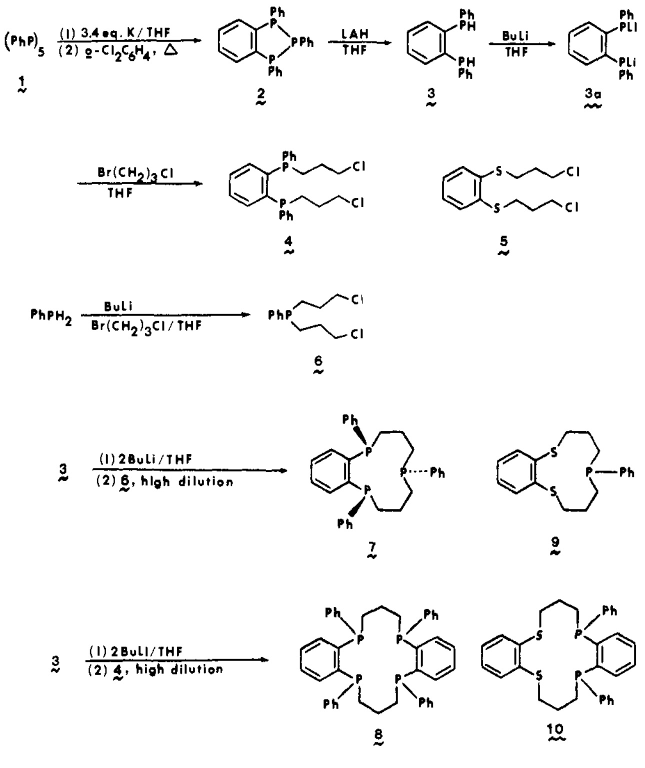
Polyphosphino Macrocyclic Ligand Systems

Sir:

There is extant a vast literature[1] concerning polyphosphorus ligand systems for transition metals. Since it is known[1f] that phosphine ligands stabilize unusual (customarily low) oxidation levels of transition metals, a major reason for interest in polyphosphine-ligated transition metals stems from the desire to develop new and unusual catalytic systems for a variety of types of reactions.[2] In light of the knowledge that cyclic ligands have enhanced ligating properties in comparison with their open-chain analogues in the area of crown ether chemistry,[3] it is at first glance surprising that no macrocyclic polyphosphine-containing species have been reported. An indication of the difficulty of the chemistry involved may be inferred from a comment on a failure to synthesize such molecules.[4] Of the several phosphorus-containing heteromacrorings described in the literature,[5] only two[5i,j] (both of which possess only a single phosphine) appear to be useful in coordination of transition metals.[6]

We now report the synthesis of the first two macrocycles containing more than two phosphino groups, along with two other macrocycles which contain phosphino groups and sulfur atoms. The benzotriphosphole **2** was obtained in 34% yield from pentaphenylcyclopentaphosphine (**1**) using a modified procedure of Mann.[7] The *o*-bis(secondary phosphine) **3** was isolated in 80% by the LiAlH$_4$ reduction of **2** in THF. The dichloride **4** was then obtained (60%) by the addition of the dilithio salt of **3** (*n*-BuLi) (**3a**) in THF to an excess of 1,3-bromochloropropane in THF. Dichlorides **5** and **6** were synthesized similarly in yields of 67 and 40%.[8] The tri- and tetraphosphinomacrocycles **7**[9] and **8** were then produced by the reaction of **3a** with **6** and **4**, respectively, under high dilution conditions.[10] Anaerobic chromatography of crude **7** on degassed silica gel using hexane–dichloroethane as eluent gave, after recrystallization from the chromatography solvent system, a white solid of mp 160.5–161.5 °C in ~5% yield, along with other fractions (amounting to ~5%) with wider melting point ranges.[11] An x-ray structure determination has confirmed the structure of the sharp-melting material to be as shown for **7** in Scheme I.[12] Presumably the crude, broad melting material contains a mixture of the three possible geometrical isomers (two meso, one *dl* pair). Interestingly, although tetraphosphine **8** has five possible isomers (three meso and two *dl* pairs), we have isolated, by recrystallization of the crude material, 22% of what appears to be predominantly one isomer (mp 229–230 °C). In a procedure similar to that above, macrocycle **9**, mp 109.5–110 °C, was synthesized from the dilithio salt of dithiocatechol[13] and **6** (45% yield), and **10**, mp 111–112 °C, from **3a** and **5** (20% yield). Species **10** can exist as two isomers (meso and *dl* pair) but here, also, it appears that one is being formed predominantly.

Scheme I



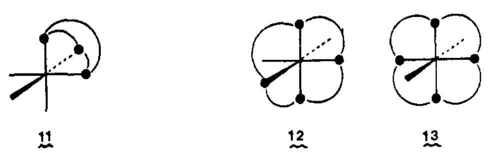


Figure 1. Modes of triligation by ligands **7** and **9** (→**11**) and tetraligation by **8** and **10** (→**12** and **13**) in octahedral complexes.

Inspection of CPK space-filling models reveals that macrorings **7**[14] and **9** must ligate metals in a three-dimensional sense. In fact they appear to have ideal geometry for *fac*-tridentate ligation in an octahedral complex **11** (Figure 1). On the other hand, **8** and **10** are sufficiently large that cis (**12**) and trans (**13**) tetraligation can occur in an octahedron. Our preliminary work shows that all of the macrocycles described here form complexes with transition metals. For example, treatment of molybdenum hexacarbonyl in a refluxing benzene solution of **7** (as a mixture of isomers[14]) with 50% aqueous sodium hydroxide and a catalytic amount of tetra-*n*-butylammonium hydroxide[15] gave, after 2 h, the diligated species **7**·Mo(CO)$_4$ as a yellow powder: mp 138–140 °C dec; IR ν_{CO} 2010, 1935, 1895, 1850 cm^{-1}.[16] On the other hand, when **7** (isomer mixture[14]) was heated in xylene with molybdenum or chromium hexacarbonyl, the corresponding tricarbonyl complexes **7**·Mo(CO)$_3$ and **7**·Cr(CO)$_3$ were isolated.[17] The complex **8**·NiClBF$_4$ was obtained using a method similar to that of King.[18] This material gave orange feather-like crystals (from chloroform) which decomposed at >390 °C.[19] Nickel(II) and cobalt(II) complexes of **9** and **10** were obtained starting with nickel(II) chloride hexahydrate and cobalt(II) chloride hexahydrate and these will be described in a later publication.

We are continuing our investigations in several directions, including the synthesis of other macrorings of various sizes containing phosphorus and other heteroatoms, the formation of transition metal complexes of these cycles, and the use of macrocycle–transition metal complexes as catalysts in organic reactions.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for support of this work (F-573).

References and Notes

(1) Inter alia see (a) C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, **17**, 165–187 (1975); (b) C. A. McAuliffe, Ed., "Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands", Wiley, New York, N.Y., 1973; (c) R. B. King, *Acc. Chem. Res.*, **5**, 177 (1972), and references contained therein; (d) G. Booth in "Organic Phosphorus Compounds", Vol. 1, G. M. Kosolapoff and L. Maier, Ed., Wiley, New York, N.Y., 1972, Chapter 3A; (e) W. Levason and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, **14**, 173–253 (1972); (f) G. Booth, *ibid.*, **6** 1–69 (1964).

(2) (a) G. N. Schrauzer, Ed., "Transition Metals in Homogeneous Catalysis", Marcel Dekker, New York, N.Y., 1971; (b) B. R. James, "Homogeneous Hydrogenation", Wiley, New York, N.Y., 1973; (c) D. Forster and J. F. Roth, Ed., *Adv. Chem. Ser.*, **No. 132** (1974).

(3) (a) G. W. Gokel and H. D. Durst, *Synthesis*, 168 (1976); (b) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).

(4) R. B. King, *J. Coord. Chem.*, **1**, 67 (1971).

(5) (a) S. D. Venkataramu, M. El-Deik, and K. D. Berlin, *Tetrahedron Lett.*, 3365 (1976); (b) T. H. Chan and B. S. Ong, *J. Org. Chem.*, **39**, 1748 (1974); (c) J. P. Albrand, J. P. Dutasta, and J. B. Robert, *J. Am. Chem. Soc.*, **96**, 4584 (1974); (d) J. P. Dutasta, A. C. Guimaraes, J. Martin, and J. B. Robert, *Tet-*

rahedron Lett., 1519 (1975); (e) J. P. Dutasta, A. C. Guimaraes, and J. B. Robert, *ibid.*, 801 (1977); (f) J. P. Dutasta, J. Martin, J. B. Robert, *J. Org. Chem.*, **42**, 1662 (1977); (g) W. C. Marsh, N. L. Paddock, C. J. Stewart, and J. Trotter, *Chem. Commun.*, 1190 (1970); (h) K. B. Yatsimirskii, L. I. Budarin, A. S. Shtepanek, A. I. Telyatnik, and V. A. Smirnov, *Teor. Eksp. Khim.*, **12**, 421 (1976) (*Chem. Abstr.*, **85**, 108726k (1976)); (i) J. Riker-Nappier and D. W. Meek, *J. Chem. Soc., Chem. Commun.*, 442 (1974); (j) J. E. Parks, B. E. Wagner, and R. H. Holm, *J. Am. Chem. Soc.*, **92**, 3500 (1970).

(6) Note that the cyclophosphononitrile described in ref 5g coordinates the transition metal via the nitrogen atoms. We do not consider the extra polymethylene chain (to make a ring) in the diphosphines described in ref 5b as a significant factor in metal complexation.

(7) (a) F. G. Mann and M. J. Pragnell, *J. Chem. Soc. C*, 916 (1966); (b) F. G. Mann and A. J. H. Mercer, *J. Chem. Soc., Perkin Trans. 1*, 1631 (1972); (c) F. G. Mann and A. J. H. Mercer, *ibid.*, 2548 (1972); (d) P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc.*, **97**, 6370 (1975).

(8) With the exception of **4**, all new compounds gave satisfactory spectroscopic and analytical data. Compounds **4** and **6** are both unstable to quaternization reactions at somewhat elevated temperatures (60–80 °C) and short periods of time, or at room temperature over extended periods of time. Consequently, **4** and **6** were routinely stored at −20 °C. We were unable to distil **4**, even using Kugelrohr conditions, and thus were unable to prepare an acceptable analytical sample. The spectroscopic properties of **4** were all consistent with the assigned structure, however.

(9) Crude 7 was obtained in 35% yield as a white solid, mp 100–130 °C. The material appeared to be homogeneous on TLC (several solvent systems on SiO_2) and gave no extraneous peaks in the mass spectrum.

(10) F. Vögtle and G. Wittig, *J. Chem. Educ.*, **50**, 650 (1973).

(11) Our experience with these macrocycles is that, at substrate to absorbent ratios of 1:10^2; only about one third of the cycle elutes no matter how much care is taken in degassing solvents and silica gel. This observation is true even when material isolated by chromatography is rechromatographed. We suspect that complexation of trace transition metals on the silica gel is the cause of the problem.

(12) We thank Professor R. E. Davis of this department for the crystal structure determination. The details of this structure, along with others now in progress will be published later.

(13) I. Degani and R. Fochi, *Synthesis*, 471 (1976).

(14) From inspection of CPK models, only the meso-cis isomer, not the meso-trans one shown, or the *dl* isomer can function as a tridentate ligand about a single metal. Since the barrier to inversion of tertiary phosphines is in the range of 30–35 kcal/mol (R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, **92**, 3090 (1970)), thermal inversion in refluxing xylene (135 °C) should allow access to the meso-cis isomer from any of the starting isomers.

(15) K.-Y. Hui and B. L. Shaw, *J. Organomet. Chem.*, **124**, 262 (1977).

(16) These frequencies are typical of cis-diphosphino metal tetracarbonyls. See, for example, (a) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964); (b) R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, **1**, 287 (1967); (c) R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).

(17) The IR CO stretching frequencies were typical of *fac*-tricarbonyl complexes (see ref 16): **7**·$Mo(CO)_3$, ν_{CO} 1940 and 1850 cm^{-1}; **7**·$Cr(CO)_3$, ν_{CO} 1940 and 1860 cm^{-1}. The ^{31}P NMR (proton decoupled, 85% H_3PO_4 external standard) spectra for both of these complexes in $CDCl_3$ solution consisted of a triplet and a doublet (intensity ratio 1:2): **7**·$Mo(CO)_3$, δ −3.76 (t, J = 26 Hz) and −52.14 (d, J = 26 Hz); **7**·$Cr(CO)_3$, δ −28.33 (t, J = 37 Hz) and −79.91 (d, J = 37 Hz). The free ligand **7** gave ^{31}P NMR resonances at δ 30.56 (s, 2 P) and 25.69 (s, 1 P).

(18) R. B. King, R. M. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).

(19) The complex **8**·$NiClBF_4$ gave a sharp singlet in the ^{31}P spectrum (chloroform-*d* solution) at δ −60.62 ppm relative to 85% H_3PO_4 external standard. Uncomplexed **8** exhibited a sharp singlet at δ 28.94 ppm.

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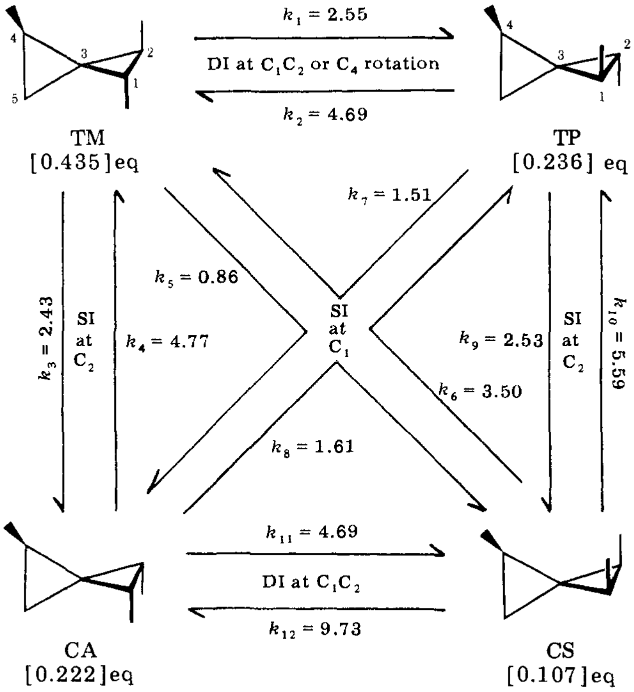
Dominant Double Rotation in the Thermally Induced 1,2,4-Trimethylspiropentane Geometric Isomerization

Sir:

The thermal geometric isomerization of vicinal centers in cyclopropane occurs predominantly by a double inversion process[1] which has been predicted to occur in a conrotatory fashion.[2] Monosubstitution of both inverting centers by small alkyl groups appears to attenuate the double inversion process such that a near-randomly-closing biradical results.[3]

Spiropentane undergoes geometric isomerization[4] by peripheral bond fission[5] faster than structural isomerization[6] to methylenecyclobutane. Double inversion has now been observed with 1,2,4-trimethylspiropentane, but a factor analysis suggests that face to face biradicals are being formed and that conrotation occurs with the trans isomers and disrotation occurs with the cis isomers.

Chart I. Rate constants (× 10^6/s) for the interconversion of the four 1,2,4-trimethylspiropentanes at 561.7 K and 150 Torr: SI = single inversion; DI = double inversion. The equilibrium concentrations are calculated.



The fact is that the four 1,2,4-trimethylspiropentanes[7] interconvert at 561.7 K with the rate constants (× 10^6/s) indicated in Chart I which in a Runge-Kutta numerical integration of the appropriate differential equations reproduces the experimental data at roughly 20% reaction.[8] The rate constants satisfy the three microscopic reversibility conditions.[9]

From the data it is clear that both double and single inversion is occurring but trans to trans or cis to cis conversions (double inversion—or, less likely, C_4 epimerization with TM and TP[10]) occur as fast as the two single inversion process, in each case suggesting a preference for double inversion.

The magnitude of the preference for double inversion is substantial if the data are dissected into contributing factors. A rate retardation factor, f_{+p}, for generating 1,4-proximal, as opposed to medial or distal, methyl relationships is 0.345 ± 0.01 from the rate constant ratio k_5/k_3 or k_8/k_{11}. A rate retardation factor, f_{-p}, for destroying 1,4-proximal, as opposed to medial or distal, methyl relationships is 0.61 ± 0.04 from the rate constant ratio k_7/k_9 or k_6/k_{10}.[11] From each spiropentane isomer there are two ratios of double to single inversion, and in each case proximal 1,4 relationships are being generated and destroyed, and cis relationships are being generated for which a rate retardation factor, f_{+c}, relative to making a trans relationship may be defined. Any given rate ratio can result from an inherent preference for double vs. single inversion, D/S, modified by the rate-retarding steric factors, f_{+p}, f_{-p}, and f_{+c}.[13] For any value of f_{+c}, the four D/S ratios from the trans isomers are within 2% of one another, and the same is true of the D/S ratios from the cis isomers (see Table I), lending confidence to the notion that steric factors are being properly considered. The cis factor, f_{+c}, determines the absolute values of the D/S ratios, and Table I gives the D/S ratios for various f_{+c} factors.[14]

If the double inversion process is conrotatory, steric effects should favor more double inversion from the trans isomers than from the cis isomers; however, this can be true only if there is a steric preference for generating a cis vicinal relationship, i.e.,