3306 *J. Am. Chem. Soc.* **1994,** *116,* 3306-3311

Tetraphosphorus Macrocycles from Phosphole Tetramers

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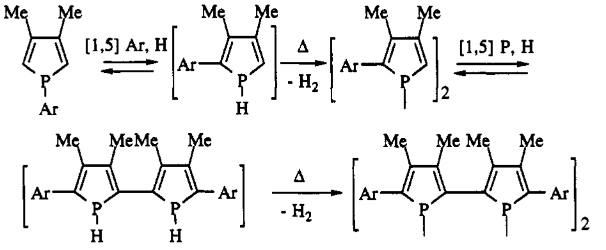
Received November 1, 1993®

Abstract: The phosphole tetramer **1**, obtained by pyrolysis of 1-phenyl-3,4-dimethylphosphole, incorporates two 2,2′-biphospholyl units linked by two P–P bonds. It is possible to cleave one or both of these bonds by naphthalene sodium in THF to yield two dianions, **2** and **4**. The reaction of **2** or **4** with dibromomethane gives either a 1,3,6,8-tetraphosphecane **5** or a 1,2,5,7-tetraphosphonane **7** in 45 and 80% yield, respectively. The reaction of **2** with tetrachloroethylene takes an unexpected course with the formation of a 1,2,5,8-tetraphosphacyclodec-6-yne **6**, whose structure was determined by X-ray analysis. The reaction of **4** with 1,4-dibromobutane affords, in 80% yield, a 1,2,5,10-tetraphosphacyclododecane **8**, whose P–P bond can be selectively cleaved by naphthalene–sodium in THF at low temperature to give further dianion **10**. In turn, **10** reacts with dibromomethane or 1,4-dibromobutane to yield the expected 13- and 16-membered macrocycles **11** and **12**. Since the phosphorus atoms of these macrocycles are all included in phosphole rings, they readily invert close to room temperature. The macrocycles can therefore adapt their conformations to the stereochemical requirements of the complexed metals. A preliminary study of the coordination chemistry of **5** and **7** has been carried out. Both macrocycles can chelate either one or two $Mo(CO)_4$ units via their diagonal phosphorus atoms. The X-ray crystal structure analyses of $\mathbf{5}\cdot Mo(CO)_4$ (**15**) and $\mathbf{7}\cdot[Mo(CO)_4]_2$ (**17**) have been performed. The structure of the cage complex **17** shows a Mo···Mo distance of 5.883 Å. Thus, it seems possible to use this kind of cage for the bimetallic activation of small molecules.

In spite of their obvious interest in coordination chemistry and homogeneous catalysis, only a few macrocyclic polyphosphines have been described in the literature to date.[1] Apart from the synthetic problems typically associated with the preparation of macrocycles, another difficulty of this chemistry is linked to the high pyramidal inversion barrier of tervalent phosphorus, which is in the range *ca.* 30–35 kcal/mol. This implies that a macrocyclic polyphosphine exists at room temperature as a complex mixture of diastereomers. Since each diastereomer has a different coordination chemistry, characteristic of the relative orientations of its lone pairs, it is necessary to carry out cumbersome separations in order to get useful ligands. When performing a template synthesis of these species, such conformational problems can be partly avoided but the decomplexation of the metal is sometimes difficult; see for example ref 2. A more definitive solution to these problems would be to reduce the pyramidal inversion barrier of phosphorus atoms so that, around room temperature, all the phosphorus atoms of the macrocycle would readily invert, thus adapting the conformation of the ring to the stereochemical requirements of the complexed metal. Such an inversion is known to exist in phospholes, where the aromaticity of the planar transition state reduces the pyramidal inversion barrier to *ca.* 16 kcal/mol.[3] Hence came the idea to build macrocyclic polyphosphines around the phosphole unit.

Results and Discussion

A possible starting point to implement such an idea was a series of phosphole tetramers which are easily obtained via a prolonged thermolysis of 1-aryl-3,4-dimethylphospholes.[4,5] The mechanism of formation of these tetramers is now reasonably well understood[6] (eq 1).



(1)

1 Ar = Ph

It implies a series of concerted [1,5] sigmatropic shifts of Ar, H, and P, plus two dehydrogenation steps whose precise mechanism is not known. These two steps are probably responsible for the modest speed and yield of the reaction. We first made the serendipitous discovery that *N,N*-dimethyl-4-bromoaniline dramatically enhances the rate and yield of the tetramerization. Previously, a typical synthesis of **1** took 5 days at 170–180 °C with a final yield of 20–25%,[4] but the same reaction with the aniline promoter can be performed in 18 h at the same temperature with a final yield of 40–45%. Since trapping experiments show that the concerted steps work efficiently,[6] we presume that the substituted aniline favors the dehydrogenation steps, but we have no idea of how it acts.

Another point of interest concerns the flexibility of the biphosphole unit. The X-ray crystal structure analysis of the complex $\mathbf{1}\cdot[Mo(CO)_5]_2$ shows a P–C–C–P torsion angle of 44.2°, whereas, in **1** itself, the same torsion angle varies between 139 and 143°.[7] Obviously, rotation around the C–C bridges readily takes place. As regards the pyramidal inversion at phosphorus, it is easy to check that the substitution pattern of the phosphole ring does not alter drastically the activation barrier of the process.

® Abstract published in *Advance ACS Abstracts,* March 15, 1994.

[1] For a recent review, see: Stelzer, O.; Langhans, K.-P.; In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: Chichester, 1990; Vol. 1, pp 226–233. See also: McAuliffe, C. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, pp 995–1004.

[2] Diel, B. N.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1982,** *104,* 4700.

[3] Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1971,** *93,* 6205.

[4] Mathey, F.; Mercier, F.; Nief, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982,** *104,* 2077.

[5] Bévierre, M.-O.; Mercier, F.; Ricard, L.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 655.

[6] Bévierre, M.-O.; Mercier, F.; Ricard, L.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992,** *129,* 1.

[7] Fischer, J.; Mitschler, A.; Mathey, F.; Mercier, F. *J. Chem. Soc., Dalton Trans.* **1983,** 841.

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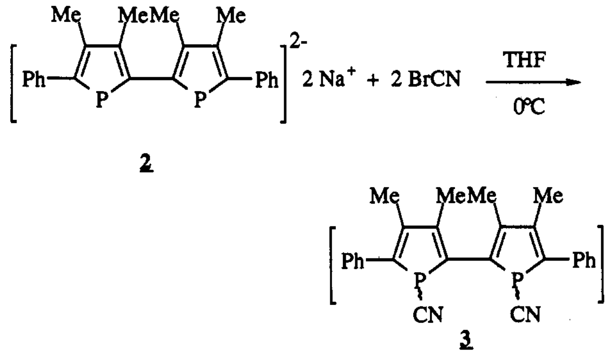
The dicyano-substituted derivative **3**, formed as shown in eq 2, is a mixture of two diastereomers: $\delta(^{31}P)$ −29.1 (major) and −33.3 (minor) ($CDCl_3$). It proved possible to selectively crystallize the major isomer by slow evaporation of a dichloromethane solution of **3**.



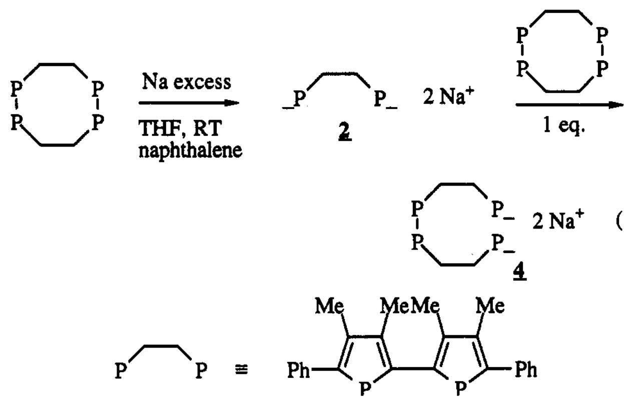
2

3

(2)

This pure diastereomer (δ −29.1) isomerizes upon standing overnight in solution at room temperature. Thus, the pyramidal inversion of phosphorus takes place in the same range of temperature for **3** and for 1-isopropyl-2-phenyl-5-methylphosphole.[3]

Returning to synthetic problems, it is possible to prepare two phosphorus anions from **1**, using the cleavage of the P–P bonds by sodium in THF (eq 3). The reaction is catalyzed by small amounts of naphthalene.

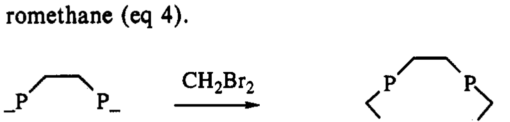


2

4

(3)

The dianion **2** is characterized by a single $\delta(^{31}P)$ resonance at +59.7 (Na^+, THF), while dianion **4** gives rise to an AA′XX′ system with two sets of resonances at −0.9 and +76.2. These two dianions proved to be versatile precursors for new tetraphosphamacrocycles. The reaction of **2** with dibromomethane affords a 10-membered macrocycle **5**, which crystallizes in dichloromethane (eq 4).



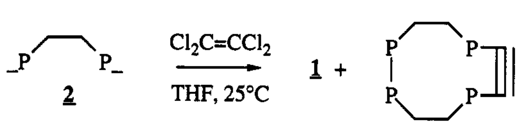
2

5 (45%)

(4)

The structure of **5** was unambiguously established by X-ray crystal analysis of one of its complexes (see later). According to ^1H NMR spectroscopy and elemental analysis, this macrocycle tenaciously retains 0.5 molecule of dichloromethane. The ^{31}P spectrum of **5** shows a singlet at 6.6 in CH_2Cl_2 and two resonances at 6.7 and 7.6 in $CDCl_3$ plus additional minor peaks. Apparently, **5** is a mixture of isomers in equilibrium whose ratio varies with the solvent.

The reaction of dianion **2** with tetrachloroethylene gives a somewhat surprising result. Besides some oxidative coupling leading to the reformation of **1**, a 10-membered acetylenic macrocycle **6** is obtained in modest yield (eq 5).



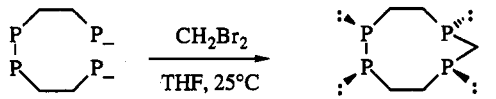
2

6 (25%)

(5)

The ^{13}C NMR spectrum of **6** ($CDCl_3$) shows the sp-carbons as a complex multiplet at δ +102. The ^{31}P NMR spectrum ($CDCl_3$) displays two resonances at −14.0 and −18.0 with no sizable ^3J(P–P) coupling. The structure of **6** was definitively established by X-ray crystal structure analysis (Figure 1). The geometry of the phosphole rings appears to be normal, and the P–P bond length at 2.204(3) Å is close to that recorded for **1**.[7] The P–spC bond lengths are short at 1.753(7) and 1.789(9) Å, as expected for an acetylenic phosphine.[8] There is some residual strain in the ring, as shown by the nonlinearity of the P–C≡C–P unit: ∠P–C≡C 170.2(8) and 173.5(6)°. The simplified view of the macrocycle (Figure 2) shows its highly distorted geometry with all the lone pairs pointing away from each other, so that no chelation is possible in that conformation.

The tetraphosphorus dianion **4** is also a convenient source for new macrocycles. The reaction of dibromomethane with **4** affords the nine-membered macrocycle **7** in excellent yield (eq 6).



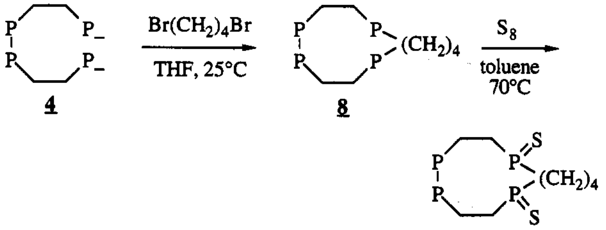
4

7 (80%)

(6)

The formula of **7** was established by elemental analysis of its toluene solvate and mass spectrometry. The ^{31}P NMR spectrum has been simulated and shows four inequivalent phosphorus atoms: δ(P1) −12.11, δ(P2) −2.41, δ(P3) 4.24, δ(P4) 8.72. The P1 and P2 atoms are directly connected, and their coupling is very strong: ^1J(P1–P2) = −336.3 Hz. This very high value implies a *cis* stereochemistry of the lone pairs at P1 and P2.[9] The inequivalency of the four phosphorus atoms in turn implies that the two other lone pairs at P3 and P4 are *trans*, as shown in eq 6.

The reaction of 1,4-dibromobutane with **4** leads to the expected 12-membered macrocycle **8** in excellent yield (eq 7).



4

8

(7)

9 (80% overall)

This macrocycle was characterized by mass spectrometry and ^{31}P NMR spectroscopy. The ^{31}P spectrum shows two quasi singlets at 22.3 and −12.9 (CH_2Cl_2). The sulfurization of **8** selectively takes place at the PC_3 phosphorus atoms, as shown by the ^{31}P NMR spectrum (CH_2Cl_2): $\delta(^{31}P)$(**9**) +63.4 (s, PC_3), −14.1 (s, P–P). The disulfide **9** has been crystallized and fully analyzed.

The reaction of **8** with sodium affords a new tetraphosphorus dianion **10** as a mixture of two diastereomers (eq 8).

The reaction must be run at low temperature in order to avoid the cleavage of the P–$(CH_2)_4$–P bridge. The ^{31}P NMR spectrum shows two AX systems: δ_{A1} +79.9, δ_{X1} +13.9, $^3J_{A1X1}$ = 76 Hz; δ_{A2} +79.2, δ_{X2} +13.7, $^3J_{A2X2}$ = 74.5 Hz. The huge ^3J(P–P)

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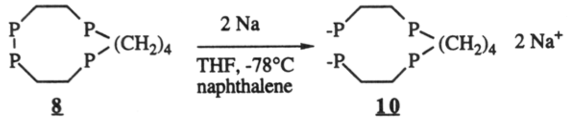
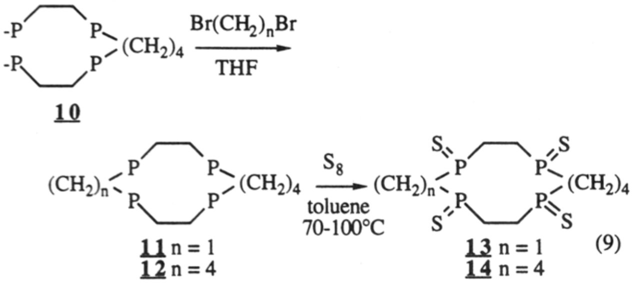
[8] Mootz, D.; Sassmannshausen, G. *Z. Anorg. Allg. Chem.* **1967**, *355*, 200.

[9] Albrand, J. P.; Faucher, H.; Gagnaire, D.; Robert, J. B. *Chem. Phys. Lett.* **1976**, *38*, 521.



(8)

couplings are especially noteworthy. The dianion **10** in turn can be used to prepare several other macrocycles, as shown in eq 9. These macrocycles were fully characterized as their tetrasulfides.

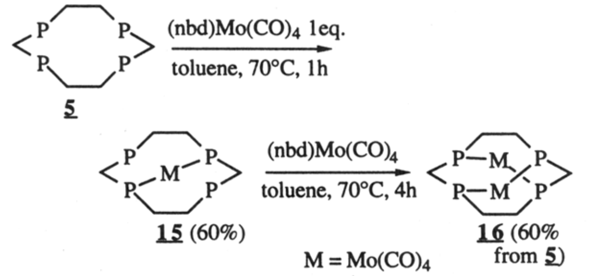


(9)

In the case of **13**, it proved possible to obtain one pure isomer by crystallization. Its ^{31}P NMR spectrum shows two inequivalent phosphorus atoms at +48.2 and +67.2 (CDCl$_3$) with no P–P coupling. In the case of **14**, a very complex mixture was obtained from which we tried to extract pure species by crystallization and chromatography. The conformations and ^{31}P NMR spectra of tetraphosphamacrocycles have been discussed by Kyba[10] and Ciampolini.[11] A priori, five isomers can be observed, four of them displaying a single ^{31}P resonance, the last one displaying four resonances corresponding to the four inequivalent phosphorus atoms (see Scheme 1).

In our case, we have isolated the isomer **14a** in the pure state. One other isomer, **14b**, with a single resonance at 58.0 (CDCl$_3$) was also obtained as a pure species. Two other isomers, **14c,d** (δ(^{31}P) +64.2 and +57.8 in CD$_2$Cl$_2$), were observed as a mixture. We cannot assign a precise stereochemistry to these species.

Having in hand a complete series of new tetraphosphamacrocycles, we performed a preliminary investigation of their coordination chemistry. The most significant results were obtained with **5** and **7**. The reaction of **5** with (norbornadiene)·Mo(CO)$_4$ first affords a monochelate **15** (eq 10), whose structure was established by X-ray analysis (Figure 3).



(10)

The macrocycle has a cradle-like conformation, and the metal is chelated between two diagonally related phosphorus atoms. The lone pairs of the noncoordinated phosphorus atoms are located on the same side of the ring as the molybdenum atom. When complex **15** is further heated with (nbd)Mo(CO)$_4$, a new complex, **16**, is formed. In the ^{31}P NMR spectrum, the AA′XX′ system corresponding to **15** ($\delta_{AA'} = -6.2$, $\delta_{XX'} = +39.9$, $J_{AX} \sim 106$ Hz) is replaced by a singlet at 38.8. In both ^{1}H and ^{13}C spectra, the four inequivalent methyl groups of **15** are replaced by only two sets of inequivalent methyls. The ^{13}C spectrum of **16** also indicates the presence of only one type of Mo(CO)$_4$ group. Elemental analysis shows that **16** is formed by addition of two Mo(CO)$_4$ units to **5**. Thus, it is clear that **16** is a bis-chelate, as shown in eq 10. This means that the two noncoordinated phosphorus atoms of **15** have undergone a pyramidal inversion in order to chelate

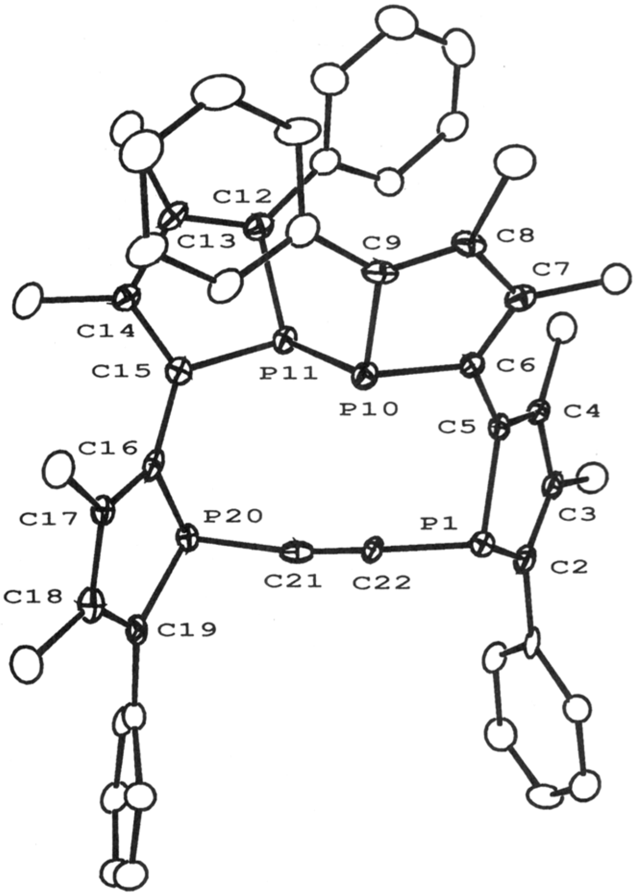


Figure 1. ORTEP drawing of one molecule of **6**. Vibrational ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity. Principal bond distances (Å) and angles (deg): P$_1$–C$_2$ 1.820(7), P$_1$–C$_5$ 1.830(9), P$_1$–C$_{22}$ 1.753(7), C$_5$–C$_6$ 1.46(1), C$_6$–P$_{10}$ 1.795(8), P$_{10}$–C$_9$ 1.799(7), P$_{10}$–P$_{11}$ 2.204(3), P$_{11}$–C$_{12}$ 1.799(9), P$_{11}$–C$_{15}$ 1.789(7), C$_{15}$–C$_{16}$ 1.48(1), C$_{16}$–P$_{20}$ 1.836(7), P$_{10}$–C$_{19}$ 1.819(8), P$_{20}$–C$_{21}$ 1.789(9), C$_{21}$–C$_{22}$ 1.21(1); C$_2$–P$_1$–C$_5$ 91.5(4), C$_5$–P$_1$–C$_{22}$ 101.1(4), P$_1$–C$_5$–C$_6$ 120.7(6), C$_5$–C$_6$–P$_{10}$ 121.2(5), C$_6$–P$_{10}$–C$_5$ 92.2(3), C$_6$–P$_{10}$–P$_{11}$ 100.5(3), P$_{10}$–P$_{11}$–C$_{15}$ 101.1(3), C$_{12}$–P$_{11}$–C$_{15}$ 91.0(4), P$_{11}$–C$_{15}$–C$_{16}$ 121.3(6), C$_{15}$–C$_{16}$–P$_{20}$ 121.0(5), C$_{16}$–P$_{20}$–C$_{15}$ 90.5(4), C$_{16}$–P$_{20}$–C$_{21}$ 100.1(3), P$_{20}$–C$_{21}$–C$_{22}$ 170.2(8), P$_1$–C$_{21}$–C$_{22}$ 173.5(6).

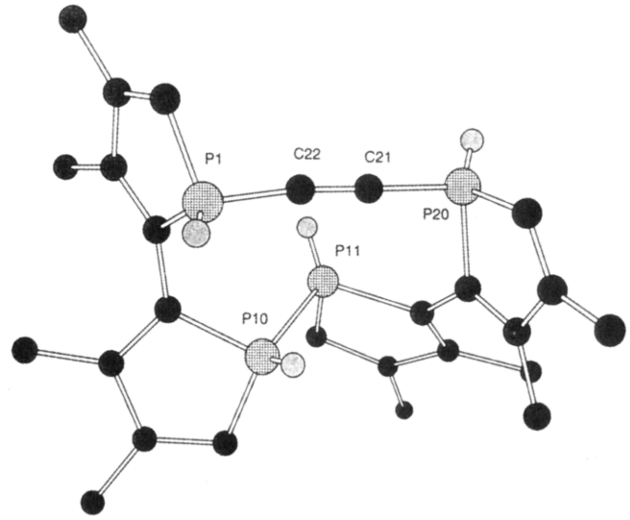


Figure 2. Chem 3D view of the central 10-membered ring of **6**. Main torsion angles (deg): P$_1$–C$_5$–C$_6$–P$_{10}$ −43.42(0.79), C$_6$–P$_{10}$–P$_{11}$–C$_{15}$ 168.41(0.38), P$_{11}$–C$_{15}$–C$_{16}$–P$_{20}$ −41.87(0.79), C$_{16}$–P$_{20}$–C$_{21}$–C$_{22}$ −75.16(4.37).

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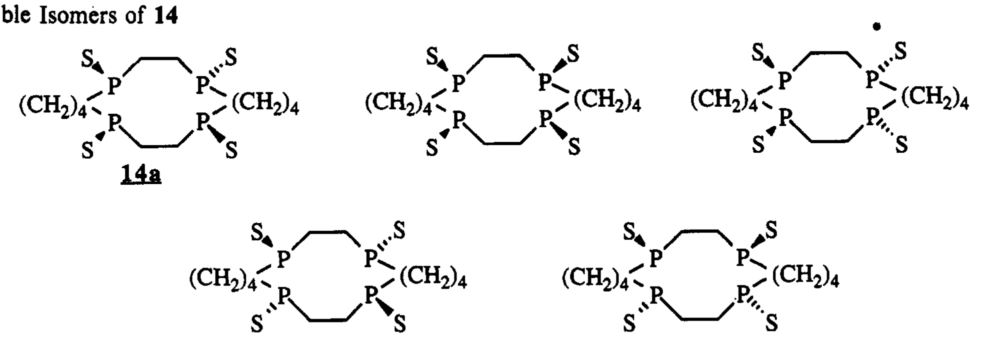
[10] Kyba, E. P.; Davis, R. E.; Hudson, C. W.; John, A. M.; Brown, S. B.; McPhaul, M. J.; Liu, L.-K.; Glover, A. C. *J. Am. Chem. Soc.* **1981**, *103*, 3868.

[11] Ciampolini, M.; Dapporto, P.; Dei, A.; Nardi, N.; Zanobini, F. *Inorg. Chem.* **1982**, *21*, 489.

Scheme 1. Possible Isomers of **14**



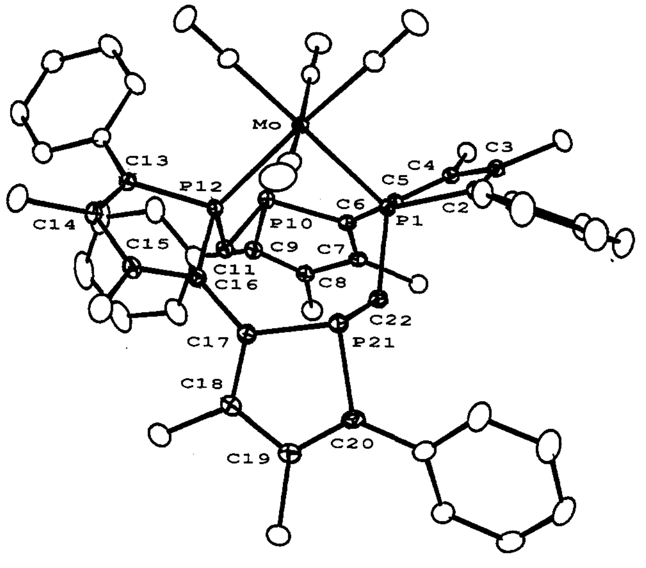
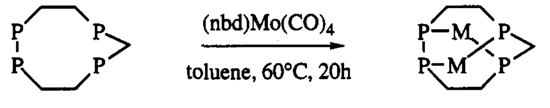


Figure 3. ORTEP drawing of one molecule of **15**. Vibrational ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Principal bond distances (Å) and angles (deg): Mo–P_1 2.5200(9), Mo–P_{12} 2.5099(9), P_1–C_5 1.808(3), P_1–C_{22} 1.839(3), C_5–C_6 1.464(4), C_6–P_{10} 1.818(3), P_{10}–C_{11} 1.854(4), C_{11}–P_{12} 1.837(3), P_{12}–C_{16} 1.816(3), C_{16}–C_{17} 1.460(5), C_{17}–P_{21} 1.814(3), P_{21}–C_{22} 1.852(4); P_1–Mo–P_{12} 86.92(3), C_5–P_1–C_{22} 104.3(2), P_1–C_{22}–P_{21} 112.9(2), C_6–P_{10}–C_{11} 104.5(2), P_{10}–C_{11}–P_{12} 113.6(2), C_{11}–P_{12}–C_{16} 104.7(2), C_{17}–P_{21}–C_{22} 106.0(2).

an additional molybdenum atom. Hence, we have a clear illustration of the conformational lability of this type of macrocycle.

Another example of this flexibility was found when studying the reaction of (nbd)Mo$(CO)_4$ with macrocycle **7** (eq 11).



(11)

7 M = Mo$(CO)_4$ **17** (60%)

The ultimate product is again a bis-chelate **17**, whose structure was established by X-ray analysis (Figure 4). The structure of **17** is very close to that proposed for complex **16**. The two metals lie on opposite sides of the macrocycle, and both are coordinated to two diagonally related phosphorus atoms. The relatively small macrocycle is obviously under strain. The P1–P21 bond is markedly longer than usual at 2.317 Å. The P10–C11–P12 unit is significantly distorted with long P–C bonds at 1.860 Å and a large PCP angle of 124.2°. This distortion may explain the abnormal deshielding of the P–*C*–P carbon at 45.26 ppm in the ^{13}C NMR spectrum of **17**. Two additional points deserve to be mentioned. Once again, the formation of the bis-complex **17** necessitates the pyramidal inversion of one phosphorus in the starting macrocycle **7**. On the other hand, **17** forms a cage whose internal radius is rather large: *d*(Mo···Mo) = 5.883 Å. It becomes conceivable to use such complexes for the bimetallic activation of small molecules provided that one of the metals is loosely coordinated to the phosphorus atoms. Clearly, the potential of this new series of macrocycles in coordination chemistry and homogeneous catalysis is high and deserves a deeper investigation.

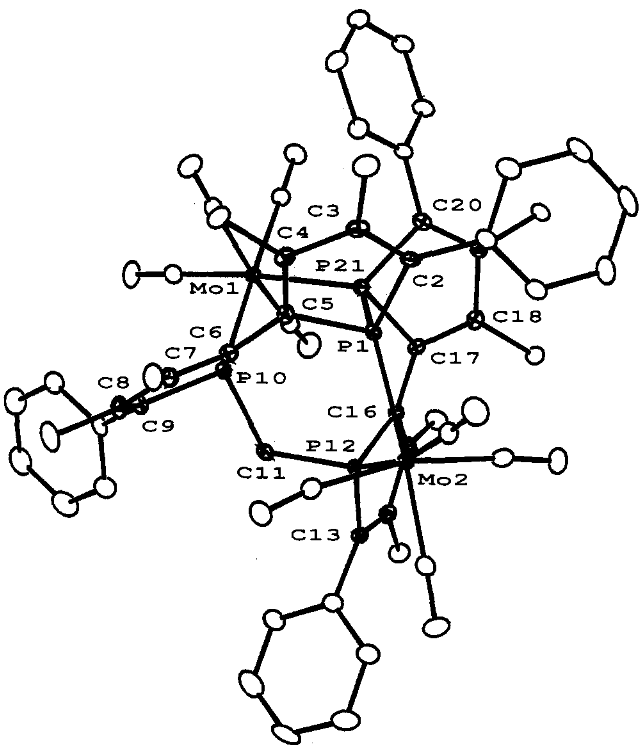


Figure 4. ORTEP drawing of one molecule of **17**. Vibrational ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity. Principal bond distances (Å) and angles (deg): Mo_1–P_{10} 2.474(1), Mo_1–P_{21} 2.480(1), Mo_2–P_1 2.533(1), Mo_2–P_{12} 2.477(1), P_1–C_5 1.810(4), C_5–C_6 1.443(5), C_6–P_{10} 1.836(4), P_{10}–C_{11} 1.860(4), C_{11}–P_{12} 1.860(4), P_{12}–C_{16} 1.829(4), C_{16}–C_{17} 1.441(5), C_{17}–P_{21} 1.817(4), P_{21}–P_1 2.317(1); P_{10}–Mo_1–P_{21} 83.23(3), P_1–Mo_2–P_{12} 82.94(3), P_{21}–P_1–C_5 98.0(1), P_1–C_5–C_6 120.7(3), C_5–C_6–P_{10} 121.8(3), C_6–P_{10}–C_{11} 107.8(2), P_{10}–C_{11}–P_{12} 124.2(2), C_{11}–P_{12}–C_{16} 108.0(2), P_{12}–C_{16}–C_{17} 122.6(3), C_{16}–C_{17}–P_{21} 120.9(3), C_{17}–P_{21}–P_1 93.3(1).

Experimental Section

All reactions were carried out under argon, and silica gel (70–230 mesh) was used for chromatographic separations. NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from internal TMS (^1H and ^{13}C) or external 85% H_3PO_4 (^{31}P). Routine mass spectra were obtained at 70 eV by the direct inlet method, with a MS-50 spectrometer (compound **6**) and with a Shimadzu GC-MS QP 1000 spectrometer for all other compounds and high-resolution mass spectra by the "Centre Régional de Mesures Physiques de l'Ouest" at Rennes, France. Elemental analyses were performed by the "Service d'analyse du CNRS" at Gif-sur-Yvette, France.

All X-ray data were collected at −150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator (unless otherwise noted). The crystal structures were solved and refined using the Enraf Nonius MOLEN package. The structures were solved by direct methods, the initial model being completed using standard Fourier techniques. Hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied in all cases.

Yields of compounds **2**, **5–9**, and **11–14** are expressed relative to tetramer **1**.

Improved Synthesis of Tetramer 1. 3,4-Dimethyl-1-phenylphosphole (2.26 g, 12 mmol) and *N*,*N'*-dimethyl-4-bromoaniline (1.8 mmol) were heated in a sealed glass tube at 180 °C for 18 h. Then, the mixture was cooled and treated with CH_2Cl_2. The insoluble red crystals of **1** were removed by filtration and dried under vacuum. Yield of **1**: 40–45%. Characterization: see ref 4.

Dianion 2. Naphthalene (0.04 g, 0.3 mmol) was stirred with an excess of sodium (~1 g) in dry THF (20 mL) until the solution became green. Tetramer **1** (1.04 g, 1.4 mmol) was then added in portions. The reaction mixture turned red and was stirred until it became green again (~2 h). Then, the excess of sodium was withdrawn. ^{31}P NMR (THF) δ 59.7.

1,1'-Dicyano-3,3',4,4'-tetramethyl-5,5'-diphenyl-2,2'-biphosphole 3. The solution of dianion **2** (2.8 mmol) was added dropwise to a solution of BrCN (5.6 mmol) in THF (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h. It was then hydrolyzed with water (20 mL), extracted with CH_2Cl_2 (40 mL), washed with water (2 × 50 mL), dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2). A 3:1 mixture of two isomers, **3a** and **3b**, was obtained. Yield of **3**: 48%. The major isomer, **3a**, was recrystallized by slow evaporation of a CH_2Cl_2 solution of **3**. According to ^{31}P NMR, the ratio between **3a** and **3b** in the mother liquor was still 3:1. Isomer **3a**: mp, ~180 °C (decomp); ^{31}P NMR ($CDCl_3$) δ −29.06; ^{1}H NMR ($CDCl_3$) δ 2.12 (pt, J(H–P) = 1.9 Hz, 6H, Me), 2.21 (s, 6H, Me), 7.32–7.49 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$) δ 16.53 (s, Me), 17.33 (s, Me), 115.72–118.43 (m, CN). Isomer **3b**: ^{31}P NMR ($CDCl_3$) δ −33.32.

Dianion 4. A solution of dianion **2** (1.4 mmol) was prepared as described above, in 15 mL of dry THF. Tetramer **1** (0.52 g, 0.7 mmol) was added in portions, and the reaction mixture was stirred until complete dissolution (~2 h): ^{31}P NMR (THF) δ −0.9 ($P_AP_{A'}$), 76.2 ($P_XP_{X'}$), $J_{AA'} \sim 299.5$ Hz, $J_{AX} \sim 96.3$ Hz, $J_{AX'} \sim 4.4$ Hz.

1,3,6,8-Tetraphosphecane 5. Dibromomethane (3 mmol) in THF (15 mL) was added dropwise to the solution of dianion **2** (2.8 mmol). The reaction mixture was hydrolyzed with water (20 mL), extracted with diethyl ether (80 mL), washed with water (2 × 50 mL), dried ($MgSO_4$), and concentrated. The residue was crystallized and recrystallized from CH_2Cl_2 to give **5** as yellow crystals, which were dried under vacuum: yield of **5**, 45%; mp, 228 °C; ^{31}P NMR ($CDCl_3$) δ 6.67, 7.55 (major peaks), 4.54, 13.09, 14.35, 20.63, 21.09 (minor peaks). Anal. Calcd for $C_{50}H_{48}P_4{\cdot}(CH_2Cl_2)_{0.5}$: C, 74.40; H, 6.06. Found: C, 74.12; H, 6.05.

1,2,5,8-Tetraphosphacyclodec-6-yne 6. Tetrachloroethylene (3 mmol) was added to the solution of dianion **2** (2.8 mmol) at 0 °C. The reaction mixture was hydrolyzed with water (20 mL), extracted with diethyl ether (60 mL), washed with water (2 × 50 mL), dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane–CH_2Cl_2, 70:30). **6** was recrystallized from toluene: yield of **6**, 25%; mp, 226 °C; ^{31}P NMR ($CDCl_3$) δ −18, −14; ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 6H, Me), 1.78 (s, 6H, Me), 2.10 (s, 6H, Me), 2.15 (s, 6H, Me), 6.95–7.48 (m, 20H, Ph); ^{13}C NMR ($CDCl_3$) δ 15.85 (s, Me), 16.38 (s, Me), 17.75 (s, Me), 17.91 (s, Me), 102 (m, $C{\equiv}C$); mass spectrum, m/e 768 (M, 90), 384 (M/2, 100). Anal. Calcd for $C_{50}H_{44}P_4$: C, 78.11; H, 5.77. Found: C, 78.29; H, 5.66.

The compound crystallizes in space group $P\bar{1}$, $a = 15.198(2)$, $b = 17.102(2)$ Å, $c = 18.975(2)$ Å, $\alpha = 64.20(1)°$, $\beta = 73.02(1)°$, $\gamma = 80.72(1)°$, $V = 4243.3(9)$ Å^3; $Z = 2$; $d_{calc} = 1.325$ g/cm^3; Cu Kα radiation ($\lambda = 1.54184$ Å); $\mu = 31.1$ cm^{-1}; $F(000) = 1768$. A total of 6361 observed reflections ($F^2 > 3.0\sigma(F^2)$) were collected in the range $2° < 2\theta < 100.0°$ and used for solution and refinement. The final agreement factors were $R = 0.081$, $R_w = 0.114$, GOF = 2.32, p factor = 0.08.

1,2,5,7-Tetraphosphonane 7. Dibromomethane (1.4 mmol) in THF (20 mL) was added dropwise to the solution of dianion **4** (2.8 mmol). The reaction mixture was hydrolyzed with water (20 mL), extracted with diethyl ether (60 mL), washed with water (2 × 50 mL), dried ($MgSO_4$), and concentrated. The residue was crystallized and recrystallized from hot toluene to give **7** as orange-yellow crystals, which were dried under vacuum: yield of **7**, 80%; mp > 260 °C; ^{31}P NMR (toluene) δ −12.11 (P_1), −2.41 (P_2), 4.24 (P_3), 8.72 (P_4), $^{1}J(P_1{-}P_2) = -366.3$ Hz, $^{3}J(P_2{-}P_3) = -7.0$ Hz, $^{2}J(P_3{-}P_4) = 5.4$ Hz; ^{1}H NMR ($CDCl_3$) δ 1.72 (pt, J(H–P) = 2.74 Hz, 3H, Me), 1.82 (pt, J(H–P) = 2.05 Hz, 3H, Me), 1.9–2 (multiplets, 9H, Me), 2.05 (br s, 3H, Me), 2.13 (d, J(H–P) = 3.94 Hz, 3H, Me), 2.28 (d, J(H–P) = 3.38 Hz, 3H, Me), 2.35 (s, Me toluene), 2.80 (m, 2H, CH_2), 6.71–7.43 (m, 20H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.84 (s, Me), 15.38 (br s, Me), 15.94 (s, Me), 16.22 (br s, Me), 17.53 (br s, Me), 21.42 (s, Me toluene), 30.85 (s, $P\mathit{C}H_2P$); mass spectrum, m/e 756 (M − 2, 30), 755 (60), 754 (64), 441 (100). Anal. Calcd for $C_{49}H_{46}P_4{\cdot}(C_7H_8)_{1.5}$: C, 79.67; H, 6.52; P, 13.81. Found: C, 79.37; H, 6.31; P, 13.84.

1,2,5,10-Tetraphosphacyclododecane 8. 1,4-Dibromobutane (1.4 mmol) in THF (20 mL) was added dropwise to the solution of dianion **4** (2.8 mmol). The reaction mixture was hydrolyzed with water (20 mL), extracted with diethyl ether (60 mL), washed with water (2 × 50 mL), dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane–CH_2Cl_2, 50:50): yield of **8** > 80%; ^{31}P NMR (CH_2Cl_2) δ −12.90, 22.33; mass spectrum, m/e 796 (M − 4, 30), 427 (100).

1,2,5,10-Tetraphosphacyclododecane 5,10-Disulfide 9. The residue of **8** was dissolved in 15 mL of toluene and reacted with sulfur (2.8 mmol) at 70 °C for 1 h. **9** crystallized as orange-yellow crystals as the solution cooled to room temperature: yield of **9**, 80%; mp 236 °C (decomp); ^{31}P NMR ($CDCl_3$) δ −13.44, 63.53; ^{1}H NMR ($CDCl_3$) δ 1.2–2.3 (m, CH_2), 1.52 (s, 6H, Me), 1.77 (m, 6H, Me), 1.93 (s, 6H, Me), 2.07 (d, J(H–P) = 2.34 Hz, 6H, Me), 7.09–7.57 (m, 20H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.85–16.06 (m, Me), 23.86 (d, ^{2}J(C–P) = 17.33 Hz, $PCH_2\mathit{C}H_2$), 30.98 (d, ^{1}J(C–P) = 43.93 Hz, PCH_2). High-resolution mass spectrum, calcd for $C_{52}H_{52}P_4S_2$: 864.246 08. Found: 864.2469.

Dianion 10. A 0.8 M THF solution of naphthalene–sodium (3.5 mL) was added to a solution of **8** (1.12 g, 1.4 mmol) in THF (15 mL) at −78 °C. Isomer **10a**: ^{31}P NMR (THF) δ 79.9 (P_A), 13.9 (P_X), $^{3}J(P_A{-}P_X) = 76$ Hz. Isomer **10b**: ^{31}P NMR (THF) δ 79.2 (P_A), 13.7 (P_X), $^{3}J(P_A{-}P_X) = 74.5$ Hz.

1,3,6,11-Tetraphosphacyclotridecane 11 and Tetrasulfide 13. The solution of dianion **10** was diluted with 100 mL of dry THF and warmed to 50 °C. Dibromomethane (1.4 mmol) in THF (50 mL) was added dropwise. The reaction mixture was allowed to cool to room temperature, hydrolyzed with water (20 mL), extracted with diethyl ether (80 mL), washed with water (2 × 50 mL), dried ($MgSO_4$), and concentrated. The peaks of **11** are apparent in the ^{31}P NMR spectrum of the residue: δ 0.06, 16.09 (in CH_2Cl_2). The residue was then dissolved in 20 mL of toluene and reacted with sulfur (6 mmol) at 100 °C for 2 h. **13** was isolated from the mother liquor by crystallization and recrystallization (toluene): yield of **13**, 15%; mp > 270 °C; ^{31}P NMR ($CDCl_3$) δ 46.16, 67.22; ^{1}H NMR ($CDCl_3$) δ 0.9–2.5 (m, CH_2), 1.91 (s, 6H, Me), 1.99 (br s, 12H, Me), 2.13 (d, ^{4}J(H–P) = 2.07 Hz, 6H, Me), 3.1 (m, CH_2), 7.15–7.69 (m, 20H, Ph); ^{13}C NMR ($CDCl_3$) δ 15.6 (m, Me), 16.90 (pt, J(C–P) = 6.24 Hz, Me), 18.79 (d, J(C–P) = 6.0 Hz, Me), 23.54 (d, ^{2}J(C–P) = 13.57 Hz, $PCH_2\mathit{C}H_2$), 33.32 (d, ^{1}J(C–P) = 45.69 Hz, $P\mathit{C}H_2$), 41.55 (t, ^{1}J(C–P) ~ 40.02 Hz, $P\mathit{C}H_2P$). Anal. Calcd for $C_{53}H_{54}P_4S_4{\cdot}C_7H_8$: C, 69.62; H, 6.03. Found: C, 70.16; H, 6.01.

1,6,9,14-Tetraphosphacyclohexadecane 12 and Tetrasulfide 14. The solution of dianion **10** was diluted with 100 mL of dry THF and warmed to 50 °C. 1,4-Dibromobutane (1.4 mmol) in THF (50 mL) was added dropwise. The reaction mixture was allowed to cool to room temperature, hydrolyzed with water (20 mL), extracted with diethyl ether (80 mL), washed with water (2 × 50 mL), dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel. **12** was isolated with hexane–CH_2Cl_2, 70:30, as the eluent (yield of **12** ~ 40%). This fraction was dissolved in 20 mL of toluene and reacted with sulfur (2.5 mmol) at 60 °C for 1 h. The solvent was evaporated, and the residue was extracted with hot toluene. A 1:1 mixture of isomers **14c** and **14d** was isolated from the solution by recrystallization. A chromatography on silica gel of the mother liquor gave isomer **14b** (CH_2Cl_2) and isomer **14a** (CH_2Cl_2–ethyl acetate, 95:5).

Isomer 14a: mp > 270 °C; ^{31}P NMR ($CDCl_3$) δ 57.25, 58.21, 59.42, 64.42; ^{1}H NMR ($CDCl_3$) δ 1–2 (m, CH_2), 1.97–2.14 (m, Me), 2.85 (m, ~1H, CH_2), 7.26–7.57 (m, 20H, Ph); ^{13}C NMR ($CDCl_3$) δ 15.37–17.46 (m, Me), 23.16 (br d, ^{2}J(C–P) ~ 14.86 Hz, 2C, $PCH_2\mathit{C}H_2CH_2CH_2P$), 24.04 (dd, ^{2}J(C–P) = 16.53 Hz, ^{3}J(C–P) = 2.27 Hz, $PCH_2\mathit{C}H_2CH_2CH_2P$), 26.43 (m, $PCH_2\mathit{C}H_2CH_2CH_2P$), 29.26 (d, ^{1}J(C–P) = 47.57 Hz, $P\mathit{C}H_2CH_2CH_2CH_2P$), 32.57 (d, ^{1}J(C–P) = 46.70 Hz, $P\mathit{C}H_2CH_2CH_2CH_2P$), 32.87 (d, ^{1}J(C–P) = 46.62 Hz, $P\mathit{C}H_2CH_2CH_2CH_2P$), 34.62 (d, ^{1}J(C–P) = 45.93 Hz, $P\mathit{C}H_2CH_2CH_2CH_2P$).

Isomer **14b**: mp > 270 °C; ^{31}P NMR ($\mathrm{CDCl_3}$) δ 58.03; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1–2.3 (m, 16H, $\mathrm{CH_2}$), 2.05 (s, 12H, Me), 2.10 (s, 12H, Me), 7.34–7.48 (m, 20H, Ph); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 15.55 (d, ^3J(C–P) = 12.83 Hz, Me), 17.26 (d, ^3J(C–P) = 11.27 Hz, Me), 22.79 (d, ^2J(C–P) = 18.27 Hz, $\mathrm{PCH_2\mathit{C}H_2\mathit{C}H_2CH_2P}$), 32.02 (d, ^1J(C–P) = 46.98 Hz, $\mathrm{P\mathit{C}H_2CH_2CH_2\mathit{C}H_2P}$), 126.87 (dd, ^1J(C–P) = 79.86 Hz, ^2J(C–P) = 11.54 Hz, $\mathrm{P\mathit{CC}P}$), 134.29 (s, *Ph*, C ipso), 134.91 (d, ^1J(C–P) = 85.22 Hz, $\mathrm{P\mathit{C}Ph}$), 147.26 (d, ^2J(C–P) = 22.61 Hz, $\mathrm{PCPh\mathit{C}Me}$), 155.11 (dd, ^2J(C–P) = 25.16 Hz, ^3J(C–P) = 5.29 Hz, $\mathrm{PC(C{-}P)\mathit{C}Me}$). High-resolution mass spectrum, calcd for $\mathrm{C_{56}H_{60}P_4S_4}$: 984.252 82. Found: 984.2565.

Mixture (1:1) of isomers **14c** and **14d**: ^{31}P NMR ($\mathrm{CD_2Cl_2}$) δ 57.82, 64.19; ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 0.6–1.8 (m, $\mathrm{CH_2}$), 1.88 (m, 12H, Me), 1.92 (d, J(H–P) = 2.29 Hz, 6H, Me), 2.04 (dd, J(H–P) ~ 2.28 Hz, 6H, Me), 3.2 (m, $\mathrm{CH_2}$), 7.18–7.57 (m, 20H, Ph); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 14.82–16.19 (m, Me), 22.29 (d, ^2J(C–P) = 18.94 Hz, $\mathrm{PCH_2\mathit{C}H_2\mathit{C}H_2CH_2P}$), 25.81 (dd, ^2J(C–P) = 17.55 Hz, ^3J(C–P) = 3.68 Hz, $\mathrm{PCH_2\mathit{C}H_2\mathit{C}H_2CH_2P}$), 29.81 (d, ^1J(C–P) = 47.54 Hz, $\mathrm{P\mathit{C}H_2CH_2CH_2\mathit{C}H_2P}$), 33.39 (d, ^1J(C–P) = 45.53 Hz, $\mathrm{P\mathit{C}H_2CH_2CH_2\mathit{C}H_2P}$), 135.29 (d, ^1J(C–P) = 71.55 Hz, $\mathrm{P\mathit{C}Ph}$), 136.68 (d, ^1J(C–P) = 75.48 Hz, $\mathrm{P\mathit{C}Ph}$), 145.26 (d, ^2J(C–P) = 20.44 Hz, $\mathrm{PCPh\mathit{C}Me}$), 145.81 (d, ^2J(C–P) = 22.18 Hz, $\mathrm{PCPh\mathit{C}Me}$), 152.6 (m, $\mathrm{PC(CP)\mathit{C}Me}$). High-resolution mass spectrum, calcd for $\mathrm{C_{56}H_{60}P_4S_4}$: 984.252 82. Found: 984.2565.

Complex 15. The macrocycle **5** (0.39 g, 0.5 mmol) was heated in toluene (15 mL) with $\mathrm{(nbd)Mo(CO)_4}$ (0.6 mmol) at 70 °C for 1 h. After evaporation of the solvent, the residue was chromatographed on silica gel (hexane–$\mathrm{CH_2Cl_2}$, 50:50). **15** was recrystallized from *o*-dichlorobenzene: yield of **15**, 60% from **5**; ^{31}P NMR ($\mathrm{C_6D_6}$) δ –6.21 ($\mathrm{P_A}$), 39.80 ($\mathrm{P_X}$), $J(\mathrm{P_A{-}P_X}) \sim 106.3$ Hz, $J(\mathrm{P_A{-}P_{X'}}) \sim 16$ Hz; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.39 (s, 6H, Me), 1.52 (s, 6H, Me), 1.72 (d, J(H–P) = 3.25 Hz, 6H, Me), 1.84 (s, 6H, Me), 2.1–2.6 (m, 4H, $\mathrm{CH_2}$), 7.03–7.98 (m, 20H, Ph); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 15.96 (s, Me), 16.13 (d, ^3J(C–P) = 6.95 Hz, Me), 17.28 (br s, Me), 17.81 (s, Me), 26.59 (m, J(C–P) ~ 30.4 Hz, J(C–P) ~ 9.70 Hz, $\mathrm{P\mathit{C}H_2P}$), 211.6 (m, CO), 214.6 (m, CO); IR ($\mathrm{CH_2Cl_2}$) ν(CO) 2018.1 m, 1910.0 s $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{54}H_{48}MoO_4P_4}$: C, 66.13; H, 4.93; P, 12.63. Found: C, 65.62; H, 4.97; P, 12.13.

The compound crystallizes in space group $P\bar{1}$, a = 13.315 (1)Å, b = 14.445(1) Å, c = 15.825(1) Å, α = 88.40(1)°, β = 78.83(1)°, γ = 81.50(1)°; V = 2953.4(4) Å^3; Z = 2; d_{calc} = 1.365 g/cm^3; μ = 4.6 $\mathrm{cm^{-1}}$; $F(000)$ = 1260. A total of 14 216 unique reflections were recorded in the range $2° < 2\theta < 56.0°$ of which 4807 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 9409 for solution and refinement. The final agreement factors were R = 0.043, R_w = 0.060, GOF = 1.14, p = 0.08.

Complex 16. $\mathrm{(nbd)Mo(CO)_4}$(0.6 mmol) was added to the crude reaction mixture of **15** and the solution stirred at 70 °C for 4 h. After evaporation of the solvent, the residue was chromatographed on silica gel (hexane–$\mathrm{CH_2Cl_2}$, 40:60). **16** was recrystallized from hexane–$\mathrm{CH_2Cl_2}$, 70:30: yield of **16**, 60% from **5**; ^{31}P NMR ($\mathrm{CDCl_3}$) δ 38.79; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.95 (s, 12H, Me), 2.01 (s, 12H, Me), 2.4 (m, 4H, $\mathrm{CH_2}$), 7.26–7.40 (m, 20H, Ph); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 16.63 (s, Me), 19.09 (s, Me), 46.33 (s, $\mathrm{P\mathit{C}H_2P}$), 135.61 (br s, *Ph*, C ipso), 140.02 (m, $\mathrm{P\mathit{CC}P}$), 144.78 (br s, $\mathrm{P\mathit{C}Ph}$), 148.41 (m, $\mathrm{PC(CP)\mathit{C}Me}$), 150.56 (br s, $\mathrm{PCPh\mathit{C}Me}$), 208.75 (m, CO), 214.24 (m, CO); IR ($\mathrm{CH_2Cl_2}$) ν(CO) 2021.3 m, 1914.6 s $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{58}H_{48}Mo_2O_8P_4}$: C, 58.60; H, 4.07; P, 10.42. Found: C, 58.28; H, 4.15; P, 9.95.

Complex 17. The macrocycle **7** (0.38 g, 0.5 mmol) was heated in toluene (15 mL) with $\mathrm{(nbd)Mo(CO)_4}$ (1.25 mmol) at 60 °C for 20 h. After evaporation of the solvent, the residue was chromatographed on silica gel ($\mathrm{CH_2Cl_2}$). **17** was recrystallized from $\mathrm{CH_2Cl_2}$–diethyl ether, 50:50: yield of **17**, 60% from **7**; ^{31}P NMR ($\mathrm{CDCl_3}$) δ 54.12; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.95 (s, 6H, Me), 1.99 (s, 6H, Me), 2.01 (s, 6H, Me), 2.09 (s, 6H, Me), 2.15 (m, 2H, $\mathrm{CH_2}$), 7.15–7.39 (m, 20H, Ph); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 15.33 (s, Me), 16.56 (s, Me), 18.04 (s, Me), 19.09 (s, Me), 45.26 (s, $\mathrm{P\mathit{C}H_2P}$), 205.7 (m, CO), 208.7 (m, CO); IR ($\mathrm{CH_2Cl_2}$) ν(CO) 2017.8 m, 1915.7 s $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{57}H_{46}Mo_2O_8P_4}$: C, 58.28; H, 3.95; O, 10.90. Found: C, 58.12; H, 4.56; O, 10.84. The compound crystallizes in space group $P\bar{1}$, a = 12.286(1) Å, b = 14.511(2) Å, c = 15.017(2) Å, α = 70.40(1)°, β = 87.10(1)°, γ = 86.61(1)°, V = 2516.5(7) Å^3; Z = 2; d_{calc} = 1.550 g/cm^3; μ = 6.7 $\mathrm{cm^{-1}}$; $F(000)$ = 1192. A total of 8827 unique reflections were recorded in the range $2° < 2\theta < 50.0°$ of which 2034 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 6793 for solution and refinement. The final agreement factors were R = 0.039, R_w = 0.052, GOF = 1.10, p = 0.08.

Supplementary Material Available: Tables of coordinates for the nonhydrogen atoms, anisotropic thermal parameters, bond distances, bond angles, and torsion angles (41 pages); tables of observed and calculated structure factor amplitudes (122 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.