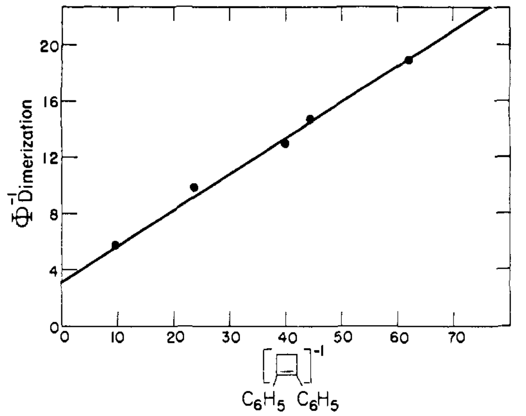

Figure 2. Plot of [quantum yield of dimerization]$^{-1}$ against [1,2-diphenylcyclobutene]$^{-1}$.

each other. We are at present seeking direct experimental evidence for the existence of a metastable eximer of I in solution at room temperature. We are also extending measurements of the kinds described here to several other small-ring unsaturated systems in hopes of determining the importance of various factors influencing the multiplicity of the photochemically active species in any given case.

**Acknowledgments.** We most gratefully acknowledge the help of Mr. Larry Costa in obtaining the fluorescence quantum yields and spectra and the help of Dr. Paul Gilman in obtaining the fluorescence lifetime limits.

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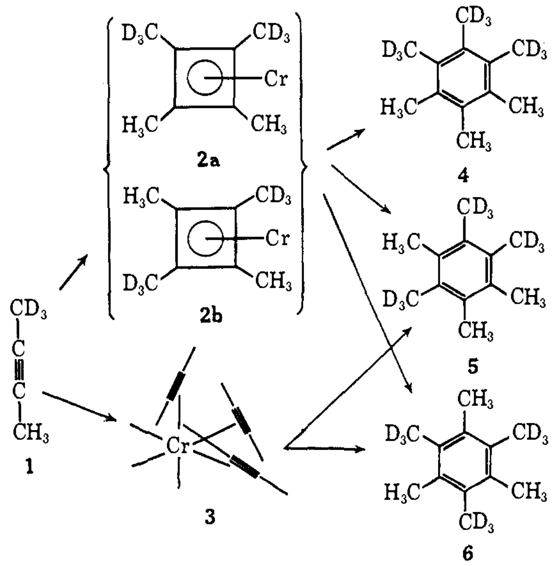
## The Cyclotrimerization of 2-Butyne-1,1,1-$d_3$ by Triphenyltris(tetrahydrofuran)chromium(III)[1]

*Sir:*

The cyclotrimerization of substituted acetylenes to benzene derivatives using organometallic catalysts is a transformation of considerable synthetic usefulness.[2,3] A controversial area in mechanistic discussions of this reaction centers around the importance of metal–cyclobutadiene complexes as reaction intermediates. The observation that various isolable transition metal complexes of cyclobutadienes react with acetylenes only in the presence of oxidizing agents or donor ligands has been interpreted as evidence against cyclobutadiene intermediates.[2,4] However, the reactivity of these stable compounds does not bear directly on that of less stable and presumably more reactive complexes which might be formed under the cyclotrimerization conditions. Labeling and product studies have provided no support for cyclobutadiene intermediates in these reactions,[5] but these experiments are amenable to a number of interpretations.[6] We wish to report the results of deuterium-labeling experiments which provide clear evidence *excluding* a chromium–tetramethylcyclobutadiene intermediate in the cyclization of 2-butyne-1,1,1-$d_3$ (**1**) to hexamethylbenzene-$d_9$ by triphenyltris(tetrahydrofuran)chromium(III).[3]

If the mechanism of this cyclotrimerization involves dimerization of **1** to a tetramethylcyclobutadiene–chromium complex, the initial stages in the cyclization must produce head-to-head and head-to-tail configurations of the labeled cyclobutadienes **2** with equal probability.[7] Further, ample experimental precedent supports the assumption that a cyclobutadiene moiety complexed with a transition metal will adopt a square geometry in which the carbon–carbon bonds of the ring are chemically equivalent.[8] In consequence, reaction of a tetramethylcyclobutadiene-containing intermediate with another molecule of **1**, either directly or following dissociation of the cyclobutadiene from the metal, will lead to a statistically determined distribution of the labeled hexamethylbenzenes **4**, **5**, and **6** (relative yields 1:5:2). In contrast, cyclotrimerization proceeding in a concerted manner through an intermediate in which three molecules of **1** are simultaneously coordinated with the metal (represented schematically by **3**), or through a metal heterocycle of the type proposed by Blomquist[4] and Collman,[9] should lead only to **5** and **6** in 3:1 relative yield.



We have distinguished experimentally between these two alternative paths by determining the yield of **4** produced in the cyclization, relative to the combined yields of **5** and **6**. Compound **4** is unique among the labeled

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(1) Supported in part by the U. S. Army Research Office (Durham), Grant ARO-D-31-124-G691, and by Eli Lilly and Co.

(2) P. M. Maitlis, *Advan. Organometal. Chem.*, **4**, 95 (1966).

(3) H. Zeiss in "Organometallic Chemistry," H. Zeiss, Ed., American Chemical Society Monograph No. 147, Reinhold Publishing Corp., New York, N. Y., 1960, p 380.

(4) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965); **88**, 623 (1966).

(5) J. C. Sauer and T. L. Cairns, *ibid.*, **79**, 2659 (1957); G. N. Schrauzer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 185 (1964).

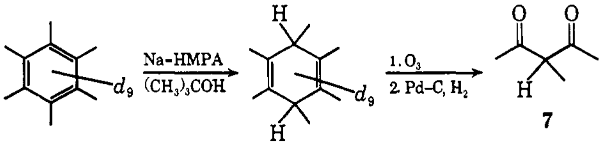
(6) For example, T. I. Bieber, *Chem. Ind.* (London), 1126 (1957). See also E. M. Arnett and J. M. Bollinger, *J. Am. Chem. Soc.*, **86**, 4729 (1964).

(7) We assume that any kinetic isotope effects in the formation and subsequent degradation (eq 1) of the hexamethylbenzenes can be neglected.

(8) R. P. Dodge and V. Schomaker, *Acta Cryst.*, **18**, 614 (1965); J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962); C. S. Yannoni, G. P. Ceasar, and B. P. Dailey, *J. Am. Chem. Soc.*, **89**, 2833 (1967).

(9) J. P. Collman and J. W. Kang, *ibid.*, **89**, 844 (1967).

hexamethylbenzenes in having three *adjacent* labeled methyl groups. Degradation of a mixture of **4**, **5**, and **6** to corresponding isotopically substituted 3-methyl-2,4-pentanediones (**7**) by reduction with sodium in hexamethylphosphoramide–*t*-butyl alcohol, followed by ozonolysis, isolates sets of three adjacent methyl groups in separate molecules (eq 1). This degradation does not scramble or exchange methyl groups; hence, mass spectral determination of the proportion of **7** having three labeled methyl groups, followed by appropriate statistical corrections to account for the distribution of labeled methyl groups expected on reduction of each of the hexamethylbenzenes, provides a method of determining the relative yield of **4**.



(1)

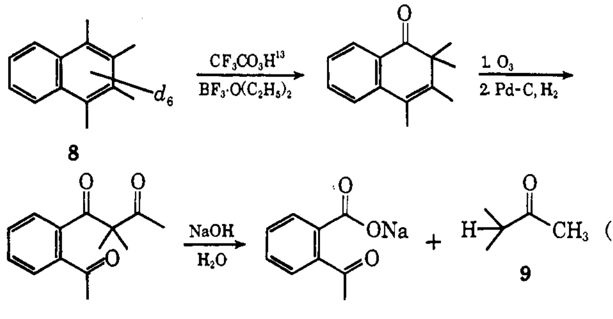
The observed isotopic composition of **7** obtained by degradation of the hexamethylbenzenes from cyclization of **1** with triphenyltris(tetrahydrofuran)chromium(III)[3] is given in Table I, together with the isotopic distribution calculated assuming that the reaction proceeds through a tetramethylcyclobutadiene intermediate and that calculated assuming a concerted cyclotrimerization (or some geometrically equivalent path).[10] Experimental results obtained by a parallel degradation of the hexamethylbenzene from cyclotrimerization of **1** using aluminum chloride in benzene are also included in this table.[11] Comparison of the observed and calculated values shows that no **7**, $(CD_3)_3$ was formed in the chromium-catalyzed reaction beyond that attributable to the isotopic composition of the starting 2-butyne and consequently indicates that within our experimental error no **4** was formed in this cyclization. The close agreement between the isotopic composition observed for the aluminum chloride catalyzed reaction and that calculated on the basis of a cyclobutadiene intermediate provides assurance that the degradation yields reliable results.[12] Taken together, these results exclude a cyclobutadiene intermediate in the cyclotrimerization of 2-butyne over triphenylchromium(III).

**Table I.** Calculated and Observed Isotopic Compositions (%)[a]

| | 7, $(CH_3)_3$ | 7, $(CH_3)_2$-$(CD_3)$ | 7, $(CH_3)$-$(CD_3)_2$ | 7, $(CD_3)_3$ |
|---|---|---|---|---|
| Calcd: concerted | 0.0 | 48.9 | 50.5 | 0.5 |
| Calcd: cyclobutadiene | 4.0 | 44.9 | 46.4 | 4.6 |
| Obsd:[b] $(C_6H_5)_3Cr(III)\cdot$ 3THF | 0.0 | 47.4 | 52.0 | 0.6 |
| Obsd:[b] $AlCl_3$ | 3.7 | 43.7 | 48.1 | 4.5 |

[a] The starting 2-butyne had isotopic composition corresponding to 98.9% $CD_3CH_3$ and 1.1% $(CD_3)_2$. The experimental compositions include contributions to the spectra from the approximately 1.1% isotopic impurity ($CHD_2$) in the $CD_3$ groups. [b] Experimental error in these values is estimated to be ±0.2%.

We have used a similar approach to demonstrate that a tetramethylcyclobutadiene–chromium complex is not an intermediate in the production of 1,2,3,4-tetramethylnaphthalene (**8**) in the chromium-catalyzed cyclization of 2-butyne. In particular, isolation of sets of *two* adjacent methyl groups from **8**, using the degradation outlined in eq 2, and mass spectral determination of the isotopic composition of **9** have established that no 1,2-dimethyl-3,4-di(methyl-$d_3$)naphthalene (**10**) is formed in the reaction of triphenyltris(tetrahydrofuran)chromium(III) with **1**.[13,14]



(2)

**Acknowledgment.** We wish to express our thanks to H. L. Mitchell and E. R. Stedronsky for their assistance in obtaining the mass spectral data.

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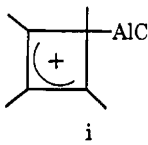
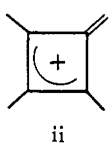
(10) Mass spectra were obtained using a nominal ionizing voltage of 8.3 eV: K. Biemann, "Mass Spectrometry—Organic Chemical Applications," McGraw-Hill Book Co. Inc., New York, N. Y., 1962, p 223 ff.

(11) W. Schäfer and H. Hellmann, *Angew. Chem. Intern. Ed. Engl.*, 6, 518 (1967).

(12) The aluminum chloride catalyzed cyclizations were carried out at 100°. Since hexamethyl(Dewar benzene) can be isolated from this reaction under milder conditions, this result is expected. Whether tetramethylcyclobutadiene is actually an intermediate in this reaction is presently a moot question since, *e.g.*, a cyclobutenyl cation of type i offers an equally satisfactory rationalization of our labeling results. However, the mass spectral data do indicate that no appreciable scrambling of deuterium between labeled and unlabeled methyl groups takes place during this cyclization. Hence cation ii is *not* an intermediate.



i



ii

(13) H. Hart and R. K. Murray, *J. Org. Chem.*, 32, 2448 (1967).

(14) This degradation was checked using an authentic sample of **10**.

(15) National Science Foundation Trainee, 1965–1966; National Institutes of Health Predoctoral Fellow, 1966–1968.

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## The Detection of Apical Interaction in Copper(II) Complexes of Potential Tridentate α-Amino Acids by Optical Rotatory Dispersion[1]

*Sir:*

Except for a number of studies involving histidine, evidence for apical coordination in copper(II) complexes by potential tridentate ligands is lacking. This communication presents optical rotatory dispersion (ORD) evidence demonstrating that tridentate coordination involving the apical position of copper does occur in a

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(1) (a) Structure and Optical Activity in Metal Complexes. IV. Part III: K. M. Wellman, S. Bogdansky, W. Mungall, and T. G. Mecca, *Tetrahedron Letters*, in press. (b) Reported in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract O-37.