

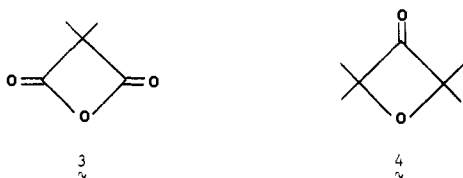
product studies provides clear evidence for the simultaneous scission of two bonds in the transition state rather than simple O–O bond breaking followed by decarboxylation.

Thus it can be argued for the peroxybutyrolactones that those compounds whose ΔH^\ddagger values are \leq that for **1a** (34.1 kcal/mol) should experience two- or three-bond homolyses in the transition states leading to their fragmentations. The products obtained from **2c** and **2d** are obviously derived from a different type of two-bond scission than the one governing the fragmentation of **1**. Activated complexes for these two types of fragmentations can be represented as A and B. With



2c and **2d**, decarboxylation does not successfully compete with deketonation even though a tertiary alkyl radical would be formed as a result of fragmentation from a type B complex. Although the ease of thermolysis of **2a–d** does appear to parallel the expected stability of the radical centers developing at C_β , the correlation may be fortuitous. Ring conformation may also play a significant role in determining the ease and mode of fragmentation; this factor may be particularly important with **2a** and **2b** since the presence of an additional sp^2 carbon would limit the available conformations of the peroxy lactone ring.

The ΔH^\ddagger for **2a** is well below that of any other γ -peroxy lactone; the transition state for it may involve concerted three-bond cleavage.¹² Neither of the compounds shown (**3** and **4**), which would be formed from alternate two-bond cleavage mechanisms, are found as reaction products. Compounds of



type **3** require temperatures >100 °C to force their decarboxylation¹³ and compound **4** is known¹⁴ to be stable up to 120 °C. Thermolysis of **2a** could be accomplished at temperatures as low as 90 °C; therefore **3** and **4** should have been observable if formed. Although **2b** has the highest ΔH^\ddagger of the compounds we studied, the value is approximately the same as the activation enthalpy for **1a**. Neither an oxetane nor a β -propiolactone has been identified as a reaction product here either, although thermolysis of **2b** does yield small amounts of compounds (five by HPLC analysis) not yet characterized and the reactions must be conducted at higher temperatures than for **2a**.

Additional work must be done with the peroxy lactones to establish ground rules, but it is clear that substituents can dictate the course of their fragmentation reactions.

References and Notes

- (1) L. A. Singer in "Organic Peroxides", Vol. I, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1970, p 265.
- (2) (a) W. Adam and Y. M. Cheng, *J. Am. Chem. Soc.*, **91**, 2109 (1969); (b) W. Adam, Y. M. Cheng, C. Wilkerson, and W. A. Zaidi, *ibid.*, **91**, 2111 (1969); (c) W. Adam and C. Wilkerson, *Chem. Commun.*, 1569 (1971).
- (3) W. Adam and L. Szendrey, *Chem. Commun.*, 1299 (1971).
- (4) D. H. Gibson and J. T. Joseph, *Tetrahedron Lett.*, 3483 (1972).
- (5) W. Adam and L. Szendrey, *J. Am. Chem. Soc.*, **96**, 7135 (1974).
- (6) Compounds **2b** and **2d** were prepared by oxidations of cyclobutanones as we described⁴ for **2a**; **2c** was prepared by acetylation of **2d**. All peroxy lactones had satisfactory elemental analyses and showed the expected spectral properties.
- (7) Thermolysis of a β -acetoxy- β -peroxy- β -propiolactone proceeds with deketonation (actually loss of acetic anhydride) as a minor competing path

(H. L. Wilson Ph.D. thesis, University of Louisville, 1975); in this case an α -lactone is formed as the other product (trapped by reaction with an alcohol).

- (8) This compound has been characterized through elemental analysis, spectral properties ($\nu_{C=O}$ 1850, 1775 cm^{-1}) and thermolysis to the enol acetate (for which satisfactory analysis was also obtained).
- (9) Caution! A neat sample of **2d** detonated when heated to 70 °C.
- (10) P. D. Bartlett and R. R. Hlatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).
- (11) W. A. Pryor and K. Smith, *J. Chem. Kinet.*, **3**, 387 (1971).
- (12) Since **2a** and **2b** are cyclic compounds, concerted three-bond cleavage of either would constitute a $[2\pi_s + 2\pi_s + 2\pi_s]$ cycloreversion reaction.
- (13) H. Staudinger, Fr. Felix, and H. Harden, *Helv. Chim. Acta*, **8**, 306 (1925).
- (14) B. L. Murr, G. B. Hoey, and C. T. Lester, *J. Am. Chem. Soc.*, **77**, 4430 (1955).

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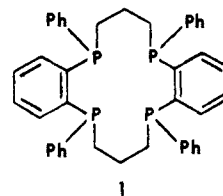
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Properties and Structure of a Tetrakis(*tert*-phosphino) Macrocycle

Sir:

We recently reported the isolation of the macrocycle **1**, a potential polydentate ligand for transition metal complexation.¹ This material, mp 229–230 °C, ³¹P NMR ($CDCl_3$) δ



–28.94 (s),² was the one of five possible isomers (three meso and two *dl* pairs) which we designate as isomer A. We wish now to report the isolation, properties, and structure of a second isomer (B),² mp ~ 160 – 165 °C, ³¹P NMR ($CDCl_3$) δ –26.10 (s).^{3,4}

At slightly above its melting point (165–170 °C) isomer B converts completely into A⁵ as evidenced by ³¹P NMR spectroscopy and the melting point of the resolidified material. However, heating either pure A or B in the melt at 240 °C (0.25 h) or in refluxing xylene (135 °C, 1 h) gave a mixture of A and B in a ratio of 1.7 ± 0.2 ,⁶ by ³¹P NMR spectroscopy. Thus the complete conversion of B \rightarrow A in the melt at ~ 165 °C is a kinetic process where A is removed from equilibrium by crystallization. Additionally, we did not observe significant amounts of the other three possible isomers (<3%) by ³¹P NMR in these thermal equilibration studies.

Both isomers A and B incorporate solvents (~ 1 mol of, e.g., benzene, cyclohexane, acetone, tetrahydrofuran) upon recrystallization, but these solvents are not bound strongly enough to allow x-ray diffraction data collection at ambient temperatures. We now report the structure of isomer B, determined at -40 °C to be the *cis-syn-cis* species. A freshly dried single crystal from acetone-THF was transferred to a Syntex P2₁ autodiffractometer where it was bathed in a cold stream of dry N₂. Crystals are tetragonal, *I*4₁/*a* (No. 88), *a* = 25.504, *c* = 13.792 Å. Density measurements indicated the presence of no more than eight molecules of B per unit cell. Thus it was known at this stage that the molecule must reside either at a crystallographic inversion center or at a crystallographic twofold axis. Intensity data were gathered for the 4392 unique reflections with $2\theta < 52^\circ$ (graphite-monochromatized Mo K α radiation). The 2390 reflections with $I \geq 2\sigma_1$ were used in the structure solution and refinement.⁷

Solution of the structure by direct methods⁸ revealed that the molecule was located at the crystallographic twofold

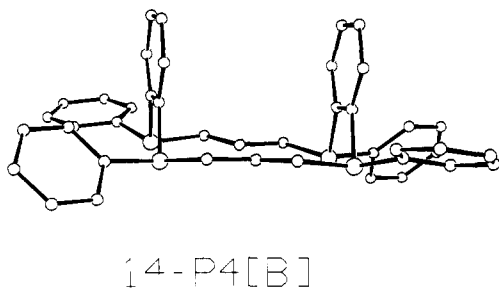


Figure 1. Molecular geometry, viewed approximately parallel to the plane of the macrocycle ring. All hydrogens are omitted.

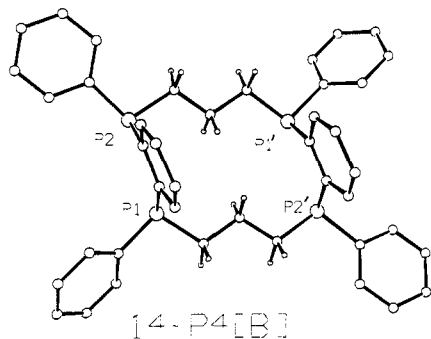


Figure 2. Molecular geometry, viewed approximately along the molecular twofold axis. Hydrogens on the benzo and phenyl rings are omitted. Nonbonded distances: $P1 \cdots P2 = 3.27$, $P1 \cdots P1' = 5.64$, $P1 \cdots P2' = 5.57$, $P2 \cdots P2' = 7.18$ Å.

rotation axis and established the molecular geometry shown in Figures 1 and 2. Comparison of observed and calculated bulk density values also suggested the presence of solvent in the crystal. Molecules of THF of solvation have been tentatively identified and the refinement continues (present $R = 0.132$) with attempts to establish their occupancy ($\sim 75\%$).

Figures 1 and 2 show the general features of molecular geometry. The ten atoms of the macrocycle, excluding the four carbons of the benzo bridges, are coplanar to within ± 0.2 Å. The benzo rings are approximately normal (92°) to the remainder of the macrocyclic ring (Figure 1). This arrangement of the fused rings is emerging as a general structural feature of the five phosphorus-containing macrocycles which have been structurally characterized;^{9a} it persists in the one metal complex for which we have obtained preliminary structural results.^{9b} As seen from a comparison of the P...P distances (Figure 2) the arrangement of the four P atoms is not rectangular. Again, this arrangement closely matches that which we observed in a 14-membered macrocycle containing both P and S.^{9c} The closest transannular H...H contact is 2.4 Å.

The conformation observed for isomer B is one in which both trimethylene diphosphino units are fully extended with P-C-C-C torsion angles near 180° (observed 177 , 176°). This cis-anti-cis stereoisomer would also allow this favorable extended conformation, and we expect that a structure determination will establish that isomer A has this stereochemistry.^{9b} Inspection of CPK models reveals that stereoisomers with phenyl groups trans to each other on the *o*-diphenylphosphino unit would require considerable distortion from the extended conformation of the trimethylene diphosphino chains. This may well be the reason for the observation of only two of the five possible stereoisomers upon thermal equilibration of either isomer A or B.

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References and Notes

- (1) E. P. Kyba, C. W. Hudson, M. J. McPhaul, and A. M. John, *J. Am. Chem. Soc.*, **99**, 8053 (1977).
- (2) Isomer A was isolated in 22% yield by crystallization and recrystallization (hexane-1,2-dichloroethane) of material obtained from a 1,2-dichloroethane extraction of the crude reaction mixture.¹ An ether extraction preceded the dichloroethane extraction, and, with considerable more difficulty, isomer B was obtained in 11% yield by crystallization and recrystallization from acetone-THF.
- (3) Resonance upfield from 85% H_3PO_4 external standard is defined as negative.
- (4) All data, spectroscopic and combustion analytical, were in accord with the formulation 1 as representing A and B.
- (5) The inversion barrier in tertiary phosphines is on the order of 35 kcal/mol: R. Baechler and K. Mislow, *J. Am. Chem. Soc.*, **92**, 3090 (1970).
- (6) This ratio did not change significantly with reactions longer than those indicated.
- (7) Crystallographic experimental and data processing procedures are as previously described: P. E. Riley and R. E. Davis, *Inorg. Chem.*, **14**, 2507 (1975).
- (8) Program MULTAN: M. M. Woolfson, J. P. Declercq, and G. Germain.
- (9) (a) Manuscripts in preparation (R.E.D.); (b) Work in progress (R.E.D.); (c) Compound 10 of ref 1. Manuscript in preparation (R.E.D.).

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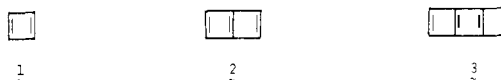
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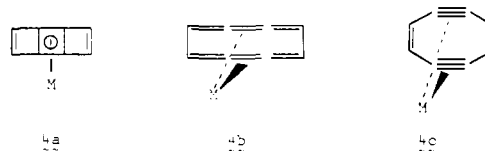
Bicyclobutadienylene(tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene)- η^5 -cyclopentadienylcobalt. A Possible Intermediate in the Remarkable Gas Phase Rearrangement of 1,2-Diethynyl- η^4 -cyclobutadiene- η^5 -cyclopentadienylcobalt

Sir:

Benzene, naphthalene, and anthracene are prototypes of the linear benzenoid aromatic acenes. A corresponding antiaromatic series may be envisaged based on the cyclobutadiene nucleus: cyclobutadiene (1), butalene (bicyclo[2.2.0]hexa-1,3,5-triene) (2), and bicyclobutadienylene¹(tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene) (3). Cyclobutadiene (1)



has been the subject of extensive investigations both as a free compound² and as a ligand to transition metals.^{2,3} Compound 2 and the isomeric *p*-benzyne have recently been implicated as reactive intermediates.⁴ The planar 8π system 3 composed of three fused cyclobutadiene rings has only been discussed from a theoretical viewpoint.⁵ We wish to report that cobalt complexed 1,2-diethynylcyclobutadienes undergo a remarkable thermal rearrangement, the topological features of which suggest the intermediate formation of a cobalt complexed bicyclobutadienylene moiety or its structural and electronic counterpart (i.e., 4a-c).⁶



Addition of a solution of bis(trimethylsilyl)butadiyne (5) (2 equiv) and η^5 -cyclopentadienyldicarbonylcobalt (6) (1 equiv) in *n*-decane to refluxing N_2 -flushed *n*-decane containing 0.2 equiv of 5 over a period of 11.5 h gave a mixture of cyclobutadiene and cyclopentadienone complexes in addition to benzenic products derived from 5.⁷ Protodesilylation of all acetylenic silyl groups in the mixture (1% KOH-EtOH, 2 h, room temperature), followed by column chromatography on