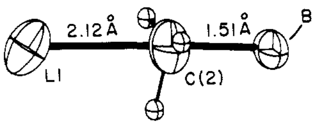


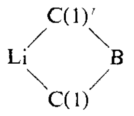
Figure 2. Linear bridge portion B–C(2)–Li illustrating the approximate stereochemistry of C(2).

to each other by symmetry operations of the space group *Pnma*. The same is true of the boron atoms, the methyl carbon atoms C(2), and the methyl carbon atoms C(3), *i.e.*, there are three structurally distinct carbon atoms, one lithium atom, and one boron atom.

The Li–C(1)–B bridge angle (75.6°) and Li–B distance (2.47 Å) are consistent with the corresponding parameters in electron-deficient compounds.[4b] It should also be noted that a completely dissimilar configuration is found for $Li_2Be(CH_3)_4$,[13] in which the Li–Be approach is 3.67 Å and Li–C distances are 2.52 Å.

The B–C(2)–Li and B–C(3)–Li groups (angles 179.6 and 177.6°) are a surprising and completely unexpected feature of the structure. The only other linear metal–methyl carbon–metal grouping which has been reported is in $(CH_3)_3In$[14] and apparently involves at most a very weak interaction with unsymmetrical In–CH_3 distances of 2.15 and 3.10 Å. In contrast, the short boron–carbon distance (B–C(2)) of 1.51 Å and lithium–carbon distance (Li–C(2)) of 2.12 Å suggest strongly coordinated linearly bridged groups. In fact, these values represent the shortest known metal–methyl carbon distances for boron and lithium and are to be compared with values of 1.590 (3) and 1.578 (1) reported for $[(CH_3)_2BH]_2$[15] and $B(CH_3)_3$[16] and 2.30 and 2.31 Å reported for $LiAl(C_2H_5)_4$[17] and CH_3Li.[18]

If the



moiety is considered to be a four-electron, four-center electron-deficient group, then the linear groups are two-electron, three-center systems. Because of the heteronuclear nature of the compound, this is undoubtedly an oversimplified view of the charge distribution. The present hydrogen atom positions, which must be regarded as somewhat tentative, are also of interest. The average HCH angles for C(1) and C(2) are 98 and 117°. The average B–C–H angle for C(2) is 102°. In short, the geometry of the methyl groups C(1) suggests a significant amount of carbanion character, while that of the five-coordinate C(2) is approaching a trigonal-bipyramidal configuration (Figure 2). The implications of the above to the stereochemistries of related boron compounds of representative and transition metal elements are currently being investigated.

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(13) E. Weiss and R. Wolfrum, *J. Organometal. Chem.*, **12**, 257 (1968).

(14) E. L. Amma and R. E. Rundle, *J. Amer. Chem. Soc.*, **80**, 4141 (1958).

(15) B. L. Carroll and L. S. Bartell, *Inorg. Chem.*, **7**, 219 (1968).

(16) L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, **42**, 3076 (1965).

(17) R. L. Gerteis, R. E. Dickerson, and T. L. Brown, *Inorg. Chem.*, **3**, 872 (1964).

(18) E. Weiss and G. Hencken, *J. Organometal. Chem.*, **21**, 265 (1970).

Interception of an Intermediate in the Addition of Diphenylcarbene to Acetylenes[1]

Sir:

Two-step addition of triplet carbenes to olefins has been demonstrated several times through the observation of nonstereospecificity in the reaction.[2] Examples typical of the known cases include methylene[3] and biscarbomethoxycarbene,[4] which give a mixture of cyclopropanes independent of the starting olefin and appropriate for product determined by the stereochemical preferences of an intermediate diradical. However, the stereochemistry of the reaction of triplet diphenylcarbene with olefins has not been determined in a system free from abstraction. Thus the stepwise nature of the addition reaction of triplet diphenylcarbene can only be presumed at this time.[5–7]

Acetylenes, which generally form cyclopropenes on reaction with carbenes,[8] lack a stereochemical "handle" through which two-step addition can be observed. Nevertheless it seemed to us that the intermediate diradical might reveal itself, provided an appropriate intramolecular trap were available. Diphenylcarbene provided the necessary triplet nature and the trap at the same time. It was hoped that the initially formed diradical **1** would attack one of the benzene rings to give the intermediate **2** which would suffer hydrogen shift to the indene **3**. With the three monosubstituted acetylenes shown, this is the course the reaction takes.[9]

No more than traces of the cyclopropenes could be formed, as nmr spectra of the crude reaction products do not show appropriate signals. Indenes **3a** and **3c** are known,[10] and were identified by a comparison of spectra. Compound **3b** is new and was identified by elemental analysis and an examination of its spectra, which closely resemble those of **3a** and **3c**.

One must now ask if the cyclopropenes could be serving as the sources of **3a–c**. Both thermal[11] and

(1) Financial support from the National Science Foundation through Grant No. GP-12759 is gratefully acknowledged.

(2) For a review of carbene chemistry see W. Kirmse, "Carbene, Carbenoide und Carbenanaloge," Verlag Chemie, Weinheim/Bergstr., Germany, 1969.

(3) C. McKnight, P. S. T. Lee, and F. S. Rowland, *J. Amer. Chem. Soc.*, **89**, 6802 (1967).

(4) M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *Tetrahedron Lett.*, 1391 (1967).

(5) G. L. Closs, *Top. Stereochem.*, **3**, 193 (1968).

(6) M. Jones, Jr., W. J. Baron, and Y. H. Shen, *J. Amer. Chem. Soc.*, **92**, 4547 (1970).

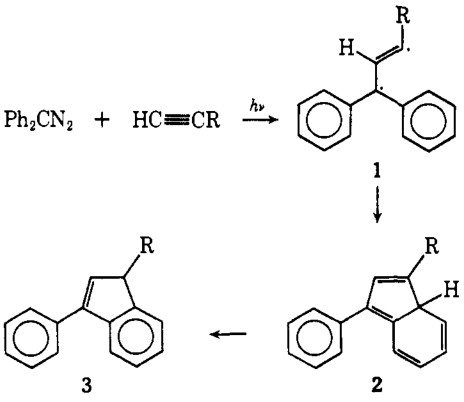
(7) The small amount of cyclopropane produced in the reaction of diphenylcarbene with *cis*- or *trans*-2-butene is formed in a largely stereospecific fashion. The cyclopropanes may well be formed largely by singlet carbene and thus not reflect the properties of the triplet.

(8) For a review see R. Fuks and H. G. Viehe in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969.

(9) A mechanism in which **1** abstracts hydrogen from a benzene ring and then recloses directly to **3** cannot be ruled out at this time, but would not alter the conclusions of this work.

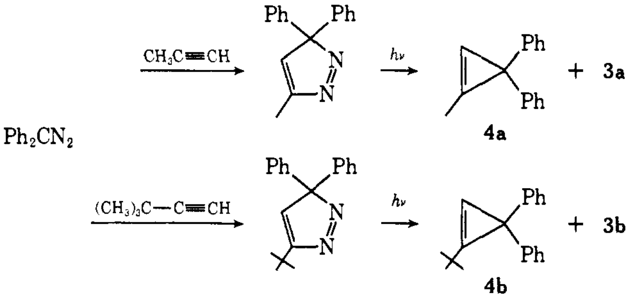
(10) B. Cheminat and R. Rambaud, *C. R. Acad. Sci. Ser. C*, **268**, 724 (1969).

(11) M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Commun.*, 907 (1967).

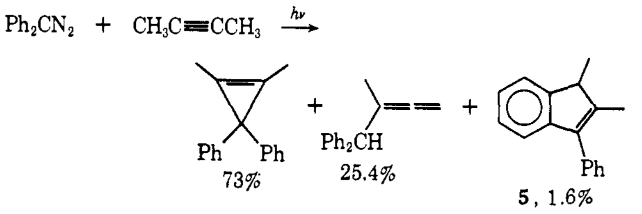


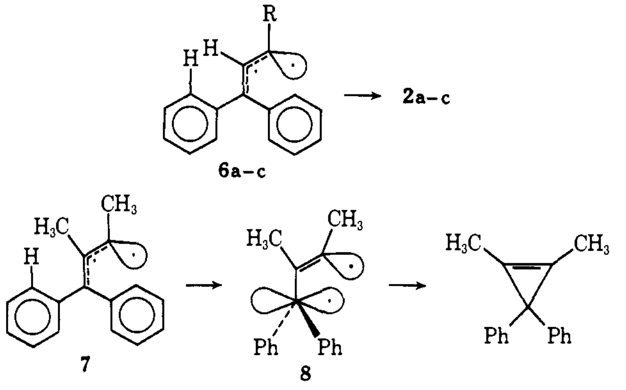
a, R = CH_3
b, R = $(CH_3)_3C$
c, R = Ph

photochemical[12] reactions of this type are known. Although the temperatures involved in this work never exceeded room temperature and are thus far below the 190–200° necessary to convert tetraphenylcyclopropene to 1,2,3-triphenylindene,[11] a photochemical rearrangement seemed distinctly possible. Accordingly, we synthesized authentic cyclopropenes **4a** and **4b** by the photochemical decomposition of the corresponding 3*H*-pyrazoles.[13] These pyrazoles are potential intermediates in the formation of indenes from diphenyldiazomethane and acetylenes. However, under a variety of conditions, including both direct and sensitized decomposition, the pyrazoles always gave substantial (20–45%) amounts of cyclopropene. Thus they cannot be intermediates in the original decompositions in which no more than traces of cyclopropene can be formed. Cyclopropenes **4a** and **4b** are not converted to indenes either by direct or by sensitized irradiation. Both benzophenone and diphenyldiazomethane were tried as sensitizers. Thus, **3a–c** are primary products of the reaction.



Curiously, irradiation of diphenyldiazomethane in dimethylacetylene produced a mixture of cyclopropene and indene strongly favoring (*ca.* 45:1) cyclopropene. The presence of the known[14] indene **5** was inferred from appropriate peaks in the nmr spectrum of the crude reaction mixture. We attribute this startling change in reaction course to a steric effect. In particular, we suspect that the intermediates responsible for indene formation are well described by **6a–c**. Rotation of one phenyl ring[15] allows formation of **2** but cyclopropenes cannot easily be produced. The diradical **7**, analogous to **6**, but formed from a disubstituted acetylene, suffers an alkyl–hydrogen interaction which is missing in **6**, and which apparently requires rotation to **8**, which is a suitable intermediate for cyclopropene formation.





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(12) D. J. Keyton, J. J. Brophy, G. W. Griffin, B. Halton, M. Kulig, and M. A. Battiste, Abstracts, 160th National Meeting of the American Chemical Society, Sept 1970, ORGN 91.

(13) G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, **90**, 173 (1968).

(14) M. Jones, Jr., M. E. Hendrick, J. C. Gilbert, and J. R. Butler, *Tetrahedron Lett.*, 845 (1970).

(15) Triplet fluorenylidene, which would produce an intermediate in which this rotation is impossible, forms only cyclopropenes.

(16) National Science Foundation Predoctoral Fellow, 1967–1971.

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Nuclear Magnetic Resonance Spectra and Ligand Substitution Reactions of Methylgold and Trimethylgold Complexes

Sir:

Our recent spectroscopic studies of the classical organogold compounds trimethylphosphinemethylgold (**1**) and trimethylphosphinetrimethylgold (**2**) have revealed some interesting phenomena, which shed new light on the relative reactivities of gold(I) and gold(III) complexes in ligand substitution processes. Compound **1**

$$\underset{\mathbf{1}}{CH_3Au \leftarrow P(CH_3)_3} \qquad \underset{\mathbf{2}}{(CH_3)_3Au \leftarrow P(CH_3)_3}$$

was obtained following the procedure described for the triethylphosphine complex by Coates and Parkin[1] and identified by its elemental analysis[2] and infrared, proton magnetic resonance, and mass spectra.

Solutions of this monomeric compound in pure anhydrous benzene exhibit the expected two proton resonances in the pmr spectra, both signals being split

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(1) G. E. Coates and C. Parkin, *J. Chem. Soc.*, 3220 (1962).

(2) Compound **1**, mp 70–71°. *Anal.* Calcd for $C_4H_{12}AuP$ (288.1): C, 16.70; H, 4.20. Found: C, 16.60; H, 4.06; mol wt (mass spectrum) 288 (no melting point, analysis, or molecular weight reported in ref 1).