in 0.4 mL of warm THF was added during 45 s to a solution of LDA (prepared from 44 μL of 1.58 M BuLi, 0.070 mmol, and 12 μL of diisopropylamine, 0.080 mmol) in 0.4 mL of THF at −78 °C. The mixture was stirred for 5 min at −78 °C and for 10 min at −10 °C and finally cooled to −78 °C. Gaseous formaldehyde (from 18 mg of paraformaldehyde depolymerized at 150 °C) was introduced for 10 min and after 5 min 1 N HCl. The reaction mixture was extracted with ether/chloroform mixture to furnish 18.5 mg of the hydroxylactone **21c** (70%) and 1 mg of the starting material after chromatographic purification: iR ($CHCl_3$) 1750 cm^{-1}; ^1H NMR δ 0.05 (s), 0.72 (s), 0.87 (s), 0.88 (d, J = 6.5 Hz), 1.00 (s), 3.1–3.7 (m), 3.7–4.1 (m), 4.3–4.8 (m), 5.1–5.3 (m).

To a solution of the lactone **21c** (17 mg, 0.032 mmol) in 0.5 mL of THF at −78 °C was added 0.2 mL of 2.1 M methyllithium, and the mixture was then warmed at 45 °C for 1 h. Methanol (0.3 mL) was added, and the mixture was concentrated. Pyridine (0.3 mL) and 0.2 mL of acetic anhydride were added, and the mixture was heated at 80 °C for 1.5 h until the initially formed monoacetate was completely converted to the diacetate. Purification of the crude product obtained after concentration gave 9.5 mg of the title diacetate **23c** (46%) as a solid (R_f 0.60, 50% ethyl acetate in hexane): MS (20 eV), m/e (rel intensity) 645 (M^+ − 1), 589 (50), 571 (26), 529 (35), 377 (55), 255 (53), 253 (45), 171 (100), 123 (74), 111 (76). FAB mass spectrum using a glycerin matrix also indicated the molecular weight of 645. ^1H NMR ($CDCl_3$, 90 MHz) δ 0.06 (s, 6 H), 0.67 (s, 3 H), 0.89 (s), 0.99 (s), 1.22 (s), 1.25 (s), 2.04 (s), 2.06 (s), 3.2–3.75 (m, 1 H), 3.8–4.4 (m centered at 4.12, 2 H), 5.03 (br d, J = 10.5 Hz), 5.29 (br d, 2 H, J = 4.0 Hz); ^{13}C NMR ($CDCl_3$) δ − 4.5, 11.9, 13.0, 18.3 (Bu–Si), 19.5, 21.1, 21.5, 24.4, 25.2 (23), 26.0 (t-Bu), 27.2 (27, 16), 28.4 (26), 32.0, 32.1, 36.6, 37.4, 39.7, 39.8, 42.9, 46.4 (24), 50.3, 53.1, 56.5, 65.9 (28), 72.7 (25), 77.7 (22), 121.0, 141.6, 170.8, 171.0.

Depresosterol Triacetate (23a). The 3-siloxy compound **23c** (3.0 mg) was dissolved in a mixture of acetic acid (30 μL), water (20 μL), and THF (50 μL) and kept for 2 days at room temperature. Volatile material was removed in vacuo and the residue was treated with a mixture of acetic anhydride (20 μL) and pyridine (30 μL) for 1 day at room temperature. After concentration, the residue was chromatographed to give 2.5 mg of the title compound as a solid (R_f 0.65, 50% ethyl acetate in hexane), which was identical with an authentic sample by the 270-MHz ^1H NMR and EI-MS spectra. The 90-MHz ^1H NMR of **23a** was identical with the silylated **23c** except for the signals due to the A-ring region.

Acknowledgment. We thank Prof. Y. Kashman for the 270-MHz ^1H NMR spectrum of the natural depresosterol, Prof. N. Ikekawa and Dr. Y. Fujimoto for helpful discussion and for the provision of steroidal aldehydes and the authentic spectra of **10a** and **15a**, Prof. O Mitsunobu for the measurement of 270-MHz spectra, and N. Nakayama for the measurement of mass spectra. Financial support from the Ministry of Education, Science, and Culture is deeply acknowledged.

Registry No. 1, 77517-54-5; **4**, 84098-44-2; **5**, 84098-53-3; **7a**, 10211-88-8; **8a**, 94956-26-0; **8a** lactone, 95042-54-9; **9b**, 63163-38-2; **10a**, 79435-62-4; **11a**, 94956-27-1; **12b**, 94956-28-2; **13a**, 95042-55-0; **13b**, 95042-56-1; **13c**, 94956-29-3; **14b**, 63160-61-2; **15a**, 63160-62-3; **16a**, 94978-08-2; **18c**, 94956-30-6; **20a**, 94956-31-7; **20c**, 94956-32-8; **21c**, 94956-33-9; **23a**, 95042-57-2; **23c**, 94956-34-0; $TiCl_4$, 7550-45-0; Ti(O-*i*-Pr)$_4$, 546-68-9; methyl bromide, 74-83-9; *tert*-butyldimethylsilyl chloride, 18162-48-6; acetone, 67-64-1; methyllithium, 917-54-4.

Synthesis of 14-Membered P_2S_2 and P_3S Macrocycles Which Contain the 1-Thio-2-(phenylphosphino)benzene Moiety. Determination of Stereochemistries of the Free Ligands and of a Pt(II) Complex

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Abstract: Three new 14-membered tetradentate (P_3S and two P_2S_2) macrocycles have been synthesized and isolated as pairs of isomers. All the isomers were separated and fully characterized, and their stereochemistries were determined or assigned. The new ligands are *cis*- and *trans*-13,17-diphenyl-13,17-diphospha-2,6-dithiatricyclo[16.4.0.0^{7,12}]docosa-7(12),8,10,1-(18),19,21-hexaene (**3C** and **3T**), *cis*- and *trans*-6,17-diphenyl-6,17-diphospha-2,13-dithiatricyclo[16.4.0.0^{7,12}]docosa-7-(12),8,10,1(18),19,21-hexaene (**4C** and **4T**), and *cis,cis*- and *cis,trans*-6,13,17-triphenyl-6,13,17-triphospha-2-thiatricyclo-[16.4.0.0^{7,12}]docosa-7(12),8,10,1(18),19,21-hexaene (**5C** and **5T**). The synthesis of **4C,T** involved the use of an S–H protecting group, CH_2OMe, which is removed quantitatively with *n*-butylthiolate in DMF. The stereochemistry of **3T** was established by a single-crystal X-ray diffraction study and that of **4C** by an X-ray study of the complex **4C**·$Pt^{II}(PF_6)_2$. The latter was a classical square-planar complex, with essentially equal Pt–S and Pt–P bond lengths, in the range 2.287–2.297 Å. The stereochemistries of **5C,T** were assigned by the comparison of the physical and spectroscopic properties with those of **3C,T**, **4C,T** as well as those of the analogous **14**-P_4**C,T** species. Crystal structures at −110 °C have been determined for **3T** and **18**. X-ray data were collected on a Syntex $P2_1$ autodiffractometer and refined by the full-matrix least-squares method. For **3T** as hexagonal plates from ethyl acetate, a = 13.4358 (22) Å, b = 14.2137 (14) Å, c = 14.0314 (21) Å, β = 93.903 (11)°, monoclinic, $P2_1/c$, Z = 4, R = 0.0520, and R_w = 0.0567 for 3383 reflections with $|F_o| \geq 6\sigma_{|F_o|}$. The structure is severely disordered, with only one PPh and one $(CH_2)_3$ chain ordered. For **18**·C_6H_6, a = 12.629 (5) Å, b = 15.304 (3) Å, c = 20.714 (6) Å, β = 104.76 (4)°, monoclinic, $P2_1/c$, Z = 4, R = 0.0530, R_w = 0.0437 for 6061 reflections with $|F_o| \geq 4\sigma_{|F_o|}$. Coordination about Pt is square planar with nearly equal Pt–P (2.297 and 2.293 Å) and Pt–S (2.296 and 2.287 Å) bond lengths. The angle S–Pt–S is 179.3°, while P–Pt–P is 170.7°. Both $\overline{SPtP(CH_2)_2CH_2}$ rings adopt the chair conformation.

Several years ago we described the synthesis and structures of several tetradentate 14-membered macrocycles which contained *tert*-phosphino sites of general type **1**.[2] One of our goals for these ligands was the systematic modification of the properties of a

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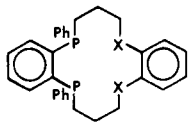
Table I. Physical Properties of Cycles Synthesized[a]

	yield, %	mp, °C	TLC[e] R_f	^{31}P NMR δ (multiplicity)	partial ^{1}H NMR (CH_2–S) δ (mult., integr.)
3C	4	127–129	0.26	−25.0 (s)	3.0 (m, 4 H)
3T	34	155–157	0.52	−27.6 (s)	3.15 (m, 4 H)
4C	4–6[c]	201–206	0.34	−22.4 (s)	3.10 (m, 4 H)
4T	20–30[c]	202–206	0.57	−26.0 (s)	3.35 (m, 2 H) 2.90 (m, 2 H)
5C	3	150–152	0.23	−24.1 (d, J = 3 Hz), −24.1 (d, J = 165 Hz), −27.0 (dd, J = 165, 3 Hz)[f]	3.05 (m, 1 H), 2.25 (m, 1 H)
5T	23	162–164	0.55	−28.5 (m)	3.50 (m, 1 H), 2.95 (m, 1 H)
1a(cis)[b]	11	158–163	0.15	−26.1 (s)	
1a(trans)[b]	25	214–216	0.61	−28.9 (s)	
12	*d*	66–68		−14.0 (s)	

[a] NMR spectra were determined on ca. 0.1 M $CDCl_3$ solutions. See Experimental Section for details. [b] Reference 2a. [c] Estimated, based on purity of the precursor to the macrocycle. See text. [d] Not determined. This species was a byproduct in several reactions. See text for details. [e] TLC was carried out on alumina with dichloromethane/hexane (1:1, v/v). [f] This spectrum was confirmed by determination at two different field strengths and by computer simulation.

transition metal (TM) coordinated in the cavity as a function of the heteroatoms X present in the cycle. As we began to develop



1

a, X = PPh
b, X = AsMe
c, X = S
d, X = O
e, X = NMe

the coordination chemistry of **1**, however, it soon became clear that our strategy would come to naught because the modifying heteroatoms X were not ligating the TM. Instead, complexes of the type $(\mathbf{1b–e})_2$TM were formed where four phosphino sites were coordinated to the metal center, as exemplified with $(\mathbf{1c})_2FeCl_2$(**2**)[3] and $(\mathbf{1d})_2CoCl_2$.[1]

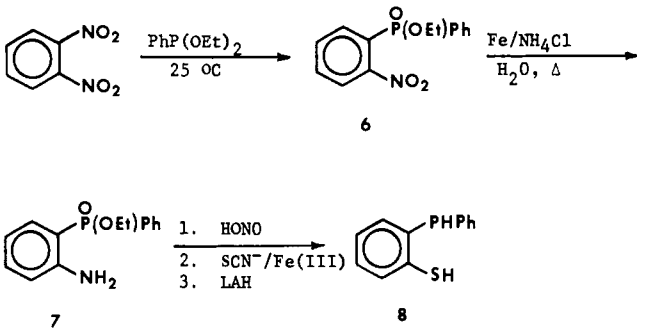
Based on examination of X-ray structures of TM complexes which involve the 1,2-diphosphinobenzo moiety,[1,3,4] we felt that if a 1-X-2-phosphinobenzo moiety were incorporated into a macrocyclic ligand, it would be highly likely that X would indeed be involved in the coordination of a TM. Thus, we set as synthetic targets ligands **3** and **4**, which we anticipated would allow us to pursue our original goal of systematic modification of TM properties as a function of the heteroatom present. We report now the synthesis of **3**, **4** (X = S), as well as **5** (X = S) and an example of a TM complex which illustrates the viability of our modified strategy.

Results and Discussion

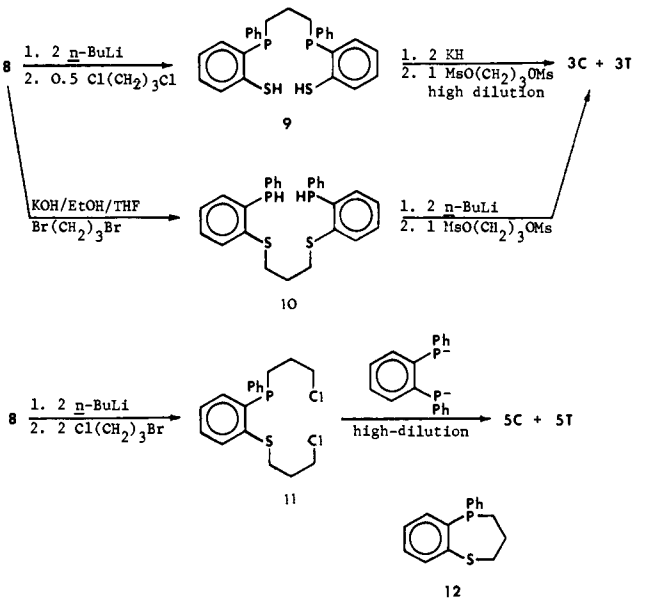
Synthesis of Ligands. The first problem to be faced in our approach to **3–5** was the synthesis of 2-(phenylphosphino)-benzenethiol (**8**), which was accomplished as shown in Scheme I.[5] This procedure allowed us to generate 50-g quantities of **8** conveniently.

Elaboration of **8** into ligands **3** and **5** was relatively straightforward, as shown in Scheme II. We utilized the much greater

Scheme I



Scheme II



nucleophilicity of a phosphide compared to a thiolate anion to selectively alkylate at phosphorus in the transformation of the dianion derived from **8** into **9**. The dipotassium salt derived from **9** was then reacted with 1,3-propanyl dimesylate under our high-dilution conditions[2b] to give **3** as a mixture of isomers. These were separated by chromatography on alumina to give **3C** (4%) and **3T** (34%) as colorless crystalline solids. See Table I for a summary of the physical properties of these ligands. We also investigated the alternative route in which **10** was generated selectively[5] and then macrocyclized in a manner similar to **9** to give **3C** and **3T** in 2 and 13% yields, respectively.

(1) Part 13 of the series "Phosphino Macrocycles". For part 12 see: Kyba, E. P.; Alexander, D. C.; Hohn, A. *Organometallics* **1982**, *1*, 1619.

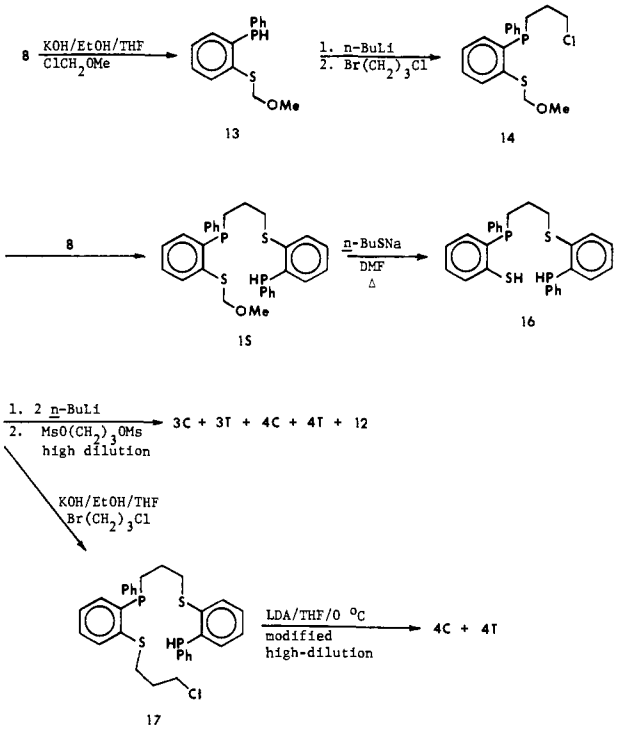
(2) (a) Kyba, E. P.; Davis, R. E.; Hudson, C. W.; John, A. M.; Brown, S. B.; McPhaul, M. J.; Liu, L.-K.; Glover, A. C. *J. Am. Chem. Soc.* **1981**, *22*, 1875. (b) Kyba, E. P.; Chou, S.-S. P. *J. Org. Chem.* **1981**, *46*, 860.

(3) Davis, R. E.; Kyba, E. P., unpublished results. The details of this structure will be published elsewhere.

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

(5) Kyba, E. P.; Clubb, C. N. *Inorg. Chem.*, in press. To our knowledge, the methoxymethyl ether has not been used as a protecting group for RSH, nor has the *n*-BuS^-/DMF method been used to remove this group.

Scheme III



Dialkylation of the dilithio salt of **8** with 1-bromo-3-chloropropane gave **11** along with a small amount of **12**. Species **11** was quite sensitive to degradation by phosphine quaternization and thus was generally not isolated but rather stored in THF solution at −20 °C until the high-dilution macrocyclization step,[2b] which gave **5** as a mixture of isomers. Separation of the isomers was effected by chromatography on alumina to give **5C** (4%) and **5T** (27%) as colorless crystals.

The synthesis of **4** (Scheme III) required considerably more strategy than those of **3** and **5**. The thiol was protected with chloromethyl methyl ether to give **13** in 76% yield.[5] The conditions used were crucial to effecting sulfur alkylation cleanly; when 1 equiv of *n*-BuLi was used instead of KOH/EtOH/THF, a mixture of products was obtained. Alkylation of the secondary phosphine in **13** was effected in high yield, using *n*-BuLi followed by 1-bromo-3-chloropropane to give **14**. The conditions for selective sulfur alkylation were then used to react **14** and **8** to give **15** in quantitative yield. It was because of this step that the sulfur protection (**13**) was carried out. Deprotection of the sulfur site was carried out in near quantitative yield by using *n*-butylthiolate in DMF to give **16**.[6] Upon macrocyclization of the dilithio salt of **16** with 1,3-propanyl dimesylate using our standard conditions,[2b] a mixture of two isomers of **4**, two isomers of **3** (major products), and **12** was obtained, as observed by ^{31}P NMR spectroscopy. A control experiment was carried out in which the dilithio salt of **16** was allowed to stand at room temperature in THF for 24 h. Examination of the resulting solution by ^{31}P NMR spectroscopy revealed a complex mixture with a ratio of **8**:**16**:**9** ≃ 1:1:3. This product distribution is based on peak heights and not calibrated for differences in relaxation times. Nonetheless, it was quite clear that this approach to **4** was not viable. We then synthesized **17** by using our standard conditions for selective sulfur alkylation. This species was very sensitive to degradation by alkylation and decomposed slowly in THF solution at room temperature. Workups such as removal of solvent greatly increased this decomposition rate. In general, we were unable to use **17** in macrocyclizations in a state of purity much higher than 60% as assessed by ^{31}P NMR. The transformation of **17** into **4** was effected in our high-dilution apparatus modified (see Experimental Section) such that **17** was added slowly to an excess of LDA at 0 °C. This procedure avoided the production of **3C**, **3T**, and **12** and gave **4**, albeit in apparently lower than usual yields; **4T** was obtained in 10–16% yields by crystallization from the crude reaction mixture and **4C** in 2–3% yields following chromatography on alumina. Since starting **17** was only about 50–60% pure prior to macrocyclization, the actual yields of **4C,T** were in the 30–35% range.

(6) Although **13** could be deprotected with 12 N HCl to give **8** in high yield, attempted deprotection of **15** to give **16** under similar conditions led to extensive degradation of **15** to products of unknown composition. It is also important to note that only highly purified DMF gave good results in the *n*-butyl thiolate deprotection.

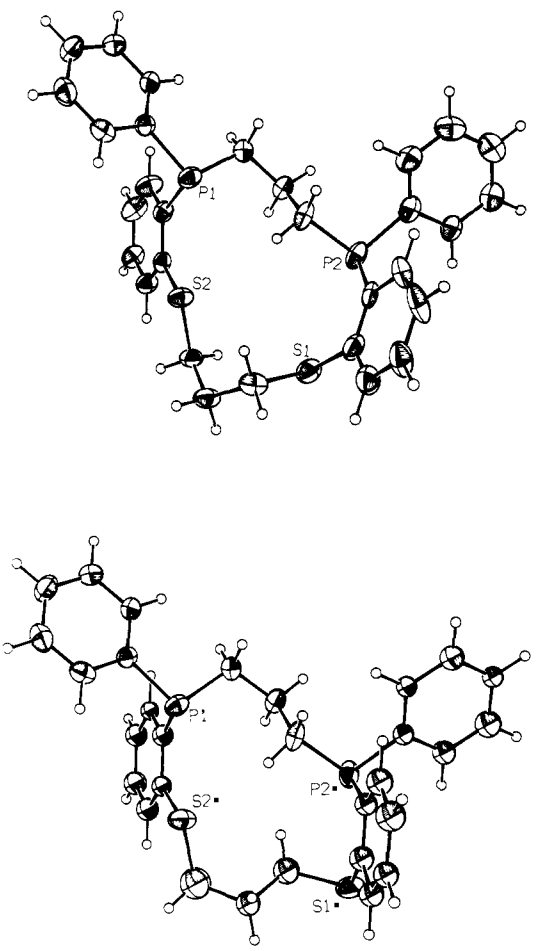


Figure 1. ORTEP plots of **3T**, with non-hydrogen atoms represented as 50% equiprobability ellipsoids. The atom numbering system is the same as that shown for the macrocycle in Figure 2 but with S1 and P2 (with its attached phenyl ring) interchanged: (a) the major conformation, **3TA**; (b) the minor conformation, **3TB**. Atoms unique to this conformation are identified by (*). Selected distances between ligating sites within the macrocycle for the major (a) [minor (b)] conformer in angstroms: P1···P2, 4.970 (2) [4.943 (4)]; P1···S1, 5.997 (2) [6.690 (4)]; P1···S2, 3.209 (2) [3.019 (4)]; P2···S1, 3.359 (2) [3.006 (6)]; P2···S2, 4.873 (2) [4.628 (6)]; S1···S2, 3.890 (2) [4.858 (6)].

Structures of the Macrocyclic Ligands. We have described in the literature the structures, determined by X-ray crystallography, of five 14-membered tetradentate cycles[2a] and five 11-membered tridentate rings.[7] In all cases, the benzo group is approximately perpendicular to the plane of the macrocycle as defined by the heteroatoms, the phenyl substituents occupy pseudoequatorial positions, and the heteroatom–$(CH_2)_3$–heteroatom′ strands exhibit a variety of conformations.

Of the pair of isomers **3C** and **3T** we have established unambiguously that **3T** is the chiral trans species. Figure 1 shows two ORTEP plots of an X-ray structure determination of **3T**. The crystal was disordered, with about 75% occupancy by one con-

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

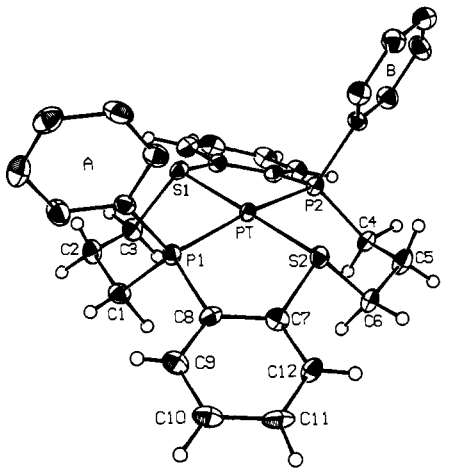
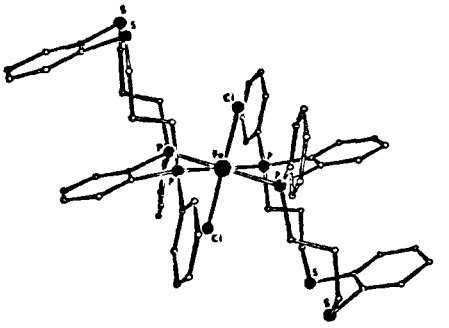


Figure 2. ORTEP plots of the dication of **18**, with non-hydrogen atoms represented as 30% equiprobability ellipsoids. The carbons of the benzo bridge spanning S1 and P2 are numbered C13–C18, with C13 bonded to S1 and C14 bonded to P2. Selected bond lengths in angstroms: P1–Pt, 2.297 (2); P2–Pt, 2.293 (2); S1–Pt, 2.296 (2); S2–Pt, 2.287 (2). Selected bond angles in degrees: P1–Pt–S2, 87.55 (8); P2–Pt–S1, 87.38 (8); P1–Pt–S1, 91.83 (8); P2–Pt–S2, 93.29 (8); P1–Pt–P2, 170.66 (8); S1–Pt–S2, 179.29 (8).

formation (Figure 1a, **3TA**) and 25% by a different conformation (Figure 1b, **3TB**). In both, it is clear that the phenyl groups are trans to each other and occupy pseudoequatorial positions, similar to all ten structures determined previously.[2a,7] The benzo groups are approximately perpendicular to the approximate plane defined by P1P2S1S2, as has been observed for **1a** (cis and trans) and **1c**.[2a] The two structures **3TA** and **3TB** differ primarily in the torsion angles of the chain $S1(CH_2)_3S2$: **3TA** [a,g,g,a], cf. **3TB** [g,a,g,a];[8] the former is different than any of the six conformations observed in the ten strands of the macrocycles determined previously.[2a] The $P1(CH_2)_3P2$ strands in both **3T** conformations are the same, [g,g,a,a], and are the same as those in the centrosymmetric structure of **1a** (trans).[2a] In order to confirm that **3C** and **3T** are isomers, each was shown to be transformed into an equilibrium mixture (ratio **3C**/**3T** = 3/7) upon heating in toluene at reflux for 3.0 h. Further heating did not change this ratio. We thus assign the configuration of isomer **3C** as that of *cis*-Ph_2.

We did not obtain crystals of X-ray quality for either isomer of **4**. Fortunately, however, our ongoing transition-metal complexation studies of these ligands has provided the configurations of **4C** and **4T**. The reaction of (1,5-cyclooctadiene)platinum dichloride with **4C** in ethanol/dichloromethane, followed by the addition of silver hexafluorophosphate, gave colorless crystals (**18**, eq 1) after workup, crystallization, and recrystallization from acetonitrile/benzene. This material featured ^{31}P NMR absorptions at δ 45.1 (J_{Pt-P} = 2150 Hz) and −107.5 (septet, J_{P-F} = 707 Hz). The result of an X-ray structure determination on **18** is shown as an ORTEP plot in Figure 2, which clearly establishes the *cis*-Ph_2 configuration. Both $SPtP(CH_2)_2CH_2$ rings adopt a chairlike conformation, and the metal is square planar, with virtually identical Pt–P and Pt–S bond lengths. We will postpone further discussion to a paper which deals with the complexation chemistry of these ligands with the metals of the Ni(II) triad. As with **3**, both **4C** and **4T** establish an equilibrium with each other upon heating at reflux in degassed toluene for 3.0 h (ratio **4C**/**4T** = 3/7). Based on the above data, we assign isomer **4T** as the *trans*-Ph_2 species.

Finally, we consider the stereochemistry of **5C** and **5T**, where we were also unable to obtain crystals of X-ray quality. Of the nine structures of phosphino macrocycles that we have determined[1,2a,7] where there was a question of the configuration of the 1,2-bis(phenylphosphino)benzene moiety, the meso–cis isomer was found without exception. We assume this to be true also with **5**, and thus the two isomers **5C** and **5T** are due to the configuration of the phosphorus atom on the thiophosphinobenzo moiety. At this point, we have three pairs of isomers of 14-membered tetradentate macrocycles whose isomerism arises from the relative configuration of phenylphosphino moieties on different benzo groups in the following cycles: **1a**(cis), **1a**(trans); **3C**,**T**; and **4C**,**T**. There are clear trends in the physical properties associated with these isomers, which are given in Table I. In general we find that the cis isomer, in comparison to its trans isomer, is formed in lower yield, has a lower melting point (if there is a difference), has a significantly lower TLC R_f value, exhibits a lower field ^{31}P NMR absorption, and shows a higher field CH_2S absorption in the ^1H NMR spectrum. Since isomer **5C** exactly matches all these characteristics, we assign it as the *cis*-Ph_2 isomer and **5T** as the trans species. As with the other macrocycles, **5C** and **5T** reach equilibrium in ca. 3.0 h in toluene at reflux (**5C**/**5T** = 3/7).



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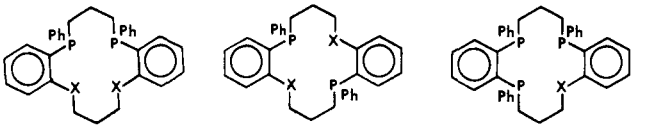


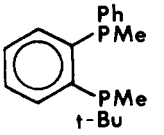
3 **4** **5**

The rather large $^3J_{P-P}$ = 165 Hz exhibited by **5C** deserves comment. There are very few vicinal dissymmetric diphosphines in the literature and even fewer whose ^{31}P NMR spectra have been reported. There are several which are linked by aliphatic carbon atoms whose three-bond phosphorus–phosphorus coupling constants are in the range 11–32 Hz.[9] There are no reports extant concerning the ^{31}P NMR spectra of dissymetric 1,2-diphosphinobenzenes. We have found recently, however, that with

$$\underset{4C}{} \xrightarrow[2.\ 2\ AgPF_6]{1.\ (1,5\text{-COD})PtCl_2} \underset{18}{[4C \cdot Pt](PF_6)_2} \qquad (1)$$

1-(phenylmethylphosphino)-2-*tert*-butylmethylphosphino)benzene (**19**), both diastereomers had $^3J_{P-P}$ = 160 Hz.[10] In light of these data, the apparently large $^3J_{P-P}$ for **5C** appears not unreasonable.

In summary, structures **20** (trans series) and **21** (cis series) represent the results of our structural determinations and deductions concerning the tetradentate P_4, P_3S, and P_2S_2 macrocycles. The trimethylene chains are symbolized with curved lines,



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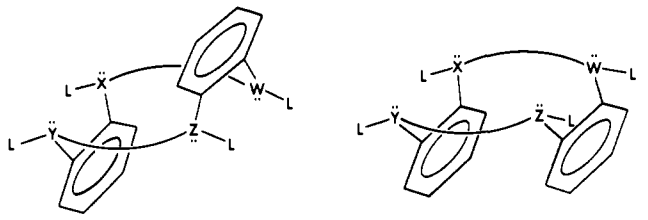
(8) As in ref 2a, the torsion angles ±(50–100°) are defined as gauche (g) and ±(145–180°) as anti (a). It is also assumed that +a ≃ −a and that the sign g is important only when measured against another g in the same strand. In fact, the conformations given are for the enantiomers of **3TA**,**B** shown in Figure 1.

(9) (a) Kyba, E. P.; Davis, R. E.; Juri, P. N.; Shirley, K. S. *Inorg. Chem.* **1981**, *20*, 3616. (b) King, R. B.; Bakos, J.; Hoff, C. D.; Marko, L. *J. Org. Chem.* **1979**, *44*, 1729. (c) King, R. B.; Bakos, J.; Hoff, C. D.; Marko, L. *Ibid.* **1979**, *44*, 3095.

(10) Kyba, E. P.; Kerby, M. C., Jr.; Rines, S. P., unpublished results.

and the benzo links are shown approximately perpendicular to the plane defined by the heteroatoms, as has been found for **1a**(trans), **1a**(cis), **1c**,[2a] and **3T** (two conformations, this work), as well as for a number of tridentate 11-membered rings.[7] We do not have direct evidence that the conformations for **4T**, **5T**, **3C**, **4C**, and **5C** are as shown, but as described above, the relative physical properties of the trans and cis series appear strongly indicative of such spacial arrangements.



20(trans) 21(cis)

1a(trans)[2a]	WL = XL = YL = ZL = PPh	1a(cis)[2a]
3T	WL = XL = PPh, YL = ZL = S	3C
4T	XL = ZL = PPh, WL = YL = S	4C
1c[2a]	XL = YL = PPh, WL = ZL = S	
5T	WL = XL = YL = PPh, ZL = S	5C

Prognosis for Coordination Chemistry. As stated in the introduction, the motivation for the synthesis of this new generation of macrocyclic ligands was to use a proximity effect (ortho substitution) to make heteroatoms which are poorer ligands than phosphines ligate a TM competitively. Structure **18** represents concrete evidence that this approach is viable. We are in the process of a study of the properties of complexes of the ligands reported here with the metals of the Ni(II) triad, in which we have found that the modifying heteroatom is indeed coordinated to the TM with ligands **3**–**5**. These studies will be described in a future publication.

Experimental Section

General Information. Proton magnetic resonance spectra were obtained on a Varian EM-390 or a Varian FT-80 spectrometer. Carbon-13 and proton-decoupled phosphorus-31 NMR spectra were determined on a Varian FT-80 spectrometer at 20.1 and 32.4 MHz, respectively. Unless otherwise stated, $CDCl_3$ solutions were used for the NMR spectroscopy. Chemical shifts are given in parts per million relative to Me_4Si for ^{13}C, and 85% H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield of the standard are defined as negative.

Infrared spectra (IR) were recorded on a Perkin-Elmer 298 grating spectrophotometer.

Mass spectra (MS or HRMS) were determined on a CEC-21-100 high-resolution instrument or a Du Pont 21-491 instrument at 70 eV.

Unless noted, all 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 aspiration pressures unless otherwise noted. Solutions were dried with anhydrous magnesium sulfate.

The phosphinothiol **8**,[5] thiomethyl methyl ether **13**,[5] and 1,2-bis(phenylphosphino)benzene[2a] were prepared as described previously.

Modified High-Dilution Apparatus. The apparatus illustrated in Figure 3 and described below is a modification of one described previously.[2b] Complete details of the types of materials and connections are given in that paper. The modified apparatus is designed to effect the high dilution at temperatures below that of the solvent under reflux and is effective only if the reaction to be carried out is very rapid. The following is a description of the operation of the apparatus.

A is a 3-L, round-bottom 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.

B is a 65-cm distillation column, insulated with glass wool and aluminum foil, which is attached to a double-surface condenser fitted with a mercury bubbler. The latter two are not shown.

C is a solvent takeoff tube.

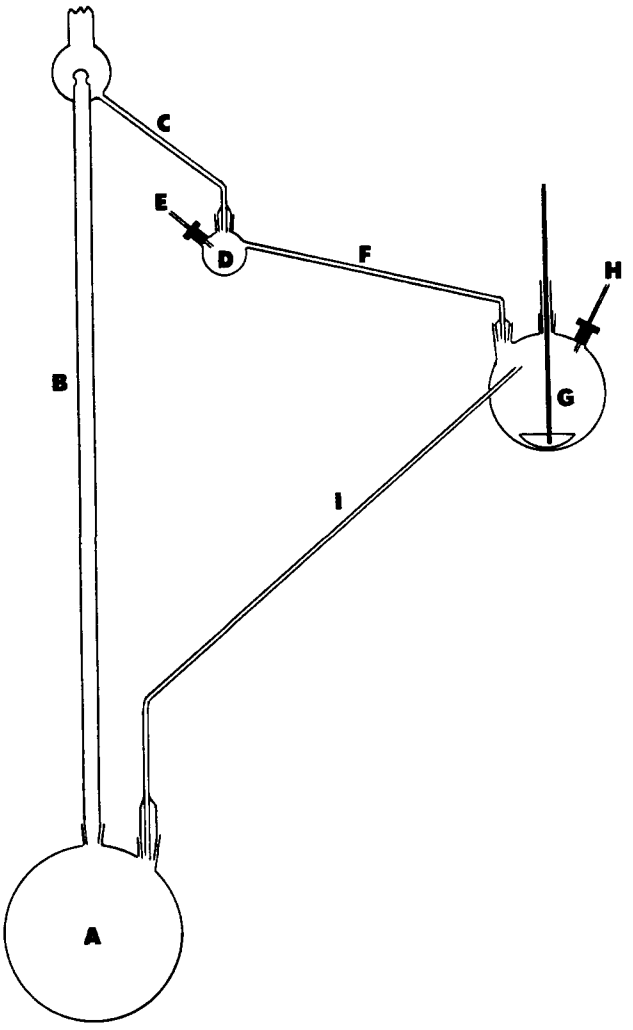


Figure 3. Modified high-dilution apparatus which allows reaction at temperatures below those of the solvent under reflux.

D is the macrocycle precursor (e.g., **17**) dilution chamber, fashioned from a 100-mL round-bottom flask and equipped with a magnetic stirring bar and stirrer.

E is a thick-walled (0.8-mm, 1.6-mm i.d.) Teflon tube attached to D and to a 250-mL syringe[7] via Ace Glass No. 7 "Mini" Ace-Thred adapters. The syringe 1 contains a solution of macrocycle precursor.

F is the overflow takeoff which feeds the diluted macrocycle precursor into G.

G is a 1-L round-bottom flask (reaction chamber) equipped with an overhead mechanical stirrer (Ace Trubore). It is surrounded (not shown) by a coolant (ethanol) in an insulated container and cooled by a FTS Flexi-cool Immersion Refrigeration Unit.

H is as E, a thick-walled Teflon tube attached to syringe 2, which contains a solution of LDA in THF at a concentration 5 times that of macrocycle precursor.

I is an overflow takeoff tube which delivers the reaction solution back to A.

The reaction is carried out as follows. Flask A is charged with ca. 2 L of purified ether, and the flask is heated with the mantle such that about 2 L/h pass through C. When the system has equilibrated, the syringe pump[7] is activated so as to deliver one drop of reactant solution every 6–8 s. This rate effects the complete addition of 250 mL in ca. 24 h.

1,3-Bis((2′,2″-thiophenyl)phenylphosphino)propane (9). The dianion of **8** was prepared by addition of a 2.80 M hexane solution of *n*-BuLi (78 mL, 218 mmol) to **8** (22.79 g, 104.5 mmol) in ether (300 mL) at −78 °C. To this solution was added 1,3-dichloropropane (4.95 mL, 52.1 mmol) and then warmed to room temperature. The mixture was quenched with 8% aqueous ammonium chloride (150 mL). The ether solution was removed and the aqueous solution extracted with dichloromethane (3 × 100 mL). The combined ether and dichloromethane extracts were dried and concentrated to leave a pale green gum (24.99 g). This was boiled at reflux in acetone and chilled to give **9** as a white powder (15.04 g, 60.5%); mp 122–124 °C; ^{31}P NMR δ −26.4; ^1H NMR δ 7.2 (m, 18 H),

4.23 (s, 2 H), 2.13 (m, 4 H), 1.63 (m, 2 H); ^{13}C NMR (partial) δ 28.6 (t, J = 13 Hz), 22.1 (t, J = 17 Hz); HRMS, m/e 476.095 91 (calcd 476.095 11).

The remaining crude material gave additional **9** (2.9 g, 90% pure) from acetone after being passed through an alumina filtration column using ethyl acetate.

1,3-Bis(2-(phenylphosphino)-1-thiophenyl)propane (10). To **8** (12.74 g, 58.4 mmol) and KOH (5.27 g, 94.0 mmol) in absolute ethanol (150 mL) and THF (150 mL) at −78 °C was added 1,3-dibromopropane (5.90 g, 29.3 mmol). The resulting solution was stirred for 1 h and concentrated. Water (100 mL) was added and extracted with ether (3 × 100 mL). The ether extracts were dried and concentrated to leave **10** as a beige oil (12.82 g, 92%); ^{31}P NMR δ −47.7; ^{1}H NMR δ 7.0–7.7 (m, 18 H), 5.25 (d, J = 224 Hz, 2 H), 2.90 (t, J = 7 Hz, 4 H), 1.80 (quintet, J = 7 Hz, 2 H); ^{13}C NMR (partial) δ 33.6 (d, J = 3.4 Hz), 28.0 (s); HRMS m/e 476.0966 (calcd 476.0951).

***trans*- and *cis*-13,17-Diphenyl-13,17-diphospha-2,6-dithiatricyclo[16.4.0.0^{7,12}]docosa-7(12),8,10,1(18),19,21-hexaene (3T and 3C). Method A.** The dithiol anion was prepared by adding dithiol **9** (17.82 g, 37.4 mmol) in THF (100 mL) to KH (9.0 g, 35% dispersion in mineral oil, 78.5 mmol) in THF (50 mL) at 0 °C. This was then diluted with THF (250 mL total volume) and reacted with 1,3-propanyl dimesylate under high dilution conditions[2b] (37 h addition time). The reaction mixture was concentrated and partitioned between water (150 mL) and dichloromethane (500 mL). The separated dichloromethane extract was dried, filtered through celite, and concentrated to give a beige oil (25.5 g). This was chromatographed on alumina (500 g) with hexane–dichloromethane (7:3, v/v) followed by hexane–dichloromethane (1:1, v/v) to give two white solids. The more chromatographically mobile solid was crystallized from ethtyl acetate to give **3T** as colorless crystals (6.52 g, 33.6%): mp 155–157 °C; ^{31}P NMR δ −27.6; ^{1}H NMR δ 7.27 (m, 14 H), 7.1 (m, 4 H), 3.15 (m, 4 H), 2.1 (m, 8 H); HRMS, m/e 516.1271 (calcd 516.1264).

Anal. Calcd. for $C_{30}H_{30}P_2S_2$: C, 69.74; H, 5.85. Found: C, 69.55; H, 5.92.

The less chromatographically mobile solid was crystallized from ethyl acetate to give **3C** as colorless crystals (722 mg, 3.7%); mp 127–129 °C; ^{31}P NMR δ −25.0; ^{1}H NMR δ 6.70–7.80 (m, 18 H), 3.00 (m, 4 H) 2.17 (m, 4 H), 1.80 (m, 4 H); HRMS, m/e 516.1281 (calcd 516.1264).

Anal. Calcd for $C_{30}H_{30}P_2S_2$: C, 69.74; H, 5.85. Found: C, 70.01; H, 5.67.

Method B. The diphosphide of **10** in THF (150 mL) prepared from **10** (12.74 g, 26.8 mmol) and *n*-BuLi (27 mmol) was reacted under high dilution conditions[2b] with 1,3-propanyl dimesylate (6.23 g, 26.8 mmol) in THF (150 mL). After the resulting solution was concentrated, water (200 mL) was added and extracted with ether (3 × 200 mL). The ether extracts were dried and concentrated to leave a sticky gum (8.0 g). The aqueous solution was then extracted with dichloromethane (3 × 150 mL). The dichloromethane extracts were dried and concentrated to leave a beige gum (5.7 g). The ether and dichloromethane extracts were each chromatographed as described in method A to give **3T** (1.74 g, 12.6%) and **3C** (0.23 g, 1.7%) upon crystallization, with identical physical and spectral properties as the materials obtained by method A. Crystals of **3T** suitable for an X-ray crystal structure analysis were obtained from ethyl acetate.

A significant amount of **12** (ca. 6%) was obtained as observed by ^{31}P NMR. In another reaction, this material was obtained as a white crystalline solid: mp 66–68 °C; ^{31}P NMR δ −14.0; ^{1}H NMR δ 7.45 (m, 6 H), 7.01 (m, 2 H), 6.60 (m, 1 H), 3.00 (m, 1 H), 2.80–1.70 (m, 5 H); HRMS, m/e 258.0636 (calcd 258.0632).

2-((3′-Chloropropyl)phenylphosphino)-1-((3″-chloropropyl)thio)benzene (11). The dianion of **8** was prepared by addition of a 1.80 M hexane solution of *n*-BuLi (73 mL, 131.0 mmol) to **8** (14.25 g, 65.4 mmol) in THF (350 mL) at −78 °C. A THF solution (50 mL) of 1-bromo-3-chloropropane (12.9 mL, 130.4 mmol) at −78 °C was added to the dianion solution and the resulting solution warmed to room temperature. This was then stored at −20 °C with no further purification to minimize loss due to quaternization: ^{31}P NMR (THF/D_2O insert) δ −13.9, −26.9, −27.2, −27.6 (peak height ratio 1:18:1:1). In a previous run, the crude **11** was obtained as a yellow oil and the following data were obtained: ^{1}H NMR δ 7.27 (m, 9 H), 3.50 (t, J = 6 Hz, 2 H), 3.47 (t, J = 6 Hz, 2 H), 2.90 (t, J = 7 Hz, 2 H), 2.0 (m, 6 H); ^{13}C NMR (partial) 45.7 (d, J = 15 Hz), 43.3 (d, J = 2 Hz), 31.7 (d, J = 7.3 Hz), 31.4 (s), 29.0 (d, J = 19 Hz), 24.9 (d, J = 13 Hz); mass spectrum, m/e 370 (M^+ for ^{35}Cl–^{35}Cl, less than 3% of base peak), 230 (base peak).

***cis,cis*- and *cis,trans*-6,13,17-Triphenyl-6,13,17-triphospha-2-thiatricyclo[16.4.0.0^{7,12}]docosa-7(12),8,10,1(18),19,21-hexaene (5C and 5T).** The diphosphide of 1,2-bis(phenylphosphino)benzene prepared from the corresponding diphosphine (19.2 g, 65.3 mmol) and a 1.80 M hexane solution of *n*-BuLi (73 mL, 131.0 mmol) at −78 °C in THF (400 mL) was reacted with the solution of **11** under high dilution conditions[2b] (addition time 78 h). The resulting solution was concentrated and partitioned between ether (400 mL) and water (300 mL). The ether was separated and the aqueous layer extracted with another portion of ether (300 mL). The combined ether extracts were dried and concentrated to give a beige gum (35.0 g). This was dissolved in hot acetone and cooled to give **5T** as a white powder (7.66 g). Concentration of the acetone and cooling gave additional **5T** (2.52 g). The combined powders were recrystallized from THF to give a white solid (8.48 g, 22%): mp 162–164 °C; ^{31}P NMR δ −28.5 (m); ^{1}H NMR δ 7.50 (m, 23 H), 3.50 (m, 1 H), 2.95 (m, 1 H), 2.25 (m, 5 H), 1.80 (m, 5 H); HRMS, m/e 592.1658 (calcd 592.1672).

Anal. Calcd for $C_{36}H_{35}P_3S$: C, 72.96; H, 5.95. Found: C, 72.71; H, 5.96.

The remaining crude product was chromatographed on alumina (375 g) initially by using hexane–dichloromethane (7:3, v/v) to elute the remaining **5T**. Crystallization from acetone gave more **5T** (1.91 g, total yield 27%). Dichloromethane was used to elute the remaining material. Further elution gave a white solid from one fraction which was recrystallized from acetone to give **5C** as a white microcrystalline solid (0.58 g): mp 150–152 °C; ^{31}P NMR δ −24.1 (P_A, d, J_{AC} = 3 Hz), −24.1 (P_B, d, J_{BC} = 165 Hz), −27.0 (P_C, dd, J_{AC} = 3, J_{BC} = 165 Hz), ν_{BC} = 2.9 ppm, the coupling constants were confirmed by using a different field strength NMR, (computer simulation using these parameters gave an identical spectrum); ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 23 H), 3.05 (m, 1 H), 2.25 and 1.75 (m, 11 H); HRMS, m/e 592.1663 (calcd 592.1672).

Anal. Calcd for $C_{36}H_{35}P_3S$: C, 72.96; H, 5.95. Found: C, 73.13; H, 6.07.

Continued elution gave impure **5C** (3.1 g), which was rechromatographed on silica gel (1460 g) by using hexane–ethyl acetate (1:19) to give a white solid. This was recrystallized from acetone to give additional **5C** (1.47 g, total yield, 5%).

((2-((3′-Chloropropyl)phenylphosphino)phenyl)thio)methyl Methyl Ether (14). The anion of **13** was prepared by addition of a 2.64 M hexane solution of *n*-BuLi (29 mL, 76.6 mmol) to **13** (19.68 g, 75.1 mmol) in THF (400 mL) at −78 °C. 1-Bromo-3-chloropropane (8.0 mL, 74.8 mmol) in THF (100 mL) at −78 °C was added to the phosphide solution and the resulting mixture warmed to room temperature. This was concentrated and partitioned between water (100 mL) and ether (150 mL). The ether layer was separated and the aqueous layer extracted with ether (2 × 150 mL). The combined ether extracts were dried and concentrated to leave **14** as a cream oil (24.45 g, 96%): ^{31}P NMR δ −26.4, −26.5 (peak height ratio 13:1); ^{1}H NMR δ 7.1–7.7 (m, 9 H), 4.8 (s, 2 H), 3.5 (t, J = 6 Hz, 2 H), 3.3 (s, 3 H), 1.7–2.3 (m, 4 H); ^{13}C NMR (partial) δ 77.4 (d, J = 8 Hz), 55.8 (s), 45.5 (d, J = 15 Hz), 28.9 (d, J = 19 Hz), 24.7 (d, J = 13 Hz); HRMS, m/e 338.065 20 (calcd 338.066 10).

((2-([3′-(1″-Thio-2″-(phenylphosphino)phenyl)propyl]phenylphosphino)phenyl)thio)methyl Methyl Ether (15). A mixture of **8** (17.5 g, 78.9 mmol) and potassium hydroxide (6.4 g, 114.0 mmol) in 95% ethanol (150 mL) and THF (150 mL) was added to **14** (24.39 g, 72.0 mmol) and stirred at room temperature for 106 h. This was concentrated and partitioned between water (150 mL) and ether (150 mL). The ether layer was separated and the aqueous layer extracted with ether (2 × 150 mL). The combined ether extracts were dried and concentrated to leave **15** as a slightly yellow oil (37.9 g, 101%); ^{31}P NMR δ −26.1, −47.6, −47.8 (peak height ratio 12:1:13); ^{1}H NMR δ 6.9–8.0 (m, 18 H), 5.27 (d, J = 222 Hz, 1 H), 4.75 (s, 2 H), 3.28 (s, 3 H), 2.93 (t, J = 6 Hz, 2 H), 1.5–2.3 (m, 4 H); ^{13}C NMR (partial) δ 77.3 (s), 55.5 (s), 35.4 (m), 25.4 (m, 2 C); HRMS, m/e 520.122 269 (calcd 520.121 32).

2-([3′-(1″-Thio-2″-(phenylphosphino)phenyl)propyl]phenylphosphino)thiobenzene (16). Sodium butylthiolate (64.8 g, 579.0 mmol) in DMF (570 mL) which had been purified by stirring with potassium hydroxide and distillation from calcium oxide was added to **15** (37.72 g, 72.5 mmol) to produce a red solution. It was essential that the DMF be purified to eliminate decomposition. The DMF solution was stirred at 80 °C for 9 h before being quenched with 25% aqueous ammonium chloride (125 mL) and concentrated by using a rotary evaporator under a high vacuum. Water (250 mL) was added and extracted with dichloromethane (3 × 200 mL). The combined dichloromethane extracts were dried and concentrated to give **16** as a green oil (35.3 g, 102%): ^{31}P NMR δ −25.7, −25.9, −46.6, −47.3, −47.6 (^{1}H-coupled, d, J = 220 Hz), (peak height ratio 1:13:1:1:13); ^{1}H NMR δ 6.6–7.9 (m, 18 H), 5.27 (d, J = 222 Hz, 1 H), 4.20 (br s, 1 H), 2.92 (t, J = 7 Hz, 2 H), 2.03 (m, 2 H), 1.70, (m, 2 H); ^{13}C NMR (partial) δ 36.0 (dd, J = 14 Hz, 4 Hz), 26.6 (d, J = 12 Hz), 25.1 (d, J = 18 Hz); HRMS, m/e 476.093 80 (calcd 476.095 11).

2-([3′-(1″-Thio-2″-(phenylphosphino)phenyl)propyl]phenylphosphino)-1-((3‴-chloropropyl)thio)benzene (17). 1-Bromo-3-chloropropane (7.8 mL, 78.9 mmol) was added with stirring to **16** (349 g, 73.0

Table II. Crystallographic Summary for **3T** and **18**·C_6H_6

	3T	**18**·C_6H_6
	A. Crystal Data (−110 °C)[a]	
a, Å	13.4358 (22)	12.629 (5)
b, Å	14.2137 (14)	15.304 (3)
c, Å	14.0314 (21)	20.714 (6)
β, deg	93.903 (11)	104.76 (4)
V, Å^3	2673.4 (7)	3871.4 (22)
d_{measd}, g cm^{-3} (21 °C)[a]	1.260	1.766
d_{calcd}, g cm^{-3} (−110 °C)	1.284	1.852
empirical formula	$C_{30}H_{30}P_2S_2$	$C_{30}H_{30}P_2S_2{\cdot}Pt{\cdot}(PF_6)_2{\cdot}C_6H_6$
fw	516.63	1079.6
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
Z	4	4
F(000), electrons	1088	2120
	B. Data Collection (−110 °C)[b]	
radiation λ, Å	Mo Kα, 0.71069	
mode	ω scan	
scan range	symmetrically over 1.0° about $K\alpha_{1,2}$ maximum	
background	offset 1.0 and −1.0° in ω from $K\alpha_{1,2}$ maximum	
scan rate, deg min^{-1}	1.5–5.0	3.0–6.0
exposure time, h	151.6	120.0
stability analysis		
computed s	−0.00020 (10)	0.00005 (4)
computed t	0.000002 (1)	−0.000001 (1)
correction range (on I)	0.984–1.005	0.994–1.004
2θ range, deg	4.0–55.0	4.0–55.0
range in hkl		
min	0,0,−18	0,0,−26
max	17,18,18	16,19,26
total reflections measd	6398	8889
data crystal vol, mm^3	0.0201	0.00482
data crystal faces	011;0$\bar{1}\bar{1}$;{11$\bar{1}$};{110} {100};2$\bar{1}$0;$\bar{2}$10;0$\bar{1}$0	{11$\bar{1}$};{100};1$\bar{1}$1;$\bar{1}$1$\bar{1}$
absorption coeff, μ(Mo Kα), cm^{-1}	3.324	10.03
transmission factor range	0.902–0.958	0.847–0.929
	C. Structure Refinement[c]	
ignorance factor p	0.04	0.02
reflections used, m ($F \geq n\sigma_F$)	3383, 6.0	6061, 4.0
no. of variables, n	364	586
goodness of fit, S	1.53	1.40
R, R_w	0.0520, 0.0567	0.0530, 0.0437
R for all data	0.1036	0.0921
max shift/esd	0.305	0.150
max peak in diff map, e Å^{-3}	0.83	1.53
min density in diff map, e Å^{-3}	−0.33	−1.68

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 45 reflections in the ranges $17.9° < 2\theta < 23.5°$ for 3T and $17.6° < 2\theta < 19.9°$ for **18**·C_6H_6. Crystal density was measured by flotation in aqueous $ZnCl_2$. For **18**·C_6H_6 the data crystal was freshly prepared, but the crystal later used to measure density had become somewhat cloudy; presumably this cloudiness is a result of partial loss of benzene of solvation, the presence of which was not known at the beginning of the study. [b] Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described in: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* **1976**, *32*, 381. Crystal and instrument stability were monitored by remeasurement of 4 check reflections after every 96 reflections. These data were analyzed as detailed in: Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B* **1975**, *31*, 1511. [c] Relevant expressions are as follows, where in this footnote F_o and F_c represent, respectively, the observed and calculated structure factor amplitudes. Function minimized was $\sum w(F_o - F_c)^2$, where $w = \sigma_F^{-2}$, $R = \sum \mathrm{abs}(F_o - F_c)/\sum F_o$. $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. $S = [\sum w(F_o - F_c)^2/(m - n)]^{1/2}$.

mmol) and KOH (9.2 g, 160.0 mmol) in THF (100 mL) and 95% ethanol (100 mL) at −78 °C. This solution was warmed to room temperature and concentrated. Water (350 mL) was added and extracted with dichloromethane (3 × 150 mL). The combined dichloromethane extracts were dried and concentrated to leave **17** as a yellow–green oil (39.5 g): ^{31}P NMR δ +30.9, −26.8, −47.1, −47.6, −47.9 (peak height ratio 5:13:2:3:13); ^1H NMR δ 7.26 (m, 18 H), 5.30 (d, J = 222 Hz, 1 H), 3.48 (t, J = 6 Hz, 2 H), 2.97 (m, 4 H), 1.40–2.30 H (m, 6 H). Mass spectrum shows no molecular ion. No further purification was done as this material undergoes quaternization quite readily. Other runs in which great care was used also resulted in decomposition.

***cis*- and *trans*-6,17-Diphenyl-6,17-diphospha-2,13-dithiatricyclo[16.4.0.0^{7,12}]docosa-7(12),8,10,1(18),19,21-hexaene (4C and 4T).** A solution of crude **17** (5.4 g) in THF (80 mL) and a solution of lithium diisopropylamide [prepared from diisopropylamine (6.8 mL, 48.5 mmol) and a 2.84 M hexane solution of *n*-BuLi (18.4 mL, 48.6 mmol) in hexane (80 mL)] were added dropwise to the modified high-dilution apparatus described above (addition time, 14 h; reflux rate, 30 L/24 h). The reaction solution was quenched with water (1 mL) and concentrated. Water (100 mL) was added and extracted with dichloromethane (3 × 75 mL). The combined dichloromethane extracts were dried and concentrated. Acetone (40 mL) was added and the resulting white solid (1.06 g) filtered. This was crystallized from chloroform to yield 4T as white crystals (502 mg, 10%); mp 202–206 °C; ^{31}P NMR δ −26.0; ^1H NMR δ 6.7–7.1 (m, 18 H), 3.35 (m, 2 H), 2.90 (m, 2 H), 1.50–2.60 (m, 8 H); HRMS, m/e 516.1250 (calcd 516.1264).

Anal. Calcd for $C_{30}H_{30}P_2S_2$: C, 69.74; H, 5.85. Found: C, 69.61; H, 5.91.

The remaining material was chromatographed on alumina (122 g) initially by using hexane–dichloromethane (1:1, v/v) followed by dichloromethane. The dichloromethane eluted an oil which gave 4C as a microcrystalline white solid (97 mg, 1.9%) from THF–ethanol: mp 201–206 °C; ^{31}P NMR δ −22.4; ^1H NMR δ 6.7–7.7 (m, 18 H), 3.10 (m, 4 H), 2.35 (m, 4 H), 1.75 (m, 4 H); HRMS, m/e 516.1255 (calcd. 516.1264).

Anal. Calcd for $C_{30}H_{30}P_2S_2$: C, 69.74; H, 5.85. Found: C, 69.50; H, 6.00.

In another reaction run the relative amount of **17** to quaternized material was evaluated by the integration of the ^{31}P NMR spectrum. This showed that only 55% of **17** was available for macrocycle formation.

In this run **4T** was obtained as a white powder in 16% yield which corresponds to a 28% yield based upon the amount of **17** available for reaction. This yield is in the range of other macrocycle synthesis yields.

(*cis*-6,17-Diphenyl-6,17-diphospha-2,13-dithiatricyclo[16.4.0.0^{7,12}]docosa-7(12),8,10,1(18),19,21-hexaene-κ^2S,κ^2P)platinum(II) Dihexafluorophosphate (18).[11] Silver hexafluorophosphate (163.8 mg, 0.648 mmol) was added to a solution of the macrocycle **4C** (165.4 mg, 0.320 mmol) and (1,5-cyclooctadiene)platinum dichloride (120.2 mg, 0.321 mmol) in ethanol (8 mL) and dichloromethane (9 mL). This was concentrated and extracted with acetonitrile (20 mL). The acetonitrile was filtered through celite and concentrated. The resulting solid was crystallized and recrystallized from acetonitrile/benzene (ca. 1:1, v/v) to give colorless crystals (57.1 mg, 17%); ^{1}H NMR (CD_3CN) δ 7.40–8.30 (m, 18 H), 7.37 (s, 6 H); ^{31}P NMR (CD_3CN) δ 45.1 (J_{Pt-P} = 2150 Hz), −107.5 (septet, J_{P-F} = 707 Hz). The crystalline solid was dried at 80 °C for 1 h under high vacuum before combustion analysis.

Anal. Calcd for $C_{30}H_{30}PtF_{12}P_4S_2$: C, 35.97; H 3.02. Found: C, 35.81; H, 3.20.

Thermal Equilibration of 3C, 3T, 4C, 4T, 5C, and 5T. The following procedure was used for each of the macrocycle isomers. Macrocycle **4C** (20.0 mg) was heated in toluene (2 mL) under reflux for 3.0 h. The toluene was removed under high vacuum. The ^{31}P NMR spectrum ($CDCl_3$) exhibited two singlets at δ −22.4 and −26.0 in an area ratio of 3:7. No further change was observed with further heating. Similarly, **4T** gave a ^{31}P NMR spectrum which exhibited two singlets at δ −22.4 and −26.0 in an area ratio of 3:7.

The ratio of **3C**:**3T** upon thermal equilibration of either isomer was 3:7 as was the ratio of **5C**:**5T**.

Crystallographic Analysis. General Comments. Crystals were grown by evaporation from ethyl acetate (**3T** as colorless flat hexagonal plates) or CH_3CN/benzene (**18**·C_6H_6 as colorless elongated prisms). For each compound, a 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 cold (−110 °C) stream of dry nitrogen for the duration of the diffraction experiments. Preliminary diffraction studies allowed determination of crystal symmetry and verification of the suitable quality of the crystals for intensity data collection. A summary of the pertinent crystal data and details of the X-ray diffraction data collection and processing is presented in Table II. The measured intensities were reduced and assigned standard deviations as described elsewhere,[12] including corrections for absorption based on measured crystal shape.

Solution and Refinement of the Structures.[13] The structures were solved by the heavy atom method, using heavy atom positions determined from a sharpened Patterson map. All structures were refined by the full-matrix least-squares method, using the program SHELX-76. Neutral atom scattering factors[14] for H, C, O, P, S, and Pt were used, including real and imaginary corrections for anomalous dispersion. In each structure, phenyl rings were treated as rigid groups, constrained with C–C = 1.395 Å, C–H = 1.00 Å, and C–C–C = C–C–H = 120°. Other non-H atoms were refined anisotropically and H atoms isotropically, except as noted below. For each structure, refinement was continued until shifts in all parameters were less than one estimated standard deviation in the respective parameter.

In the structure solution of **3**, early difference density maps showed multiple peaks for all atoms except one P and its phenyl ring and the trimethylene chain attached to it, indicating severe disorder. The occupancy ratio of the two conformers is 75:25, determined by refinement of the occupancies with thermal parameters fixed. Only H atoms on phenyl ring 1 were observed in a difference density map; hence, H atoms were placed at ideal positions and allowed to ride on their carbons. Non-hydrogen atoms of the major conformation were treated anisotropically, while only the heteroatoms and those atoms of the minor form in common with the major form were treated anisotropically. Benzo bridges were fixed as rigid groups, as described above for phenyl groups. Thermal parameters for hydrogen atoms of the major form were varied, but thermal parameters for hydrogen atoms of the minor form not in common with the major form were set to 1.0 × U(C) for the trimethylene bridge and 1.5 × U(C) for the phenyl rings and benzo bridges. The major and minor conformations were refined in alternate cycles of the least-squares calculations, 307 and 165 parameters, respectively.

After location and partial refinement of the atoms of **18**·C_6H_6, a difference density map clearly showed one benzene molecule of solvation per asymmetric unit. In the structure refinement, only the phenyl rings were treated as rigid groups. All non-hydrogen atoms, including those of the rigid phenyl groups, were refined anisotropically, and isotropic thermal parameters were refined for all hydrogens. Because of the large total number of parameters refined, the refinement was carried out in blocks with refinement of the cation (382 parameters) and refinement of the two PF_6^- and the solvent benzene in alternate cycles (205 parameters).

Further details of the refinements appear in Table II. Observed and calculated structure amplitudes, final crystallographic coordinates and thermal parameters, full tables of bond lengths, bond angles and selected torsion angles, and selected least-squares planes are available.[15]

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Registry No. 3c, 94890-87-6; **3T**, 94890-88-7; **4C**, 94890-89-8; **4T**, 94890-90-1; **5C**, 94890-91-2; **5T**, 94942-82-2; **8**, 93383-27-8; **9**, 94890-92-3; **10**, 94890-93-4; **11**, 94890-94-5; **12**, 94890-95-6; **13**, 94890-96-7; **14**, 94890-97-8; **15**, 94890-98-9; **16**, 94904-40-2; **17**, 94890-99-0; **18**, 94904-42-4; **18**·C_6H_6, 94904-43-5; 1,3-dichloropropane, 142-28-9; 1,3-dibromopropane, 109-64-8; 1-bromo-3-chloropropane, 109-70-6; 1,3-propane dimesylate, 15886-84-7; 1,2-bis(phenylphosphino)benzene, 38023-29-9; sodium butylthiolate, 4779-86-6; silver hexafluorophosphate, 26042-63-7; (1,5-cyclooctadiene)platinum dichloride, 12080-32-9.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, fractional crystallographic coordinates, thermal parameters, full listings of bond lengths and angles, selected torsion angles, and selected least-squares planes (95 pages). Ordering information is given on any current masthead.

(11) For a description of the "κ" nomenclature, see: Sloan, T. E.; Busch, D. H. *Inorg. Chem.* **1978**, *17*, 2043.

(12) Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* **1976**, *32*, 381.

(13) Principal computer programs: least-squares lattice parameters, LSLAT by K. N. Trueblood; absorption correction, SYABS, a local version of ORABS by W. R. Busing and H. A. Levy as modified by J. M. Williams; full-matrix least-squares and Fourier calculations, SHELX-76 by G. M. Sheldrick; least-squares planes, PLANE by A. W. Cordes; thermal ellipsoid plots, ORTEP-II by C. K. Johnson. Various data processing programs of local origin, including: statistical analysis of check reflections, SYSTD by T.-H. Hseu; data reduction, INCON by R. E. Davis; preparation of computer-typed tables of atomic parameters, bond lengths, bond angles, and torsion angles for publication, FUER by S. B. Larson; listing of structure factor amplitudes, XLFC by S. B. Larson.

(14) Scattering factors for H, C, O, S, and P were used as programmed in SHELX-76. Values for Pt were obtained from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(15) See note at the end of the paper regarding availability of supplementary material.