

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

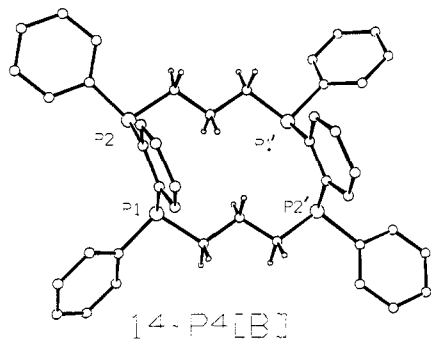


Figure 2. Molecular geometry, viewed approximately along the molecular twofold axis. Hydrogens on the benzo and phenyl rings are omitted. Nonbonded distances: $P1 \cdots P2 = 3.27$, $P1 \cdots P1' = 5.64$, $P1 \cdots P2' = 5.57$, $P2 \cdots P2' = 7.18$ Å.

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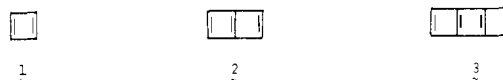
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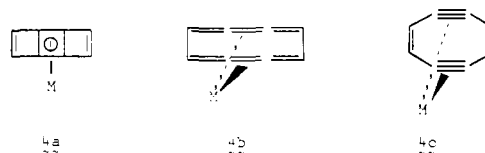
Bicyclobutadienylene(tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene)- η^5 -cyclopentadienylcobalt. A Possible Intermediate in the Remarkable Gas Phase Rearrangement of 1,2-Diethynyl- η^4 -cyclobutadiene- η^5 -cyclopentadienylcobalt

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)

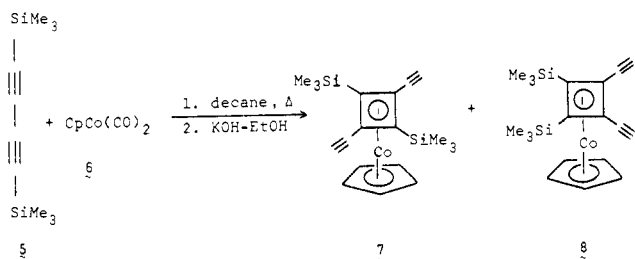


has been the subject of extensive investigations both as a free compound² and as a ligand to transition metals.^{2,3} Compound 2 and the isomeric *p*-benzyne have recently been implicated as reactive intermediates.⁴ The planar 8π system 3 composed of three fused cyclobutadiene rings has only been discussed 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

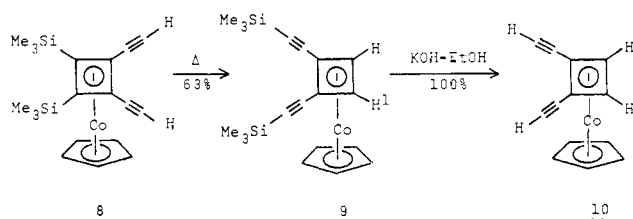


Addition of a solution of bis(trimethylsilyl)butadiyne (5) (2 equiv) and η^5 -cyclopentadienyldicarbonylcobalt (6) (1 equiv) in *n*-decane to refluxing N_2 -flushed *n*-decane containing 0.2 equiv of 5 over a period of 11.5 h gave a mixture of cyclobutadiene and cyclopentadienone complexes in addition 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

neutral alumina, gave, among other products,⁷ in order of elution **7** (50%)⁹ and **8** (2%)⁹ as yellow crystalline air-, heat- and acid-sensitive products after sublimation.⁸ The relative structural assignment was based on the spectral, particularly mass spectral,^{9,10} and chemical properties (*vide infra*).



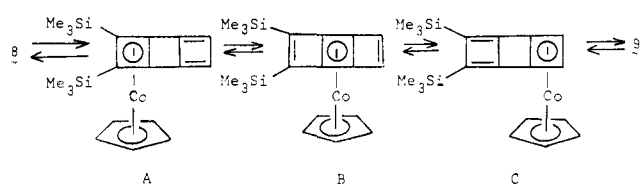
Vacuum sublimation¹¹ of **8** through a hot quartz tube (525 °C (10^{-4} Torr)) initiated a completely unprecedented clean rearrangement to isomer **9** which collects as crystalline material on the other side of the pyrolysis oven.⁸⁻¹⁰ That the neighboring arrangement of the two acetylene substituents had been maintained was indicated by spectral comparison within the 1,2 series^{9,10} and with model systems,¹² by the ¹³C-satellite ¹H NMR spectrum (180 MHz),¹³ and by conversion of **9** to **10**⁸⁻¹⁰ and comparison with the isomeric 1,3-diethynylcyclobutadienecyclopentadienylcobalt (**11**),⁸⁻¹⁰ obtained from **7** by treatment with tetramethylammonium fluoride (Me_4SO , N_2 , 1 h).¹⁴ Under the conditions of the pyrolysis, 1,3 isomer **7** is sublimed completely unchanged up to 700 °C.



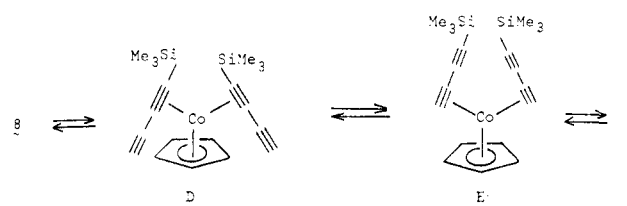
An attractive, simple mechanism for the conversion of **8** to **9** is shown in Scheme I. It involves a formal [2 + 2] cycloaddition of the two acetylene units in **8** to provide a bicyclobutadienylene ligand with three fused cyclobutadiene rings, each of which is a potential site for metal complexation. The CpCo moiety migrates back and forth along the tricycle establishing an equilibrium among the three possible isomers A, B, and C. C may undergo a formal retro-[2 + 2] reaction of the original ligand cyclobutadiene to give **9**. The driving force for the overall transformation is the release of steric strain of the two neighboring trimethylsilyl groups in **8** and the relative electronic stabilization of silicon bound to the more electronegative sp carbon.¹⁵

An alternative mechanism may be proposed (Scheme II) involving the selective formation of a metal diacetylene complex (D) and subsequent "sliding" of the ligands to give E followed by recyclization, presumably through metallocyclic intermediates.¹⁶ If this mechanism were to operate, in which relatively unhindered rotation around the cobalt-acetylene bond in D and E might be anticipated, the selective formation of **9** and the inertness of **7** under the pyrolysis conditions would require mutual kinetic protection of the 1,2- and 1,3-

Scheme I

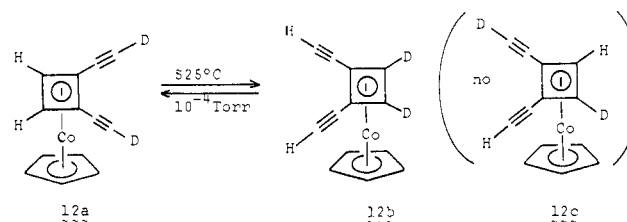


Scheme II



diethynylcyclobutadiene manifold from each other. Otherwise one might have expected **8** to give **7** or its silylacetylenic isomer (if either 1,3-diethynyl isomer were to be more stable than **8** and **9**), or alternatively (if **9** were more stable than **7**) one would have anticipated **7** to lead to **9**. This kinetic protection amounts to an unlikely high barrier to ring closure of rotamers of D and E to give 1,3-diethynylcyclobutadiene isomers, or an equally unlikely high barrier to ring opening of **7**. Even if one invoked restricted rotation around the cobalt-acetylene bond,¹⁷ one might have expected **7** to rearrange to 1,3-bis(trimethylsilyl)ethynylcyclobutadienecyclopentadienylcobalt.

To rigorously exclude the "sliding-rotation mechanism", the dideuterated derivative **12a** (obtained from **9** or **10** by treatment with 1.7% $\text{CH}_3\text{OK}/\text{CH}_3\text{OD}$ and D_2O workup)⁸⁻¹⁰ was exposed to the pyrolysis conditions. If the mechanism outlined in Scheme II were operating in the anticipated rearrangement of **12a**, then random single and double "slides" and rotations followed by ring closure within the 1,2-diethynylcyclobutadiene energy surface would be anticipated to generate a statistical (1:1:2) mixture of **12a**, **12b**, and **12c**. In fact, when



12a was pyrolyzed, the resulting product consisted of a clean 1:1 mixture of the two dideuterio isomers **12a** and **12b**, related to each other by pairwise exchange of the deuterium label, as required by the mechanism suggested in Scheme I.

The absence of isomer **12c** was ascertained by washing out the acetylenic deuterium from the product mixture (KOH-MeOH) and subsequent mass spectral analysis: only molecular ions for **10** (m/e 224) and its 3,4-dideuterio analogue **12b** (m/e 226) were detected.¹⁸

Knowledge of the true nature of the intermediate in these unusual rearrangements (e.g., **4a-c**)¹⁹ will have to await the outcome of trapping experiments underway in our laboratories.

Acknowledgments. We thank R. L. Funk, A. Naiman, and P. Perkins for useful discussions and the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, National Institute of Health, Chevron Research Co., Pressure Chemical Corp., and Silar Laboratories Inc. for generous financial and material support of our programs. One of us (K.P.C.V.) wishes to dedicate this paper to the memory of Dr. Ing. H. Vollhardt who succumbed to cancer on Feb 12, 1978, after a prolonged and spirited battle.

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- This name was coined in analogy to biphenylene.
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- (7) Details will be reported in a full paper.
- (8) Satisfactory analytical and spectral data were obtained for all new compounds.
- (9) Compound 7: yellow crystals; mp 49–51 °C; *m/e* 368 (M⁺, 30%), 246 (CpCoMe₃SiC₂H, 34%); τ (CCl₄) 5.13 (s, 5 H), 7.17 (s, 2 H), 9.70 (s, 18 H); ν_{CCH} 3310 cm⁻¹, $\nu_{\text{C}=\text{C}}$ 2090 cm⁻¹. 8: yellow crystals; mp 82.5–84.5 °C; *m/e* 368.0822 (calcd 368.0827, M⁺, 100%), 294 (CpCoMe₃SiC₂SiMe₃, 28%), 246 (CpCoMe₃SiC₂H, 62%), 198 (CpCoC₆H₂, 6%); τ (CCl₄) 5.10 (s, 5 H), 7.00 (s, 2 H), 9.80 (s, 18 H); ν_{CCH} 3310 cm⁻¹, $\nu_{\text{C}=\text{C}}$ 2090 cm⁻¹. 9: yellow crystals; mp 62–63 °C; *m/e* 368.0820 (calcd 368.0827, M⁺, 62%), 342 (CpCoMe₃SiC₆SiMe₃, 1%), 294 (CpCoMe₃SiC₂SiMe₃, 2%), 246 (CpCoMe₃SiC₂H, 7%); τ (CCl₄) 5.10 (s, 5 H), 6.03 (s, 2 H), 9.77 (s, 18 H); ¹³C NMR (parts per million from Me₄Si, in C₆D₆) δ 0.7, 59.7, 62.9, 82.3, 98.1, 102.8; $\nu_{\text{C}=\text{C}}$ 2140 cm⁻¹. 10: yellow oil; *m/e* 224.0032 (calcd 224.0036, M⁺, 84%), 198 (CpCoC₆H₂, 7%), 165 (M - Co, 100%), 124 (CpCo, 81%); τ (CCl₄) 5.07 (s, 5 H), 6.03 (s, 2 H), 7.07 (s, 2 H); ν_{CCH} 3280 cm⁻¹, $\nu_{\text{C}=\text{C}}$ 2095 cm⁻¹. 11: yellow crystals; mp 94–96 °C; *m/e* 224 (M⁺, 59%), 165 (M - Co, 100%), 124 (CpCo, 91%); τ (CCl₄) 5.04 (s, 5 H), 5.55 (s, 2 H), 7.23 (s, 2 H); ν_{CCH} 3300 cm⁻¹, $\nu_{\text{C}=\text{C}}$ 2110, 2085 cm⁻¹. 12a: *m/e* 226 (M⁺, 65%), 200 (CpCoC₆H₂, 4%), 175 (CpCoC₄H₂, 5%), 167 (M - Co, 95%), 150 (CpCoC₂H₂, 1.5%), 124 (CpCo, 100%); $\nu_{\text{C}=\text{C}}$ 2590 cm⁻¹, $\nu_{\text{C}=\text{C}}$ 1975 cm⁻¹.
- (10) Mass spectra of "cis"- and "trans"-disubstituted η^5 -cyclopentadienyl- η^4 -cyclobutadiene-cobalt complexes exhibit diagnostic fragmentation patterns on electron impact: M. D. Rausch, I. Bernal, B. R. Davies, A. Siegel, F. A. Higbie, and G. F. Westover, *J. Coord. Chem.*, **3**, 149 (1973).
- (11) Heating 8 to 140 °C in toluene for 4 h gives a complex mixture of products.
- (12) W. H. Okamura and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 5991 (1967).
- (13) We observe $J(^{13}\text{C}-\text{H}) = 191 \text{ Hz}$, $J(\text{H}-\text{H}) \leq 0.4 \text{ Hz}$, $J(\text{H}-\text{H})$ expected for 1,2-disubstitution $< 0.7 \text{ Hz}$, $J(\text{H}-\text{H})$ for 1,3-disubstitution = 9 Hz. See H. A. Brune, H. P. Wolff, and H. Hüther, *Z. Naturforsch., B*, **23**, 1184 (1968); J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
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- (18) Irradiation of this mixture through Pyrex with a medium-pressure Hg lamp gave unchanged starting material.
- (19) In addition to the mechanisms outlined in Schemes I and II, more complicated processes involving metallocyclic intermediates and a series of sigmatropic shifts are conceivable.⁷
- (20) (a) Recipient of a Regents' Predoctoral Fellowship. (b) Fellow of the A. P. Sloan Foundation, 1976–1980.

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Existence and Structure of the Molecular Ion 18-Vanadate(IV)

Sir:

We wish to report the existence of a large spherical oxo anion of vanadium(IV) having the composition V₁₈O₄₂¹²⁻, and to describe briefly its structure as determined by x-ray diffraction

from a crystal of its potassium salt, K₁₂V₁₈O₄₂·16H₂O. Heretofore the only large discrete ion of vanadium identified in a definite structural sense has been the orange decavanadate(V), V₁₀O₂₈⁶⁻.¹ The latter species (with its protonated forms) is known to be the dominant oligomer produced when V₂O₅ is treated with a limited amount of strong base.² On the basis of the work described in this preliminary communication, we now believe that the deep red-brown species V₁₈O₄₂¹²⁻ occupies a position in the aqueous chemistry of vanadium(IV) analogous to that of V₁₀O₂₈⁶⁻ in the chemistry of vanadium(V).

Relatively little has been known of the constitution of the brown solutions obtained by treating VO₂ (or VO²⁺) with hydroxide, even though this reaction was first described by Berzelius in 1831. These solutions are stable in the pH range 9–13(+) in the absence of oxygen, and from them brown to black salts can be crystallized. (The early work is cited in ref 3a.) The sodium and potassium salts were studied carefully ~20 years ago by Weiske⁴ who formulated them as [Na₂V₃O₇·4H₂O]_x and [K₂V₃O₇·2.5H₂O]_x. Several types of measurements made on their solutions convinced him that a very large anion was present in these compounds. The value of x that correctly describes both of these salts is shown below to be 6.

Both the sodium and the potassium salts were prepared by combining solutions of VOSO₄ with the appropriate hydroxide (OH⁻/V, ~5) at 60–70 °C under nitrogen or argon. The resulting deep reddish brown solutions, which were 0.5–0.7 M in vanadium(IV) and near pH 14, were filtered as necessary and chilled for several hours at 0 °C, after which flaky brown crystalline products were separated. The crude products were redissolved to saturation in 0.2 N hydroxide at 70 °C (~6 wt %) under inert gas. Standing for 1–3 days at room temperature produced sharp black tetragonal (Na) or monoclinic (K) prisms, which were recovered in 50–80% overall yields.

Prepared salts were protected against water loss and oxidation. Vanadium was determined by sequential potentiometric titrations with cerium(IV) and iron(II) in 2 N H₂SO₄. The average oxidation state inferred by this means was 4.01 (Na) and 4.00 (K). Potassium was determined as the tetraphenyl borate, sodium by atomic absorption, and water by weight loss in vacuo at 160 and 300 °C.

Calcd for Na₁₂V₁₈O₄₂·24H₂O: V, 39.92; Na, 12.01; H₂O, 18.82. Found: V, 39.6; Na, 13.0; H₂O, 19.43. Calcd for K₁₂V₁₈O₄₂·16H₂O: V, 39.08; K, 20.00; H₂O, 12.29. Found: V, 38.95; K, 20.07; H₂O, 12.48. Several other salts were prepared and analyzed, including those of Ba²⁺, Tl⁺, Cs⁺, Rb⁺, and Na⁺/Cs⁺.

For the sodium salt the dimensions of the tetragonal unit cell, as obtained by the precession method, are $a = 20.83$, $c = 14.40 \text{ \AA}$. The density, as obtained by the flotation method, is 2.45 g/mL. From these and analytical data, the cell was calculated to contain a group of 17.9 V atoms in each asymmetric unit. Preliminary results for the monoclinic potassium salt (refined data given below) implied 17.7 V atoms in each asymmetric unit. This was taken as evidence for the persistence of an 18-vanadate ion in two different space groups, and therefore probably also in the solutions from which the salts crystallized.

A crystal of the potassium salt 0.25 × 0.13 × 0.18 mm was protected in a glass capillary during collection of Mo K α x-ray diffraction data with a Picker four-circle diffractometer. Nineteen hand-centered reflections gave a refined unit cell of dimensions $a = 12.580(1)$, $b = 37.661(4)$, $c = 12.724(1) \text{ \AA}$; $\beta = 97.606(4)^\circ$; $Z = 4$; $D_x = 2.608$, $D_m = 2.58 \text{ g/mL}$.

A total of 3490 symmetry-independent counter data were collected by the θ - 2θ scan method, of which 2984 were considered observed. After all appropriate adjustments of the data, the structure was solved in the uniquely assignable space group