet to be observed in such macrocycles. We have been unable to resolve the remaining isomers in the crude mixture. With the spectral data for **6C** in hand it is clear that the ^{31}P NMR absorption of the crude reaction mixture at −25.7 ppm was in fact due to at least two components, one of which was **6C** and another which obscured the AB quartet of **6C**.

We have commented earlier about the stereochemistry of the key macrocyclization step using **1b** as the initial nucleophile.[5] On the basis of the study of models, the formation of the *cis*-Ph_2 species appeared entirely reasonable on the basis of consideration of the solvation requirements of Li^+ and the steric bulk of Ph. It was also apparent with **2d** (Y = PPh, L = Cl) as the electrophile that although the *dl* isomer is present, it yields no macrocyclic product, for example, with **1b**, and proceeds to polymer instead.[6] On the basis of the formation of only one isomer each of **3** and **4**, it appears that macrocyclization using **1a** as the nucleophile also gives only cis substituents. In the synthesis of **5**, the *meso*-**2c** electrophile would lead to **5A** and **5B**, but now, with the much smaller methyl substituents on the *dl*-**2c**, some **5C** is formed also. A similar analysis would apply to the synthesis of **6C** and its isomers. Furthermore, one would predict that had the electrophile–nucleophile combination been "reversed" [**1a** + **2d** (Y = PPh, L = Cl) instead of **1b** + **2c**] only **6A** and **6B** would have been formed. This is because the *dl*-**2d** could lead only to **6C'**, presumably a thermodynamically much less attractive molecule. We have not as yet attempted this reaction.

Experimental Section

General Methods. Melting points were obtained by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Chemalytics, Inc., or Galbraith Laboratories, Inc.

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, and 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. 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 on 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 × 0.188 in. or 6 ft × 0.125 in.). Peak area measurements were obtained with the aid of a Vidar 6300 digital integrator.

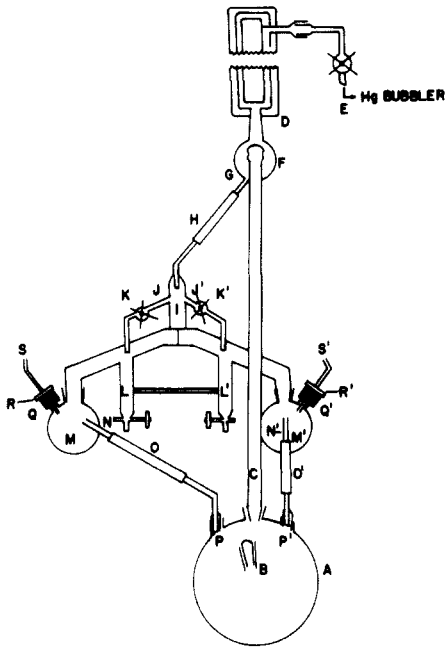


Figure 1. High-dilution apparatus shown in toto except for the syringes which are attached at S and S[1] and shown in Figure 3.

Unless noted, all of the reactions, manipulations, and purification steps involving phosphines and arsines were performed under a dry nitrogen or argon atmosphere. Air-sensitive liquids were transferred by Teflon Flex-needles (Aldrich) with 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. THF for high-dilution reactions was distilled from LAH under a nitrogen atmosphere.

The following compounds have been described elsewhere: *o*-bis[(lithiomethyl)arsino]benzene (**1a**),[7] *o*-bis[(lithiophenyl)-phosphino]benzene (**1b**),[5] *o*-bis[3-(methanesulfonyloxy)propoxy]benzene (**2a**).[6]

High-Dilution Apparatus.[12] The apparatus shown in Figure 1 allows the easily controlled, slow, simultaneous addition of two reagents in dilute solution to a reaction chamber containing boiling solvent, all under an inert atmosphere. The description follows the lettered assignments of the various parts of the appartus.

A is a 3-L, round-bottomed reaction flask containing a large (length 2.75 in., diameter 1 in.), egg-shaped magnetic stirring bar. The flask is fitted with a heating mantle and magnetic stirrer. It is charged with about 1.5 L of solvent, generally THF.

B is a 24/40 F joint which allows connection to a vacuum pump to evacuate the system and fill it with dry nitrogen several times.

C is a distillation column, insulated with glass wool and aluminum foil.

D is a double surface condenser, necessary because of the high reflux rates used.

E is an adapter with stopcock which leads via rubber tubing to a mercury bubbler, which is connected to a dry-nitrogen line.

F is a solvent collection chamber.

G is a solvent takeoff tube.

H is thick-walled (2 mm) Teflon tubing (6 mm i.d.) to allow flexibility in this three-dimensional apparatus.

I is a solvent-splitting chamber in which solvent overflows through tubes J and J[1]. The rate of flow in each direction can be controlled by using Teflon stopcocks K and K[1] or, preferably, by physically adjusting the relative levels of M and M[1] with jacks.

L and L[1] are collection chambers (10 mL) which allow the measurement of solvent flow through J and J[1].

M and M[1] are reactant dilution chambers fashioned from 100-mL flasks and equipped with magnetic stirring bars and stirrers.

(12) We are most grateful to John K. Somerville (glassblower), Grady K. Rollins (machinist), and F. C. Jack Maseles (electronics) for their considerable help in developing this apparatus.

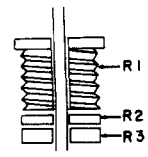


Figure 2. Teflon adapters to provide airtight seal for Teflon tubes which convey reactant solutions. These are used at positions Q and Q[1] (Figure 1) and T1 and T2 (Figure 3).

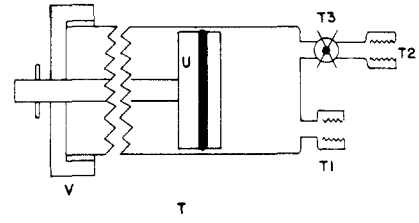


Figure 3. Airtight, 250-mL syringe which delivers reactant solution to dilution chambers M(M[1]) via S(S[1]) shown in Figure 1.

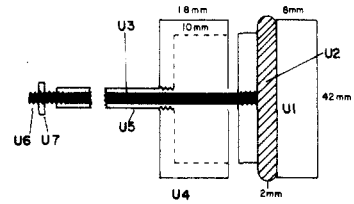


Figure 4. Plunger assembly for syringe shown in Figure 3.

N and N[1] are reactant overflow takeoffs which maintain the volume of solvent in the chamber at ca. 90 mL.

O and O[1] are Teflon tubing connectors as in H.

P and P[1] are drip-tip introducers of diluted reactants into reaction chamber A.

Q and Q[1] are reactant introducers fashioned from Ace Glass no. 7 "Mini" Ace-Thred adapters. The reactant solutions are introduced via thick-walled (0.8 mm) Teflon tubes (1.6 mm i.d.) S and S[1].

R and R[1] are Teflon adapters which give an airtight seal between S,S[1] and Q,Q[1]. As shown in Figure 2, the adapter is fashioned from a Teflon plug (Ace Glass) which has bored through it an appropriately sized hole and has about 3 mm sliced from the tip to give two pieces R1 and R3. A gasket fashioned from EPR rubber which fits tightly around the Teflon tubing is placed between R1 and R3. When the bushing is screwed into Q, R1 and R3 compress R2 and give an airtight seal.

T and T[1] are airtight syringes (Figure 3) fashioned from heavy-wall (0.1875 in.) Pyrex glass *precision* tubing (1.6805 in. i.d. from Wilmad Glass, 22 cm in length) which hold 250 mL of solution. Fittings T1 and T2 are as described for Q and R, except that T2 is also equipped with Teflon stopcock T3.

U and U[1] are plungers which allow airtight seals, as shown in Figure 4, and have several parts. U1, the plunger head, is fashioned from high-density polyethylene, with the front portion being 42 mm in diameter and the back portion being 38 mm in diameter. Into this is screwed a brass rod (6 mm in diameter, 24 cm in length), U3. A Teflon covered O-ring (U2, Ace Glass, size 128) fits up against the edge of U1 as shown. The plunger tail (U4) is also made from high-density polyethylene, (outer diameter 42 mm) and is hollowed out with a diameter slightly greater than 38 mm so that it can fit over the back portion of U1 and up against U2. A brass tube (U5, 7 mm i.d., 20 cm in length) is screwed into U4 such that U3 fits through U5. U3 is threaded at its end (U6) and is fitted with a nut which can be screwed up against the end of U5. When all the pieces are fitted together and U7 is screwed up against the end of U5, this brings U4 and U1 closer together which squeezes the Teflon-covered O-ring outward, giving a plunger which has an adjustable diameter. This allows the generation of a tight seal to the wall of the syringe barrel. In addition, since reagents such as **1a** and **1b** are corrosive toward Teflon, when the O-ring is worn out it is a simple matter to replace it.

V is a plunger guide made from high density polyethylene.

The syringe pump is critical in this apparatus because it must have sufficient power to overcome the considerable friction generated by having the Teflon O-rings tight against the barrels of the syringes. We have found, for example, that the Sage Model 355 has insufficient power for these purposes. The pump that we employ is a Harvard Apparatus infusion/withdrawal pump, which has been modified for our syringes and also for continuous variation of speed instead of 12-step variations. With this we can easily control the rate of addition from 50 mL/min to 200 mL/3–4 days (1–2 drops/min).

The high-dilution reaction is run in this apparatus after it has been evacuated at B (E closed, and Teflon plugs at Q) for several hours and filled with dry nitrogen. Teflon tubes (S) are attached at Q under positive nitrogen pressure, and chamber A is charged with ca. 1.5 L of THF by using Flex-needle techniques. Flask A is then heated and stirred until the appropriate reflux rate is established as measured at L and L^1. This is usually about 25 L/day each through J and J^1. The reagents are then added from the syringes to M and M^1 which are vigorously stirred at a rate of ca. 3–4 drops/min (250 mL/24 h).

***o*-Bis[[(3-chloropropyl)methyl]arsino]benzene (2c).** To a mixture of *o*-bis(methylarsino)benzene (6.3 g, 24.4 mmol) and 1-bromo-3-chloropropane (115 g, 730 mmol) in anhydrous THF (250 mL) at −78 °C was added dropwise a 3.2 M hexane solution of *n*-butyllithium (15.2 mL, 48.8 mmol) in 1.5 h. The reaction mixture was slowly warmed to room temperature and stirred for 1 h before it was evaporated at 40 °C (50 μm).

The residue was partitioned between ether (300 mL) and water (2 × 50 mL). The ether layer was washed with brine (100 mL), dried, and concentrated to give a pale yellow oil (7.0 g) which was chromatographed on silica gel (100 g) with hexane–dichloromethane (5:1 v/v) as eluent to yield a colorless oil: 3.75 g (37%); ^{1}H NMR ($CDCl_3$) δ 7.31 (m, 4 H), 3.48 (m, 4 H), 1.80 (m, 8 H), 1.20 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 146.9, 130.0, 128.6, 46.2, 29.9, 26.0, 8.4; mass spectrum, *m/e* 410 (M^+ for ^{35}Cl–^{35}Cl). This material was used without further purification in the macrocyclization described below.

***cis*-2,17-Dimethyl-2,17-diarsa-6,13-dioxatricyclo-[16.4.0.0^{7,12}]docosa-7(12),8,10,18(1),19,21-hexaene (3).** The following description is typical of all the macrocyclizations carried out in this work. The dianion **1a** [from *o*-bis(methylarsino)benzene (4.9 g, 18.99 mmol) and 3.2 M *n*-butyllithium in hexane (11.8 mL, 38.0 mmol)] in THF (132 mL) and **2a** (7.25 g, 18.99 mmol) in THF (143 mL) were reacted in the high-dilution apparatus described above (addition time, 20 h). The reaction mixture was concentrated on a rotary evaporator, and the residue was dissolved in ether (500 mL). This was washed with saturated aqueous ammonium chloride (100 mL), water (2 × 100 mL), and brine (100 mL) and dried. Upon concentration of the mixture under vacuum, a pale yellow solid (6.45 g) was obtained, which was filtered through a column of silica gel (50 g) with dichloromethane–hexane (1:1 v/v) as eluent to give a white solid, 3.2 g (37%). Recrystallization from benzene–hexane gave **3** as a white crystalline solid: 2.5 g (30%); mp 105–106 °C; ^{1}H NMR ($CDCl_3$) δ 7.31 (m, 4 H), 6.82 (m, 4 H), 4.00 (m, 4 H), 1.88 (m, 8 H), 1.15 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 149.6, 147.2, 130.3, 128.2, 121.6, 115.6, 70.1, 26.3, 25.9, 7.6; mass spectrum, *m/e* 448 (M^+).

Anal. Calcd for $C_{20}H_{26}As_2O_2$: C, 53.59; H, 5.85. Found: C, 53.70; H, 5.92.

***cis*-2,17-Dimethyl-2,17-diarsa-6,13-dithiatricyclo-[16.4.0.0^{7,12}]docosa-7(12),8,10,18(1),19,21-hexaene (4).** Reaction of **1a** (3.0 g, 11.6 mmol) and **2b** (4.8 g, 11.6 mmol) as described for **3** above gave, after the extractive and evaporative workup, a pale yellow semisolid (5.3 g). This was chromatographed on silica gel (80 g) with dichloromethane–hexane (1:1 v/v) as eluent to give a white solid. This was further purified by recrystallization from chloroform–hexane to give **4** as a white crystalline solid: 1.87 g (34%); mp 118.5–119.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.17 (m, 8 H), 2.87 (m, 4 H), 1.63 (m, 8 H), 1.05 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 147.11, 137.44, 130.82, 130.26, 128.34, 126.69, 36.10, 28.16, 25.69, 8.32; mass spectrum, *m/e* 480 (M^+).

Anal. Calcd for $C_{20}H_{26}As_2S_2$: C, 50.00; H, 5.46. Found: C, 49.94; H, 5.46.

2,6,13,17-Tetramethyl-2,6,13,17-tetrarsatricyclo-[16.4.0.0^{7,12}]docosa-7(12),8,10,18(1),19,21-hexaene (5). Reaction of **1a** (3.2 g, 12.4 mmol) and **2c** (5.1 g, 12.4 mmol) as described for **3** above gave, after the extractive and evaporative workup, a pale yellow semisolid (5.65 g). This was chromatographed on silica gel (100 g) with hexane–dichloromethane (3:1 v/v) as eluent to give three compounds. The chromatographically most mobile material, **5A** (R_f 0.22, with the above solvent system), was obtained as a white solid, 0.25 g. Recrystallization from benzene–hexane–chloroform gave a white, crystalline solid: 0.20 g (2.7%); mp 206–207.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 8 H), 1.67 (m, 12 H), 1.11 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 148.1, 130.3, 128.6, 33.0, 24.7, 9.5; mass spectrum, *m/e* 596 (M^+). The material of intermediate mobility, **5B** (R_f 0.05), was also a white crystalline solid (0.167 g, 2.2%) after recrystallization from benzene–hexane: mp 121–122 °C; ^{1}H NMR ($CDCl_3$) δ 7.02 (m, 8 H), 1.60 (m, 12 H), 1.08 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 146.8, 129.8, 128.2, 30.6, 23.5, 8.1; mass spectrum, *m/e* 596 (M^+). The chromatographically least mobile material, **5C** (R_f 0.03), was obtained as a white crystalline solid (0.10 g, 1.3%) by recrystallization from acetone: mp 117.5–118.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 8 H), 1.8 (m, 12 H), 1.26 (s, 3 H), 1.23 (s, 3 H), 1.17 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 148.0, 147.5, 146, 132.7, 121.9, 130.3, 130.1, 128.1, 127.9, 32.7, 32.0, 31.5, 31.0, 24.4, 23.6, 8.9, 8.7, 8.2, 7.7 (the last ten absorptions are of equal intensity); mass spectrum, *m/e* 596 (M^+).

Anal. Calcd for $C_{22}H_{32}As_4$: C, 44.32; H, 5.41. Found for **5A**: C, 44.47; H, 5.56. Found for **5B**: C, 44.36; H, 5.54. Found for **5C**: C, 44.54; H, 5.49.

2,17-Dimethyl-6,13-diphenyl-2,17-diarsa-6,13-diphosphatricyclo[16.4.0.0^{7,12}]docosa-7(12),8,10,18(1),19,21-hexaene (6). Reaction of dianion **1b** [from *o*-bis(phenylphosphino)benzene[5] (4.33 g, 14.67 mmol) and 3.2 M *n*-butyllithium in hexane (9.2 mL, 29.34 mmol)] and **2c** (6.03 g, 14.67 mmol) as described for **3** above gave, after the extractive (dichloromethane was used as the solvent) and evaporative workup, a pale yellow, viscous liquid, 6.6 g. This material was purified by column chromatography on silica gel (200 g) with hexane–dichloromethane as eluent to give **6** as a mixture of isomers: 1.8 g (20%); ^{1}H NMR ($CDCl_3$) δ 7.35 (m), 1.31 (s), 1.27 (s); ^{13}C NMR ($CDCl_3$) δ 147.5, 127.7, 31.7, 31.6, 30.2, 29.9, 24.4, 24.1, 8.7, 8.5; ^{31}P NMR ($CDCl_3$) δ −25.8, −29.2 (area ratio, 0.73:1). Crystallization and recrystallization from toluene–hexane gave one isomer of **6** as a white crystalline solid: 0.25 g (3%); mp 138.5–139.5 °C; ^{1}H NMR (CD_2Cl_2) δ 7.5–7.0 (m, 18 H), 2.3–1.5 (m, 12 H), 1.31 (s, 3 H), 1.27 (s, 3 H); ^{13}C NMR (CD_2Cl_2) δ 147–127 (complex absorptions), 31.2, 30.5, 29.1 (t, J = 6 Hz), 23.6 (t, J = 12 Hz), 8.0, 8.6; ^{31}P NMR (CD_2Cl_2) δ −25.8 (AB q, J_{pp} = 29.6 Hz, ν_{AB} = 33.1 Hz); mass spectrum, *m/e* 617 (M^+).

Anal. Calcd for $C_{32}H_{36}As_2P_2$: C, 60.77; H, 5.74. Found: C, 60.57; H, 5.82.

Acknowledgment. We are most grateful to the National Science Foundation (Grant No. CHE 78-11543), the Air Force Office of Scientific Research (Grant No. AFOSR-79-0090), and the Robert A. Welch Foundation (Grant No. F-573) for generous support of this work. Helpful discussions concerning the high-dilution apparatus with Dr. Heinz H. Heumüller are gratefully acknowledged.

Registry No. **1a**, 75396-01-9; **1b**, 65113-32-8; **2a**, 76010-86-1; **2b**, 76010-87-2; *meso*-**2c**, 76010-88-3; *dl*-**2c**, 76010-89-4; **3**, 76010-90-7; **4**, 76010-91-8; **5A**, 76010-92-9; **5B**, 76035-37-5; **5C**, 76035-38-6; **6C**, 76010-93-0; *o*-bis(methylarsino)benzene, 34664-59-0; 1-bromo-3-chloropropane, 109-70-6.