The Mechanism of Formation of 1,2,3,4-Tetramethylnaphthalene from 2-Butyne and Triphenyltris(tetrahydrofuran)chromium(III)[1]

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Abstract: Reaction of triphenyltris(tetrahydrofuran)chromium(III) (**1**) with 2-butyne yields, *inter alia*, 1,2,3,4-tetramethylnaphthalene (**2**). A free or metal-complexed tetramethylcyclobutadiene has been excluded as an intermediate in this reaction by the observation that 1,2-dimethyl-3,4-di(methyl-d_3)naphthalene (**6**) is not a product of **1** and 2-butyne-1,1,1-d_3 (**3**). Examination of the relative yields of 1,2,3,4,5-pentamethylnaphthalene (**15**) and 1,2,3,4,6-pentamethylnaphthalene (**16**) formed in reaction of 2-butyne with tri-*o*-tolyl-, tri-*m*-tolyl-, and tri-*p*-tolyltris(tetrahydrofuran)chromium(III) demonstrates that a long-lived aryne–chromium complex is also not an intermediate in these cyclizations. Labeling and kinetic isotope experiments using partially deuterated derivatives of **1** further discredit benzyne complexes as intermediates in the formation of **2**. The reaction of trimesityltris(tetrahydrofuran)chromium(III) with 2-butyne to form *cis*-2-mesitylbut-2-ene suggests that an initial step in these reactions may be insertion of 2-butyne into a carbon–chromium bond with formation of an intermediate vinylic chromium reagent (**24**). The additional observations that 2-biphenylmagnesium bromide and trichlorotris(tetrahydrofuran)chromium(III) react to form 5-(2-biphenyl)dibenzchromole (**29**), and that this chromocycle reacts with 2-butyne to yield 9,10-dimethylphenanthrene, implicate an analogous chromocycle 3,4-dimethyl-5-phenylbenzchromole (**34**) in the formation of **2**. Taken together with further deuterium exchange and labeling experiments, these observations lead to the proposal that the reaction of **1** with 2-butyne proceeds by initial insertion of one molecule of 2-butyne into a phenyl–chromium bond of **1**, cyclization of the resulting vinylic chromium compound with elimination of benzene to form chromocycle **34**, and reaction of the chromocycle with a second molecule of 2-butyne to yield **2** (Scheme VII).

Cyclooligomerization of acetylene by transition metal catalysts provides the basis for a number of useful organic syntheses.[3] Attempts to establish mechanisms for this class of reactions have been hindered by difficulties in identifying the active organometallic catalysts. Although a variety of structures have been postulated for these catalysts, it has proved possible to isolate and characterize mechanistically significant reaction intermediates or by-products in only a small number of reactions.[4,5] Precedents derived from the extensively explored chemistry of transition-metal acetylene complexes suggest that these cyclooligomerization reactions are initiated by coordination of one or more molecules of acetylenic substrate to a metal atom or metal atom cluster of the catalyst.[3,6] The process(es) by which the coordinated acetylenes are subsequently converted to product has been variously suggested to involve metallocyclic,[4,7,8] π-allylic,[5a,9,10] or cyclobutadiene[8,10–13] intermediates, or to proceed by a concerted "π-multicenter" reaction path.[11,13] Of these suggested and not necessarily exclusive mechanisms, only the metallocyclic pathway has received positive support.[4,5] Unfortunately, without knowing either the structures of the active catalysts, or, in most cases, even elementary details of stoichiometry, reaction order, or material balance, the design and interpretation of experiments bearing on the mechanisms of these reactions remains a difficult and subjective matter.

Our interest in the mechanism of transition metal catalyzed cyclooligomerization reactions has prompted us to examine a related *noncatalytic* cyclization involving a transition metal organometallic reagent: *viz.*, the reaction of 2-butyne with triphenyltris(tetrahydrofuran)chromium(III) (**1**) to yield, *inter alia*, 1,2,3,4-tetramethylnaphthalene (**2**).[11,12,14] This reaction is a considerably more tractable subject for mechanistic examination than the catalytic cyclooligomerizations

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[3] Reviews: (a) C. Hoogzand and W. Hübel in "Organic Syntheses via Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, pp 343 ff; (b) F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev., Sect. A*, **3**, 227 (1968); (c) E. Ochiai, *Coord. Chem. Rev.*, **3**, 49 (1968); (d) J. P. Collman, *Transition Metal Chem.*, **2**, 1 (1966).

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

[5] (a) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 187 (1964); (b) R. P. Dodge and V. Schomaker, *J. Organometal. Chem.*, **3**, 274 (1965); (c) J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hübel, *J. Amer. Chem. Soc.*, **88**, 292 (1966); J. T. Mague, *ibid.*, **91**, 3983 (1969); L. R. Bateman, P. M. Maitlis, and L. F. Dahl, *ibid.*, **91**, 7292 (1969).

[6] W. Hübel, "Organic Syntheses via Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, p 273 ff.

[7] L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **27**, 3930 (1962); W. Keim, *J. Organometal Chem.*, **16**, 191 (1969); E.-A. Reinsch, *Theor. Chem. Acta*, **11**, 296 (1968).

[8] For related proposals of metal-coordinated butadiene 1,4-diradicals as reaction intermediates, see R. C. Cookson and D. W. Jones, *Proc. Chem. Soc.*, 115 (1963); H. P. Throndsen, W. Metlesics, and H. Zeiss, *J. Organometal. Chem.*, **5**, 176 (1966).

[9] G. Wilke, *et al.*, *Angew. Chem., Int. Ed. Engl.*, **5**, 151 (1966); A. T. Blomquist and P. M. Maitlis, *J. Amer. Chem. Soc.*, **84**, 2329 (1962); P. M. Maitlis, *et al.*, *ibid.*, **90**, 5321 (1968).

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

[11] H. Zeiss in "Organometallic Chemistry," H. Zeiss, Ed., American Chemical Society Monograph No. 147, Reinhold, New York, N. Y., 1960, pp 386 ff.

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

[13] 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).

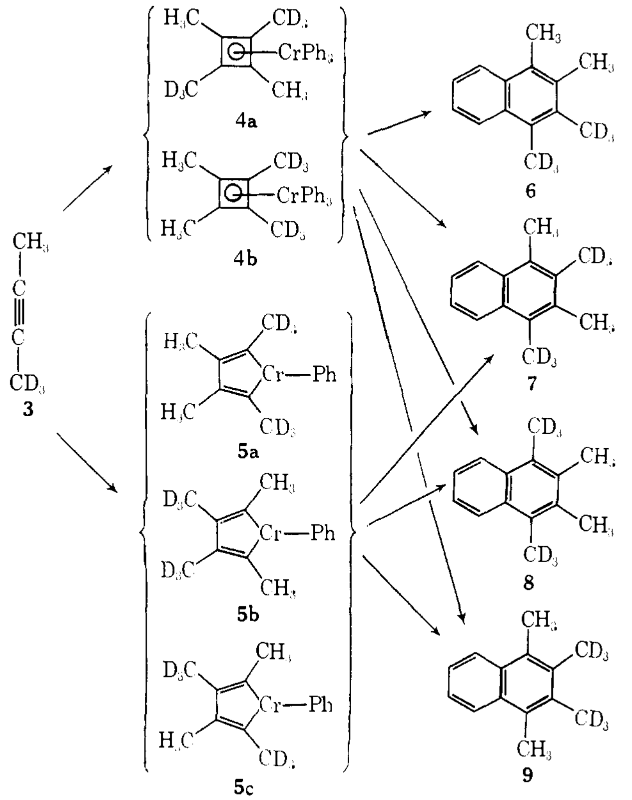
[14] Related reactions have been observed with diphenylnickel [M. Tsutsui and H. Zeiss, *J. Amer. Chem. Soc.*, **81**, 6090 (1959)] and with cyclopentadienylmethyliron dicarbonyl and cyclopentadienylethylmolybdenum tricarbonyl [A. Nakamura and N. Hagihara, *Nippon Kagaku Zasshi*, **84**, 344 (1963); *Chem. Abstr.*, **59**, 14021*d* (1963)].

for several reasons. First, the composition and structure of the starting organometallic reagent **1** are reasonably well defined.[11,12,15] Second, the fact that conversion of a σ-bonded phenylchromium moiety into tetramethylnaphthalene necessarily involves the cleavage of an *ortho* carbon–hydrogen bond provides an opportunity to apply a number of standard mechanistic tests to those steps of the reaction in which the carbon–hydrogen bond is broken and the corresponding carbon–carbon bond formed. Finally, since the organochromium reagent is directly involved as a reagent, and since it is not regenerated, there is no ambiguity concerning the nature of the "active" organometallic species in the reaction. Nonetheless, despite the obvious differences between this noncatalytic cyclization and the catalytic cyclooligomerization reactions, there are also enough parallels to suggest that information concerning the mechanism of the former should be pertinent to mechanistic questions concerning the latter.

Results and Discussion

Mechanisms Involving a Cyclobutadiene Intermediate. The initial objective of this study was to determine if either tetramethylcyclobutadiene or a chromium–tetramethylcyclobutadiene complex were an intermediate in the conversion of **1** to **2**. Previous deuterium-labeling studies of the cyclotrimerization of 2-butyne to hexamethylbenzene by an organochromium compound of unknown composition derived from **1** had demonstrated that a chromium-tetramethylcyclobutadiene complex was *not* an intermediate in the reaction.[16] Although it seemed probable that the same result would be found for the noncatalytic conversion of **1** into **2**, the fact that these earlier labeling studies[16] had established that the mechanism of catalytic cyclotrimerization varied with the catalyst indicated that it would be prudent to treat this point explicitly.

The same experimental probe used to test the catalytic cyclotrimerizations of 2-butyne-1,1,1-d_3 (**3**) to hexamethylbenzene-d_9 for intermediates of tetramethylcyclobutadiene-like symmetry served, with some modification, to exclude this type of intermediate in the conversion of **3** to tetramethylnaphthalene-d_6. This experimental test is based on the supposition that the four ring carbon–carbon bonds of free or metal-complexed tetramethylcyclobutadiene are chemically equivalent.[17] With this supposition, reaction of **1** with **3** taking place by way of an intermediate of cyclobutadiene-like symmetry would lead first, with equal probabilities, to intermediates containing the head-to-head and head-to-tail tetramethylcyclobutadiene-d_6 moieties represented by **4a** and **4b**, and ultimately by a pathway whose precise mechanism need not be specified to the four isotopically substituted tetramethylnaphthalenes **6**, **7**, **8**, and **9** in relative yields 25%:50%:12.5%:12.5%.[18] Conversion of **3** to tetramethylnaphthalene-d_6 by way of π-allylic or metallocyclic intermediates, represented schematically by **5a–c**, or by way of any other "linear" cyclooligomerization pathway that does not allow the four methyl groups derived from the two reacting molecules of **3** to become equivalent, will lead to **6**, **7**, **8**, and **9** in relative yields of 0%:50%:25%:25%.[18] Thus, a clear distinction between the mechanistic alternatives under consideration can be made on the basis of the relative yield of **6** formed in the mixture of deuterated tetramethylnaphthalene isomers: the observation that 1,2-dimethyl-3,4-di(methyl-d_3)naphthalene (**6**) is *not* a product of reaction of **3** with **1** is sufficient evidence to *exclude* a free or complexed tetramethylcyclobutadiene as a reaction intermediate.



The relative yield of **6** in the mixture of tetramethylnaphthalenes **6**, **7**, **8**, and **9** obtained by reaction of **1** and **3** was established using a chemical degradation designed to capitalize on the fact that only **6** contains adjacent labeled methyl groups at the 1 and 2 positions of the naphthalene ring (Scheme I). Oxidation of the mixture of isotopically labeled tetramethylnaphthalenes with trifluoroperacetic acid and boron trifluoride etherate yields a mixture of the labeled ketones **10**, **11**, and **12**.[19] Ozonolysis of this mixture without separation into individual components, followed by catalytic reduction of the resulting ozonides, yields **13**, among other products. Cleavage of **13** with aqueous sodium hydroxide yields methyl isopropyl ketone (**14**) and sodium 2-acetylbenzoate.[20]

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[15] For a crystal structure of the related compound p-$CH_3C_6H_4$-$CrCl_2\cdot 3THF$, see J. J. Daly, R. P. A. Sneeden, and H. H. Zeiss, *J. Amer. Chem. Soc.*, **88**, 4287 (1966).

[16] G. M. Whitesides and W. J. Ehmann, *ibid.*, **91**, 3800 (1969).

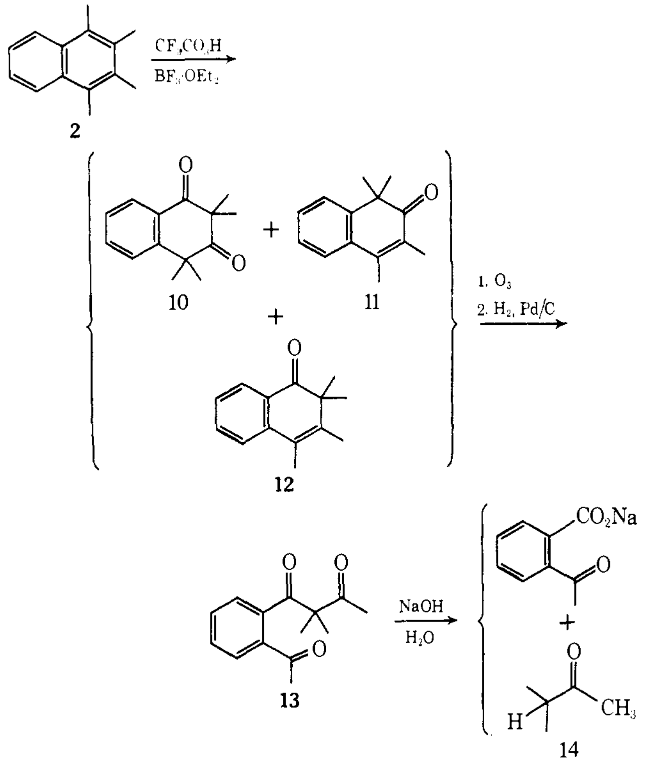
[17] R. P. Dodge and V. Schomaker, *Acta Crystallogr.*, **18**, 614 (1965); J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962); C. S. Yannoni, G. P. Ceasar, and B. P. Dailey, *J. Amer. Chem. Soc.*, **89**, 2833 (1967); H. Oberhammer and H. A. Brune, *Z. Naturforsch.*, **24a**, 607 (1969).

[18] We assume as previously[16] that any deuterium kinetic isotope effects in the formation of the deuterated tetramethylnaphthalene isomers 6–9 are negligible, and that the relative yields of these isomers expected from each of the reaction paths considered can be calculated entirely from statistical considerations.

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

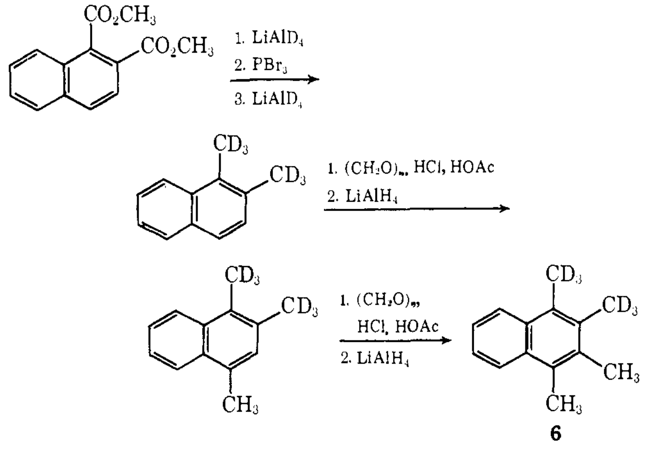
[20] For similar base-catalyzed cleavage reactions of substituted β-diketones, see R. G. Pearson and E. A. Mayerle, *J. Amer. Chem. Soc.*, **73**, 926 (1951). Although the cleavage of **13** might *a priori* have proceeded by scission of the carbon–carbon bond adjacent to that broken in Scheme I, yielding sodium acetate and 2′-acetyl-2-methylpropiophenone, only the mode of cleavage indicated in this scheme was observed.

Scheme I. Degradation of 1,2,3,4-Tetramethylnaphthalene-d_6



This sequence of reactions isolates adjacent methyl groups from the 1 and 2 positions of tetramethylnaphthalene in the isopropyl group of **14**. The reaction conditions for the cleavage **13** → **14** were specifically adjusted so that any deuterium present in the methyl group directly bonded to the carbonyl moiety in **14** was washed out during the course of the reaction.[21] Consequently, the methyl isopropyl ketone obtained by degradation of **7**, **8**, or **9** using this sequence should be entirely **14**-d_3, while that obtained from **6** should be a 1:1 mixture of **14**-d_6 and **14**-d_0.[18] Thus mass spectroscopic analysis of the deuterium distribution in the methyl isopropyl ketone obtained from degradation of the mixture of labeled tetramethylnaphthalene-d_6 isomers isolated from reaction of **1** and **3** can be simply related to the relative yield of **6** in this mixture.

Scheme II. Synthesis of 1,2-Dimethyl-3,4-di(methyl-d_3)naphthalene 6



In order to be certain that scrambling of the deuterium label present in **6** does not take place during this degradation, an authentic sample of **6** was synthesized, using the sequence of Scheme II, and degraded; mass spectroscopic analysis of the resulting methyl isopropyl ketones yielded the distribution of deuterium label summarized in Table I. The observation that no detectable yield of **14**-d_3 results from the degradation of authentic 1,2-dimethyl-3,4-di(methyl-d_3)-naphthalene (**6**) establishes that no scrambling of methyl groups or of deuterium atoms occurs during degradation, and indicates that the analytical scheme outlined in Scheme I should be capable of detecting any significant concentration of **6** admixed with **7**, **8**, and **9**.[22]

Degradation of the mixture of tetramethylnaphthalene-d_3 isomers obtained by reaction of triphenyltris(tetrahydrofuran)chromium(III) with 2-butyne-1,1,1-d_3, followed by mass spectrometric analysis of the resulting **14**, yielded results also listed in Table I. 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 the **3**: that is, they represent the yields that would be observed for reactions of triphenylchromium with pure **3**. For comparison, Table I also contains the relative abundances of the isotopically substituted derivatives of **14**, calculated on the assumption that the reaction proceeds entirely by way of a cyclobutadiene intermediate (**4**) and those calculated on the assumption of a noncyclobutadiene process involving only intermediates of the type represented schematically by **5** (called "linear" in this table).

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

Tetramethylnaphthalene source	14-d_0	14-d_3	14-d_6
6	58.2	0.5	41.2
Reaction of 1 and 3	0.0	99.8	0.2
Calcd: cyclobutadiene	12.5	75.0	12.5
Calcd: "linear"	0.0	100.0	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 ~±1%.

Within the limits of detection of this procedure (±1%) no **14**-d_0 or **14**-d_6 was obtained from this degradation. Hence, no **6** was present in the starting mixture of tetramethylnaphthalene-d_6 isomers. This observation establishes that neither tetramethylcyclobutadiene nor any other intermediate of similar effective symmetry is involved in the conversion of **1** to **2**.

Mechanisms Involving a Benzyne Intermediate. Zeiss and Sneeden have advanced the proposal that conversion of triphenyltris(tetrahydrofuran)chromium (**1**) to tetramethylnaphthalene (**2**) takes place by a mechanism involving an intermediate benzyne–chromium

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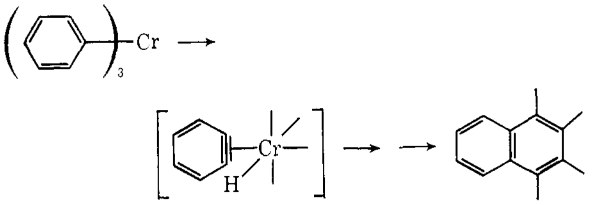
(21) When unlabeled methyl isopropyl ketone was subjected to the reaction conditions used for the conversion of **13** to **14**, using D_2O as solvent, the recovered ketone was found to contain >90% d_3 material by mass spectroscopic analysis.

(22) The observation that the normalized abundance from authentic **6** of **14**-d_0 is ~20% higher than that of **14**-d_6 remains unexplained. One possible origin of this anomaly might be a deuterium isotope effect in the degradation of tetramethylnaphthalene-d_6. However, regardless of its source, it clearly does not affect the conclusions drawn from these analyses. For isotopic effects in methyl group migration see W. M. Schubert and P. H. LeFevre, *J. Amer. Chem. Soc.*, **91**, 7746 (1969).

complex, derived from elimination of a chromium hydride fragment from **1**.[23] This proposal finds little support in the available literature dealing with benzyne chemistry.[24] Although a complex of benzyne with silver(I) has been implicated as a transitory intermediate in the thermal decomposition of benzenediazonium-2-carboxylate in the presence of silver ion[25] and a stable complex of a fluorinated cyclohexyne derivative with cobalt has been prepared,[26] extensive efforts to synthesize authentic benzyne–transition metal complexes have been unsuccessful.[24,27,28] Nevertheless, tetramethylnaphthalene *is* formally derived from the elements of one molecule of benzyne and two molecules of 2-butyne; further, chromium compounds in various valence states have been implicated as hydrogen atom or hydride ion acceptors in the Etard reaction[29a] and in other reactions of organochromium reagents.[23,29b] Thus, mechanisms for formation of **2** related to that represented by eq 1, although improbable, cannot be disregarded arbitrarily.



(1)

We have carried out several experiments designed to exclude certain classes of mechanisms for the conversion of **1** to **2** requiring benzyne intermediates. These experiments do not provide sufficient evidence to exclude *all* possible mechanisms for **1** → **2** involving benzyne intermediates, and additional experiments theoretically capable of excluding the remaining classes of mechanisms do not seem to be practical in the reaction system under study. Nevertheless, the observations reported here, together with evidence contained in the following section, combine effectively to exclude benzyne pathways for formation of **2**.

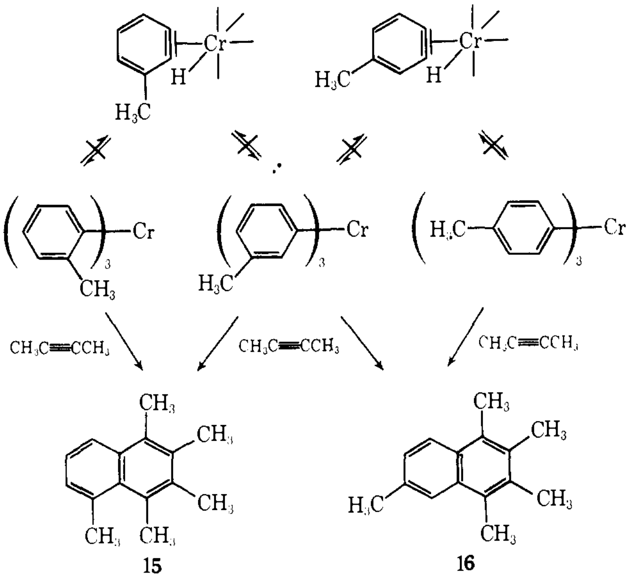
Stereochemical evidence against *reversible* elimination of a chromium hydride moiety during the reaction of triarylchromium reagents with acetylenes was obtained by examining the yields of 1,2,3,4,5-pentamethylnaphthalene (**15**) and 1,2,3,4,6-pentamethylnaphthalene (**16**) formed in reaction of tri-*o*-tolyl-, tri-*m*-tolyl-, and tri-*p*-tolyltris(tetrahydrofuran)chromium(III) with 2-butyne (Table II). Equilibration of these tritolylchromium compounds with dehydrotoluene–chromium complexes should provide a pathway for interconversion of *o*-, *m*-, and *p*-tolyl groups (Scheme III). The observation that reaction of 2-butyne with tri-*p*-tolylchromium yields no **15**, and that reaction with tri-*o*-tolylchromium yields no **16**, demonstrates that the tolylchromium reagents do *not* equilibrate under these reaction conditions. However, isomerization of, *e.g.*, *o*- to *m*-tolylchromium by way of an intermediate dehydrotoluene–chromium complex would require that the lifetime of this intermediate be sufficient to permit the torsion around the aryne–chromium bond necessary to transfer the hydride ligand from its coordination site on the metal to the carbon atom originally bonded to the metal. Thus, reversible chromium hydride elimination from these tritolylchromium reagents could be reconciled with the data of Table II, provided that the rate of collapse of the dehydrotoluene complex to σ-tolylchromium reagent was much more rapid than the rate of torsion around the aryne–chromium bond. There is presently no way of estimating the barrier to this type of torsional motion in the hypothetical benzyne–chromium complexes, although *a priori* torsion of a benzyne in an octahedral complex might be expected to be more rapid than that observed for ethylene in square planar rhodium[30] or platinum[31] complexes.

Table II. Yields of Pentamethylnaphthalenes from Reaction of Tritolylchromium(III) Reagents with 2-Butyne

	Yield, %[a]	
$R_3Cr\cdot3THF$	**15**	**16**
$(o\text{-Tolyl})_3Cr\cdot3THF$	60	0.0[b]
$(m\text{-Tolyl})_3Cr\cdot3THF$	5.1	47
$(p\text{-Tolyl})_3Cr\cdot3THF$	0.0[b]	69

[a] Yields are based on the assumption that formation of 1 equiv of pentamethylnaphthalene per equivalent of triarylchromium reagent would constitute a 100% yield. Reactions were carried out in THF solution at 25°. [b] Less than 0.5% could have been detected.

Scheme III. Formation of Pentamethylnaphthalenes



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(23) (a) H. H. Zeiss and R. P. A. Sneeden, *Angew. Chem., Int. Ed. Engl.*, 6, 435 (1967); (b) R. P. A. Sneeden and H. H. Zeiss, *J. Organometal. Chem.*, 20, 153 (1969).

(24) Survey: R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967.

(25) L. Friedman, *J. Amer. Chem. Soc.*, **89**, 3071 (1967).

(26) R. L. Hunt and G. Wilkinson, *Inorg. Chem.*, **4**, 1270 (1965); N. A. Bailey, M. R. Churchill, R. Hunt, R. Mason, and G. Wilkinson, *Proc. Chem. Soc.*, 401 (1964).

(27) G. Wittig and F. Bickelhaupt, *Chem. Ber.*, **91**, 883 (1958); H. Hellmann and G. M. Scheytt, *Ann. Chem.*, **642**, 22 (1961); H. J. S. Winkler and G. Wittig, *J. Org. Chem.*, **28**, 1733 (1963).

(28) A compound suggested to be a benzyne–nickel complex has been reported, but evidence confirming its structure has not appeared: *cf.*, E. W. Gowling, S. F. A. Kettle, and G. M. Sharples, *Chem. Commun.*, 21 (1968).

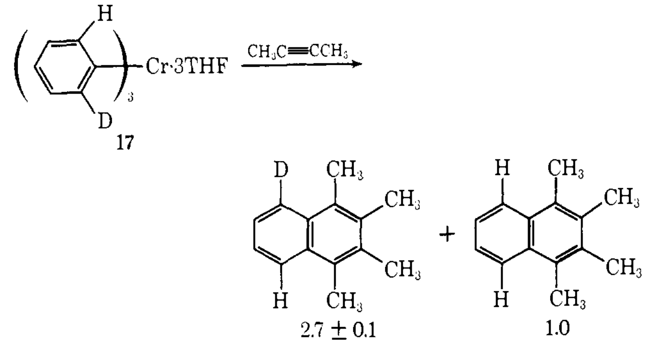
(29) (a) K. B. Wiberg and R. Eisenthal, *Tetrahedron*, **20**, 1151 (1964); I. Necsoiu, V. Przemetchi, A. Ghenciulescu, C. N. Rentea, and C. D. Nenitzescu, *ibid.*, **22**, 3037 (1966); (b) G. Henrici-Olivé and S. Olivé, *J. Organometal. Chem.*, **9**, 325 (1967).

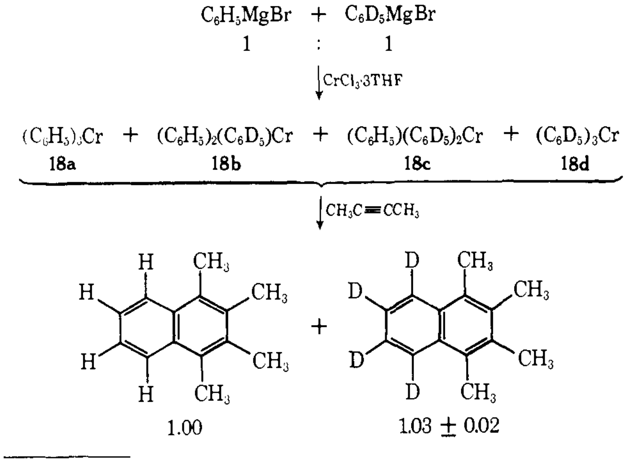
(30) R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 2519 (1969).

(31) A. R. Brause, F. Kaplan, and M. Orchin, *ibid.*, **89**, 2661 (1967); C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 53 (1969).

Thus, the data of Table II indicate qualitatively that the conversion of tritolyl- and presumably other triarylchromium reagents to the corresponding tetramethylnaphthalenes does not involve reversible formation of a long-lived aryne–chromium intermediate, but they do not permit a rigorous estimate of the lower limit for the lifetime of a benzyne–metal intermediate which would be compatible with the absence of observable positional isomerization during the reaction.

Two complimentary deuterium kinetic isotope effect measurements relate to the possible intermediacy of metal-complexed benzyne as a transitory intermediate in the conversion of **1** to **2**. First, the isotope effect on the rate of cleavage of the carbon–hydrogen bond of the phenyl ring incorporated into the tetramethylnaphthalene was determined to be $k_H/k_D = 2.7 \pm 0.1$[32] by mass spectrometric determination of the ratio of tetramethylnaphthalene-d_1 to tetramethylnaphthalene-d_0 formed during reaction of tri(phenyl-2-d_1)tris(tetrahydrofuran)chromium(III) (**17**) with 2-butyne. Second, the isotope effect characterizing the selection of a phenyl group from among undeuterated and perdeuterated phenyl groups bonded to chromium was established to be $k_H/k_D = 0.97 \pm 0.02$ (or 0.99 per *ortho* carbon–hydrogen bond) by mass spectrometric examination of the ratio of tetramethylnaphthalene-d_0 to tetramethylnaphthalene-d_4 formed on reaction of 2-butyne with the mixture of organochromium compounds obtained on treatment of chromium trichloride with a 1:1 mixture of phenylmagnesium bromide and phenyl-d_5-magnesium bromide. The relative yields of the four possible labeled triphenylchromium compounds obtained in this reaction is that expected from statistical considerations: **18a**:**18b**:**18c**:**18d** 1:3:3:1. Clearly, in this mixture, only **18b** and **18c** offer the possibility of an intramolecular choice of deuterated and nondeuterated phenyl groups during the step in which the reaction sequence resulting in conversion of a particular phenyl group to tetramethylnaphthalene is initiated. However, these compounds constitute the majority of the mixture, and the presence of **18a** and **18d** does nothing to obscure the conclusion that there is no isotope effect on the reaction in which phenyl group selection takes place.

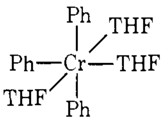




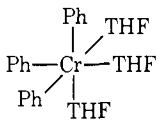
Control experiments established that the relative yields of tetramethylnaphthalene-d_0 and -d_4 were independent of the extent of conversion of the mixture of compounds **18a–d** to products. Thus, the *absolute* rates of formation of these compounds, and by inference the absolute rates of reaction of **18b** and **18c**, are equal throughout the course of the reaction.

These kinetic isotope effect data lead immediately to one important conclusion concerning the mechanism of conversion of **1** to **2**. The moderate isotope effect observed in the reaction of **17** with 2-butyne establishes that a carbon–hydrogen bond is broken in the reaction that determines which of the two geometrically equivalent carbon atoms originally *ortho* to the chromium atom is to form a ring juncture in the tetramethylnaphthalene product. This same reaction, regardless of its precise nature, obviously occurs during conversion of **18b** and **18c** to products. However, the negligible kinetic isotope effect observed in the latter reaction indicates that the reaction that determines which of the three phenyl rings of **1** is ultimately converted to **2** does *not* involve carbon–hydrogen bond breaking, since the isotope effect for the reaction involving competition between corresponding C–H and C–D bonds in different phenyl groups should be the same as that characterizing the competition between C–H and C–D bonds in the same phenyl group. Clearly the phenyl group cannot be selected in a reaction taking place *after* the C–H bond is broken. Thus, the phenyl ring incorporated into tetramethylnaphthalene is selected in a reaction which takes place *before* the *ortho* carbon–hydrogen bond is broken.

Further interpretation of these isotope effects in terms of specific mechanisms involving benzyne intermediates is complicated by ignorance of the geometry of **1**: both *meridional* (**1a**) or *facial* (**1b**) arrangements of the phenyl groups of this compound are conceivable. There is no experimental evidence available that bears directly on the geometry of **1**; however, the *meridional* isomer seems the more probable of the two possibilities.[33] On the hypothesis that the observed isotope



1a



1b

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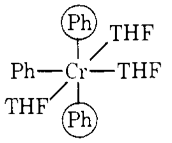
[32] It is possible (*vide infra*) that the rate of the reaction which is the reverse of the step in which the hydrogen is removed from the phenyl group is competitive with the subsequent steps of the conversion of **17** or **18** to products. Hence, the observed ratio of **2**-d_1 to **2**-d_0 produced in the reaction of **17** should be considered to yield a lower limit for the kinetic isotope effect describing the breaking of the carbon–hydrogen bond.

[33] Dichloro(*p*-tolyl)tris(tetrahydrofuran)chromium exists in a meridional configuration;[15] bis(trimethylamine)trichlorochromium(III) is a trigonal bipyramid.[34]

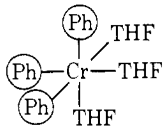
[34] G. W. A. Fowles, P. T. Greene, and J. S. Wood, *Chem. Commun.*, 971 (1967).

effects arise during chromium hydride elimination, any mechanism that converts one of two (or three) geometrically *equivalent* phenyl groups to benzyne, regardless of the nature of its rate-determining step, can be rigorously excluded on the grounds that it should give rise to similar isotope effects in reactions of **17** and **18**. On the other hand, mechanisms which involve conversion of a geometrically *unique* phenyl group to benzyne require further consideration, since at the most elementary level of interpretation, mechanisms of this type would be compatible with the conclusion (*vide supra*) that the selection of the phenyl ring converted to tetramethylnaphthalene must precede breaking of carbon–hydrogen bond of this ring.

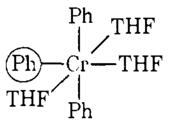
Thus, for example, the isotope effect data are incompatible with mechanisms requiring extrusion of benzyne from one of the circled phenyl groups of complexes **19** and **20**, regardless of the position of the rate-limiting step for the reaction; their compatibility with mechanisms involving elimination of the indicated phenyl group of **21**, in which the phenyl group converted to benzyne is unique by virtue of its relation to the two remaining phenyl groups, or from **22**, in which it is unique by virtue of its relation to the coordinated acetylenic ligands,[35] depends on the position of the rate-determining step. If benzyne formation from complexes **21** or **22** were rate limiting, tetramethylnaphthalene-d_0 should be formed more rapidly than tetramethylnaphthalene-d_4 in the early stages of the reaction of 2-butyne with the mixture of compounds **18a–d**, because the kinetic isotope effect observed for reaction of **17** with 2-butyne would influence the relative rates of formation of benzyne-d_0 and -d_4. If, on the other hand, benzyne were formed in an equilibrium established before the rate-determining step, some combination of a (presumably) small equilibrium isotope effect and a subsequent kinetic isotope effect involving, *e.g.*, cleavage of a chromium–hydride (or deuteride) bond, would be responsible for overall isotope effect observed for **17**. This combination would again ensure that tetramethylnaphthalene-d_0 was formed more rapidly than tetramethylnaphthalene-d_4 in the early stages of reaction of **18a–d**. The observation that the ratio of tetramethylnaphthalene-d_0 to -d_4 remains constant throughout the reaction excludes both of these possibilities.



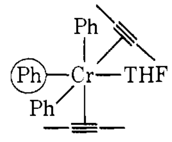
19



20



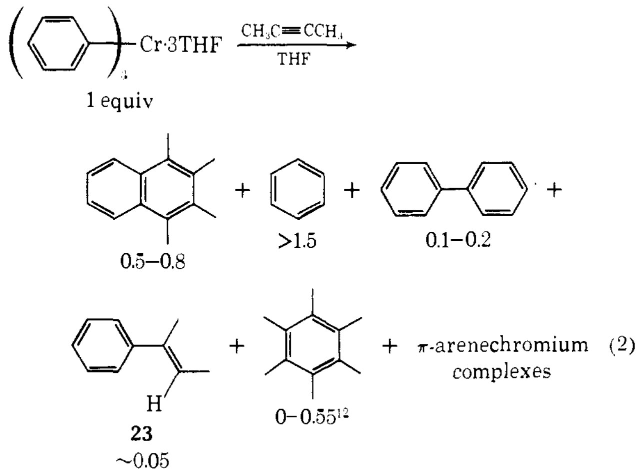
21

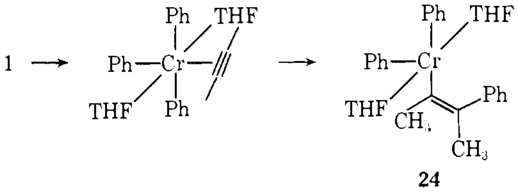


22

However, a mechanism for conversion of **1** to **2** requiring extrusion of benzyne from a geometrically unique phenyl group of either the starting organochromium reagent or an organochromium intermediate such as **21** or **22** would be compatible with the isotope effect data, *provided* that this extrusion took place *after* the rate-limiting step for the overall reaction.[35]

Mechanisms Involving a Metallocyclic Intermediate. The first substantial clues concerning the mechanism of conversion of **1** to **2** lay among the other products formed in this reaction (eq 2). Triarylchromium(III) compounds rearrange thermally in the absence of stabilizing ligands to a complex mixture of aromatic hydrocarbons and benzene- and biphenylchromium(I) π-arene complexes;[36] thus, the presence of these compounds in the reaction mixture is of no assistance in deducing a mechanism for the reaction. Hexamethylbenzene is produced in significant quantities only when 2-butyne is present in large excess,[11,12] and is probably formed in a process unrelated to the conversion of **1** to **2**. On the other hand, the observation of small quantities of *cis*-2-phenylbut-2-ene in the product mixture after hydrolysis suggests that insertion of 2-butyne into a carbon–chromium bond of **1** or some related organochromium compound may be an initial step in conversion of **1** to products.[37] This supposition is strengthened by the related observation, first reported by Zeiss and confirmed in our work, that reaction of trimesityltris(tetrahydrofuran)chromium(III) with 2-butyne, followed by hydrolysis, yields *cis*-2-mesitylbut-2-ene in high yield.[38] Normal cyclization of the type which would lead to a product analogous to tetramethylnaphthalene is, of course, suppressed in this reaction by the substitution of methyl groups for hydrogen atoms in the positions *ortho* to the carbon–chromium bond, although an "abnormal" cyclization yielding 2,3,4,6-tetramethylindene (**26**) is observed.





24

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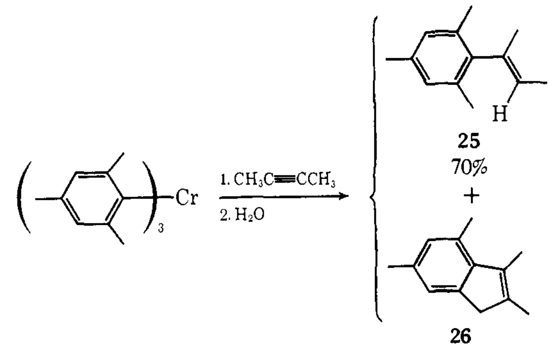
[35] Hähle and Stolze have shown that one molecule of THF is lost selectively from $CrPh_3 \cdot 3THF$ to yield $CrPh_3 \cdot 2THF$. If a reaction of this sort occurs in THF solution, a molecule of 2-butyne could complex with the $CrPh_3 \cdot 2THF$ in a manner that would "select" the phenyl group to be involved in the subsequent cyclization. J. Hähle and G. Stolze, *Z. Naturforsh.*, **19b**, 1081 (1964).

[36] M. Tsuisui and H. Zeiss, *J. Amer. Chem. Soc.*, **81**, 1367 (1959); J. Hähle and G. Stolze, *J. Organometal. Chem.*, **8**, 311 (1967).

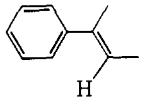
[37] R. F. Heck, *Advan. Chem. Ser.*, No. **49**, 181 (1965).

[38] W. Metlesics and H. Zeiss, *J. Amer. Chem. Soc.*, **81**, 4117 (1959).

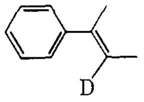


26
20%

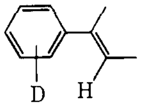
In order to confirm that the substituted styrenes **23** and **25** are in fact derived from the analogous styrylchromium compounds by hydrolysis, the extent of deuterium incorporation into these compounds following treatment of the reaction mixtures obtained from 2-butyne and triphenyl- or trimesityltris(tetrahydrofuran)chromium with deuterium oxide was examined. Mass spectrometric analysis established that the isotopic composition of **25** isolated under these conditions was 1% d_2, 54% d_1, and 45% d_0, and was consistent with initial insertion of 2-butyne into the carbon–chromium bond of trimesitylchromium to yield an intermediate styrylchromium reagent. Mass spectrometric analysis of **23** obtained following a deuterium oxide quench of partially reacted **1** revealed a more complicated labeling pattern: *viz.*, a mixture of d_0, d_1, and, surprisingly, d_2 species were present. The position of the deuterium in these isomers was localized by oxidizing the **23** to a mixture of isotopically substituted benzoic-d_0 (56%) and -d_1 (44%) acid with potassium permanganate. On the assumptions that deuterium was present in the side chain of the labeled **23** only at the vinylic position as was indicated by the nmr spectrum, and that no deuterium was washed out of the ring during permanganate oxidation, comparison of the isotopic composition of the **23** before cleavage with permanganate with that of the benzoic acid isolated after cleavage indicated that the deuterated 2-phenylbut-2-ene was composed of a mixture of four isomers (**23a–d**). Of these isomers, **23b** is the compound expected from hydrolysis of the styrylchromium compound which would be formed as a product of insertion of 2-butyne into a carbon–chromium bond of **1**, and **23a** might be formed by decomposition of the styrylchromium by some pathway that would involve transfer of a hydrogen to the β position.[39] The ring-deuterated compounds **23c** and **23d** clearly cannot be derived in a direct manner from hydrolysis of a simple styrylchromium intermediate. Although the position of the ring deuterium atoms in **23c** and **23d** is not known with certainty, by analogy with the behavior of related organochromium compounds to be discussed below, it is presumed that the label is localized in the *ortho* positions.



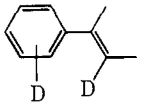
23a
(22%)



23b
(34%)

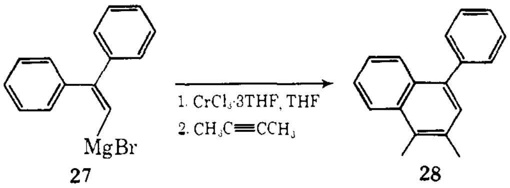


23c
(12%)



23d
(32%)

In testing the hypothesis that the first intermediate formed in the conversion of **1** and **2** is a styrylchromium compound **24**, it was important to have independent information concerning the reactivity of organochromium compounds of this type toward 2-butyne. Clearly, if reaction of an authentic styrylchromium compound with 2-butyne leads to a spectrum of products similar to that obtained from **1**, the case for an intermediate styrychromium reagent in the latter reaction is strengthened. In initial experiments, the products of reaction of the organometallic compound derived from trichlorotris(tetrahydrofuran)chromium(III) and 2,2-diphenylethenylmagnesium bromide (**27**) with 2-butyne were examined.[40] The styrylchromium compound which is presumed to be an intermediate in these conversions does react with 2-butyne to form a cyclic aromatic product analogous to **2**; however, the yield of this product is significantly lower than the yield of **2** obtained by reaction of triphenylchromium(III) with 2-butyne. Whether this difference in yield is mechanistically significant is unclear. Since styrylchromium reagents appear to be thermally much less stable than **1**, their rapid thermal conversion to the corresponding butadiene dimers may be more facile than in the case of the organochromium reagent, **24**, in which only one labile styryl moiety is bonded to each chromium atom.



27

28
12%

In an effort to circumvent some of the ambiguities originating in the thermal instability of the styrylchromium reagents, the preparation of tris(2-biphenyl)-tris(tetrahydrofuran)chromium(III) was attempted. Our interest in this compound as a potential model for **24** rested on two considerations: first, since the chromium atom of this substance would be directly bonded to an aromatic carbon atom, its constituent carbon–chromium σ bonds might be expected to have reasonable thermal stability; and second, the geometry of the carbon–chromium bond of this material with respect to the *o*-phenyl group of the biphenyl moiety would be expected to resemble closely that characterizing the styrylchromium reagent **24**.

Treatment of 2-biphenylmagnesium bromide with trichlorotris(tetrahydrofuran)chromium(III), followed by reaction of the resulting organochromium compound with 2-butyne, did, in fact, yield 9,10-dimethylphenanthrene (**30**) in 80% yield based on chromium.[41] Thus, the reactions leading to cyclization and aromatization in the reaction sequence leading to **30** take place with yield and efficiency comparable to those characterizing the conversion of **1** to **2**. However, more interesting from a mechanistic viewpoint is the obser-

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[39] The absence of any significant amount of the *trans* isomer of **23a** excludes decomposition by any pathway involving a free radical. G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4541 (1966).

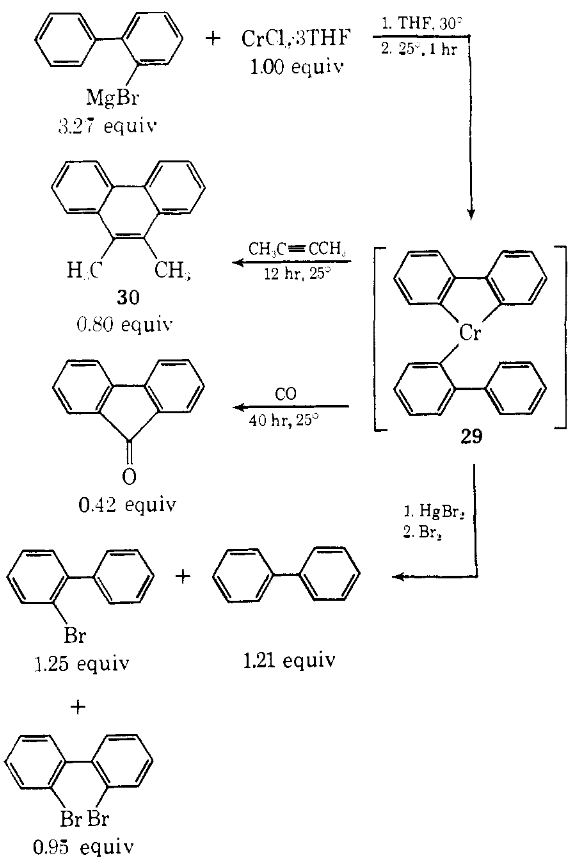
[40] The interpretation of similar reactions using *cis*-styrylmagnesium bromide was made ambiguous by apparent isomerization of the olefinic double bond of the intermediate styrylchromium reagent.

[41] If carbon monoxide is substituted for 2-butyne in the reaction, fluorenone is produced in a 42% yield.

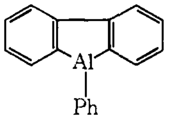
vation that the intermediate organochromium compound present in solution at the point at which 2-butyne is added to the reaction mixture is *not* the expected tris(2-biphenyl)chromium(III), but rather a compound assigned the structure **29** on the basis of analysis of products obtained by a degradation designed to establish the locations of carbon–chromium bonds.

Direct reaction of arylchromium reagents with bromine yields a mixture of products, including aryl bromides and biaryls, and as such is unsuitable as a quantitative method of identifying the locations of carbon–chromium bonds.[42] However, arylchromium reagents react smoothly with mercury(II) bromide, yielding the corresponding arylmercury(II) bromides.[42] The carbon–mercury bonds of these substances, in turn, are cleaved by bromine in high yield to aryl bromide and mercury(II) bromide.[43] Treatment of a solution obtained by reaction of 2-biphenylmagnesium bromide in turn with chromium trichloride, mercuric bromide, and bromine yields a solution containing 2,2′-dibromobiphenyl, 2-bromobiphenyl, and biphenyl in the yields shown in Scheme IV. Taking into account the slight excess of Grignard reagent used, and the presence of small amounts of biphenyl in the solution of this Grignard reagent, these yields establish clearly that *ca.* 1 equivalent of biphenyl has been produced at some stage of the reaction of Grignard reagent and chromium trichloride, and that one further equivalent of the biphenyl Grignard reagent has been converted to a substance having carbon–metal bonds in both 2 and 2′ positions. These observations strongly suggest that **29** correctly represents the structure of the organometallic intermediate in this reaction. It is not clear from our data whether a tris(2-biphenyl)chromium compound or, *e.g.*, a derivative of chlorobis(2-biphenyl)chromium or dichloro(2-biphenyl)chromium is the compound from which cyclization to produce the metallocyclic moiety of **29** occurs.

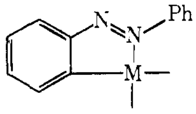
Scheme IV. Formation and Reactions of 5-(2-Biphenyl)-dibenzchromole (**29**)



A number of sound precedents support the proposed formation of a metallocyclic compound of chromium(III) by intramolecular attack on an adjacent carbon site: *viz.*, pyrolysis of diphenyl(2-biphenyl)aluminum yields the closely analogous 5-phenyldibenzaluminole **31**;[44] reaction of azobenzene with potassium tetrachloroplatinate,[45] palladium dichloride;[45] or nickelocene[46] yields compounds of structure **32**; and arylphosphine complexes of rhodium,[47,48] iridium,[49] ruthenium,[48,50] cobalt,[50] and iron[51,52] undergo reactions which either require or implicate oxidative addition of an *ortho* carbon–hydrogen bond to the metal with formation of cyclic intermediates represented schematically by **33**. These and related[53] examples have established that formation of four- or five-membered metallocyclic rings by cyclization onto a benzene ring is a general and facile reaction type. Combined with the experimental data summarized in Scheme IV, they make the structure **29** a very reasonable formulation for the stable organochromium substance formed under our reaction



31



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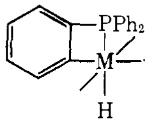

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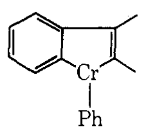

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[42] W. Herwig and H. H. Zeiss, *J. Amer. Chem. Soc.*, **81**, 4798 (1959).

[43] F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968 pp 75 ff.

[44] J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, **88**, 2976 (1966).

[45] A. C. Cope and R. W. Siekman, *ibid.*, **87**, 3272 (1965); see also R. F. Heck, *ibid.*, **90**, 313 (1968).

[46] J. P. Kleiman and M. Dubeck, *ibid.*, **85**, 1544 (1963); see also N. W. Alcock, R. C. Spencer, R. H. Prince, and O. Kennard, *J. Chem. Soc., A*, 2383 (1968).

[47] W. Keim, *J. Organometal. Chem.*, **14**, 179 (1968).

[48] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965), have observed oxidative addition of the carbon–hydrogen bonds of coordinated $P{-}CH_3$ and naphthalene groups to ruthenium, and S. D. Ibekwe, B. T. Kilbourn, U. A. Raeburn, and D. R. Russell, *Chem. Commun.*, 433 (1969), have determined the crystal structure of $(\sigma\text{-}C_{10}H_7)RuH[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$ by X-ray diffraction.

[49] M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967); *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

[50] G. W. Parshall, *J. Amer. Chem. Soc.*, **90**, 1669 (1968); G. W. Parshall, W. H. Knoth, and R. A. Schunn, *ibid.*, **91**, 4990 (1969).

[51] G. Hata, H. Kondo, and A. Miyake, *ibid.*, **90**, 2278 (1968).

[52] A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968); see also P. L. Pauson, *Pure Applied Chem.*, **17**, 235 (1968); M. M. Bagga, W. T. Flannigan, G. R. Knox, P. L. Pauson, F. J. Preston, and R. I. Reed, *J. Chem. Soc. C*, 36 (1968).

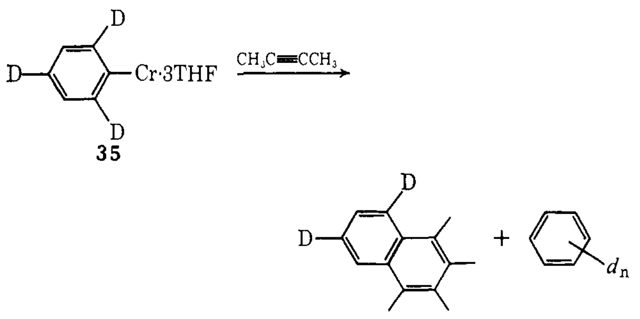
[53] R. Koster, *Advan. Organometal. Chem.*, **2**, 257 (1964); R. Köster and M. A. Grassberger, *Ann. Chem.*, **719**, 169 (1968); D. Hellwinkel, *Chem. Ber.*, **99**, 3660 (1966).

conditions by reaction of 2-biphenylmagnesium bromide and chromium trichloride.

The observation of the dibenzchromole **29** as a stable organometallic intermediate and the demonstration that the reaction of **29** with 2-butyne proceeds smoothly to 9,10-dimethylphenanthrene obviously suggest that the related chromocycle, 3,4-dimethyl-5-phenylbenzchromole (**34**), might be an intermediate in the conversion of **1** to **2**. We have not been able to obtain clearcut evidence for this benzchromole as an *intermediate* in this conversion. Although the formation of *cis*-2-phenylbut-2-ene-d_2 (**23d**) on treatment of a reacting mixture of **1** and **3** with deuterium oxide strongly implicates **34** as a solution component, the yield of **23d**, and by inference **34**, is always low. These yields are easily compatible with the hypothesis of **34** as an intermediate on the pathway leading to tetramethylnaphthalene, provided that the rate of reaction of **34** with 2-butyne is rapid compared with its rate of formation. However, in the absence of other evidence, it is also conceivable, although unlikely, that **34** might be simply the product of a side reaction unrelated to the path connecting **1** with **2**. Regardless, it is clear that the conversion of 2-biphenylmagnesium bromide to 9,10-dimethylphenanthrene involves initial formation of the dibenzchromole **29** as an intermediate, followed by subsequent reaction of this substance with 2-butyne. A similar pathway for the conversion of **1** to **2** seems very probable.

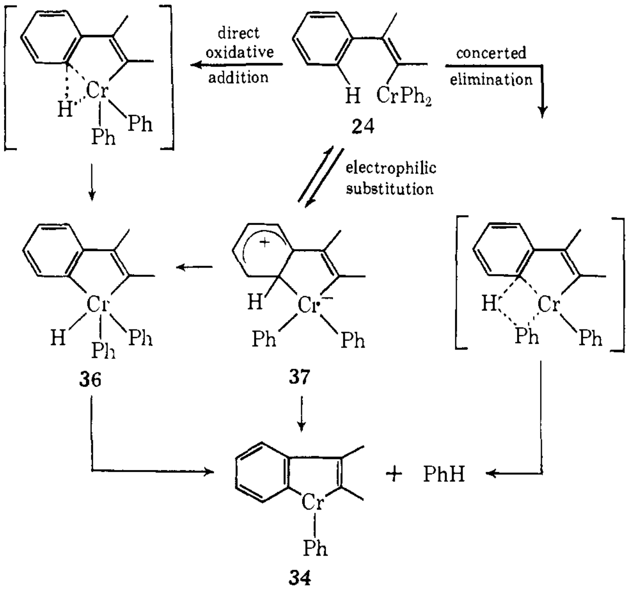
The kinetic isotope effects, discussed earlier in connection with the question of the intermediacy of benzyne–chromium complexes in reaction of triphenylchromium with 2-butyne, now bear reexamination in light of the evidence indicating that the most significant intermediate is in fact a benzchromole, formed by insertion of 2-butyne into a carbon–chromium bond followed by cyclization. The observation that there is no isotope effect on the reaction of compounds **18a–d** with 2-butyne is entirely consistent with this mechanistic hypothesis, again provided that the rate-determining step for the reaction occurs before the cyclization. Clearly, only a small secondary isotope effect would be expected to attend a mechanism whose rate-determining step was insertion of 2-butyne into the carbon–chromium bond of triphenylchromium to form **24**, or coordination of 2-butyne to the chromium atom of this metal compound. Further, the postulate that the slow step in conversion of triphenylchromium to tetramethylnaphthalene involves coordination or insertion of 2-butyne, and that the subsequent formation and further reaction of the benzchromole **34** are fast, is consistent with the failure to detect any significant buildup of intermediate organochromium compounds during the reaction.

Mechanistic interpretation of the deuterium isotope effect observed for reaction of tri(phenyl-2-d_1)tris(tetrahydrofuran)chromium (**17**) with 2-butyne requires knowledge of the fate of the hydrogen atom lost from the *ortho* position of the phenyl ring. This information was obtained by reaction of tri(phenyl-2,4,6-d_3)tris(tetrahydrofuran)chromium(III) **35** with 2-butyne to give among other products, tetramethylnaphthalene-d_2 and a mixture of deuterated benzenes. The mixture of benzenes was separated from the reaction mixture, and its isotopic composition determined by mass spectroscopy. Knowledge of the isolated yield and isotopic composition of the benzene, and of the yield of tetramethylnaphthalene-d_2, was sufficient to establish that >0.5 equiv of $C_6H_2D_4$ was produced for each equivalent of tetramethylnaphthalene formed in the reaction. Since some of the benzene produced in this transformation is held as π-benzenechromium(0) or chromium(I) complexes, and as such would not have been isolated as benzene under the conditions used in working up these experiments, it appears that most or all of the *o*-hydrogen which disappears from one phenyl ring of triphenylchromium in forming tetramethylnaphthalene is transferred to a second phenyl ring and ultimately appears as benzene.



At least three basic mechanistic schemes deserve consideration as possible descriptions of the cyclization step. The ring closure might take place by direct insertion of the chromium(III) atom into the *ortho* carbon–hydrogen bond of the phenyl ring to give a chromium(V) hydride (**36**) as an intermediate, followed by loss of benzene; it might take place by electrophilic attack by the chromium(III) atom on the phenyl ring to yield a σ complex (**37**), followed either by direct loss of benzene or by a 1,2-proton shift to yield the product of oxidative addition **36**; or it might take place by a process in which expulsion of benzene was concerted in some unspecified manner with carbon–chromium bond formation.

Scheme V. Formation of 1,2-Dimethyl-5-phenylbenzchromole

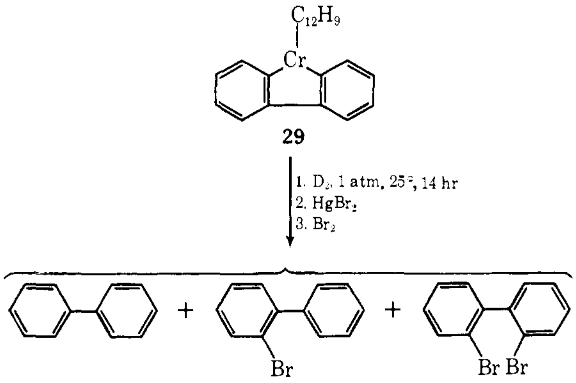


Comparison of the isotope effect obtained during reaction of tri(phenyl-2-d_1)chromium (**17**) and 2-butyne with those observed for representative electrophilic substitution reactions at aromatic carbon permits one clear condition to be placed on the mechanisms outlined in Scheme V: if intermediate **37** does lie along the reaction path between **24** and **34**, its formation from **24** must take place in a rapid preequilibrium step, and its conversion to **36** or **34** must be rate determining. The α-deuterium isotope effect on the rate of formation of a σ complex is normally small in electrophilic substitution reactions, since little carbon–hydrogen bond stretching takes place during attack of the electrophile on the ring.[54,55] Thus, the isotope effect observed for reaction of **17** with 2-butyne ($k_H/k_D = 2.7$)[56] is too large to be compatible with rate-limiting attack of the chromium atom on the aromatic ring.

Further differentiation between the mechanistic alternatives of Scheme V is difficult on the basis of the available information. The difference between the two paths connecting compounds **24** and **36** is primarily one of timing in formation of the carbon–chromium bond. While it is clear from other work that sp^2 hybridization at carbon is not required for oxidative addition of carbon–hydrogen bonds to transition metals,[57,58] there is no firm evidence indicating that oxidative addition of *aromatic* carbon–hydrogen bonds to metals does not in fact procced through intermediates analogous to **37** by a pathway involving initial attack of the metal on carbon rather than by insertion of the metal into a carbon–hydrogen bond. However, there is also no direct evidence establishing the intermediacy of compounds resembling either **36** or **37** in reactions of these chromium compounds. Nevertheless, two lines of evidence lend support to the suggestion that conversion of **24** to **34** takes place either by oxidative addition of a carbon–hydrogen bond to the chromium atom or by concerted addition–elimination, rather than by a reaction resembling electrophilic substitution at carbon.

The first of these lines derives from an examination of the reactions of triphenylchromium (**1**) and 5-(2-biphenyl)dibenzchromole (**29**) with deuterium gas. Reaction of **1** in THF with deuterium for 14 hr at 1 atm pressure and 25° resulted in slow deuterolysis of the carbon–chromium bond, yielding a mixture of benzene-d_1 (58%) and -d_0 (42%) as the primary organic products. The benzene-d_0 detected in this reaction is probably produced by thermally induced homolytic scission of carbon–chromium bonds of some partially deuterolyzed species and reaction of the resulting free or metal-complexed phenyl radicals with solvent. No deuterium was exchanged into the triphenylchromium under these conditions.

Reaction of deuterium with **29** under similar conditions resulted in analogous cleavage of the carbon–chromium bonds to yield biphenyl. However, if the reaction with **29** was carried to partial completion, and the remaining organochromium compound converted to the corresponding aryl bromides by reaction with mercury(II) bromide and bromine, mass spectroscopic analysis established that appreciable deuterium had been exchanged into the rings. Degradation of the biphenyls established that the deuterium which had exchanged into the chromium reagents has been incorporated predominantly or exclusively into the 2 positions of the biphenyl ring (see the Experimental Section).



29

(1.65 equiv)	(0.31 equiv)	(0.17 equiv)
94.0% d_0	69.5% d_0	80.5% d_0
5.6% d_1	27.3% d_1	17.9% d_1
4.0% d_2	3.2% d_2	1.6% d_2

The pertinence of these results to the mechanism of cyclization of **24** to **34** depends on the resemblance of the process by which the carbon–chromium bonds of the dibenzchromole **29** are converted to carbon–deuterium bonds to the reverse of the reaction sequence in which the carbon–hydrogen bonds of the immediate precursors of **29** and **34** are converted to carbon–chromium bonds. At the very least the observation that deuterium is exchanged into the *ortho* positions of the biphenyl groups demonstrates that carbon–hydrogen bond cleavage is reversible under some conditions.

The phenomenological similarity of the isotopic exchange observed on treatment of **29** with deuterium to that observed by Parshall, Knoth, and Schunn for the *o*-hydrogens of the phenyl rings of $HCo(N_2)(PPh_3)_3$ and related compounds[50] is sufficiently close to make the suggestions of analogous mechanisms attractive. Following the scheme proposed by these authors, exchange would take place by oxidative addition of deuterium to **29** to yield a species represented schematically by **35** followed either by an irreversible cleavage of

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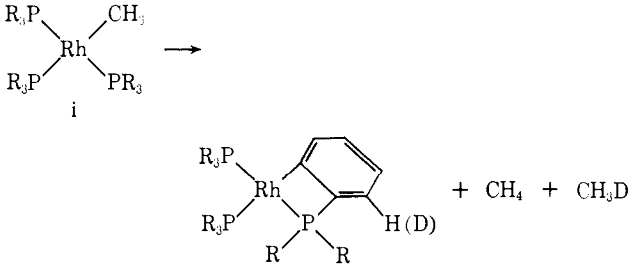
(54) Review: H. Zollinger, *Advan. Phys. Org. Chem.*, **2,** 163 (1964).

(55) For isotope effects in intramolecular electrophilic substitution reactions of several compounds closely related to those considered in this work, *viz.*, derivatives of 2-(phenyl-2-d_1)benzoic acid, see D. B. Denney and P. P. Klemchuk, *J. Amer. Chem. Soc.*, **80,** 3285 (1958).

(56) A related reaction, the thermal decompsition of methyltris[tri-(phenyl-2-*d*)phosphine]rhodium (i) to ii, methane, and methane-d_1, presumably *via* oxidative addition of an *ortho* carbon–hydrogen (deuterium) bond to rhodium,[47] exhibits an isotope effect of $k_H/k_D \leq 4.2$, as measured by the ratio of CH_4 to CH_3D evolved (see Experimental Section). This number is comparable with the isotope effect of 2.7 observed for the reaction of **17**[32] and supports the contention that the reaction **1** → **2** proceeds *via* oxidative addition.



i

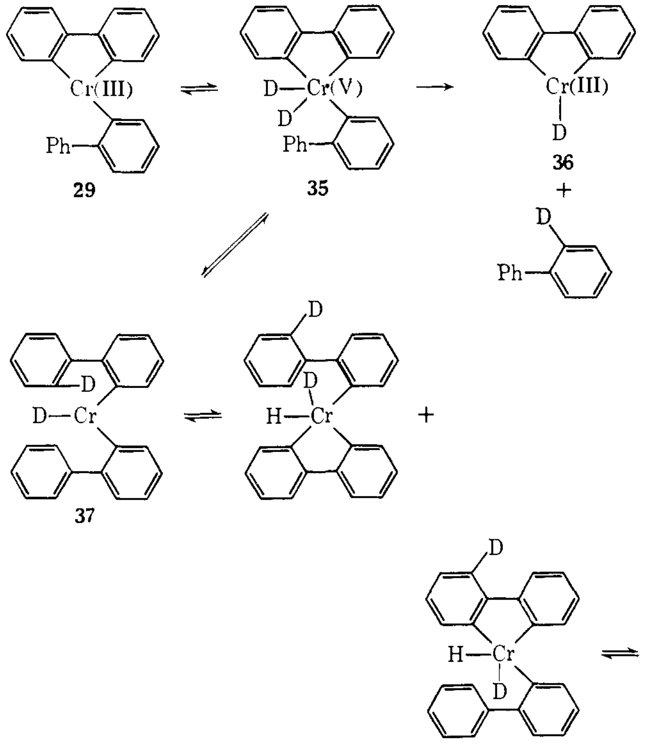
ii

R = *o*-C_6H_4D

(57) S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968); F. Piacenti, *et al.*, *J. Amer. Chem. Soc.*, **90,** 6848 (1968).

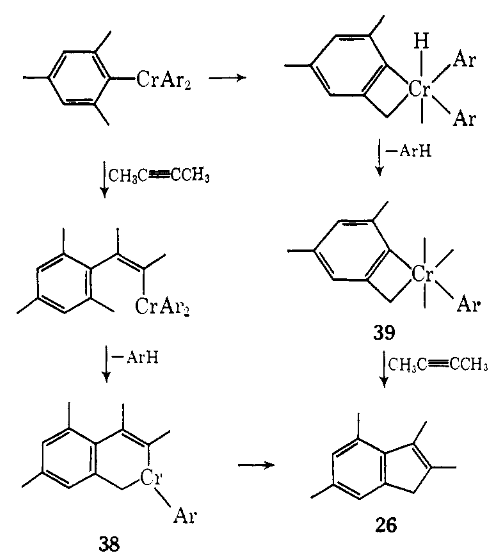
(58) M. A. Bennett and P. A. Longstaff, *ibid.*, 6266 (1969).

the chromium–biphenyl σ bond (**35** → **36**), or by a competing and potentially reversible cleavage of a chromium–carbon bond of the dibenzchromole (**35** → **37**). However, there is no direct evidence in this work (or indeed in much of the directly analogous work with d^8 complexes) for discrete hydridic intermediates derived from oxidative addition. On the basis of evidence presently available, these classes of reactions might take place by a reaction sequence in which oxidative addition to form an intermediate hydride and subsequent elimination were separate steps, or by a process analogous to that labeled "concerted elimination" in Scheme V in which addition and elimination merge to a single step[59]



The second datum supporting the hypothesis that conversion of **24** to **34** requires a step involving oxidative addition of a carbon–hydrogen bond to chromium has already been mentioned in another connection. The adduct of trimesitylchromium and 2-butyne cannot cyclize by substitution at an *ortho* carbon–hydrogen bond; instead, cyclization takes place by attack on a methyl group, ultimately yielding **26**. The formation of this product can be rationalized using a mechanism very similar to that of Scheme VI proceeding through a six-membered chromocycle **38**, or by direct cyclization to the four-membered chromocycle **39**. Again, no experimental evidence provides direct support for either alternative. However, reaction of trimesitylchromium with deuterium to partial completion, followed by degradation of the remaining organochromium reagents using mercury(II) bromide and bromine, yielded 2-bromomesitylene with composition 61.7% d_0 and 34.8% d_1, together with small quantities of more highly deuterated material. Deuterium incorporation into a mesityl group bonded to chromium is in clear contrast with the results of similar experiments using triphenylchromium, but is compatible with an intermediate resembling **39**. The oxidative addition of a methyl carbon–hydrogen bond to chromium implicated by structure **39** has some precedent.[48,58,63] However, regardless of the precise mechanism of formation of **26**, the demonstration that the ability of organochromium reagents to yield cyclic products does not depend on the availability of an aromatic carbon atom to act as one ring terminus provides support for those mechanisms for cyclization which do not resemble aromatic substitution.

Scheme VI



Summary and Conclusions

This work indicates that the conversion of triphenylchromium to tetramethylnaphthalene on reaction with 2-butyne takes place in three distinct steps: insertion of 2-butyne in a phenylchromium σ bond of **1** to form a styrylchromium reagent; cyclization of this styrylchromium reagent to a benzchromole; and reaction of the benzchromole with a second molecule of 2-butyne to form tetramethylnaphthalene (Scheme VII). In brief summary, four kinds of evidence support this mechanism. First, labeling experiments using 2-butyne-1,1,1-d_3, product studies based on reactions of *o*-, *m*-, and *p*-tolylchromium reagents, and deuterium kinetic isotope effect determinations carried out with **17** and **18** combine effectively to exclude mechanisms involving intermediates of tetramethylcyclobutadiene- or benzyne-like symmetry. Second, isolation of *cis*-2-mesitylbut-

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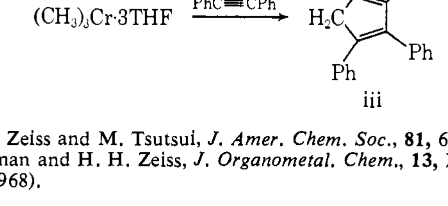
[59] Organolithium[60] and -magnesium[60] reagents, sodium naphthalide,[61] and hydroxide ion,[62] react readily with hydrogen, presumably by a mechanism involving nucleophilic attack. A related mechanism might also be possible for the reaction of arylchromium reagents with hydrogen.

[60] K. Clauss and H. Bestian, *Ann. Chem.*, **654**, 8 (1962); W. E. Becker and E. C. Ashby, *J. Org. Chem.*, **29**, 954 (1964).

[61] S. Bank and T. A. Lois, *J. Amer. Chem. Soc.*, **90**, 4505 (1968).

[62] C. Walling and L. Bollyky, *ibid.*, **86**, 3750 (1964).

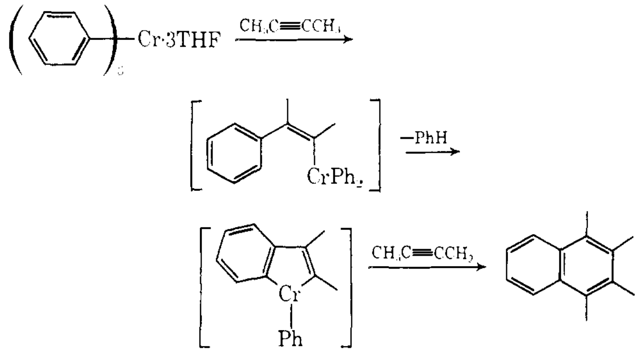
[63] Mechanisms similar to those outlined in Scheme VI provide a rationalization for production of tetraphenylcyclopentadiene iii on reaction of trimethyltris(tetrahydrofuran)chromium with tolane.[64]



iii

[64] H. Zeiss and M. Tsutsui, *J. Amer. Chem. Soc.*, **81**, 6090 (1959); M. Michman and H. H. Zeiss, *J. Organometal. Chem.*, **13**, P23 (1968); **15**, 139 (1968).

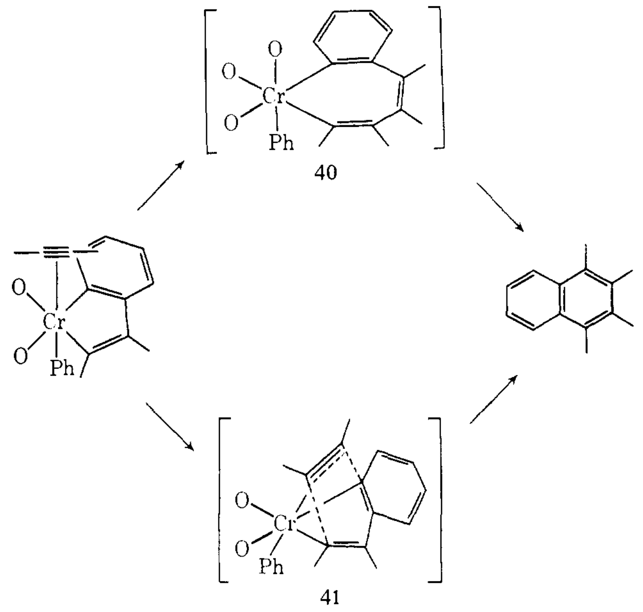
Scheme VII. Schematic Mechanism for Conversion of Triphenyltris(tetrahydrofuran)chromium(III) to 1,2,3,4-Tetramethylnaphthalene



2-ene and *cis*-2-phenylbut-2-ene from reacting mixtures of trimesityl- and triphenylchromium support the proposed initial insertion of 2-butyne into the aryl–chromium bond. Third, the isolation of *cis*-(phenyl-2-*d*)-but-2-ene-3-*d* (**23d**) following deuterolysis of a reacting mixture of triphenylchromium and 2-butyne, and the facile formation of 5-(2-biphenyl)dibenzchromole (**29**) on reaction of 2-biphenylmagnesium bromide with chromium trichloride, provide evidence for five-membered chromium heterocycles as reaction intermediates. Finally, several deuterium kinetic isotope and labeling studies appear to be consistent with the proposed reaction sequence.

The insertion of 2-butyne into a carbon–metal bond implicated in the first step of this mechanism is unexceptional, and deserves no further comment.[65] Cyclization of the resulting styrylchromium compound to a chromium-containing heterocycle is more interesting on two counts. First, it provides further support for the supposition[4,5] that five-membered metallocycles are important as intermediates in organometallic reactions. Second, the close analogy between the ring-closing and ring-opening reactions of the chromium(III) compounds examined here, and similar reactions of d^8 complexes, suggests that the former may take place by mechanisms involving oxidative addition of carbon–hydrogen bonds to chromium. Oxidative addition of an aromatic carbon–hydrogen bond to a d^3 chromium(III) ion to give compound formally containing a d^1 chromium(V) ion has no precedent.[66] However, the stability of substances such as Ph_6CrLi_3,[67] $Li_3Cr_2H_3Ph_6$,[68] $(CH_3)_6CrLi_3$[69] is sufficient to establish that chromium(III) is capable of forming compounds containing multiple carbon–chromium σ bonds. Corresponding compounds of chromium(V) are not known as stable entities, but might not be prohibitively energetic as intermediates or transition states in mechanisms requiring oxidative addition to chromium(III).

Only negative evidence is available concerning the nature of the final stage of the proposed mechanism, in which the chromium(III) heterocycle reacts with 2-butyne to yield tetramethylnaphthalene. At least three alternative mechanisms appear conceivable for this step: reaction might take place by insertion of a second molecule of 2-butyne into a carbon–chromium bond to give a seven-membered chromium heterocycle (*e.g.*, **40**), by a concerted, front-side displacement, or by a Diels–Alder reaction, in which formation of both carbon–carbon bonds to the entering acetylene occur concurrently. We have never detected products in the reaction mixtures from the formation of **2** or **30** which suggest compounds resembling **40** as a precursor; and on the basis of this weak evidence, we prefer a mechanism for incorporation of the second molecule of 2-butyne into the tetramethylnaphthalene ring proceeding through an intermediate or transition state resembling **41**.



Experimental Section[70]

General Methods. All reactions involving organometallic compounds were carried out in flame-dried glassware under an inert atmosphere of prepurified nitrogen using 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.

Triphenyltris(tetrahydrofuran)chromium(III) (1)[12] **and 2-butyne-1,1,1-d_3 (3)**[16] were prepared as described previously. **Trichlorotris(tetrahydrofuran)chromium(III)** was prepared using a procedure based on that of Zeiss.[72] The desired quantities of anhydrous chromium(III) chloride and tetrahydrofuran were placed in a flame-

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[65] For examples of additions of other organometallic molecules to acetylenes, see ref 3 and P. M. Maitlis, *Advan. Organometal. Chem.*, **4**, 95 (1966).

[66] Reviews: J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968); L. Vaska, *ibid.*, **1**, 335 (1968); J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 54 (1968); G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

[67] F. Hein and R. Weiss, *Z. Anorg. Allg. Chem.*, **295**, 145 (1958).

[68] F. Hein and B. Heyn, *Monatsber. Deut. Akad. Wiss. Berlin*, **4**, 223 (1962); *Naturwissenschaften*, **46**, 321 (1959).

[69] E. Kurras and J. Otto, *J. Organometal. Chem.*, **4**, 114 (1965); J. Krause, Proceedings 9th International Conference on Coordination Chemistry, St. Moritz, Sept 1966, p 168.

[70] 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 237B 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 minimal ionizing voltage.[71] Microanalysis was performed by Midwest Microlab, Inc., Indianapolis, Ind. Glpc analyses were carried out using an F & M Model 810 flame ionization instrument. Samples for mass spectroscopic analyses were collected from an F & M Model 720 instrument equipped with a thermal conductivity detector. Normally SE-52 or UC-W98 columns were used for both analytical and preparative work.

[71] K. Biemann, "Mass Spectrometry-Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962, pp 223 ff. Samples for deuterium analysis were purified by glpc, taking care to collect as much of the peak as possible to avoid isotopic fractionation.

[72] W. Herwig and H. Zeiss, *J. Org. Chem.*, **23**, 1404 (1958).

dried flask, together with a small quantity of chromium(II) chloride [~1–5% by weight of Cr(III)Cl$_3$].[73] The mixture was heated under nitrogen with stirring at a temperature between 50° and reflux temperature until a homogeneous solution was obtained, typically 1–2 hr.

1,2,3,4-Tetramethylnaphthalene (2). The general procedure used for these reactions is based on the procedure developed by Zeiss.[12] The Grignard reagent from 0.52 g (3.3 mmol) of bromobenzene in 10 ml of tetrahydrofuran was added dropwise to 1.0 mmol of trichlorotris(tetrahydrofuran)chromium(III) in 15 ml of tetrahydrofuran at −30° to which heptadecane had been added as internal standard. After stirring 1–2 hr at room temperature, 0.2 ml (*ca* 3 mmol) of 2-butyne was added and the solution stirred overnight. Hydrolysis of a 1-ml aliquot of the reaction mixture in 1 ml of 10% aqueous hydrochloric acid and analysis by glpc showed a 50–75% yield of tetramethylnaphthalene. Samples for mass spectral analysis were obtained by hydrolysis of the reaction mixture in 10 ml of 10% aqueous hydrochloric acid, concentration of the organic phase under vacuum, and the collection of the 1,2,3,4-tetramethylnaphthalene from glpc.

To prepare quantities of 1,2,3,4-tetramethylnaphthalene larger than 10 mmol, the same procedure, modified by omission of the internal standard, was followed. The product obtained from concentration of the hydrolyzed reaction mixture was recrystallized from hexane to yield 30–50% of 1,2,3,4-tetramethylnaphthalene having mp 105–106°; lit.[12] mp 106°.

1,2,3,4-Tetramethylnaphthalene-d_6. Triphenyltris(tetrahydrofuran)chromium(III) prepared from 7.3 g (46 mmol) of CrCl$_3$·3THF was allowed to react with 7.9 ml of 2-butyne-1,1,1-d_3 (*ca.* 5.0 g, 97 mmol) following the procedure described above to yield 1.2 g (6.3 mmol) of 1,2,3,4-tetramethylnaphthalene-d_6 having mp 106–106.5° (lit.[12] mp for an undeuterated sample 106°). The isotopic composition of this material determined mass spectrometrically (8.3 eV) was 2.4% d_9, 93.8% d_6, and 3.7% d_5.[74]

1,2-Bis(hydroxymethyl-d_2)naphthalene. A solution of 40 g (0.16 mol) of dimethylnaphthalene-1,2-dicarboxylate[75] in 200 ml of dry tetrahydrofuran (THF) was cautiously added to 7.6 g (0.18 mol) of lithium aluminum deuteride[76] in 100 ml of THF over 30 min. The solution was heated at reflux temperature for 2 hr, cooled, hydrolyzed, and made acidic with 30% aqueous hydrochloric acid. The organic layer was separated and the aqueous layer washed with 100 ml of chloroform. The combined organic layers were washed with aqueous sodium bicarbonate, dried (MgSO$_4$), and concentrated to yield 31.5 g (79%) of 1,2-bis(hydroxymethyl-d_2)naphthalene having mp 148.5–149.5° (mp of an undeuterated sample 149–149.5°).

Anal. of undeuterated sample Calcd for C$_{12}$H$_{12}$O$_2$: C, 76.57; H, 6.43. Found: C, 76.61; H, 6.39.

1,2-Bis(bromomethyl-d_2)naphthalene. To a mixture of 20 g (0.11 mol) of 1,2-bis(hydroxymethyl-d_2)naphthalene and 50 ml of benzene at 0° was added 30 ml (*ca.* a threefold excess) of phosphorus tribromide. The mixture was warmed to room temperature, stirred for 8 hr, poured onto ice, and extracted with 50 ml of chloroform. The chloroform solution was washed with aqueous sodium bicarbonate, dried (MgSO$_4$), and concentrated to yield 31.5 g (87%) of 1,2-bis(bromomethyl-d_2)naphthalene having mp 148.5–149.5° (mp of an undeuterated sample prepared by an alternative procedure[77] 148.5–149.5°).

1,2-Di(methyl-d_3)naphthalene. A solution of 26 g (82 mmol) of 1,2-bis(bromomethyl-d_2)naphthalene in 500 ml of dry THF was added to 3.8 g (90 mmol) of lithium aluminum deuteride in 200 ml of tetrahydrofuran over a period of 30 min, during which time the solution began to reflux. Refluxing was continued with external heating for an additional 18 hr. The solution was hydrolyzed, made acidic with 30% hydrochloric acid, and the THF removed under vacuum. The residue was extracted with ether and the ether layer dried (MgSO$_4$), concentrated, and distilled under vacuum to yield 11.5 g (87%) of 1,2-di(methyl-d_3)naphthalene[78] having bp 66–67° (0.10 mm); mass spectral isotopic analysis (8.3 eV) 94.4% d_6 and 5.6% d_5.

4-Chloromethyl-1,2-di(methyl-d_3)naphthalene. Chloromethylation of 10.9 g (67 mmol) of 1,2-di(methyl-d_3)naphthalene using the procedure of Hewett,[79] with 20 g (670 mmol) of paraformaldehyde and 100 ml of acetic acid yielded 8.0 g (60%) of 4-chloromethyl-1,2-di(methyl-d_3)naphthalene having mp 74.5–75° (lit.[79] mp for an undeuterated sample 72°).

1,2-Di(methyl-d_3)-4-methylnaphthalene. The reduction of 7.5 g (37 mmol) of 4-chloromethyl-1,2-di(methyl-d_3) with 1.6 g (42 mmol) of lithium aluminum hydride in 50 ml of THF was carried out using the procedure described for the reduction of di(bromomethyl-d_2)-naphthalene with LAD. Concentration of the ether extract yielded 6.0 g (92%) of 1,2-di(methyl-d_3)-4-methylnaphthalene having mp 49–50° (lit.[79] mp of an undeuterated sample 49–50°); mass spectral isotopic composition (8.3 eV) 94.3% d_6 and 5.7% d_5.

2-Chloromethyl-3,4-di(methyl-d_3)-1-methylnaphthalene. Chloromethylation of 5.5 g (31 mmol) of 1,2-di(methyl-d_3)-4-methylnaphthalene using 4.5 g (150 mmol) of paraformaldehyde and 40 ml of acetic acid was carried out using the procedure of Hewett.[79] A reaction time of 4 days produced 2.2 g (32%) of 2-chloromethyl-3,4-di(methyl-d_3)-1-methylnaphthalene having mp 87–88°.

1,2-Dimethyl-3,4-(dimethyl-d_3)naphthalene (6). The reduction of 2.0 g (8.9 mmol) of 2-chloromethyl-3,4-di(methyl-d_3)-1-methylnaphthalene with 0.38 g (10 mmol) of lithium aluminum hydride using the procedure described above yielded 1.6 g (100%) of 1,2-dimethyl-3,4-di(methyl-d_3)naphthalene having mp 105–106° (lit.[12] mp for undeuterated sample 106°); mass spectral isotopic composition (8.3 eV) 93.5% d_6 and 6.5% d_5.

Degradation of 1,2,3,4-Tetramethylnaphthalene-d_6. A sample of deuterated 1,2,3,4-tetramethylnaphthalene (0.5 g, 3.6 mmol) was oxidized using the procedure of Hart and Murray.[19] The resulting oily mixture of **10**, **11**, and **12** was dissolved in 15 ml of methanol and cooled to −20°. Ozone was bubbled through the solution until the effluent gas turned an aqueous solution of potassium iodide brown (*ca.* 3 min). Excess ozone was removed by bubbling a stream of nitrogen through the solution briefly. Ozonides were reduced catalytically using ~100 mg of 5% Pd–C and 1 atm of hydrogen. The methanolic solution was filtered and concentrated under vacuum to yield *ca.* 250 mg of an oil. To this oil was added 10 ml of 10% aqueous sodium hydroxide, and the mixture was stirred for 24 hr at ambient temperature. The solution was extracted with 1.0 ml of decane and the decane solution dried over 4A Molecular Sieves. Samples of methyl isopropyl ketone (**14**) for mass spectral analysis were purified by glpc using an SE-30 column. The mass spectrum of **14** prepared in this manner from undeuterated tetramethylnaphthalene was identical with that of an authentic sample of **14**.

Reaction of Tri-*m*-tolyltris(tetrahydrofuran)chromium with 2-Butyne. To a solution of 2.0 mmol of CrCl$_3$·3THF and 0.211 g of eicosane in 20 ml of tetrahydrofuran at −30° was added the Grignard reagent prepared from 1.2 g (7.0 mmol) of *m*-bromotoluene in 15 ml of tetrahydrofuran. After stirring the reaction mixture for 1 hr at room temperature, 0.4 ml (*ca.* 6 mmol) of 2-butyne was added and the solution stirred for 10 hr. A 2-ml aliquot of the mixture was then quenched in 2 ml of 10% aqueous hydrochloric acid and analyzed by glpc. This analysis established the presence of 0.186 g (47.0%) of 1,2,3,4,6-pentamethylnaphthalene and 0.0203 g (5.1%) of 1,2,3,4,5-pentamethylnaphthalene in the reaction mixture.

1,2,3,4,5-Pentamethylnaphthalene (15). Tri-*o*-tolylchromium (2.04 mmol) was prepared[80] and allowed to react with 2-butyne following the procedure used for the *m*-tolyl isomer to yield 220 mg (60%) of 1,2,3,4,5-pentamethylnaphthalene having mp 70–71°: nmr (CDCl$_3$) δ ~7.0–8.0 ppm (m, 3, aromatic),[81] 2.75 (s, 3), 2.60 (s, 3) 2.50 (s, 3) and 2.28 (s, 6).

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[73] The chromous ion appears to catalyze the dissolution of trichlorochromium(III). In Zeiss's procedures small quantities of chromous ion were generated *in situ* by reduction with zinc. For small scale preparations, the procedure described here is the more convenient.

[74] Isotopic compositions reported throughout 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 molecular ion had relative abundance <1.0%, if not reported explicitly.

[75] E. F. Bradbrook and R. P. Linstead, *J. Chem. Soc.*, 1739 (1936); R. Meier and H. G. Lotter, *Chem. Ber.*, **90**, 222 (1957).

[76] Purchased from Metal Hydrides; isotopic purity 99% deuterium.

[77] W. Ried and H. Boden, *Chem. Ber.*, **89**, 708 (1956).

[78] An undeuterated sample prepared by this sequence exhibited an ir spectrum identical with a commercial sample obtained from K & K Laboratories.

[79] C. W. Hewett, *J. Chem. Soc.*, 293 (1940).

[80] The *o*-bromotoluene used in this experiment was prepared by esterification of *o*-bromobenzoic acid, reduction of the ester with LAH, bromination of the alcohol with PBr$_3$, and reduction of the dibromide with LAH to give isomerically pure (>99% by nmr) *o*-bromotoluene.

[81] This aromatic multiplet was analyzed as an ABC spin system using the iterative nmr program LAOCN3:[82] δ_A = 7.80, δ_B = 7.19, δ_C = 7.12, J_{AB} = 8.3 Hz, J_{AC} = 1.9 Hz, J_{BC} = 6.9 Hz. The magnitudes of these coupling constants are consistent with those expected for **15**, but are inconsistent with those expected for **16**.[83]

Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.86; H, 9.07.

1,2,3,4,6-Pentamethylnaphthalene (16). Tri-*p*-tolylchromium (1.08 mmol) was prepared and allowed to react with 2-butyne following the procedure used for the *m*-tolyl isomer to yield 148 mg (69%) of 1,2,3,4,6-pentamethylnaphthalene having mp 85–86°; nmr ($CDCl_3$) δ ~7.1–8.1 ppm (m, 3, aromatic),[84] 2.53 (s, 6), 2.50 (s, 3), and 2.30 (s, 6).

Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.72; H, 9.40.

Chlorobenzene-2-*d*. A mixture of 100 g (0.42 mol) of 1-chloro-2-iodobenzene, 200 ml of dioxane, 80 ml of deuterium oxide, and 80 g of zinc powder was refluxed for 7 hr, filtered, and the organic layer separated. The aqueous layer was washed with 150 ml of ether and the combined ether layers were washed with two 100-ml portions of water, dried ($MgSO_4$), and concentrated by distillation through a 50-cm Vigreux column. The residue was distilled through a 50-cm spinning band column to yield 28.1 g (57%) of chlorobenzene-2-*d*; this material has mass spectral composition 97.1% d_1, 2.9% d_0.

Bromobenzene-2-*d*. Benzoic-2-*d* acid (10 g, 82 mmol), prepared from N,N-dimethylbenzylamine by the procedure of Hauser[85] using butyllithium in a 3:1 hexane–ether solution as metallating agent, was converted to bromobenzene-2-*d* (10.7 g, 84%) using the procedure of Oppenheimer and Bergmann;[86] this material had mass spectroscopic isotopic composition (9.0 eV) 98.1% d_1, 1.9% d_0.

Reaction of Tri(phenyl-2-*d*-)tris(tetrahydrofuran)chromium(III) with 2-Butyne. A solution of 63 mmol of tri(phenyl-2-*d*)chromium(III) was allowed to react with 1.5 ml (*ca.* 160 mmol) of 2-butyne using the procedure described above for reaction of undeuterated triphenylchromium. A sample of the resulting tetramethylnaphthalene, isolated by glpc, had mass spectroscopic isotopic composition (8.8 eV) 71.6 d_1, 28.4% d_0.

Bromobenzene-d_5. Bromine (60 g, 0.37 mol) was added over 1 hr to 25 g (0.3 mol) of benzene-d_6[87] containing 1 g of iron filings. The solution was poured into 50 ml of 1 *N* sodium hydroxide and filtered. The organic layer was separated, dried ($MgSO_4$), and distilled to yield 29 g (84%) of bromobenzene-d_5, bp 55–56° (15 Torr); mass spectral isotopic composition 95.8% d_5, 4.2% d_4.

Reaction of 2-Butyne with a Mixture of $(C_6H_5)_3Cr$, $(C_6H_5)_2(C_6D_5)Cr$, $(C_6H_5)(C_6D_5)_2Cr$, and $(C_6D_5)_3Cr$ (18a–d). An approximately 1:1 mixture of bromobenzene-d_0 and bromobenzene-d_5 was prepared (49.6% d_0, 50.4% $d_4 + d_5$[88]). The Grignard reagent solution prepared from 1.1 g (*ca.* 7.0 mmol) of this mixture of bromobenzenes and magnesium in 20 ml of THF was added dropwise to 1.99 mmol of **1** in 30 ml of tetrahydrofuran at +30°, containing 0.1693 g of heptadecane as an internal standard. After stirring for 1 hr at room temperature, a 10-ml aliquot of the resulting solution of **18a–d** was added to 1.0 g of mercury(II) bromide, the resulting organomercurial was cleaved with an excess of bromine, and the excess bromine was decomposed by addition of 10 ml of 10% aqueous sodium bisulfite. After concentration of the organic phase under vacuum, a sample of bromobenzene was collected by glpc for mass spectral isotopic analysis: 48.8 mol% $d_4 + d_5$. To the remainder of the solution of **18a–d** was added 0.5 ml (*ca.* 6 mmol) of 2-butyne. During the course of the ensuing exothermic reaction, 10-ml aliquots of the reaction mixture were quenched in 5 ml of 10% aqueous hydrochloric acid and the yields of tetramethylnaphthalene determined by glpc. After concentration of each quenched aliquot under vacuum, samples of 1,2,3,4-tetramethylnaphthalene were collected by glpc for mass spectral isotopic analysis. Yields and isotopic analyses are summarized in Table III. The kinetic isotope effect was obtained by comparison of the isotopic composition of the tetramethylnaphthalene with that of the bromobenzene obtained by mercuration and bromination of the starting solution of **18a–d**.

Table III. Yields and Isotopic Composition of Tetramethylnaphthalenes Isolated from Reaction of 2-Butyne with **18a–d**

	Tetramethylnaphthalene			
		Isotopic composition, %		Isotope effect,
Time,[a] min	Yield, %	d_0	$d_3 + d_4$	k_H/k_D[b]
2.0	24	50.5	49.5	0.97
3.5	37	50.1	49.9	0.96
5.0	41	50.5	49.5	0.97
90	74	50.5	49.5	0.97

[a] Time after adding 2-butyne to the solution of **18a–d**. [b] Obtained by comparison with the isotopic composition of the mixture of bromobenzene-d_0, -d_4, and -d_5 obtained by mercuration and bromination of **18a–d**.

Reaction of Trimesityltris(tetrahydrofuran)chromium(III) with 2-Butyne. A solution of 6.3 mmol of trichlorotris(tetrahydrofuran)-chromium(III) in 100 ml of THF to which 0.7456 g of hexadecane had been added as internal glpc standard was cooled to −30°. To this solution was added the Grignard reagent solution prepared from 4.0 g (20 mmol) of 2-bromomesitylene and an excess of magnesium in 50 ml of THF. The reaction mixture was allowed to warm to room temperature, with appearance of a characteristic blue color. After stirring the solution at room temperature for 2 hr, 1.5 ml (*ca.* 17 mmol) of 2-butyne was added. The course of the ensuing reaction was monitored by glpc analysis of hydrolyzed aliquots and was complete after 0.5 hr. Hydrolysis, followed by component isolation and spectroscopic analysis, established that the reaction yielded 0.771 g (70%) of *cis*-2-mesitylbut-2-ene (**25**)[40] having bp 42–43° (0.03 Torr), and 0.223 g (21%) of a compound, bp 70–73° (0.04 Torr), deduced to be 2,3,4,6-tetramethylindene (**26**) on the basis of the following evidence: nmr ($CDCl_3$) δ 6.89 (s, 1, aromatic), 6.70 (s, 1, aromatic), 3.06 (broad singlet, 2, CH_2), 2.48 (s, 3, ArCH_3), 2.22 (s, 3, ArCH_3), 2.15 (broad singlet, 3, 2-CH_3), 1.98 (s, 3, 3-CH_3); mass spectrum (70 eV) *m/e* 172 (molecular ion).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.58; H, 9.36.

Hydrolysis of a reaction mixture with deuterium oxide yielded *cis*-2-mesitylbut-2-ene having isotopic composition (9.0 eV) 1% d_2, 54% d_1, and 45% d_0.

Isolation of *cis*-2-Phenylbut-2-ene (23) from Reaction of 1- and 2-Butyne. To 20 mmol of **1** in 200 ml of THF was added 3.0 ml (*ca.* 35 mmol) of 2-butyne. Fifteen minutes after the beginning of the exothermic reaction (105 min after the addition of 2-butyne), 2.0 ml of deuterium oxide was added. The mixture was poured into 100 ml of 10% hydrochloric acid and extracted with 20 ml of ether. The ether was washed three times with 50-ml portions of water, dried ($MgSO_4$), and concentrated. Deuterated *cis*-2-phenylbut-2-ene was isolated by glpc in ~2% overall yield, based on chromium. Its mass spectroscopic isotopic composition (8.8 eV) was 32.4% d_2, 45.4% d_1, and 22.2% d_0. An undeuterated sample prepared by an analogous procedure had an ir spectrum in good agreement with that of an authentic sample.[89]

Degradation of Deuterated *cis*-2-Phenylbut-2-ene. A mixture of 50 μl of deuterated *cis*-2-phenylbut-2-ene, 160 mg (1.0 mmol) of potassium permanganate, and 20 ml of water was stirred for 2 hr. Excess permanganate was decomposed with sodium bisulfite and the solution was filtered, made acidic with hydrochloric acid, and extracted with 5 ml of ether. The ether was concentrated under vacuum and benzoic acid was isolated from the residue by collection from glpc. This material had mass spectroscopic isotopic composition (8.8 eV) 44.2% d_1 and 55.8% d_0.

Reaction of Tris(2,2-diphenylethenyl)chromium(III) with 2-Butyne. The Grignard reagent solution prepared from 6.0 g (23 mmol) of 2-bromo-1,1-diphenylethylene[90] and excess magnesium in 30 ml of THF was added to a solution of 6.4 mmol of $CrCl_3 \cdot 3THF$ and 0.181 g of eicosane (glpc standard) in 60 ml of THF at −30°. To this solution was added 2.5 ml (*ca.* 33 mmol) of 2-butyne in one portion, and the resulting solution was allowed to warm to room

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(82) A. A. Bothner-By and S. M. Castellano in "Computer Programs for Chemistry," Vol. I, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, p 10.

(83) A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965); S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(84) Analysis of this multiplet yielded $\delta_A = 7.96$, $\delta_B = 7.86$, $\delta_C = 7.23$, $J_{AB} = 0.8$ Hz, $J_{AC} = 9.8$ Hz, $J_{BC} = 2.2$ Hz. These coupling constants are compatible with **16**.

(85) F. N. Jones, M. F. Zinn, and C. R. Hauser, *J. Org. Chem.*, **28**, 663 (1963).

(86) J. Blum, E. Oppenheimer, and E. D. Bergmann, *J. Amer. Chem. Soc.*, **89**, 2338 (1967).

(87) Purchased from Stohler Isotope Chemicals.

(88) The ratio of bromobenzene-d_4 to -d_5 was approximately invarient throughout this experiment. For convenience, only the sum of these two species is reported.

(89) Sadtler Catalogue, spectrum no. 1619.

(90) D. Y. Curtin and E. W. Flynn, *J. Amer. Chem. Soc.*, **81**, 4714 (1959).

temperature and stirred for 2 hr. Analysis of the mixture by glpc showed the presence of 0.155 g (11%) of a product identified by comparison of its retention time and mass spectrum with those of an authentic sample of 1,2-dimethyl-4-phenylnaphthalene (**28**). Hydrolysis of the reaction mixture, concentration, and extraction with ether yielded 1.0 g (25% based on chromium) of a white solid, slightly soluble in ether, which was identified as 1,1,4,4-tetraphenylbutadiene by comparison of its ir spectrum with that of a known sample.[91]

1,2-Dimethyl-4-phenylnaphthalene (28) was prepared by oxidative coupling of a mixed copper(I) ate complex.[92] Solutions of phenyllithium prepared from 15 g (94 mmol) of bromobenzene and excess lithium wire in 100 ml of ether, and of 4-lithio-1,2-dimethylnaphthalene, prepared from 2.6 g (11 mmol) of 4-bromo-1,2-dimethylnaphthalene[79] and lithium wire in 30 ml of ether, were added to 7.2 g (50 mmol) of copper(I) bromide at 0°. Oxygen was bubbled through the solution at 0° for ~5 min, and the reaction mixture was hydrolyzed with 50 ml of water. The ether layer was separated, dried ($MgSO_4$), and concentrated. Much of the biphenyl formed as the major product of the reaction was removed by sublimation at 70° (0.1 Torr). The residue from the sublimation was distilled under vacuum to yield 0.8 g (34% based on naphthalene precursor) of 1,2-dimethyl-4-phenylnaphthalene having bp 122.4° (0.05 Torr) and nmr ($CDCl_3$) δ 7.1–8.2 (m, 10, aromatic), 2.70 (s, 3, CH_3), and 2.48 (s, 3, CH_3).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.91; H, 7.06.

5-(2-Biphenyl)dibenzchromole (29), and Its Reaction with 2-Butyne. The Grignard reagent prepared from 0.8223 g (3.53 mmol) of 2-bromobiphenyl and excess magnesium in 15 ml of THF containing 0.1707 g of heptadecane as internal glpc standard at *ca.* 45°[93] was slowly added to a solution composed of 1.08 mmol of $CrCl_3 \cdot 3THF$ in 20 ml of THF at −20°, containing 0.1093 g of eicosane as a second internal glpc standard. After the solution had warmed to room temperature and stirred for 1 hr, a 10-ml aliquot was allowed to react with 0.5 g of mercury(II) bromide at room temperature. Bromine (150 mg) was added to the resulting mixture of organomercury compounds, and the solution analyzed by glpc for biphenyl, 2-bromobiphenyl, and 2,2′-dibromobiphenyl.

To the remaining reaction mixture was added 0.2 ml (*ca.* 3 mmol) of 2-butyne, and the solution was stirred for 6 hr at 25°. A 1-ml aliquot was hydrolyzed with 5% hydrochloric acid and analyzed for 9,10-dimethylphenanthrene[94] by glpc. A 10-ml aliquot was worked up with mercury(II) bromide using the procedure described above. Products were isolated by glpc and identified by comparison of ir and mass spectra with those of authentic samples. In a separate experiment in which the reaction mixture was quenched with deuterium oxide, mass spectral analysis of the 9,10-dimethylphenanthrene formed showed no incorporation of deuterium.

Fluorenone. A solution of 2.05 mmol of 5-(2-biphenyl)dibenzchromole (**29**) in 40 ml of THF, containing 0.1446 g of heptadecane as internal standard, prepared as described above, was stirred for 1 hr at room temperature. After stirring for an additional 40 hr under an atmosphere of carbon monoxide at room temperature, a 2-ml aliquot was hydrolyzed with 1 ml of 10% aqueous hydrochloric acid and analyzed by glpc to show 0.153 g (42% based on chromium) of fluorenone. The remaining solution was concentrated under vacuum, hydrolyzed, made acidic with 20% aqueous hydrochloric acid, and extracted with 20 ml of ether. The ether solution was concentrated and a sample of fluorenone, collected by glpc, was shown to exhibit an ir spectrum matching that of an authentic sample.

Reaction of Tri(phenyl-2,4,6-d_3)chromium (35) with 2-Butyne. A solution of 1.0 mmol of $CrCl_3 \cdot 3THF$ in 10 ml of tetrahydrofuran containing 0.0762 g of heptadecane and 0.2136 g of decane as in-

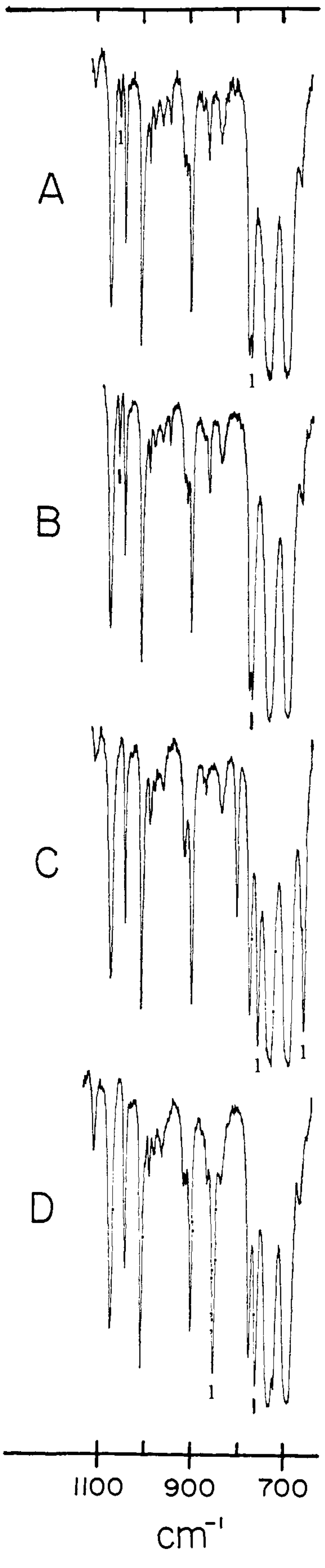

Figure 1. The infrared spectra of biphenyl-*d* obtained from the reaction of **29** with deuterium (A) and from mixtures of biphenyl-d_0 with ~25% of biphenyl-2-*d* (B), biphenyl-3-*d* (C), and biphenyl-4-*d* (D). Bands characteristic of each deuterated species are indicated on the spectra.

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(91) Sadtler Catalogue, spectra no. 14255, 20511.

(92) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969); G. M. Whitesides, J. San Filippo, Jr., C. P. Casey, and E. J. Panek, *ibid.*, **89**, 5302 (1967).

(93) The solubility of biphenyl-2-magnesium bromide in THF is inconveniently low at temperature <40°.

(94) An authentic sample of 9,10-dimethylphenanthrene, mp 142–142.5°, was prepared using literature procedures: C. A. Dormfeld, J. E. Callen, and G. H. Coleman, "Organic Syntheses," Coll. Vol. III, Wiley, New York, N. Y., 1955, p 134; B. M. Mikhailov and N. G. Chernova, *J. Gen. Chem. USSR*, **21**, 1659 (1951).

ternal standards were cooled to −30° and 3.8 mmol of phenyl-2,4,6-d_3-magnesium bromide[95] in 10 ml of tetrahydrofuran was added slowly. After stirring the reaction mixture for 12 hr at room temperature, the reaction was quenched with 2 ml of 5 *M* hydrochloric acid. Analysis by glpc showed 112 mg (1.44 mmol) of benzene and 89 mg (0.48 mmol) of 1,2,3,4-tetramethylnaphthalene. The reaction mixture was then diluted with 50 ml of water and extracted with 10 ml of ether. The ether extract was washed with 50 ml of water, dried ($MgSO_4$), and concentrated by distillation through a 30-cm Vigreux column. Mass spectral analysis of a sample of benzene collected by glpc showed isotopic composition 15% d_4, 83.3% d_3, and 1.7% d_2.

Reaction of Triphenyltris(tetrahydrofuran)chromium(III) with D_2. A solution of 2.0 mmol of triphenyltris(tetrahydrofuran)chromium(III) in 25 ml of tetrahydrofuran was stirred for 90 min at room temperature in a 125-ml flask under an atmosphere of deuterium. Approximately one-half of the solution was added to 1.5 g of mercury(II) bromide and the resulting mercury compounds were cleaved with an excess of bromine. Excess bromine was decomposed with 10 ml of a 10% aqueous sodium bisulfite solution. The solution was then diluted with 50 ml of water and extracted with 10 ml of pentane. The pentane was concentrated and a portion of bromobenzene was collected by glpc. Mass spectral analysis established its isotopic composition to be >99.5% d_0. The remaining triphenylchromium was stirred a total of 14 hr, poured into 100 ml of water, made acidic with hydrochloric acid, and extracted with 10 ml of pentane. The pentane solution was concentrated and benzene was collected by glpc. Mass spectral analysis established its isotopic composition to be 57.6% d_1 and 42.4% d_0.

Reaction of 5-(2-Biphenyl)dibenzchromole (29) with Deuterium. The same general procedure was used for several experiments. The Grignard reagent obtained from 3.5 mmol of 2-bromobiphenyl was allowed to react with 1.0 mmol of $CrCl_3 \cdot 3THF$ at −30° in THF as described previously. The nitrogen atmosphere over the organometallic solution was replaced by deuterium (1 atm), and the mixture was allowed to warm to room temperature and stir for the desired length of time. It was then quenched by addition to 1.5 g of mercury(II) bromide followed by bromine. The mixture was filtered and concentrated. Samples of biphenyl, 2-bromobiphenyl, and 2,2′-dibromobiphenyl used for mass spectral deuterium analysis were isolated by glpc.

Qualitatively, the extent of deuterium incorporation into each of these materials depended on the extent to which the reaction of **20** with deuterium was allowed to proceed, the higher incorporation into the 2-bromo- and 2,2′-dibromobiphenyl being observed after longer reaction times. The most extensive incorporation into these materials was observed in materials isolated from reaction between ∼1 mmol of **20** and 2 mmol of D_2 carried out at 25° for 14 hr. Here, isotopic compositions of the biphenyl derivatives were: biphenyl (83.6% d_0, 11.3% d_1, 4.7% d_2, and 0.3% d_3), 2-bromobiphenyl (52.5% d_0, 38.8% d_1, 7.8% d_1, and 0.8% d_3), and 2,2′-dibromobiphenyl (71.9% d_0, 26.7% d_1, and 2.3% d_2).

Biphenyl-2-d_1, biphenyl-3-d_1, and biphenyl-4-d_1 were prepared by reaction of the corresponding Grignard reagents with deuterium oxide in THF solution, and were purified by crystallization followed by sublimation. Melting points and mass spectroscopic isotopic compositions of each isomer were: biphenyl-2-*d*, mp 69–70°, 92.1% d_1, 7.4% d_0; biphenyl-3-*d*, mp 68.5–69.5°, 62.4% d_1, 37.6% d_0; biphenyl-4-*d*, mp 69.5–70°, 88.0% d_1, 12.0% d_0. Ir spectra (CCl_4) of mixtures of biphenyl-d_0 and these compounds in the 650–1100 cm^{-1} region are reproduced in Figure 1.

Determination of the Site of Deuteration of the Biphenyls Obtained by Reaction of 29 with Deuterium. The crude mixture of organic products obtained by reaction of ∼5 mmol of **29** and 3 mmol of D_2 for 14 hr at 25°, followed by reaction with mercury(II) bromide and bromine, was distilled through a short-path column to separate the biphenyl derivatives from nonvolatile inorganic and organometallic substances. This distillate, which included the major part of the biphenyl, 2-bromobiphenyl, and 2,2′-dibromobiphenyl present in the crude reaction mixture, was allowed to react with excess magnesium in 5 ml of THF. The solution was cooled to 0° to precipitate the biphenyl-2-magnesium bromide and biphenyl-2,2′-di(magnesium bromide), the precipitate was compacted by centrifugation at 0°, and the supernatant solution decanted. The solid residue was allowed to react with ∼1 ml of water, and the resulting biphenyls isolated using conventional procedures, and purified by sublimation (mp 67–70°). The isolated yield of biphenyl was ∼100 mg; its ir spectrum in the 650–1100 cm^{-1} region is given in Figure 1; mass spectral isotopic analysis showed 81.0% d_0, 17.4% d_1, and 1.5% d_2.

Reaction of Trimesitylchromium with Deuterium. A solution of 1.0 mmol of trimesitylchromium[38] in 25 ml of tetrahydrofuran was stirred under 1 atm of deuterium in a 100-ml flask for 12 hr. The solution was then added to 1.0 g of mercury(II) bromide, followed by 0.2 ml of bromine. Excess bromine was decomposed with aqueous sodium bisulfite and the resulting mixture poured into 50 ml of water and extracted with 35 ml of ether. The ether was dried ($MgSO_4$) and concentrated under vacuum. A sample of 2-bromomesitylene, purified by glpc, was analyzed by mass spectrometry to show 61.7% d_0, 34.8% d_1, 0.6% d_2, 1.3% d_3, 0.9% d_4, 0.6% d_5, and a trace of d_6 and d_7 isomers.

Tri(phenyl-2-*d*)phosphine. (Phenyl-2-*d*)magnesium chloride was prepared by refluxing 15 g (0.13 mol) of chlorobenzene-2-*d* with 0.4 g (0.17 mol) of powdered magnesium in 150 ml of THF for 4 hr. The Grignard reagent was then decanted through a cannula, cooled to 0°, and 3.2 g (0.023 mol) of phosphorus trichloride was added dropwise over 20 min. The solution was warmed to room temperature and hydrolyzed with 100 ml of 20% aqueous ammonium chloride, the layers were separated, and the aqueous layer was washed with 30 ml of ether. The combined organic layers were dried ($MgSO_4$), concentrated under vacuum, and the last traces of solvent were removed by heating the residue to 60° (0.1 Torr) for 10 min. The residue was crystallized from ethanol to yield 5.2 g (85%) of tri(phenyl-2-*d*)phosphine having mp 79–80°; mass spectral isotopic analysis: 0.6% d_1, 7.4% d_2, and 92.1% d_3.

Tris[tri(phenyl-2-*d*)phosphine]rhodium(I) Chloride. Tris[tri(phenyl-2-*d*)phosphine]rhodium(I) chloride was prepared in 96% yield from 4.1 g (15.5 mmol) of tri(phenyl-2-*d*)phosphine and 0.70 g (2.7 mmol) of rhodium(III) chloride hydrate according to the procedure of Wilkinson:[96] mp 155–157° (lit.[96] mp for an undeuterated sample 157–158°).

Decomposition of Methyltris[tri(phenyl-2-*d*)phosphine]rhodium(I). Methyltris[tri(phenyl-2-*d*)phosphine]rhodium(I), prepared from 0.50 g of tris[tri(phenyl-2-*d*)phosphine]rhodium(I) chloride according to the procedure of Keim,[47] was heated for 4 hr at 120°. The methane evolved, after having been passed over alumina to remove traces of residual ether, was analyzed for deuterium by mass spectroscopy. The methane was shown to contain 81.3% CH_4 and 18.7% CH_3D, giving, after correction for undeuterated phenyl groups in the triphenylphosphine ligand, an isotope effect of $k_H/k_D = 4.2 \pm 0.1$.

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[95] Prepared from bromobenzene-2,4,6-d_3, synthesized using the procedure of J. M. Scarborough, U. S. Atomic Energy Commission, NAA-SR-2144 (1957); *Chem. Abstr.*, **52**, 9042*d* (1958).

[96] J. A. Osborn, F. H. Sardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).