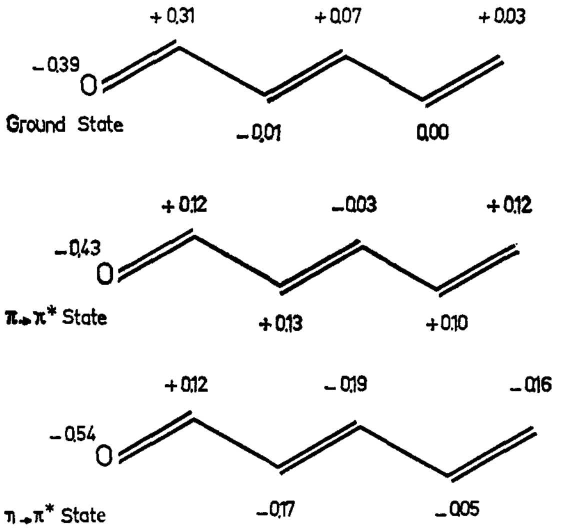

Figure 8. Net π charges in β,δ-hexadienone system.

a large stabilization energy during the dimerization, or (b) to react in a triplet state, where the intermolecular stabilization is unfavorable but a significant energy compensation (again of the order of 1 eV) is received prior to the reaction *via* intersystem crossing from singlet to triplet manifold.

Conclusion

The major weakness of the theory and its applications lies in the consideration of the π electrons alone. We are fully aware that the calculated reaction paths are valid only in the very intial stages of the cycloadditions. The σ electrons must be included to get full reaction paths. Also the neglect of the σ core makes the theory unreliable for the study of photodimerizations such as that of cyclopentenone,[32] where n → π* states could be involved. Again the low, often negative, interaction energies which are obtained by sole consideration of these π electrons clearly indicate that the major source of the activation energy lies in the rearrangement of the σ core. However, the primordial role of the π electrons in *guiding* concerted reactions is apparent from their importance in determining the selection rules for permissible reactions.[33]

With these facts in mind, it is still quite remarkable that the theory can account quantitatively for the nature of the stable cycloadducts in the dimerizations of such complicated systems as unsaturated keto steroids.

Acknowledgments. The authors wish to thank Mr. C. Deniau for kind help with the photographs, and the Quantum Chemistry Program Exchange for providing the molecular SCF program.

(32) (a) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962); (b) P. E. Eaton and W. S. Hurst, *ibid.*, **88**, 5038 (1966).

(33) (a) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968); (b) G. B. Gill, *Quart. Rev.* (London), **22**, 338 (1968).

The Cyclotrimerization of 2-Butyne-1,1,1-d_3 by Transition Metal Catalysts[1]

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Abstract: The observation that 1,2,3-trimethyl-4,5,6-tri(methyl-d_3)benzene (**6**) is not a product of the cyclotrimerization of 2-butyne-1,1,1-d_3 (**4**) using a metallic catalyst is sufficient evidence to establish that the activity of the catalyst does not depend on the generation of free or metal-complexed tetramethylcyclobutadiene-d_6 as a reaction intermediate. The relative yield of **6** in the mixtures of the three hexamethylbenzene-d_9 isomers, **6**, 1,2,4-trimethyl-3,5,6-tri(methyl-d_3)benzene (**7**), and 1,3,5-trimethyl-2,4,6-tri(methyl-d_3)benzene (**8**), obtained on catalytic cyclotrimerization of **4** is conveniently established by degradation of the mixture of deuterated 3-methylpentane-2,4-diones (**12**), using a reaction sequence which does not interchange methyl groups, followed by mass spectrometric examination of the deuterium distribution in these materials. Application of this degradation to the hexamethylbenzene-d_9 isomers obtained on cyclotrimerization of **4** using triphenyltris(tetrahydrofuran)chromium(III), dimesitylcobalt(II), dicobalt octacarbonyl, bis(acrylonitrile)nickel(0), and a titanium tetrachloride–triisobutylaluminum Ziegler catalyst has demonstrated that **6** is not a product of these reactions, and consequently that these cyclizations do *not* take place through tetramethylcyclobutadiene intermediates. The relative yield of **6** produced from **4** using aluminum trichloride as catalyst (~12%) is consistent with the intervention of an intermediate of cyclobutadiene-like symmetry during the cyclization. The yield of **6** produced using dichlorobis(benzonitrile)palladium(II) (~9.5%) is intermediate between these two extremes.

The cyclotrimerization of disubstituted acetylenes to derivatives of benzene by transition metal catalysts is one of the simplest of a number of important organic syntheses that utilize metallic reagents to polymerize or cyclooligomerize olefins and acetylenes.[3,4] As such,

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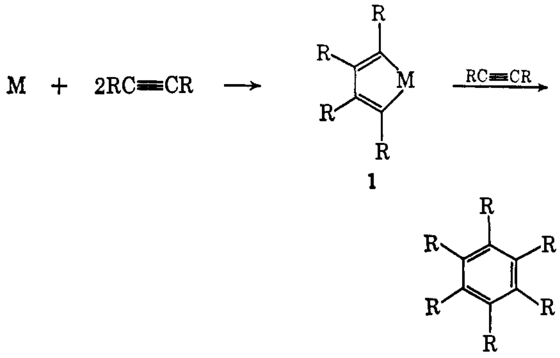
(1) Supported in part by the U. S. Army Research Office (Durham), Grant ARO-D-31-124-G691, and by Eli Lilly and Co.

(2) National Science Foundation Trainee, 1965–1966; National Institutes of Health Predoctoral Fellow, 1966–1969.

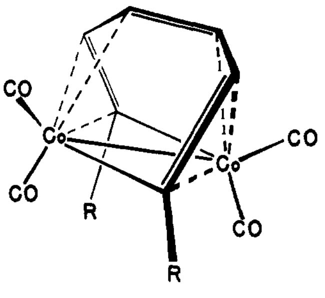
(3) Reviews: F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, *A*, 3 227 (1968); P. M. Maitlis, *Advan. Organometal. Chem.*, **4**,

studies of the mechanisms of these reactions are of interest, both in their own right, and for their pertinence to more general questions concerning the mechanisms of transition metal catalysis of organic reactions. The practical difficulties involved in characterizing the thermally labile catalysts and reaction intermediates encountered in these reactions have so far precluded a complete investigation of the mechanism of any acetylene trimerization. However, despite the primitive level of present understanding of many of the individual steps in these trimerizations, the elegant series of X-ray diffraction studies of compounds isolated from reactions of $Fe_3(CO)_{12}$ with diphenylacetylene[5] and more recent chemical and spectroscopic elaboration of the structures of the organometallic compounds formed in the reaction of $(Ph_3P)_2IrClN_2$ with dimethyl acetylenedicarboxylate[6] have firmly established the existence of a cyclotrimerization pathway requiring a five-membered metallocycle (**1**) as a reaction intermediate.



(1)

Accumulating structural evidence[6,7] suggests that heterocyclic organometallic compounds of type **1** may prove to be common reactive intermediates in transition metal catalyzed reactions.[6,8,9] Nevertheless, at this time there is no compelling reason to believe that all acetylene cyclotrimerizations share closely related mechanisms. A number of plausible mechanistic alternatives to the reaction pathway represented schematically by eq 1 are also worth consideration. One, suggested by the structure of the compound $Co_2(CO)_4(C_2H_2)(HC_2C(CH_3)_3)_2$ (**2**) isolated from a mixed cyclotrimerization reaction,[10] and supported by studies of a variety of related olefin and diene cyclization reactions,[11] involves metal–π-allyl complexes as intermediates. A second requires simultaneous coordination of three molecules of acetylene to a central metal atom (**3**), followed by concerted collapse to an arene or a metal–π-arene complex without further significant intermediates.[12] A third invokes metal–cyclobutadiene complexes as reactive intermediates.[13]



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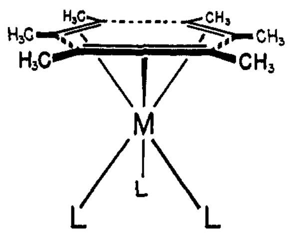

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Although the early theoretical prediction of stability for transition metal–cyclobutadiene complexes[14] and the subsequent isolation and characterization of a number of complexes containing cyclobutadiene ligands focused attention on their potential interest as reaction intermediates, the well-established unreactivity of these cyclotrimerization reactions has been interpreted as evidence that they do not play an important role in acetylene cyclotrimerization.[3] In addition, labeling and product studies in several acetylene oligomerization reactions have provided no support for cyclobutadiene intermediates.[12,15] Moreover, the distribution of products from cyclization of unsymmetrically substituted acetylenes has been taken as evidence against cyclobutadiene intermediates; thus, for example, monosubstituted acetylenes yield 1,2,4- and 1,3,5-trisubstituted benzenes, but have not normally been observed to give 1,2,3-substituted products (however, *vide infra*). Despite these arguments, uncomplexed cyclobutadiene and many of its derivatives clearly *are* reactive toward acetylenes.[16,17] Furthermore, greater reactivity would be expected from labile cyclobutadiene–metal complexes than from their stable analogs.[18] Many of the transition metal catalyzed cyclotrimerization reactions are carried out using conditions under which an unstable or reactive cyclobutadiene–metal complex would go undetected. Moreover, these catalyst systems often contain strong donor ligands or oxidizing agents of the type known to labilize certain of the isolable cyclobutadiene complexes.[3,17] Thus, neither the available data concerning the reactivity of isolable cyclobutadiene

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95 (1966); V. O. Reikhsfel'd and K. L. Makovetskii, *Russian Chem. Rev.*, **35**, 510 (1967).

[4] E. Ochiai, *Coord. Chem. Rev.*, **3**, 49 (1968); J. P. Collman, *Transition Metal Chem.*, **2**, 1 (1966).

[5] R. P. Dodge and V. Schomaker, *J. Organometal. Chem.* (Amsterdam), **3**, 274 (1965); J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hübel, *J. Amer. Chem. Soc.*, **88**, 292 (1966); see also A. A. Hock and O. S. Mills, *Acta Cryst.*, **14**, 139 (1961).

[6] J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, **7**, 1298 (1968), and references therein.

[7] M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 120 (1967); J. T. Mague and G. Wilkinson, *Inorg. Chem.*, 7, 542 (1968).

[8] L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **27**, 3930 (1962).

[9] A. T. Blomquist and P. M. Maitlis, *J. Amer. Chem. Soc.*, **84**, 2329 (1962).

[10] O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 187 (1964).

[11] G. Wilke, *et al.*, *Angew. Chem. Int. Ed. Engl.*, **5**, 151 (1966); P. Heimbach and W. Brenner, *ibid.*, **6**, 800 (1967); D. A. Harbourne, D. T. Rosevear, and F. G. A. Stone, *Inorg. Nucl. Chem. Letters*, **2**, 247 (1966).

[12] For example, G. N. Schrauzer, P. Glockner, and S. Eichler, *Angew. Chem. Int. Ed. Engl.*, **3**, 185 (1964); G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 550 (1962).

[13] H. Zeiss in "Organometallic Chemistry," H. Zeiss, Ed., American Chemical Society Monograph No. 147, Reinhold Publishing Corp., New York, N. Y., 1960, p 380; E. M. Arnett and J. M. Bollinger, *J. Amer. Chem. Soc.*, **86**, 4729 (1964).

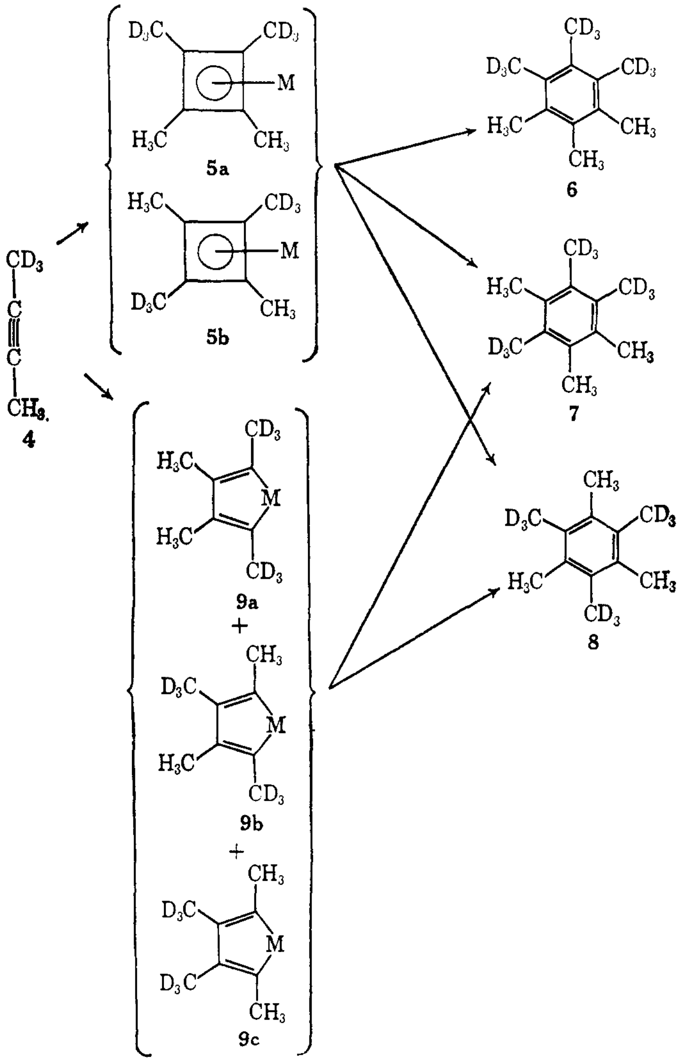
[14] H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

[15] J. C. Sauer and T. L. Cairns, *J. Amer. Chem. Soc.*, **79**, 2659 (1957); see, however, T. I. Bieber, *Chem. Ind.* (London), 1126 (1957); G. N. Schrauzer, *J. Amer. Chem. Soc.*, **81**, 5310 (1959).

[16] M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Organic Chemistry Monographs Vol. 10, Academic Press, New York, N. Y., 1967.

[17] L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965); **88**, 623 (1966).

[18] The complexes $(Ph_4C_4)Mo(CO)(PhC_2Ph)_2$ and $(Ph_4C_4)_2(PhC_2Ph)Mo_2(CO)_4$ are reported to decompose to give small yields of hexaphenylbenzene on heating. Although these transformations may take place by reaction of coordinated tetraphenylcyclobutadiene and diphenylacetylene, other unrelated reaction paths can equally well account for the benzene production: *cf.* W. Hübel and R. G. Merényi, *J. Organometal. Chem.* (Amsterdam), **2**, 213 (1964).



metal complexes toward acetylenes nor the results of previous mechanistic examinations have provided an unambiguous answer to the question of the intermediacy of labile complexes of cyclobutadiene in metal catalyzed cyclotrimerization reactions.

As part of a program of investigation of transition metal catalyzed cyclooligomerization reactions, we felt it worthwhile to survey a number of metal-catalyzed cyclotrimerizations of 2-butyne to hexamethylbenzene using a mechanistic probe specifically intended to detect intermediate metal–tetramethylcyclobutadiene complexes. We present the results of these studies in this paper.[19]

Results

The criterion used to differentiate between cyclotrimerization mechanisms involving intermediates having the effective symmetry of tetramethylcyclobutadiene and mechanisms having only intermediate metallocycles, metal–acetylene complexes, or π-allylic organometallic compounds rests on the well-founded premise that the four ring carbon atoms and carbon–carbon bonds of a metal–cyclobutadiene complex are chemically equivalent.[20] With this premise, if a metal–cyclobutadiene complex is an intermediate in acetylene cyclotrimerization, it is clearly impossible without labeling experiments to distinguish the pairs of atoms in the C_4 ring that were bonded together in the original acetylene molecules. Since any one of the four carbon–carbon bonds of the ring could be broken in forming an arene product, the two carbon atoms derived from a single acetylene need not be adjacent in the product arene. In contrast, adjacent carbon atoms in an acetylene that undergoes cyclotrimerization only by way of intermediates **1**, **2**, or **3** will remain adjacent in the resulting arene.

Thus, cyclotrimerization of 2-butyne-1,1,1-d_3 (**4**) *via* a metal–tetramethylcyclobutadiene intermediate will lead first to the head-to-head and head-to-tail dimers **5a** and **5b**, and ultimately to the three isotopically substituted hexamethylbenzenes **6**, **7**, and **8**. Making the assumption that deuterium kinetic isotope effects can be neglected in these reactions,[21] and the further assumption that conversion of **5** to **6**, **7**, and **8** would take place by initial 2 + 4 cycloaddition to yield hexamethyl(Dewar benzene)-d_9, followed by ring opening, or by some equivalent path, the expected relative yields of the hexamethylbenzene-d_9 isomers can be calculated from simple statistical considerations,

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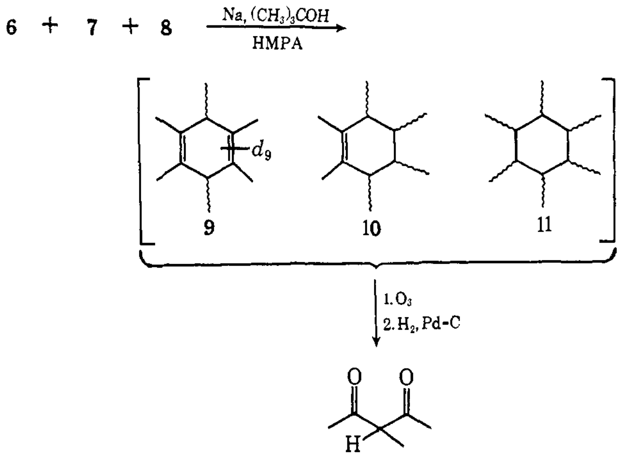
[19] Part of this work has been communicated: G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, **90**, 804 (1968).

[20] 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. Amer. Chem. Soc.*, **89**, 2833 (1967).

[21] The deuterium kinetic isotope effect for a related cycloaddition reaction, the reverse Diels–Alder reaction of the *exo* adduct of maleic anhydride and 2-(methyl-d_3)furan, is $k_H/k_D \sim 1.03$; *cf.* S. Seltzer, *ibid.*, **87**, 1534 (1965).

giving the ratio of **6**:**7**:**8** as 12.5:62.5:25.0 (in per cent). On the other hand, cyclotrimerization proceeding either by initial reaction of two molecules of **4** to form a mixture of metallocycles **9** followed by a subsequent Diels–Alder or carbon–metal bond-insertion reaction, by an intermediate resembling **2**, or by a concerted trimerization (**3**) would lead directly only to the hexamethylbenzene isomers **7** and **8**. In each of these mechanisms, again assuming negligible deuterium isotope effects and a statistically determined product distribution, the relative yields **6**:**7**:**8** would be 0:75:25 (in per cent). It is thus possible to make one rigorous mechanistic distinction from an examination of the products of cyclization of **4**: if **6** is *not* a product, neither tetramethylcyclobutadiene-d_6 nor a metal complex of this compound could have been a reaction intermediate. Of course, the converse of this statement is incorrect, since a variety of mechanisms *not* involving a cyclobutadiene intermediate are capable of yielding **6**.[22]

The 2-butyne-1,1,1-d_3 (**4**) used in our experiments was prepared by reaction of propynyllithium with methyl-d_3 iodide. Its isotopic purity was limited by the presence of ~0.5% of CHD_2I in the CD_3I and by contamination by 1–3% of 2-butyne-d_6, presumably originating in acetylene present in the starting propyne. Determination of the yield of **6** formed in the cyclotrimerization of **4**, relative to the yields of **7** and **8**, was accomplished by taking advantage of the fact that of these three compounds, only **6** has three *adjacent* CD_3 groups. The mixture of **6**, **7**, and **8** was converted to a mixture of isotopically substituted 3-methylpentane-2,4-diones (**12**) using a sequence of reactions which did not interchange the positions of methyl groups during the degradation, and the proportion of **6** in the starting mixture inferred from the yield of **12**-d_9, relative to the combined yield of **12**-d_6, and **12**-d_3. Reduction of the mixture of deuterated hexamethylbenzene isomers with sodium and *t*-butyl alcohol in hexamethylphosphoramide (HMPA) yielded a mixture of deuterated hexamethylcyclohexa-1,4-diene (**9**) (40–50%) and two other compounds tentatively identified as hexamethylcyclohexene (**10**) and hexamethylcyclohexane (**11**).[23] Ozonolysis of this mixture, without separating the **9**, **10**, and **11**, followed by reduction of the resulting ozonides, converted **9** to **12**. Compound **12** was isolated by glpc under conditions that minimized deuterium exchange and its isotopic composition determined mass spectrometrically.



12

In order to relate the isotopic composition of **12** to the relative yield of **6** formed in the cyclotrimerization, the assumption was again made that there were no deuterium kinetic isotope effects in the reduction and ozonolysis steps of the degradation; thus the yields of **12**-d_0, -d_3, -d_6, and -d_9 formed during the degradation of **6** were assumed to be the ratios 1:2:2:1 while the corresponding ratios formed on degradation of **7** or **8** were assumed to be 0:1:1:0. With this assumption, calculation of the relative yields of **12**-d_0, -d_3, -d_6, and -d_9 expected from the degradation of any particular mixture of **6**, **7**, and **8** becomes a straightforward exercise in probabilities, involving determination of the relative abundances of each of the isotopically substituted derivatives of **12** expected from random cleavage of the rings of **6**, **7**, and **8** separately, classification of these derivatives according to mass, weighting according to the relative quantities of **6**, **7**, and **8** in the mixture under consideration, summation, and normalization.

The isotopic compositions of the **12** isolated from the degradation of the mixture of deuterated hexamethylbenzene isomers obtained from cyclotrimerization of **4** using triphenyltris(tetrahydrofuran)chromium(III),[24] dimesitylcobalt,[25] dicobalt octacarbonyl,[26] bis(acrylonitrile)nickel(0),[27] a titanium tetrachloride–triisobutylaluminum Ziegler catalyst,[28] dichlorobis(benzonitrile)palladium(II),[29] and aluminum chloride[30] are given in Table I along with the yields of **6** calculated from these compositions. These numbers are normalized, and have been corrected for contributions to the mass spectra arising from naturally abundant ^{13}C and from the 2-butyne-d_6 and 2-butyne-1,1-d_2 present as impurities in **4**; that is, they represent the yields that would be observed for cyclization of pure **4**. For comparison, this table also contains the relative abundances of the isotopically substituted derivatives of **12** calculated on the assumption that the cyclization proceeds entirely by way of a cyclobutadiene intermediate (**5**) and those

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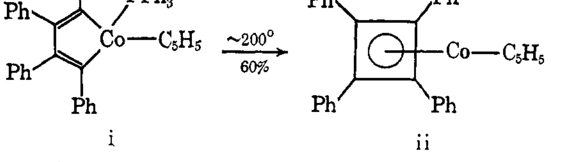
(22) It is worthwhile to point out explicitly that the observation of products derived from an intermediate cyclobutadiene would not preclude a metallocyclic intermediate either earlier or later in the course of the reaction. For example, the conversion of a compound believed to be the metallocycle i to $(Ph_4C_4)(C_5H_5)Co$ (ii) has been reported: H. Yamazaki and N. Hagihara, *J. Organometal. Chem.* (Amsterdam), **7**, P22 (1967).



i ii

(23) Previous attempts to carry out the reduction of hexamethylbenzene using calcium in ammonia and lithium in ethylenediamine had been unsuccessful: H. Boer and P. M. Duinker, *Rec. Trav. Chim. Pays-Bas*, **77**, 346 (1958); J. D. Brooks, R. A. Durie, and H. Silberman, *Aust. J. Chem.*, **17**, 55 (1964).

(24) W. Herwig, W. Metlesics, and H. Zeiss, *J. Amer. Chem. Soc.*, **81**, 6203 (1959).

(25) M. Tsutsui and H. Zeiss, *ibid.*, **83**, 825 (1961).

(26) W. Hübel and C. Hoogzand, *Chem. Ber.*, **93**, 103 (1960); U. Krüerke and W. Hübel, *ibid.*, **94**, 2829 (1961).

(27) G. N. Schrauzer, *ibid.*, **94**, 1403 (1961).

(28) B. Franzus, P. J. Canterino, and R. A. Wickliffe, *J. Amer. Chem. Soc.*, **81**, 1514 (1959); A. J. Hubert, *J. Chem. Soc., C*, 6, 1967.

(29) H. Reinheimer, H. Dietl, J. Moffat, D. Wolff, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **90**, 5321 (1968).

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

Table I. Normalized Calculated and Observed[a,b] Isotopic Compositions (%)[c]

Catalyst	**12**-$(CH_3)_3$	**12**-$(CH_3)_2(CD_3)$	**12**-$(CH_3)(CD_3)_2$	**12**-$(CD_3)_3$	Normalized yield of **6**
1. $Ph_3Cr \cdot 3THF$	0.0	48.4	51.5	0.1	0.3
2. $Mes_2Co(II)$	*c*	47.0	53.0	0.0	0.0
3. Co_2CO_8	*c*	47.9	52.1	0.0	0.0
4. $(CH_2CHCN)_2Ni(0)$	*c*	46.0	53.8	0.1	0.3
5. $TiCl_4 + (i\text{-}C_4H_9)_3Al$	*c*	47.4	52.4	−0.1	<0.0
6. $(C_6H_5CN)_2Pd(II)Cl_2$[d]	3.7	43.7	48.9	3.2	9.6
7. $(C_6H_5CN)_2Pd(II)Cl_2$[d]	3.1	44.5	49.1	3.2	9.6
8. $(C_6H_5CN)_2Pd(II)Cl_2$[e]	(3.1)[f]	45.8	47.9	3.3	9.9
9. $AlCl_3$	3.5	44.5	48.4	4.0	12.0
10. $AlCl_3$[e]	(3.5)[f]	43.4	49.1	3.9	11.7
Calcd: cyclobutadiene	4.16	45.84	45.84	4.16	12.5
Calcd: "concerted"	0.00	50.00	50.00	0.00	0.0

[a] Corrected for $CD_3C\equiv CCD_3$ and $CD_2HC\equiv CCH_3$ present as impurities in the starting $CD_3C\equiv CCH_3$. [b] The estimated precision in these numbers is $\sim\pm 2\%$ for **21**-$(CH_3)_2(CD_3)$ and **12**-$(CH_3)(CD_3)_2$, and $<\pm 0.5\%$ for **12**-$(CD_3)_3$. [c] Observed by background. [d] Duplicate runs. [e] Experiment to check for Lewis acid catalyzed scrambling: see text for discussion. [f] Assumed value.

calculated on the assumption of a noncyclobutadiene process involving only intermediates such as **1**, **2**, or **3** (called "concerted" in this table and throughout the remainder of the paper).

For purposes of comparison of the observed and calculated values, the most important numbers in Table I are those representing the relative yields of **12**-$(CD_3)_3$, since these yields are directly related to the yield of **6** formed in the cyclization. Within the limits of detection of this experimental procedure ($\sim\pm 0.5\%$) no **12**-$(CD_3)_3$, and by inference no **6**, is formed in the reactions involving triphenylchromium(III), dimesitylcobalt(II), dicobalt octacarbonyl, bis(acrylonitrile)-nickel(0), and the Ziegler catalyst. Therefore it is immediately clear that these reactions do *not* involve intermediate tetramethylcyclobutadienes. The normalized yield of the **12**-$(CD_3)_3$ derived from the aluminum chloride catalyzed cyclization is in agreement with that expected from an intermediate having the same effective symmetry as a tetramethylcyclobutadiene. The yield of **12**-$(CD_3)_3$ from the cyclization catalyzed by bis(benzonitrile)palladium dichloride is intermediate between these two extremes.

In order to evaluate the significance of these results, it is important to have some idea of the practical precision of the data. Three pairs of experiments in Table I permit an empirical evaluation of this precision. First, entries 6 and 7 in this table represent duplicate experiments carried out using dichlorobis(benzonitrile)-palladium(II). Clearly the reproducibility of the observed normalized yields of **12**-$(CD_3)_3$ in these experiments is good. Although the reproducibility of the values of the normalized yields of the remaining isotopically labeled derivatives of **12** appears less satisfactory, the relative error in all these numbers is approximately the same.

Entries 9 and 10 in Table I provide similar information. The experiments summarized under entries 8 and 10 were carried out in order to determine if the **6** formed in the aluminum chloride catalyzed reaction of entry 9 was produced directly by the cyclotrimerization, or if it was an artifact resulting from slow Lewis acid catalyzed conversion of **8** and **7** to **6** under the conditions of the cyclization.[31] To test the latter possibility, the mixture of hexamethylbenzene-d_9 isomers isolated from aluminum chloride catalyzed cyclization of **4** (entry 9) was added to a reaction mixture in which nondeuterated 2-butyne was allowed to cyclotrimerize to hexamethylbenzene, using aluminum chloride catalyst and reaction conditions very similar to those used in the original cyclization of **4**. Isolation and degradation of the resulting mixture of labeled and unlabeled hexamethylbenzenes were carried out and the yields of the labeled derivatives of **12** were normalized on the assumption that the **12**-$(CD_3)_3$ and **12**-$(CH_3)_3$ in this mixture were in the same ratio as had been observed in entry 9. The resulting distribution of the label in **12** demonstrated that the yield of **6** relative to the yields of **7** and **8** was not changed by extended exposure to the cyclization conditions. Further, examination of the isotopic distribution in the hexamethylbenzenes *before* degradation showed no evidence of species such as hexamethylbenzenes-d_3 or -d_6 resulting from intermolecular exchange of methyl groups, or of increased yields of hexamethylbenzene-d_8 or -d_7 resulting from loss of deuterium from the hexamethylbenzene-d_9. Very similar results were obtained using the mixture of hexamethylbenzene-d_9 isomers obtained from bis(benzonitrile)palladium(II) dichloride catalyzed cyclization (entry 8). Thus, it appears that aluminum chloride does not catalyze either inter- or intramolecular scrambling of methyl groups or hydrogen atoms under the condtions used in these cyclotrimerization reactions. Entries 9 and 10 of Table I therefore represent, in essence, two separate degradations of the same mixture of **6**, **7**, and **8** diluted with different quantities of hexamethylbenzene-d_0. The absolute agreement between the data of entries 7 and 8, and 9 and 10 is approximately the same as between that of entries 6 and 7, and is sufficient to suggest that the normalized yields of **12**-$(CD_3)_3$ throughout Table I should be considered precise to $<\pm 0.5\%$.

One feature of Table I remains puzzling: *viz.*, the normalized yields of **12**-$(CH_3)(CD_3)_2$ are consistently 3–6% higher than those of **12**-$(CH_3)_2(CD_3)$ despite the fact that these yields should be equal for almost any reasonable cyclization mechanism. These differences in yield are sufficiently large and sufficiently consistent that they are undoubtedly real. They may be a

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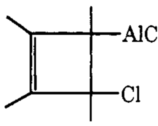
(31) The fast intramolecular rearrangement of methyl groups in heptamethylbenzenenonium ion would provide a possible precedent: V. A. Koptyug, V. G. Shubin, and A. I. Rezukhin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 192 (1965); M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. G. Malmström, and T. Vänngärd, Ed., Pergamon Press, Oxford, 1967, p 85; W. von E. Doering and M. Saunders, *Tetrahedron*, **4**, 178 (1958).

reflection of systematic instrumental error or an artifact of the analytical method.[32] A proportional error in the relative yields of **12**-$(CD_3)_3$ might lead to values as much as 0.4% too high. However, a systematic error of this type is clearly of no concern in those cyclizations which do not yield **6**. Moreover, although such errors are potentially troublesome in the cyclizations using aluminum chloride and bis(benzonitrile)palladium dichloride which *do* result in appreciable yields of **6**, there is good reason to believe that the observed yield of **12**-$(CD_3)_3$ for the former catalyst is in fact correct (*vide infra*). Hence, we will assume in the discussion which follows that the observed normalized yields of **12**-$(CD_3)_3$ reported in Table I do not contain appreciable contributions from systematic error in procedure or analysis.

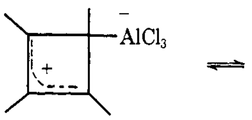
Discussion

The absence of **12**-$(CD_3)_3$ among the degradation products from the hexamethylbenzene-d_9 prepared by cyclotrimerization of **4** using triphenyltris(tetrahydrofuran)chromium(III), dimesitylcobalt(II), bis(acrylonitrile)nickel(0), dicobalt octacarbonyl, and titanium tetrachloride–triisobutylaluminum demonstrates that **6** is not a product of these cyclizations and, consequently, that neither free tetramethylcyclobutadiene, nor any derivative having the effective symmetry of this molecule, is an intermediate in these reactions.[33] Taken as a group, these five catalysts represent the majority of structural types commonly associated with transition metal reagents displaying activity in acetylene cyclotrimerization reactions. The conclusion that the mechanisms by which they effect this catalysis does not involve the generation of reactive cyclobutadiene intermediates suggests that such intermediates are not of *general* importance in acetylene cyclotrimerization and is in agreement with the conclusions of previous studies.[3,4,6,8,9,12]

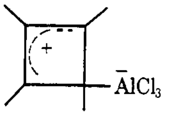
In clear contrast, within the limits of sensitivity of our experimental method, cyclotrimerization of **4** with aluminum trichloride produces the yield of **6** expected on the basis of an intermediate tetramethylcyclobutadiene. Whether this reaction actually generates tetramethylcyclobutadiene is a question which cannot be answered on the basis of the available data. If the reaction is run under milder conditions than those used here, hexamethyl(Dewar benzene) can be isolated in good yield.[29] The formation of this species is certainly compatible with a tetramethylcyclobutadiene intermediate; consequently, the yield of **6** was anticipated. However, the labeling results are equally compatable with a mechanism involving only intermediates of the type **13** or **14**, provided that the rate of migration of the covalently bonded groups around the ring in these species (*e.g.*, **14a** $\rightleftharpoons$ **14b**) is fast compared with that of further reaction with 2-butyne.[35] The absence of detectable deuterium exchange between CH_3 and CD_3 groups *does* exclude **15** as an intermediate. Similarly, the observation that no hexamethylbenzene-d_6 is detected among the cyclization products of **4** with this catalyst demonstrates that the species in which the cyclobutadiene-like symmetrization takes place, whatever its structure, is not in equilibrium with 2-butyne.[36]



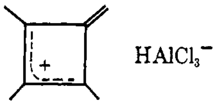
13



14a



14b



15

The cyclotrimerization of **4** with dichlorobis(benzonitrile)palladium(II) provides an interesting and at present unsolved problem in interpretation. The relative yield of **6** obtained using this catalyst is ~9.6% (Table I). The yield of **6** expected from a "concerted" cyclization is of course 0%; that from a tetramethylcyclobutadiene intermediate is 12.5%. The observed yield is thus intermediate between these two limiting extremes.

Dietl and Maitlis recently reported the isolation of 1,2,3-trimethyl-4,5,6-triphenylbenzene (**16**), a cyclic trimer structurally analogous to **6**, in 3% relative yield from the cyclotrimerization of phenylmethylacetylene with this catalyst.[39] Provided that both this yield and that inferred for **6** are correct and comparable, their difference suggests that the reaction which leads to this partial symmetrization is sensitive to substituents in such a manner that formation of the isomer having the substitution pattern represented by **6** and **16** is suppressed by unsymmetrical substitution. In earlier studies of the mechanism of catalytic action of dichlorobis(benzonitrile)palladium(II), Blomquist and Maitlis demonstrated that a tetraphenylcyclobutadienepalladium(II) complex is unreactive toward diphenylacetylene under the conditions used to effect the cyclotrimerization of this compound.[9] The unreactivity of the one complex identified by Blomquist and Maitlis does not, however, preclude the existence of another

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(32) An important fragmentation in the mass spectrum of 12 appears to be a McLafferty rearrangement (see the Experimental Section). A deuterium isotope effect in this fragmentation might enhance the intensity of $[12\text{-}(CD_3)_2(CH_3)]^+$ relative to $[12\text{-}(CD_3)(CH_3)_2]^+$, and thus provide one satisfactory rationalization for the difference in the yields of these species reported in Table I. *Cf.* J. K. MacLeod and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 5182 (1967).

(33) The major difference in the distribution of isotopically labeled isomers from the Ziegler and aluminum chloride catalyst systems indicates that the active catalyst in the former is not simply aluminum trichloride or isobutylaluminum dichloride derived from the reaction between the two catalyst components, but rather that it is probably a coordinatively unsaturated Ti(IV) or Ti(III) species of the type commonly involked in discussions of α-olefin polymerization.[34] This conclusion is in accord with observations made by R. F. Lutz, *J. Amer. Chem. Soc.*, **83**, 2551 (1961).

(34) L. Reich and A. Schindler "Polymerization by Organometallic Compounds," Interscience Publishers, New York, N. Y., 1966; G. Henrici-Olivé and S. Olivé, *Angew. Chem. Int. Ed. Engl.*, **6**, 790 (1967).

(35) For nmr studies of related exchange processes, see E. H. Gold and T. J. Katz, *J. Org. Chem.*, **31**, 372 (1966); H. H. Freedman and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 734 (1964).

(36) Similar intermediates are probably involved in the reduction of 3,4-dichlorotetramethylcyclobutene with zinc[37] and of 3,4-diiodotetramethylcyclobutene with mercury.[38]

(37) C. E. Berkoff, R. C. Cookson, J. Hudec, D. W. Jones, and R. O. Williams, *J. Chem. Soc.*, 194 (1965).

(38) R. Criegee and F. Zanker, *Chem. Ber.*, **98**, 3838 (1965).

(39) H. Dietl and P. M. Maitlis, *Chem. Commun.*, 481 (1968).

reactive cyclobutadiene complex, or of a complex having similar symmetry, as an intermediate in the trimerization of acetylenes. In short, it is not clear whether formation of **6** in our experiments with dichlorobis(benzonitrile)palladium(II) is due to the intervention of a tetramethylcyclobutadiene intermediate, or to some entirely unrelated symmetrizing process. However, the observation that the relative yield of **6** is more than 75% of that expected on the basis of a fully symmetric cyclobutadiene-like intermediate indicates that the reaction responsible for this symmetrization, whatever its nature, is not a minor one. Further speculation concerning the mechanism of the palladium(II)-catalyzed cyclotrimerization will be deferred until additional experimental data are available.[40]

Experimental Section[41]

General Methods. All reactions involving organometallic compounds were carried out in flame-dried glassware under an inert atmosphere of prepurified nitrogen using the standard techniques for handling oxygen- and water-sensitive reagents. Ether and tetrahydrofuran were distilled from lithium aluminum hydride under a nitrogen atmosphere immediately before use. Dioxane was distilled from a dark purple solution of sodium benzophenone dianion. Hexane was stirred with concentrated sulfuric acid and distilled from a suspension of sodium benzophenone dianion. Reagent grade benzene was used directly. Hexamethylphosphoramide (HMPA) was stirred with sodium until the solution was dark blue, then distilled at ~0.01 mm through a 10-cm Vigreux column.

2-Butyne-1,1,1-d_3 (4). Propyne was bubbled into 100 ml (~1.6 *N*, 0.16 mol) of commercial *n*-butyllithium in hexane, held at room temperature by a water bath, until gas absorption ceased. Ether was added as necessary to replace solvent lost by evaporation. Solvent was removed from the resulting white precipitate of propynyllithium by bulb-to-bulb distillation, and 100 ml of freshly distilled triglyme was added to the solid residue.[43] Methyl-d_3 iodide (20 g, 0.14 mol, 99.5% CD_3I, 0.5% CD_2HI; Stohler Isotope Chemicals) was added in four portions over 40 min, while holding the temperature of the reaction mixture below 20° with a water bath. After the initial exothermic reaction had subsided, the mixture was stirred for 30 min. The product was isolated by passing a slow stream of nitrogen through the reaction mixture while slowly raising its temperature to ~70°; **4** (6.7 g, 88%) was condensed from the nitrogen stream at the temperature of a Dry Ice–isopropyl alcohol bath. Mass spectral analysis indicated isotopic composition for a typical sample of **4** prepared using this procedure of 1.1% d_6, 95.7% d_3, and 3.2% d_2.[44] This isotopic distribution varied slightly from preparation to preparation; hence, the isotopic composition of the hexamethylbenzenes isolated from different cyclotrimerization reactions should not be expected to remain constant.

Cyclotrimerization of 2-butyne-1,1,1-d_3 using triphenyltris(tetrahydrofuran)chromium(III) was modeled on the procedure of Zeiss,[24] starting with ~33 mmol of triphenylchromium and 178 mmol of **4**. A mixture of hexamethylbenzene-d_9 and 1,2,3,4-tetramethylnaphthalene-d_6 was obtained from the cyclization reaction. This mixture was distilled through a short column at atmospheric pressure (bp ~245–250°), and the first fraction was recrystallized from absolute ethanol to yield 1.0 g (10%) of a mixture of deuterated hexamethylbenzenes, having mp 164–165° (lit.[24] mp 165–167° for hexamethylbenzene), and mass spectral isotopic composition 3.1% d_{12}, 92.3% d_9, and 4.6% d_8.

Using Dimesitylcobalt(II). Using the procedure of Tsutsui and Zeiss,[25] **4** (1.5 ml, ~18 mmol) was allowed to react with ~1.0 mmol of dimesitylcobalt(II). The mixture of deuterated hexamethylbenzenes (245 mg, ~24%) isolated after recrystallization from absolute ethanol had mp 163–164°, and mass spectral isotopic composition 1.9% d_{12}, 93.3% d_9, and 4.9% d_8.

Using Dicobalt Octacarbonyl. A mixture of 0.150 g of $Co_2(CO)_8$ (Alfa Inorganics, Inc.) and 1.2 ml (~15 mmol) of **4** in 4 ml of dioxane was refluxed for 48 hr.[26] The reaction mixture was cooled and poured into 20 ml of 30% aqueous nitric acid. The nitric acid solution was extracted with ether, and the ether was washed with water, dried ($MgSO_4$), and concentrated under vacuum. The residue was recrystallized from ethanol to yield 450 mg (~54%) of hexamethylbenzenes having mp 164–165°, and isotopic composition 1.8% d_{12}, 93.6% d_9, and 4.6% d_8.

Using the Ziegler Catalyst System.[28] To 5 ml of dry hexane was added 0.1 ml of titanium tetrachloride and 1.0 ml of a 25% solution of triisobutylaluminum in hexane. The solution was cooled to 0° and 1.1 ml of **4** was added. The mixture was allowed to warm to room temperature overnight with stirring, quenched with 2 ml of methanol, and poured into 10 ml of water. The hexane layer was separated, washed with water, dried ($MgSO_4$), and concentrated under vacuum. The residue was recrystallized from ethanol to yield 500 mg (~65%) of product, mp 166–166.5°, isotopic composition 3.0% d_{12}, 92.3% d_9, and 4.6% d_8.

Using Bis(acrylonitrile)nickel(0).[27] A mixture of 0.9 g of bis(acrylonitrile) nickel,[45] 3.5 ml of **3**, and 4 ml of dioxane was refluxed for 48 hr. The reaction mixture was poured into 30 ml of 30% aqueous nitric acid and extracted into ether. The ether layer was washed with water, dried ($MgSO_4$), and concentrated. The residue was crystallized from ethanol to yield 540 mg (22%) of product, mp 165–166°, isotopic composition 1.1% d_{12}, 93.9% d_9, and 5.0% d_8.

Using Dichlorobis(benzonitrile)palladium(II).[29] Addition of 2.5 ml of **4** to a solution of 3.0 g of dichlorobis(benzonitrile)palladium(II)[46] in 70 ml of reagent benzene resulted in a mildly exothermic reaction. The reaction mixture was heated at reflux temperature for 20 hr, cooled, and poured into 50 ml of 30% aqueous nitric acid. The benzene layer was separated, washed with water, dried ($MgSO_4$), and concentrated. The residue was chromatographed on 30 g of silicic acid using hexane. The mixture of deuterated hexamethylbenzenes eluted first, and was recrystallized from ethanol to yield 320 mg (18%) of material having isotopic composition 0.9% d_{12}, 94.5% d_9, and 4.6% d_8.

Using Aluminum Chloride. A modification of the procedure developed by Schäfer and Hellmann was used in this reaction.[30] A mixture of 1.1 g of **4**, 1 ml of benzene, and 100 mg of aluminum chloride (from a freshly opened bottle) was sealed in a glass tube and heated in a steam bath for 26 hr. The tube was opened, and the contents were dissolved in benzene, washed with water, dried ($MgSO_4$), and concentrated. The residue was recrystallized from ethanol to yield 430 mg (39%) of **6**, **7**, and **8**, having mp 163–164° and isotopic composition 3.3% d_{12}, 93.4% d_9, and 3.3% d_8.

To check for inter- and intramolecular scrambling of methyl groups among the deuterated hexamethylbenzenes under the influence of the catalyst system, a mixture of 1 ml of benzene, 100 mg of $AlCl_3$, 1 ml of 2-butyne, and 120 mg of the mixture of **6**, **7**, and **8** formed in the preceding experiment was carried through the experimental procedure outlined above. The resulting mixture of hexamethylbenzene isomers was isolated as before, and had isotopic composition 3.2% d_{12}, 93.2% d_9, and 3.5% d_8. A similar experiment carried out using a mixture of **6**, **7**, and **8** from the bis(benzonitrile)palladium dichloride catalyzed cyclization described above yielded hexamethylbenzenes having composition 0.6% d_{12}, 93.5% d_9, 4.9% d_8, 0.4% d_7, and 0.5% d_6.

Degradation of Hexamethylbenzenes. The same general procedure was used for all degradations.[47] To 18 ml of HMPA was added 170 mg (1.0 mmol) of a mixture of deuterated hexamethylbenzenes and 200 mg of sodium cut into small pieces. When the

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(40) This reaction is being examined further in collaboration with Professor Maitlis and coworkers.

(41) Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. Nmr spectra were run on a Varian A-60 spectrometer. Infrared spectra were taken in sodium chloride cells using a Perkin-Elmer Model 237 B grating spectrophotometer. Mass spectra were determined on a Hitachi-Perkin-Elmer RMU-6D mass spectrometer. All spectra used for deuterium analysis were obtained using a nominal ionizing voltage of 8.3 eV.[42] Microanalysis was performed by Midwest Microlab, Inc., Indianapolis, Ind.

(42) K. Biemann, "Mass Spectrometry-Organic Chemical Applications," McGraw-Hill Book, Co., Inc., New York, N. Y., 1962, p 223 ff.

(43) In our hands commercially available propynyllithium (Alfa Inorganics, Inc.) proved unsuitable for this reaction.

(44) Isotopic compositions reported thoughout the experimental section are derived from intensity data corrected for ^{13}C. The ionizing voltage at which spectra were taken was such that the intensity of the $M - 1$ peak was negligible. Any ion of mass between M^+ and $M^+ + 12$ had relative abundance <0.1%, if not reported explicitly.

(45) G. N. Schrauzer, *J. Amer. Chem. Soc.*, **81**, 5310 (1959).

(46) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *ibid.*, 60, 882 (1938).

(47) We are indebted to Professor H. O. House and Mr. R. W. Giese for advice concerning the HMPA reduction.

solution had turned blue, 0.5 ml of *t*-butyl alcohol freshly distilled from sodium was added. Additional portions of 0.2, 0.2, and 0.1 ml of *t*-butyl alcohol were added at 1-hr intervals. In most reductions, the blue color vanished.[48] The resulting reduction mixture was poured into 80 ml of water and extracted with 20 ml of ether. The ether layer was washed with water and dried ($MgSO_4$). Analysis of the resulting ether solution by glpc showed only **9**, **10**, and **11**. The structure of **9** was assigned on the basis of spectral evidence and elemental analysis: nmr (CCl_4) δ 2.40 (m, 2, $CHCH_3$), 1.62 (s, 12, allylic CH_3), and 1.05 ppm (s, 6, J = 7 Hz, $CHCH_3$); mass spectrum (70 eV) *m/e* (relative intensity) 164 (32), 150 (10), 149 (100), 134 (25), 133 (26), 119 (12), 105 (6), 91 (9), 83 (7), 77 (5), 55(5), 39(5).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.63; H, 12.10.

The structures for **10** and **11** were tentatively assigned on the basis of their mass spectra (70 eV). **10**: 166 (19), 164 (27), 152 (24), 151 (12), 150 (100), 134 (23), 133 (23), 119 (12), 110 (20), 109 (11), 105 (9), 83 (27). **11**: 168 (26), 166 (20), 153 (29) 151 (28), 110 (40), 97 (48), 95 (33), 84 (14), 83 (100), 69 (44).

The ether solution of **9**, **10**, and **11** was cooled to −20°, and ozone was bubbled through the solution until the effluent gas turned an aqueous potassium iodide solution brown (3–5 min). Excess ozone was removed by bubbling a stream of nitrogen through the solution briefly, and the ozonides were then reduced catalytically using ~100 mg of 10% Pd–C and 1 atm of hydrogen. The resulting ether solution was dried ($MgSO_4$) and the solution concentrated by distillation through a 2-ft Vigreux column. Samples of **12** for mass spectral analysis were collected from glpc (SE-52 column at 105°). The mass spectrum of **12** prepared from undeuterated hexamethylbenzene using this procedure was identical with that of a sample prepared by an alternative procedure.[49]

Mass Spectral Analyses. Samples of **12** for deuterium analysis were purified by glpc, taking care to collect as much of the peak as possible to avoid isotopic fractionation.[42] Spectra were run at a nominal ionizing voltage of 8.3 eV. At this voltage, the intensity of the M − 1 ion was negligible. Typical spectra over the range *m/e* 114–124 for deuterated samples of **12** obtained from the degradation are shown in Figure 1. The method used for partitioning the intensities of these ions among the species of interest was somewhat arbitrary, and will be briefly outlined here. Peaks at *m/e* 114, 117, 120, and 123 were assigned respectively to **12**-d_0, -d_3, -d_6, and -d_9. The peak at *m/e* 121 was assigned the composition **12**-d_6 + ^{13}C or **12**-d_7, and the ratio r_1 of intensities of the peaks at 120 and 121 was calculated: $r_1 = I_{121}/I_{120}$. The peak at *m/e* 122 was partitioned between species of **12** having two and three labeled methyl groups assuming that the contribution to the former was $r_1{}^2I_{120}$, and that to the latter was $(I_{122} - r_1{}^2I_{120})$. The peak at *m/e* 119 was assumed to **12**-d_5, and the ratio $r_2 = I_{119}/I_{120}$ calculated. The *m/e* 118 peak was partitioned between species of **12** having one and two labeled methyl groups by allocating $r_2{}^2I_{120}$ to the latter, and $(1 - r_2{}^2)I_{120}$ to the former.

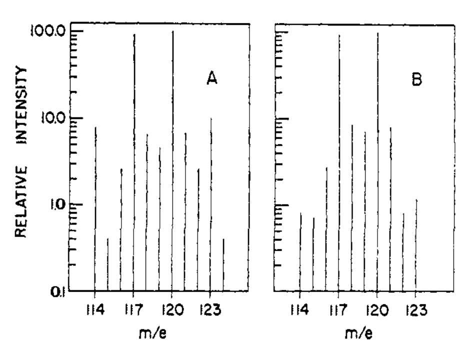

Figure 1. Typical mass spectra in the region of M^+ for the mixture of deuterated isomers of **12** obtained on degradation of the hexamethylbenzene-d_9 isomers from cyclotrimerization of **4** with aluminum chloride (A) and the Ziegler catalyst (**B**). The ordinate is a logarithmic scale in order to emphasize the lower intensity peaks.

Extending a similar treatment to the remaining ions, the relative quantities of the various labeled isomers of **12** are given below; these numbers are *not* corrected for contributions to the ion intensities from products arising from degradation of **12**-d_{12} present as an impurity in the **12**-d_9. These spectra were run under conditions

$$\mathbf{12}\text{-}(CD_3)_3 = I_{123}(1 + r_1) + (I_{122} - r_1{}^2I_{120})$$

$$\mathbf{12}\text{-}(CD_3)_2(CH_3) = I_{120} + I_{121} + r_1{}^2I_{122} + I_{119} + r_2{}^2I_{120}$$

$$\mathbf{12}\text{-}(CD_3)(CH_3)_2 = I_{117} + (I_{118} - r_2{}^2I_{120}) + I_{116} + (I_{115} - r_1I_{114})$$

$$\mathbf{12}\text{-}(CH_3)_3 = I_{114}(1 + r_1)$$

in which background was unimportant for all ions except *m/e* 114. When significant background intensity was observed at this value of *m/e*, the peak was simply ignored if in addition there was no significant peak at *m/e* 123.

Once the intensities in the region *m/e* 114–123 had been partitioned as described above, the resulting relative yields of the labeled isomers of **12** were first normalized, and then corrected for contributions due to hexamethylbenzene-d_{12}. From the uncorrected numbers, it was readily apparent whether the sample being examined fell into the "cyclobutadiene" or "concerted" classification. Degradation of hexamethylbenzene-d_{12} produced by a "cyclobutadiene" pathway would result in **12**-$(CD_3)_3$, **12**-$(CH_3)(CD_3)_2$, and **12**-$(CH_3)_2(CD_3)$ in relative yields 18.75:62.5:18.75. By a "concerted" mechanism, the corresponding relative yields would be 16.67:66.67:16.67. To correct for contributions to the labeled isomers of **12** from this source, the fraction of hexamethylbenzene-d_{12} in the mixture of labeled hexamethylbenzenes isolated from a particular cyclization was determined by mass spectroscopy, the corresponding contributions to the apparent yields of **12**-$(CD_3)_3$, -$(CH_3)(CD_3)_2$, -$(CH_3)_2(CD_3)$, and -$(CH_3)_3$ from this source calculated using the "cyclobutadiene" or "concerted" ratios, whichever was appropriate, these contributions subtracted from the uncorrected normalized yields for these species obtained above, and the resulting corrected values then renormalized to give the entries in Table I.

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(48) If the color had not vanished after 4.5 hr, an aliquot of the mixture was hydrolyzed and analyzed by glpc. If the reaction appeared to be complete, excess sodium was destroyed by cautious addition of 0.5 ml of water and the mixture worked up as indicated.

(49) A. W. Johnson, E. Markham, and R. Price, *Org. Syn.*, **42**, 75 (1962).