

AD-A251 017



INFORMATION PAGE

Form Approved  
OMB No. 0704-0188

2

estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Avenue, S.W., Washington, DC 20543, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

REPORT DATE  
May 26, 1992

3. REPORT TYPE AND DATES COVERED  
Technical Report

4. TITLE AND SUBTITLE

The Unexpected Formation of 1,5-Bis(cyclobuta)-3,4,7,8-tetramethylcyclooctatetraene from a Zirconacyclopentadiene

5. FUNDING NUMBERS

G-N00014-91-J-1043

6. AUTHOR(S)

Rupert E.v.H. Spence, Stephen L. Buchwald, and John F. Richardson

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemistry  
Massachusetts Institute of Technology  
77 Massachusetts Avenue  
Cambridge, MA 02139

8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report No. 1

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research  
Department of the Navy  
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Prepared for publication in *Acta Chemica Scandinavica*

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release, distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Attempts to convert 2,2'-cyclobuta-1,1'-dimethylzirconacyclopentadiene into the corresponding bismole by treatment with phenylbismuth dibromide, led instead to the formation of 1,5-Bis(cyclobuta)-3,4,7,8-tetramethylcyclooctatetraene. A preliminary mechanistic study of this unusual transformation was also carried out.

DTIC  
ELECTE  
JUN 03 1992  
S A D

14. SUBJECT TERMS

main group metallacycles, cyclooctatetraene synthesis

15. NUMBER OF PAGES

12

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT

Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE

Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT

Unclassified

20. LIMITATION OF ABSTRACT

UL

OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1043

R & T code 4135014

Technical Report No. 1

The Unexpected Formation of 1,5-Bis(cyclobuta)-3,4,7,8-tetramethylcyclooctatetraene  
from a Zirconacyclopentadiene

by

Rupert E.v.H. Spence, Stephen L. Buchwald, and John F. Richardson

Prepared for Publication

in

*Acta Chemica Scandinavica*

Massachusetts Institute of Technology  
Department of Chemistry  
Cambridge, MA 02139

May 25, 1992

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale, its distribution is unlimited.

**92-14254**



92 5 29 025

Author responsible for correspondence and proofs: Prof. Stephen L. Buchwald,  
Department of Chemistry, Massachusetts Institute of Technology, Cambridge,  
Massachusetts 02139, USA.

The Unexpected Formation of 1,5-Bis(cyclobuta)-3,4,7,8-tetramethylcyclooctatetraene  
from a Zirconacyclopentadiene.

Rupert E. v. H. Spence and Stephen L. Buchwald\*

Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139, USA

John F. Richardson<sup>a</sup>

Department of Chemistry  
University of Louisville  
Louisville, Kentucky 40292, USA

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification .....	
By .....	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

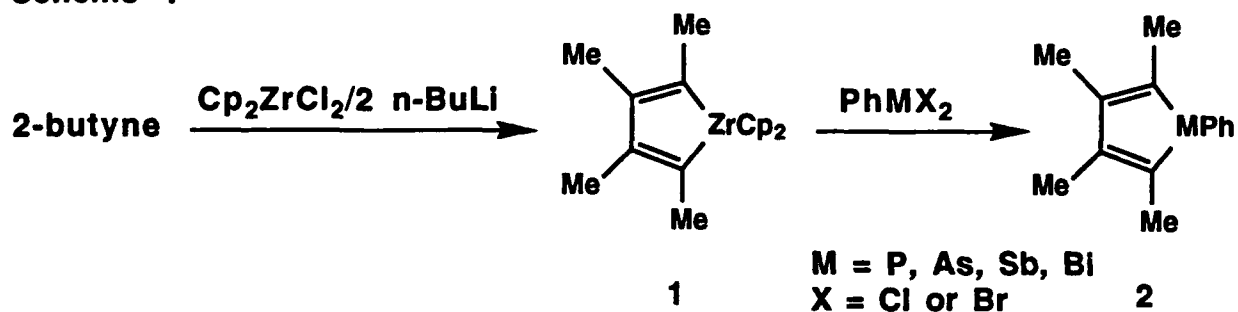


Dedicated to Professor Salo Gronowitz on the occasion of his 65th birthday.

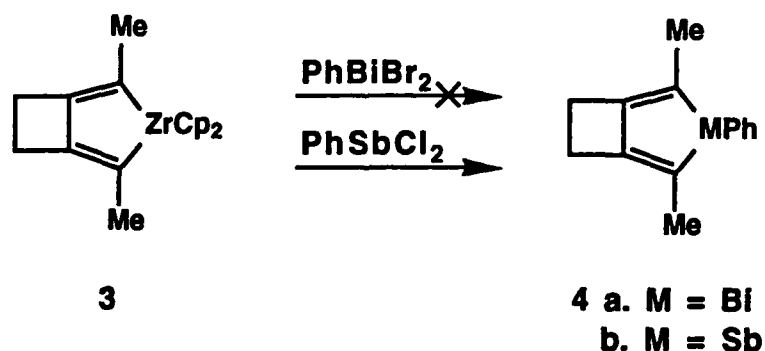
<sup>a</sup>Author to whom questions regarding crystallography should be addressed.

The conversion of readily prepared zirconacyclopentadienes<sup>1</sup> to the corresponding main group heterocycles by the Fagan-Nugent method has been shown to be extremely versatile.<sup>2,3</sup> For example, reaction of zirconacycle **1** (prepared by the sequential addition of 2 equivalents n-BuLi and 2-butyne to zirconocene dichloride)<sup>1e</sup> with phenylpnictogen dihalides gives the respective main group heterocycles **2** in high isolated yields (Scheme 1).<sup>2</sup> During the course of our study on the synthesis of antimony and bismuth heterocycles,<sup>3</sup> we were therefore surprised to find that treatment of phenylbismuth dibromide with an equivalent of zirconacycle **3**<sup>1d</sup> failed to give the desired phenylbismole **4a** (Scheme 2). Instead, cyclooctatetraene **5**<sup>4</sup> was produced (Scheme 3). In contrast, in previous work from our laboratory, only the expected phenylstibole **4b** was obtained upon treatment of **3** with PhSbCl<sub>2</sub> (Scheme 2).<sup>5,6</sup>

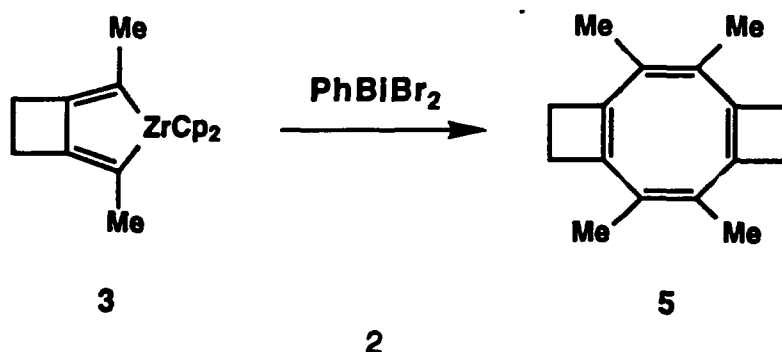
Scheme 1



Scheme 2



Scheme 3



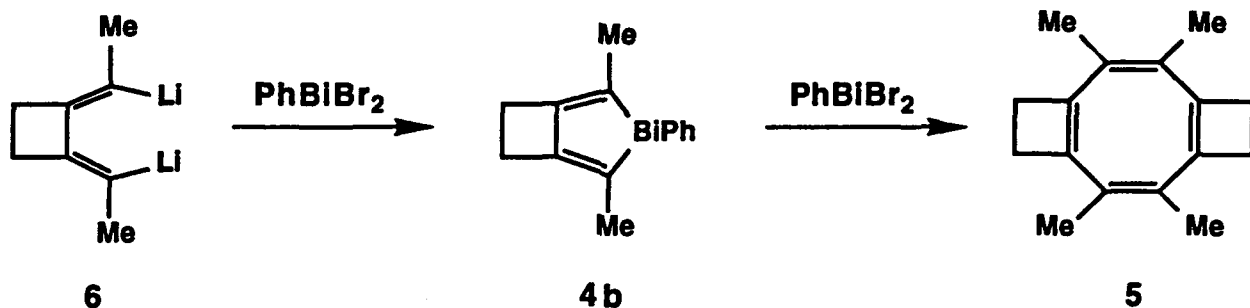
Cyclooctatetraene **5** can be isolated in 83% yield as a bright yellow crystalline solid from the addition of **3** to PhBiBr<sub>2</sub>. The <sup>1</sup>H NMR spectrum of the crude reaction mixture indicates that **5** is the major organic product and that the by-products of the reaction include Cp<sub>2</sub>ZrBr<sub>2</sub>, Ph<sub>3</sub>Bi and Ph<sub>2</sub>BiBr and other unidentified zirconocene species. A black precipitate also forms which we believe to be elemental bismuth.

In order to fully characterize compound **5**, its X-ray structure was determined. A view of the molecule is shown in Figure 1 and selected bond lengths and angles are given in Table 2. The molecule adopts a tub conformation and, in general, the bond lengths and angles are similar to those found in other cyclooctatetraene structures.<sup>7</sup> Interestingly, the double bonds of the cyclooctatetraene ring are found to be endocyclic to the fused four membered rings (similar to related cyclooctatetraene structures),<sup>7g,h</sup> while in the precursor zirconacycle **3**<sup>1d</sup> the double bonds are found exocyclic to the cyclobutane ring. The torsion angle of 49° defined by C(2)-C(1)-C(8)-C(7) is less than that found in the parent cyclooctatetraene (55°),<sup>7a</sup> octamethylcyclooctatetraene (68°)<sup>7c,d</sup> and other cyclooctatetraene structures.<sup>7c,i,j</sup> This flattening of the molecule, relative to the parent compound, is most likely due to the cyclobutene rings (perfluorotetracyclobuta-1,3,5,7-cyclooctatetraene, with four fused cyclobutene rings, is planar).<sup>7g,8,9</sup> Consistent with this solid state flattening, the solution ring inversion barrier of **5** is found to be 10 ± 0.2 Kcal/mol (coalescence occurs at -67 °C in THF-d<sub>6</sub> as determined by variable temperature <sup>1</sup>H NMR) significantly less than that observed for the parent cyclooctatetraene (13.7 Kcal/mol)<sup>10a</sup> and tetramethylcyclooctatetraene (23 Kcal/mol).<sup>10b</sup>

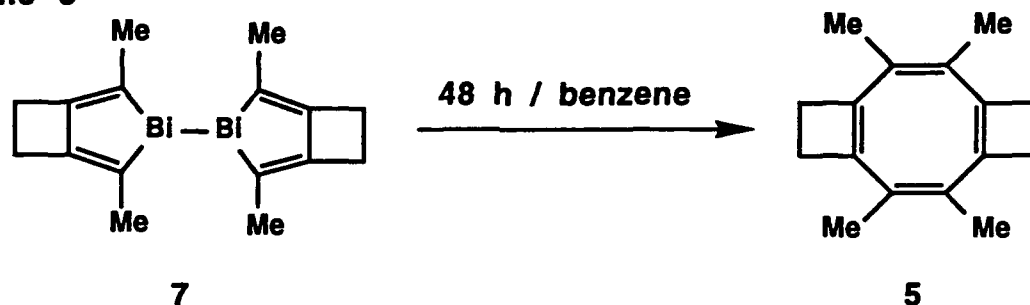
Bismole **4a** has been prepared from the dilithio salt **6** (Scheme 4) and is found to be stable both in solution and the solid state.<sup>11</sup> However, addition of PhBiBr<sub>2</sub> to **4a** cleanly gives cyclooctatetraene **5**. Importantly, slow addition of PhBiBr<sub>2</sub> (1 equivalent) to an excess of zirconacycle **3** (4 equivalents) in benzene gives significant amounts of bismole **4a** together with compound **5** and unreacted **3**. Consequently, we believe that addition of zirconacycle **3** to PhBiBr<sub>2</sub> leads to the formation of bismole **4a**, but subsequent reaction with PhBiBr<sub>2</sub> gives cyclooctatetraene **5**.

Interestingly, treatment of **3** with BiBr<sub>3</sub>, SbCl<sub>3</sub> and GaCl<sub>3</sub> also gives **5** as the major organic product, as determined by <sup>1</sup>H NMR. Furthermore, when benzene solutions of bismole **7** (Scheme 5), prepared from the reductive coupling of **4b**,<sup>11</sup> are stored at room temperature for 48 h, compound **5** forms in >90% yield and elemental bismuth precipitates. It is therefore apparent that there is some thermodynamic preference for the formation of cyclooctatetraene **5**.

### Scheme 4

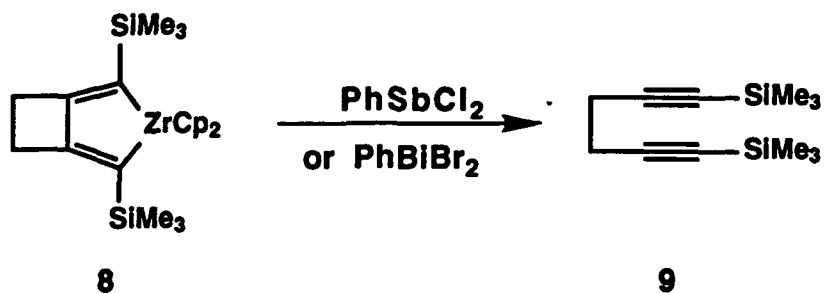


### Scheme 5



Attempts to convert other pnictoles or zirconacycles to the corresponding cyclooctatetraenes have, to date, been unsuccessful. Interestingly, we have found that introduction of a cyclobutane ring into the 3,4 position of zirconacyclopentadienes can promote the formal oxidation of the zirconium bound carbon fragment.<sup>12</sup> For example, zirconacyclopentadiene **8** upon treatment with  $\text{PhSbCl}_2$  and  $\text{PhBiBr}_2$  clearly reverts to 1,6-bis(trimethylsilyl)hexa-1,5-diyne, **9**, the initial organic precursor to **8** (Scheme 6). Clearly, the differing steric and electronic effects of the trimethylsilyl groups relative to methyl groups leads to alternative products for **3** and **8**.

### Scheme 6



**Acknowledgement.** We thank the Office of Naval Research for partial support of this research. SLB is an Alfred P. Sloan Fellow (1988-92) and a Camille & Hentry Dreyfus Teacher-Scholar. JFR acknowledges the award of an NSF equipment grant (CHE-9016978). NMR spectra were obtained with the help of Christopher Willoughby.

## Experimental

*Preparation of 1,5-Bis(cyclobuta)-3,4,7,8-tetramethylcyclooctatetraene, 5.* To a suspension of phenylbismuth dibromide (446 mg, 1 mmol) in benzene (15 mL) was added a solution of zirconacycle **3**<sup>1d</sup> (327 mg, 1 mmol; C<sub>6</sub>H<sub>6</sub> 15 mL), under argon. The reaction quickly darkened and on stirring overnight a yellow solution with black ppt formed. The benzene was removed *in vacuo*, diethyl ether was added and the solution then passed through a column of neutral alumina. Subsequent chromatography (silica column/hexane elutant) removed the Ph<sub>3</sub>Bi by-product and gave pure **5**, which can be recrystallised from hexane at -80 °C.

Yield, 88 mg, 83 %. Mp 131-132 °C. Anal. C<sub>16</sub>H<sub>20</sub>: C 90.51; H 9.49.

MS [IP 70 ev;  $m/e$  (% rel. int.)]: 212 (91, M), 197 (73), 183 (77), 182 (75), 169 (100), 167 (80).

<sup>1</sup>H (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 2.30 (8H, s), 1.53 (12H, s).

<sup>1</sup>H (500 MHz, d<sup>8</sup>-THF, -100 °C): δ 2.25 (4H, d, 10.7 Hz), 2.15 (4H, d, 10.7 Hz), 1.53 (12H, s).

<sup>13</sup>C{<sup>1</sup>H} (300MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 144.3, 131.4, 26.6, 16.4.

*X-Ray Diffraction Analysis:* A crystal of **5** with dimensions of 0.12 x 0.24 x 0.27 mm<sup>3</sup> was mounted on a glass fiber. An Enraf-Nonius CAD-4 diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) was used to measure the unit cell dimensions and to collect data. Unit-cell constants were obtained from least squares refinement, using the setting angles of 25 accurately centered reflections in the range 15° <  $\theta$  < 18°. Crystal data were determined to be: a = 12.588(2) Å; b = 7.843(1) Å; c = 13.804(2) Å;  $\beta = 108.98(2)^\circ$ ; V = 1288.3 Å<sup>3</sup>; Z = 4; M = 212.34 amu; D<sub>x</sub> = 1.09 g cm<sup>-3</sup>; F(000) = 464;  $\mu = 0.6 \text{ cm}^{-1}$ . The space group was determined to be P2<sub>1</sub>/n (alternate no. 14) from systematic absences.

The data were collected at 23(2) °C using the  $\omega$ -2 $\theta$  scan technique (scan width = 0.8 + 0.34tan $\theta$ ). The scan rate was varied from 1 to 3 ° min<sup>-1</sup>(in  $\theta$ ) and data were collected to a maximum 2 $\theta$  of 50°. A total of 2379 reflections were collected, of which

2269 were unique; 1399 with  $I > 3\sigma(I_o)$  were included in structural analysis. As a check on crystal stability three standard reflections were monitored every 60 min. and showed a decay of 6%; decay corrections ranged from 1.00 to 1.03. Lorentz and polarisation corrections were applied to the data but no absorption correction was made. A secondary extinction correction was applied  $(5.4(5) \times 10^{-7})$ .<sup>13</sup>

The structure was solved by direct methods (MULTAN80).<sup>14</sup> A total of 8 carbon atoms were located from an E-map and the remaining atoms were located from a series of difference Fourier maps. Hydrogen atoms were located and their positions refined with isotropic thermal parameters fixed at 1.3Beq of the bonded C atom. The structure was refined in full-matrix least-squares where the function minimized was  $\sum w(|F_o| - |F_c|)^2$  and the weight was defined as  $w = [\sigma(F)^2 + (0.005F)^2 + 0.3]^{-1}$ .<sup>15</sup> Scattering factors were taken from Cromer and Waber<sup>16</sup> and anomalous dispersion effects were included in  $F_c$ .<sup>17</sup> The final cycle of refinement included 206 parameters and converged (largest parameter shift was 0.1 times its esd) with  $R = \sum ||F_o| - |F_c|| / \sum F_o = 0.046$ ,  $R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2} = 0.043$  and  $S = 1.13$ . The final difference electron density map showed maximum and minimum values of 0.18 (3) and -0.18 (3)  $e\text{\AA}^{-3}$ .

The atomic parameters are presented in Table 1. Selected bond lengths and angles are given in Table 2 and a view of the molecule is shown in Figure 1. Anisotropic thermal parameters, H parameters and structure factor tables are available upon request.

## References

1. (a) Buchwald, S. L. and Nielson, R. B. *Chem. Rev.* **88** (1988), 1047. (b) Buchwald, S. L., Watson, B. T. and Huffman, J. C. *J. Am. Chem. Soc.* **109** (1987), 2544. (c) Buchwald, S. L., Lum, R. T. and Dewan, J. C. *J. Am. Chem. Soc.* **108** (1986), 7441. (d) Nugent, W. A., Thorn, D. L. and Harlow, R. L. *J. Am. Chem. Soc.* **109** (1987), 2788. (e) Negishi, E., Cederbaum, F. E. and Takahashi, T. *Tetrahedron Lett.* **27** (1986), 2829. (f) Negishi, E., Holmes, S. J., Tour, J. M., Miller, J. A., Cederbaum, F. E., Swanson, D. R. and Takahashi, T. *J. Am. Chem. Soc.* **111** (1989), 3336.
2. Fagan, P. J. and Nugent, W. A. *J. Am. Chem. Soc.* **110** (1988) 2310.
3. Buchwald, S. L., Fisher, R. A. and Foxman, B. M. *Angew. Chem., Int. Ed. Engl.* **29** (1990) 771. Buchwald, S. L., Fisher, R. A. and Davis, W. M. *Organometallics* **8** (1989), 2082. Fisher, R. A., Nielsen, R. B., Davis, W. M. and Buchwald, S. L. *J. Am. Chem. Soc.* **113** (1991), 165.
4. For reviews of various aspects of and further references on cyclooctatetraene chemistry see (a) Paquette, L. A. *Tetrahedron* **31** (1975), 2855 and (b) Paquette, L. A. *Pure Appl. Chem.* **54** (1982), 987.
5. Hsu, D. *PhD Thesis* (1991), Massachusetts Institute of Technology.
6. In the reactions we have examined, for example between **3** and  $\text{PhMX}_2$  ( $\text{M} = \text{Sb}, \text{Bi}$ ), the products obtained are not dependent upon whether the zirconacycle is added to the pnictogen or the pnictogen is added to the zirconacycle.
7. (a) Claus, K. H. and Kruger, C. *Acta Crystallogr.* **C44** (1988), 1632. (b) Avitabile, G., Ganis, P. and Petraccone, V. *J. Phys. Chem.* **73** (1969), 2378. (c) Laird, B. B. and Davis, R. E. *Acta Crystallogr.* **B38** (1982), 678. (d) Bordner, J., Parker, R. G. and Stanford, R. H., Jr. *Acta Crystallogr.* **B28** (1972), 1069. See, however, ref. 6(c). (e) Wheatley, P. J. *J. Chem. Soc.* (1965), 3136. (f) Pawley, G. S., Lipscomb, W. N. and Freedman, H. H. *J. Am. Chem. Soc.* **86** (1964), 4725. (g) Einstein, F. W. B., Willis, A. C., Cullen, W. R. and Soulen, R. L. *J. Chem. Soc., Chem. Comm.* (1981), 526. (h) Cobblestick, R. E. and Einstein, F. W. B. *Acta Crystallogr.* **B33** (1977), 2339. (i) Diercks, R., Stamp, L. and tom Dieck, H. *Chem. Ber.* **117** (1984), 1913. (j) tom Dieck, H., Lauer, A. M., Stamp, L. and Diercks, R., *J. Mol. Catal.* **35** (1986), 317. (k) Furmanova, N. G. and Struchkov, Yu. T. *Cryst. Struct. Comm.* **7** (1978), 693.
8. Mak, T. C. W. and Li, W-K *THEOCHEM*, **6** (1982), 281.
9. Trindle, C. and Wolfskill, T. *J. Org. Chem.* **56** (1991), 5426

10. (a) Anet, F. A. L. *J. Am. Chem. Soc.* **84** (1962), 671. (b) Ganis, P., Musco, A. and Temussi, P. A. *J. Phys. Chem.* **73** (1969), 3201.
11. Spence, R. E. v. H. and Buchwald, S. L. unpublished results.
12. We have observed, in our laboratory, similar behavior in related systems. Warner, B. P. and Buchwald, S. L. unpublished results.
13. Zachariasen, W. H. *Acta Crystallogr.* **16** (1963), 1139.
14. All computer programs were part of the MolEN package: MolEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands (1990)
15. Killean, R. C. G. and Lawrence, J. L. *Acta Crystallogr.* **25B** (1973), 1750.
16. Cromer, D. T. and Waber, J. T. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4 Table 2.2B (Present distributor: Kluwer Academic Publishers, Dordrecht and Boston).
17. D. T. Cromer, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4 Table 2.3.1.

**Table 1: Table of Positional Parameters and Their Estimated Standard Deviations.**

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>Beq (Å<sup>2</sup>)<sup>a</sup></u>
C1	0.4870 (2)	0.3155 (3)	0.6263 (2)	3.29 (6)
C2	0.4715 (2)	0.4649 (3)	0.6669 (2)	3.30 (5)
C3	0.3845 (2)	0.5420 (3)	0.7030 (2)	3.34 (6)
C4	0.2758 (2)	0.5397 (3)	0.6471 (2)	3.43 (5)
C5	0.2345 (2)	0.4568 (3)	0.5460 (2)	3.30 (6)
C6	0.2494 (2)	0.3061 (3)	0.5063 (2)	3.44 (6)
C7	0.3154 (2)	0.1508 (4)	0.5430 (2)	3.60 (6)
C8	0.4243 (2)	0.1547 (3)	0.5984 (2)	3.44 (5)
C9	0.6029 (2)	0.3620 (4)	0.6235 (2)	4.28 (7)
C10	0.5856 (2)	0.5349 (4)	0.6710 (2)	4.44 (7)
C11	0.4289 (2)	0.6270 (4)	0.8057 (2)	5.03 (7)
C12	0.1858 (2)	0.6241 (4)	0.6797 (2)	5.28 (7)
C13	0.1460 (2)	0.5169 (4)	0.4478 (2)	4.54 (7)
C14	0.1630 (2)	0.3421 (4)	0.4025 (2)	4.86 (7)
C15	0.2509 (3)	-0.0123 (4)	0.5092 (2)	5.66 (8)
C16	0.4938 (3)	-0.0034 (4)	0.6333 (2)	4.95 (7)
H9A	0.664 (2)	0.290 (3)	0.670 (2)	5.5*
H9B	0.612 (2)	0.369 (3)	0.553 (2)	5.5*

<sup>a</sup>Beq is defined as  $(4/3) \cdot [a^2\beta_{11} + b^2\beta_{22} + \dots ab(\cos\gamma)\beta_{12} + \dots]$

Table 2. Table of Selected Bond Lengths (Å) and Angles (°) for Compound 5.

C(1)-C(2)	1.340 (4)	C(5)-C(6)	1.341 (4)
C(1)-C(8)	1.471 (4)	C(5)-C(13)	1.523 (3)
C(1)-C(9)	1.517 (4)	C(6)-C(7)	1.469 (4)
C(2)-C(3)	1.473 (4)	C(6)-C(14)	1.518 (3)
C(2)-C(10)	1.522 (4)	C(7)-C(8)	1.334 (3)
C(3)-C(4)	1.334 (3)	C(7)-C(15)	1.505 (4)
C(3)-C(11)	1.501 (4)	C(8)-C(16)	1.504 (4)
C(4)-C(5)	1.473 (3)	C(9)-C(10)	1.552 (4)
C(4)-C(12)	1.501 (4)	C(13)-C(14)	1.551 (5)
C(2)-C(1)-C(8)	136.1 (3)	C(6)-C(5)-C(13)	93.9 (2)
C(2)-C(1)-C(9)	94.1 (2)	C(5)-C(6)-C(7)	136.8 (2)
C(8)-C(1)-C(9)	129.7 (2)	C(5)-C(6)-C(14)	94.0 (2)
C(1)-C(2)-C(3)	136.6 (2)	C(7)-C(6)-C(14)	129.1 (2)
C(1)-C(2)-C(10)	93.9 (2)	C(6)-C(7)-C(8)	122.6 (2)
C(3)-C(2)-C(10)	129.5 (2)	C(6)-C(7)-C(15)	114.2 (2)
C(2)-C(3)-C(4)	122.3 (2)	C(8)-C(7)-C(15)	123.1 (2)
C(2)-C(3)-C(11)	114.4 (2)	C(1)-C(8)-C(7)	122.2 (2)
C(4)-C(3)-C(11)	123.3 (3)	C(1)-C(8)-C(16)	114.6 (2)
C(3)-C(4)-C(5)	122.2 (2)	C(7)-C(8)-C(16)	123.1 (2)
C(3)-C(4)-C(12)	123.5 (2)	C(1)-C(9)-C(10)	86.0 (2)
C(5)-C(4)-C(12)	114.2 (2)	C(2)-C(10)-C(9)	85.9 (2)
C(4)-C(5)-C(6)	136.3 (2)	C(5)-C(13)-C(14)	85.9 (2)
C(4)-C(5)-C(13)	129.6 (2)	C(6)-C(14)-C(13)	86.2 (2)

**Figure 1: Crystallographic View of 5.**

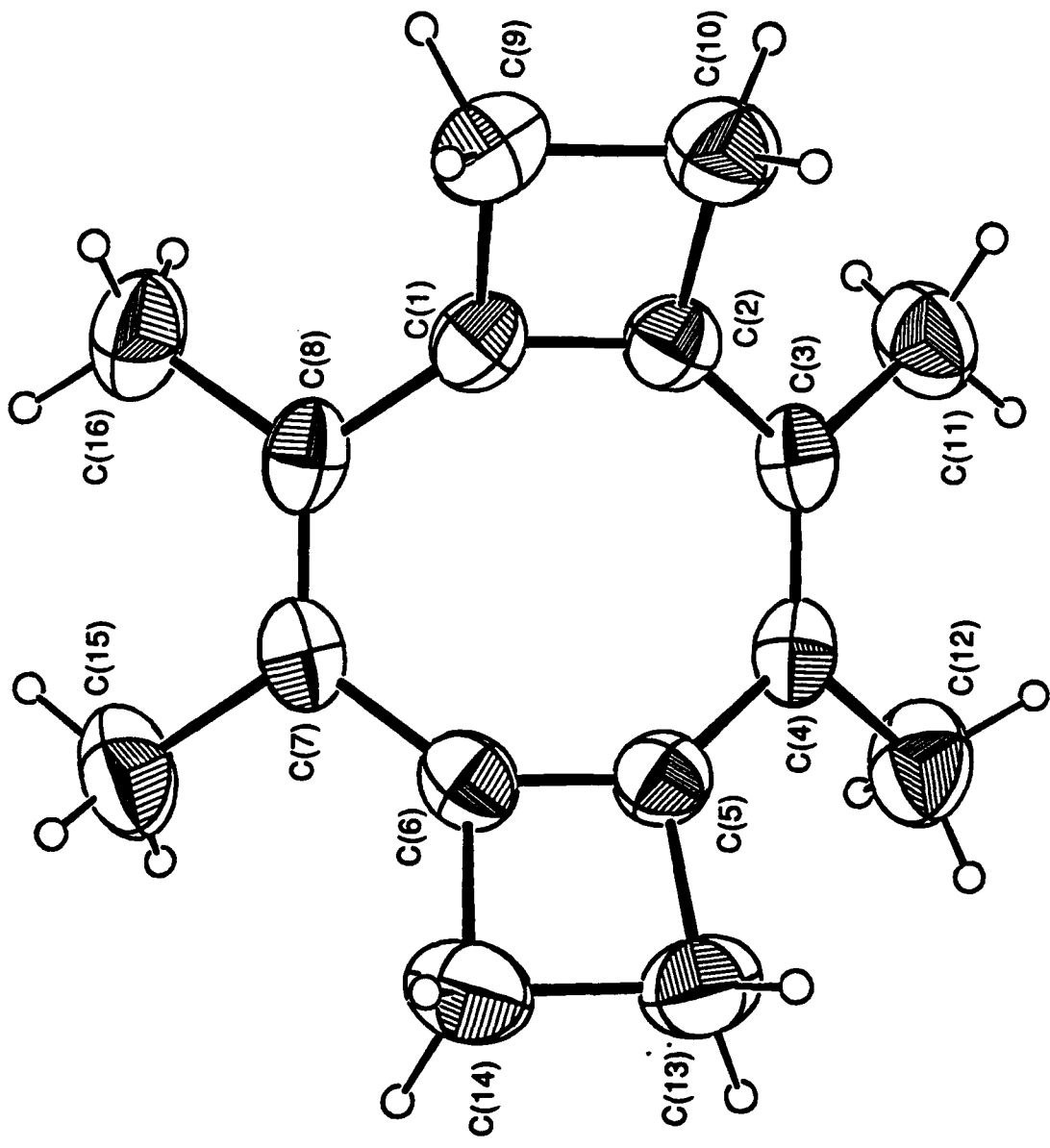
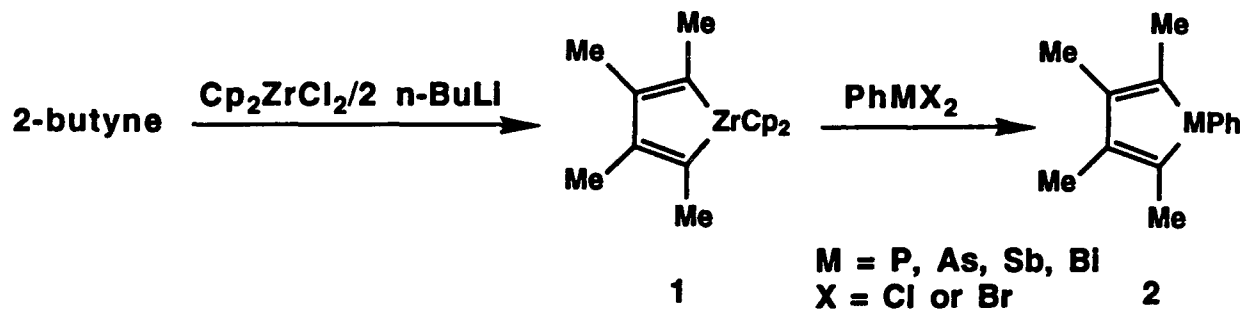
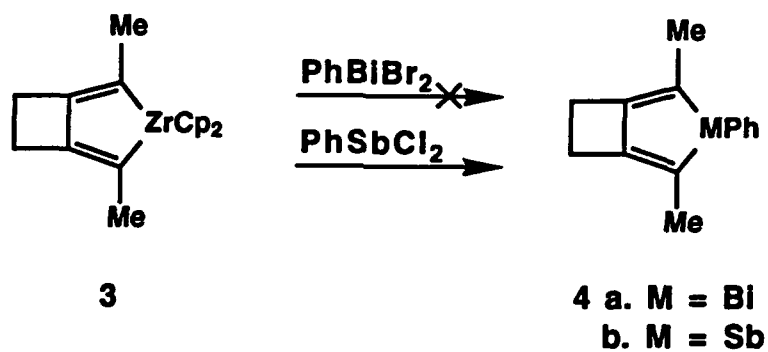


Figure 1. Space  
Buchwald and  
Fichardson

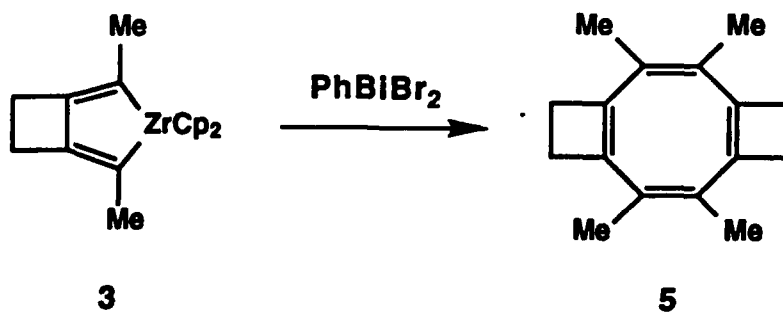
**Scheme 1**



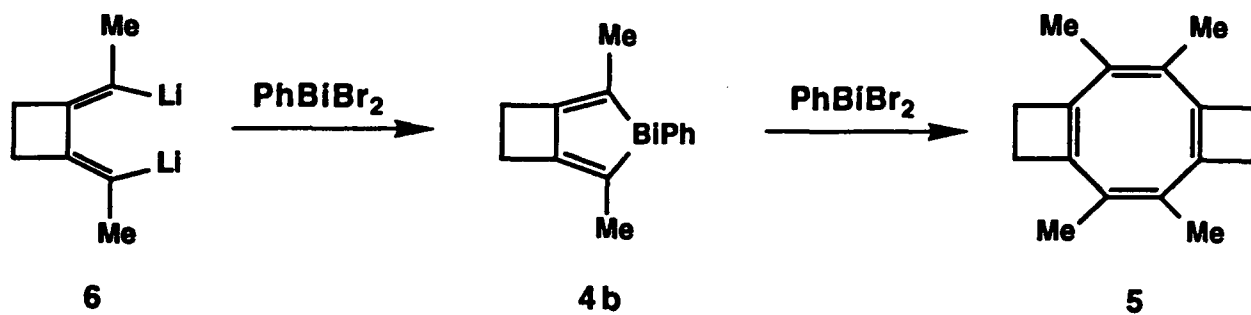
**Scheme 2**



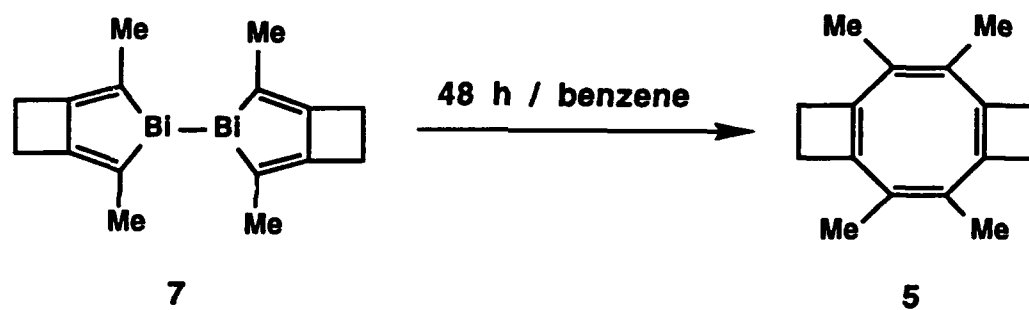
**Scheme 3**



**Scheme 4**



**Scheme 5**



**Scheme 6**

