

The four vinyl protons of the COD ligand are thus nonequivalent in the static structure (two cis to the methylated sulfur and two trans, two above the coordination plane and two below).

Since only two vinyl resonances are observed in the low temperature spectrum down to  $-80^\circ$ , we suggest that two dynamic processes are occurring in solution which equilibrate pairs of vinyl protons with only one of these processes observed on the nmr time scale in the present study. Possible averaging processes include: (a) inversion at the pyramidal sulfur;<sup>5</sup> (b) twofold twist of one chelate ring going through a tetrahedral transition state; (c) dissociation of a Rh-olefin bond, rotation of the diolefin, and recombination; and (d) a process similar to (c) in which the Rh-S(CH<sub>3</sub>) bond cleaves. Because of the loss of methyl proton-rhodium coupling in going from  $-20^\circ$  to room temperature, we tend to favor (d) as the observed process with inversion at sulfur (a) as the rapid equilibrating process which we are unable to freeze out on the nmr time scale. However, (b) cannot be ruled out as the observed process because of coalescence temperatures of 0 and  $-50^\circ$  for Rh(COD)(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-mnt) and Rh(NBD)(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-mnt), respectively. In the twofold twist mechanism, steric interactions between the diene and the sulfur donor ligands should be reduced for the NBD complex and thus lead to the observed lower barrier for equilibration in that system. The low activation energy implicit in our assumption about inversion at sulfur seems reasonable since the transition state for process (a) should be stabilized by a delocalized dithiolene resonance structure. In addition, the solid state structure of Rh(COD)(CH<sub>3</sub>-mnt) shows the alkylated sulfur to be slightly less pyramidal than those found in other metal complexes.<sup>6</sup> The magnitude of  $J_{\text{Rh-H}}$  in the present case is similar to that found in structurally related systems.<sup>7</sup> Further studies including detailed spectral analyses will be reported.

Alkylation of dithiolate sulfur atoms has been observed previously.<sup>8</sup> In the present study the adduct complexes remain as d<sup>8</sup> Rh(I) systems potentially capable of undergoing oxidative addition reactions. The thiolate S donor lone pairs function as nucleophiles in attack on oxidative addition substrates and thus raise the possibility of utilizing such ligand lone pairs in certain multi-step, metal complex promoted reactions.

**Acknowledgment.** We thank the National Science Foundation (GP-40088X) for support of this research

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(6) To assess the pyramidal nature of the alkylated sulfur in this system, we have summed the three bond angles about S(1) and compared that sum with trivalent sulfur in other systems. The larger the sum, the greater the s character in the sulfur  $\sigma$ -bonding orbitals and the closer the sulfur is to the  $360^\circ$  value for a planar, trigonal atom. The values for representative systems are as follows:  $322^\circ$  (present case);  $316^\circ$  in  $\text{Re}_2\text{Cl}_5(\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3)_4$  [M. J. Bennett, F. A. Cotton, and R. A. Walton, *Proc. Roy. Soc., Ser. A*, **303**, 175 (1968)];  $315^\circ$  in  $\text{Ni}(\text{TSP})\text{Cl}^+$  (L. P. Haugen and R. Eisenberg, *Inorg. Chem.*, **8**, 1072 (1969));  $310^\circ$  in  $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{S}^+$  (A. Lopez-Castro and M. R. Truter, *Acta Crystallogr.*, **17**, 465 (1964)).

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(9) Alfred P. Sloan Foundation Fellow, 1972-1974.

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**Supplementary Material Available.** The table of final positional and thermal parameters for the structure will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-4994.

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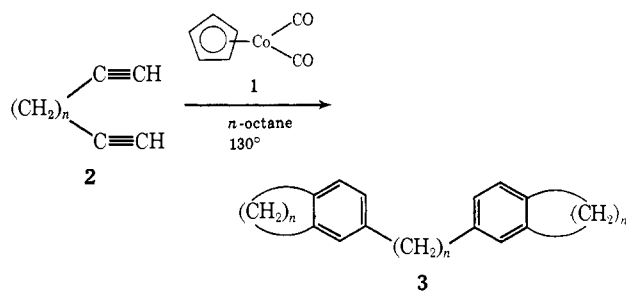
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### A One-Step Synthesis of Benzocyclobutenes Involving Cooligomerization of Linear Mono- and Diacetylenes Catalyzed by $\eta^5$ -Cyclopentadienylcobalt Dicarboxyl

Sir:

We wish to report that commercially available  $\eta^5$ -cyclopentadienylcobalt dicarbonyl ( $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$ ) (**1**) reacts catalytically with linear 1, *m*-diacetylenes to produce, in good to moderate yield, trimers the formation of which involves the interaction of six acetylene functions. The product-forming intermediates in these reactions can be intercepted either by other acetylenes, leading to a versatile one-step synthesis of benzocyclobutenes, or by nitriles, leading to complex pyridines.

Our first observation was made in the reaction of 1,5-hexadiyne (**2**,  $n = 2$ ) with **1** in refluxing *n*-octane (con-



ditions similar to those described by King and Efraty<sup>1</sup> and by Macomber<sup>2</sup>). Chromatography of the reaction mixture gave a product (45% yield) containing neither acetylene, carbonyl, nor metal, the spectral data of which were consistent with benzocyclobutene structure **3** ( $n = 2$ ). This material was identical with the sample of **3** ( $n = 2$ ) reported earlier as having been isolated in 13% yield on reaction of **2** with a Ziegler-Natta catalyst.<sup>3</sup>

The reaction is apparently general for linear terminal diacetylenes. Compounds **2** ( $4 \geq n \geq 2$ ) all produce **3** in reasonable yield along with only trace amounts of colored by-products, easily removed by column chromatography. The reaction is even cleaner when carried out catalytically; a 1:20 mole ratio of **1** to **2** leads to comparable yields of **3** in better purity and at about the same rate.

(1) R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, **94**, 3021 (1972).

(2) R. S. Macomber, *J. Org. Chem.*, **38**, 816 (1973).

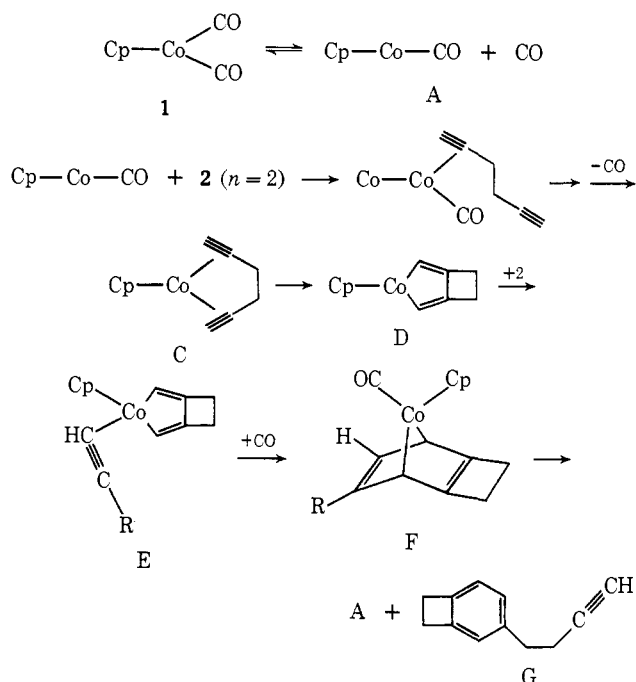
(3) (a) A. J. Hubert and J. D. Dale, *J. Chem. Soc.*, 3160 (1965); A. Hubert, *J. Chem. Soc. C*, 6 (1967); see also (c) E. L. Colthup and L. S. Meriwether, *J. Org. Chem.*, **26**, 5169 (1961); (d) R. D. Stephens, *ibid.*, **38**, 2260 (1973).

**Table I.** Reactions of Acetylenes and Nitriles Catalyzed by  $\eta^5$ -Cyclopentadienylcobalt Dicarbonyl (**1**)<sup>a</sup>

Reactants	Product	% yield <sup>c</sup>
<b>2</b> ( $n = 2$ )	<b>3</b> ( $n = 2$ )	45
<b>2</b> ( $n = 3$ )	<b>3</b> ( $n = 3$ )	25
<b>2</b> ( $n = 4$ )	<b>3</b> ( $n = 4$ )	20
<b>2</b> ( $n = 2$ ) + <b>5</b> ( $R_2 = H, R_3 = n$ -hexyl)	<b>6</b> ( $R_2 = H, R_3 = n$ -hexyl)	
<b>2</b> ( $n = 2$ ) + <b>5</b> ( $R_2 = R_3 = C_6H_5$ )	<b>6</b> ( $R_2 = R_3 = C_6H_5$ )	48
<b>2</b> ( $n = 2$ ) + <b>5</b> ( $R_2 = R_3 = CO_2CH_3$ )	<b>6</b> ( $R_2 = R_3 = CO_2CH_3$ )	14
<b>2</b> ( $n = 2$ ) + <b>5</b> ( $R_2 = H, R_3 = C_6H_5$ )	<b>6</b> ( $R_2 = H, R_3 = C_6H_5$ )	17
<b>2</b> ( $n = 2$ ) + <b>5</b> ( $R_2 = H, R_3 = CH_2OH$ )	<b>6</b> ( $R_2 = H, R_3 = CH_2OH$ )	14 <sup>b</sup>
<b>2</b> ( $n = 2$ ) + $C_6H_5CN$	<b>8</b>	29
<b>9</b> + $C_6H_5C\equiv CC_6H_5$	<b>10</b>	28
<b>4</b> + <b>5</b> ( $R_2 = R_3 = CO_2CH_3$ )	<b>7</b> ( $R_2 = R_3 = CO_2CH_3$ ) <sup>d</sup>	

<sup>a</sup> Typical reaction conditions are as follows. A 1:1 molar mixture of mono- and bisacetylene in *n*-octane (varying amounts of toluene can be added to effect dissolution of octane-insoluble acetylenes) is slowly added to a solution of *ca.* 50 mg of **1** (used as obtained from Pressure Chemical Co., Pittsburgh, Pa.) in refluxing *n*-octane. After 14 hr the solvent is evaporated and the residue chromatographed on alumina. Hydrocarbons elute with 2% ether in pentane, others with higher ether contents in pentane solvent. Most of the catalyst can usually be recovered by eluting with pentane. <sup>b</sup> An excess of propargyl alcohol was employed in this reaction. <sup>c</sup> Isolated yield. In most cases, conditions are not optimized. Our results with **2** ( $n = 2$ ) indicate that higher dilution increases the yield of product. <sup>d</sup> Lit. (P. Heimbach and R. Schimpf, *Angew. Chem., Int. Ed. Eng.*, **8**, 206 (1969)).

On the basis of recent work by Collman, Yamazaki, Müller, and others,<sup>4</sup> we assume that the mechanism outlined in Scheme I for **2** ( $n = 2$ ) is a reasonable path

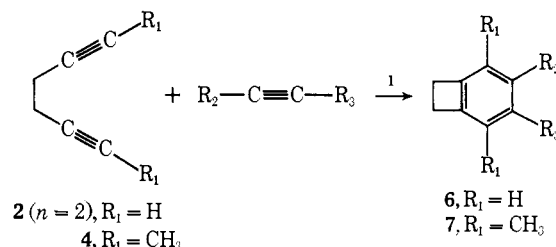
**Scheme I**

for these reactions. The fact that the presence of excess CO retards the overall reaction rate suggests that the first step is rate determining. A crucial step in this scheme involves oxidative addition of the  $\eta^2$ -complexed diacetylene to cobalt(I) in intermediate C, leading to a cobalt(III) metallacyclobutene (D) which is coordinately unsaturated and can incorporate another molecule of **2**. Formation of two new C-C bonds in E might lead to intermediate F, which could extrude monocarbonyl A (for reentry into the catalytic cycle), and leave com-

(4) (a) J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, **7**, 1298 (1968); (b) H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, **21**, 431 (1970); (c) E. Müller and C. Beissner, *Chem. Ztg.*, **97**, 207 (1973); (d) S. A. Gardner, P. S. Andrews, and M. D. Rausch, *Inorg. Chem.*, **12**, 2396 (1973); (e) P. M. Maitlis, *Pure Appl. Chem.*, **33**, 489 (1973); (f) L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **27**, 3930 (1962); (g) A. T. Blomquist and P. M. Maitlis, *J. Amer. Chem. Soc.*, **84**, 2329 (1962); (h) G. M. Whitesides and W. J. Ehrmann, *ibid.*, **91**, 3800 (1969).

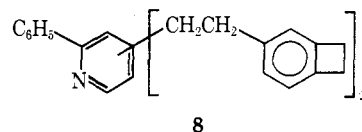
pound G. Reaction of G with another molecule of D would lead ultimately to the final product **3**.

Consideration of this mechanism suggested that it might be possible to divert intermediate D with other acetylenes, and thus create a general one-step syn-



thesis of benzocyclobutenes<sup>5</sup> in which extensive control of substitution might be available. This proved successful; as shown in Table I, in the presence of added monoacetylenes, negligible amounts of trimer **3** are formed and reasonable yields of a variety of benzocyclobutenes can be obtained.<sup>6</sup>

In an attempt to intercept D with benzonitrile,<sup>7</sup> the reaction took a somewhat different course. Isolated after 14 hr of reflux in *n*-octane and separated by preparative thin-layer chromatography were several compounds having general structure **8** (these materials



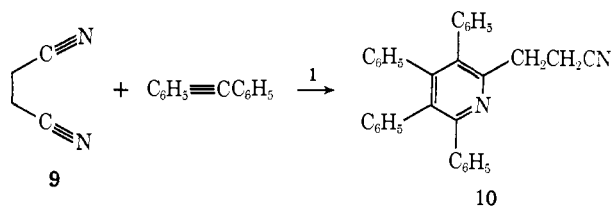
appear to be positional isomers of one another). Similarly, succinonitrile (**9**) cannot be used to simply mimic the role of diacetylene **2**—in the presence of **1** and diphenylacetylene, the reaction leads to pyridine **10** in 28% yield.

Although the mechanism outlined in Scheme I provides a reasonable working hypothesis for understand-

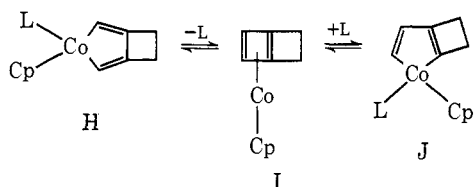
(5) For some previously reported available routes to individual benzocyclobutenes, see (a) I. Klundt, *Chem. Rev.*, **70**, 471 (1970); (b) P. Radlick and L. R. Brown, *J. Org. Chem.*, **38**, 3412 (1973); (c) A. Sanders and W. P. Giering, *ibid.*, **38**, 3055 (1973); (d) M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2255 (1958); (e) J. Oliver and P. Ongley, *Chem. Ind. (London)*, 1024 (1965).

(6) All new compounds reported gave satisfactory analytical and spectral data.

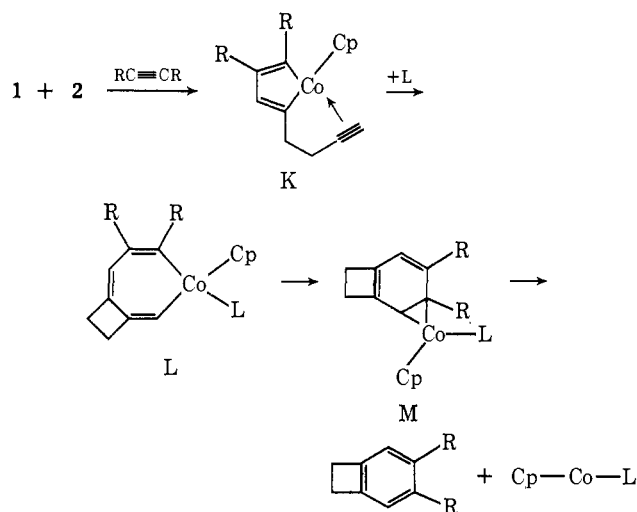
(7) For related reactions, see Y. Wakatsuki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 280 (1973); *Tetrahedron Lett.*, 3383 (1973).



ing these reactions, some comment on other possible routes is warranted. We believe that the absence of 2,3-disubstituted benzocyclobutenes in the cooligomerizations reported here makes it unnecessary to invoke metalocycle rearrangement *via* a complexed cyclobutadiene intermediate<sup>4h</sup> (*i.e.*,  $H \rightleftharpoons I \rightleftharpoons J$ ).



However, it is conceivable that the first metalocycle formed in the cooligomerization is K, which arises



from interaction of two different acetylene molecules. Formation of product would then require direct insertion of the third acetylene group into the Co—C bond, leading to L, which could extrude the metal *via* "metalloncaradiene" M (insertion into the Co—C bond is, of course, also a possibility in E). Finally, it is quite possible that cluster complexes such as those formed<sup>8</sup> during the photochemistry of 1 are also produced thermally, and that these are involved in the acetylene dimerizations. Experiments are now under way aimed at distinguishing these alternatives.

**Acknowledgments.** We are grateful to Professors John E. Bercaw and Robert H. Grubbs for helpful discussions and to the National Science Foundation, the National Institutes of Health, and the Chevron Research Corporation for financial support.

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(9) Camille and Henry Dreyfus Teacher-Scholar, 1970-1975.

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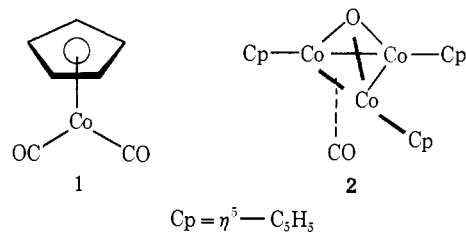
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### Isolation of Unstable Bis( $\eta^5$ -cyclopentadienylcobalt) Tricarbonyl from the Irradiation of $\eta^5$ -Cyclopentadienylcobalt Dicarbonyl. Thermal Reactions of This Binuclear Complex Leading to Starting Material and Trinuclear and Tetranuclear Cobalt(I) Complexes

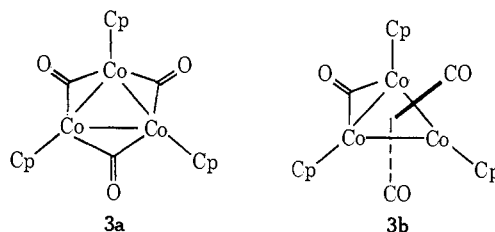
Sir:

Irradiation of  $\eta^5$ -cyclopentadienylcobalt dicarbonyl<sup>1</sup> ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Co(CO)<sub>2</sub>; 1) efficiently produces a new bi-



nuclear cobalt complex which reverts to starting material at room temperature in solution. Because (a) our observations significantly amplify earlier accounts<sup>2,3</sup> of the photochemistry of 1, (b) this reaction can be used as the starting point in the preparation of two additional polynuclear cobalt complexes, one of them a new compound, and (c) these substances are effective acetylene trimerization<sup>4</sup> catalysts,<sup>5</sup> we wish to report our preliminary results here.

Irradiation of 1 in *n*-hexane for long periods of time has been reported by King to yield black crystalline precipitates.<sup>2</sup> This material was separated<sup>2</sup> into two fractions, which were assumed to be two forms of a trinuclear complex possibly having structure 3a or 3b. Dahl isolated from a similar irradiation a small



amount of black crystals determined to have structure 2 by X-ray diffraction.<sup>3</sup>

We have studied the course of this irradiation more closely using nmr techniques. Under normal conditions extensive line-broadening occurs, rendering nmr observation difficult; this complication disappears, however, when oxygen and water are rigorously excluded and the irradiation is carried out in a sealed nmr tube. Employing this technique we find that 1-2 hr of irradiation of 1 in benzene-*d*<sub>6</sub>, cyclohexane, or

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(2) R. B. King, *Inorg. Chem.*, **5**, 2227 (1966).

(3) V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 3763 (1969).

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(5) K. P. C. Vollhardt and R. G. Bergman, *J. Amer. Chem. Soc.*, **96**, 4996 (1974).