

The Unexpected Formation of 3,4,7,8-Tetramethyl-1,2,5,6-tetrahydrodicyclobuta[*a, e*]cyclooctene from a Zirconacyclopentadiene

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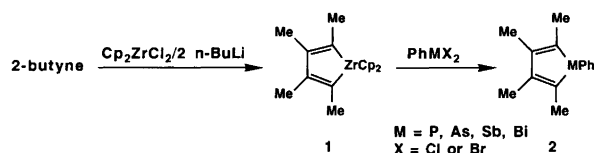
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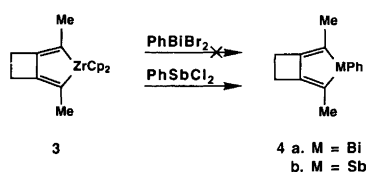
Dedicated to Professor Salo Gronowitz on the occasion of his 65th birthday.

The conversion of readily prepared zirconacyclopentadienes¹ into the corresponding main-group heterocycles by the Fagan–Nugent method has been shown to be extremely versatile.^{2,3} For example, reaction of zirconacycle **1** (prepared by the sequential addition of 2 equivalents *n*-BuLi and 2-butyne to zirconocene dichloride)^{1e} with phenylpnictogen dihalides gives the respective main-group heterocycles **2** in high isolated yields (Scheme 1).² During the course of our study on



Scheme 1.

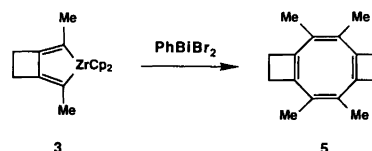
the synthesis of antimony and bismuth heterocycles,³ we were therefore surprised to find that treatment of phenylbismuth dibromide with an equivalent of the zirconacycle **3**^{1d} failed to give the desired phenylbismole **4a** (Scheme 2). Instead, the cyclooctatetraene **5**⁴ was



Scheme 2.

produced (Scheme 3). In contrast, in previous work from our laboratory, only the expected phenylstibole

4b was obtained upon treatment of **3** with PhSbCl₂ (Scheme 2).^{5,6}



Scheme 3.

Cyclooctatetraene **5** can be isolated in 83% yield as a bright yellow crystalline solid from the addition of **3** to PhBiBr₂. The ¹H NMR spectrum of the crude reaction mixture indicates that **5** is the major organic product and that the by-products of the reaction include Cp₂ZrBr₂, Ph₃Bi and Ph₂BiBr and other unidentified zirconocene species. A black precipitate also forms which we believe to be elemental bismuth.

In order fully to characterize compound **5**, we determined its X-ray structure. A view of the molecule is shown in Fig. 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.⁷ Interestingly, the double bonds of the cyclooctatetraene ring are found to be endocyclic to the fused four-membered rings (similar to related cyclooctatetraene structures),^{7g,h} while in the precursor zirconacycle **3**^{1d} 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°),^{7a} octamethylcyclooctatetraene (68°)^{7c,d} and other cyclooctatetraene structures.^{7c,i,j} 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).^{7g,8,9} Consistent with this solid-state flattening,

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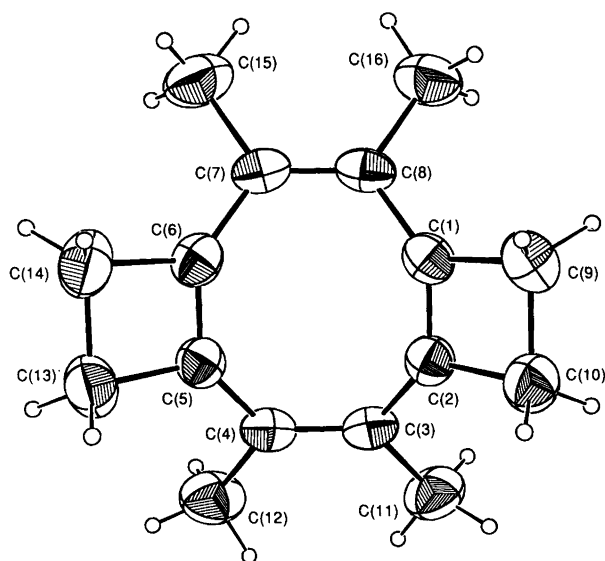
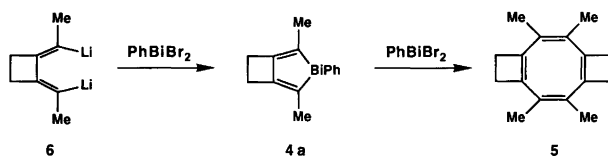


Fig. 1. Crystallographic view of **5**.

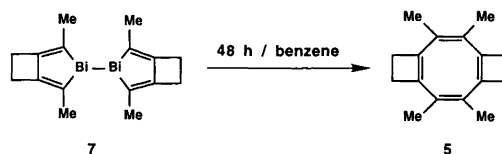
the solution ring inversion barrier of **5** is found to be 10 ± 0.2 kcal mol⁻¹ [$41.8 \pm .84$ kJ mol⁻¹] (coalescence occurs at -67°C in THF-*d*₆ as determined by variable-temperature ¹H NMR spectroscopy) significantly less than that observed for the parent cyclooctatetraene (13.7 kcal mol⁻¹ [57.3 kJ mol⁻¹])^{10a} and tetramethylcyclooctatetraene (23 kcal mol⁻¹ [96.2 kJ mol⁻¹]).^{10b}

The 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.¹¹ However, addition of PhBiBr₂ to **4a** cleanly gives the cyclooctatetraene **5**. Importantly, slow addition of PhBiBr₂ (1 equiv.) to an excess of zirconacycle **3** (4 equiv.) in benzene gives significant amounts of the bismole **4a** together with compound **5** and unchanged **3**. Consequently, we believe that addition of the zirconacycle **3** to PhBiBr₂ leads to the formation of the bismole **4a**, but subsequent reaction with PhBiBr₂ gives the cyclooctatetraene **5**.



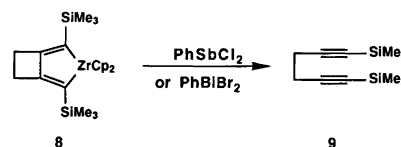
Scheme 4.

Interestingly, treatment of **3** with BiBr₃, SbCl₃ and GaCl₃ also gives **5** as the major organic product, as determined by ¹H NMR spectroscopy. Furthermore, when benzene solutions of the bibismole **7** (Scheme 5), prepared from the reductive coupling of **4a**,¹¹ 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 the cyclooctatetraene **5**.



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.¹² For example, the zirconacyclopentadiene **8** upon treatment with PhSbCl₂ and PhBiBr₂ cleanly 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 lead to alternative products for **3** and **8**.



Scheme 6.

Experimental

Preparation of 3,4,7,8-tetramethyl-1,2,5,6-tetrahydrodicyclobuta[*a, e*]cyclooctene 5. To a suspension of phenylbismuth dibromide (446 mg, 1 mmol) in benzene (15 ml) was added a solution of the zirconacycle **3**^{1d} (327 mg, 1 mmol; C₆H₆ 15 ml), under argon. The reaction quickly darkened and after overnight stirring a yellow solution with a 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 eluant) removed the Ph₃Bi by-product and gave pure **5**, which can be recrystallized from hexane at -80°C . Yield, 88 mg, 83%. M.p. $131\text{--}132^\circ\text{C}$. Anal. C₁₆H₂₀: C 90.51; H 9.49. MS [IP 70 eV; *m/z* (% rel. int.)]: 212 (91, *M*), 197 (73), 183 (77), 182 (75), 169 (100), 167 (80). ¹H NMR (300 MHz, C₆D₆, 25°C): δ 2.30 (8 H, s), 1.53 (12 H, s). ¹H NMR (500 MHz, THF-*d*₈, -100°C): δ 2.25 (4 H, d, 10.7 Hz), 2.15 (4 H, d, 10.7 Hz), 1.53 (12 H, s). ¹³C{¹H} NMR (300 MHz, C₆D₆, 25°C): δ 144.3, 131.4, 26.6, 16.4.

X-Ray diffraction analysis. A crystal of **5** with dimensions of $0.12 \times 0.24 \times 0.27$ mm³ was mounted on a glass fiber. An Enraf-Nonius CAD-4 diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) 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 $15 < \theta < 18^\circ$. Crystal data were determined to be: $a = 12.588(2) \text{ \AA}$; $b = 7.843(1) \text{ \AA}$; $c = 13.804(2) \text{ \AA}$; $\beta = 108.98(2)^\circ$; $V = 1288.3 \text{ \AA}^3$; $Z = 4$; $M = 212.34 \text{ amu}$; $D_x = 1.09 \text{ g cm}^{-3}$; $F(000) = 464$; $\mu = 0.6 \text{ cm}^{-1}$. The space group was determined to be $P2_1/n$ (No. 14) from systematic absences.

The data were collected at $23(2)^\circ\text{C}$ using the ω - 2θ scan technique (scan width = $0.8 + 0.34\tan\theta$). The scan rate was varied from 1 to 3° min^{-1} (in θ) and data were collected to a maximum 2θ 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 [$5.4(5) \times 10^{-7}$].¹³

The structure was solved by direct methods (MULTAN80).¹⁴ A total of eight 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 $1.3B_{\text{eq}}$ 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 $w = [\sigma(F)^2 + (0.005F)^2 + 0.3]^{-1}$.¹⁵ Scattering factors were taken from Cromer and Waber¹⁶ and anomalous dispersion effects were included in F_c .¹⁷ The final cycle of refinement included 206 parameters and converged (largest parameter shift was 0.1 times its esd) with $R = \sum \|F_o| - |F_c|/\sum |F_o| = 0.046$, $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.043$ and $S = 1.13$. The final difference electron density map

Table 1. Table of positional parameters and their estimated standard deviations.

Atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$
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)

^a B_{eq} is defined as $(4/3) * [a^2\beta_{11} + b^2\beta_{22} + \dots ab(\cos \gamma) \beta_{12} + \dots]$.

Table 2. Table of selected bond lengths (\AA) and angles ($^\circ$) 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)

showed maximum and minimum values of 0.18(3) and $-0.18(3) \text{ e \AA}^{-3}$.

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 Fig. 1. Anisotropic thermal parameters, H parameters and structure factor tables are available upon request.

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