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Synthesis and Structure of a Tricyclic Bis(zirconacyclopentadiene) Compound

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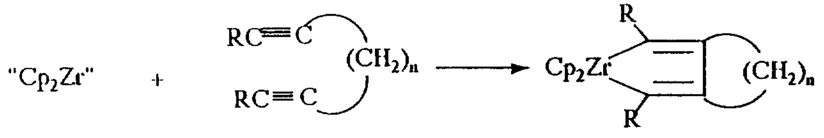
Abstract: 1,5-Bis(trimethylsilyl)penta-1,4-diyne was synthesized from trimethylsilylacetylide and 1-trimethylsilyl-3-bromo-1-propyne, and used in a reaction with "Cp_2Zr", giving as the major product 4,6,10,12-tetrakis(trimethylsilyl)-5,5,11,11-tetrakis(η^5-cyclopentadienyl)-5,11-dizirconatricyclo[7,3,0,$0^{3,7}$]dodeca-1(12), 3,6,9-tetraene, which was characterized by ^1H and ^{13}C NMR spectroscopy and x-ray diffraction studies.

Introduction

Bicyclic metallacyclpentadienes of the group 4 transition metals are synthesized from the putative "Cp_2M" (M = Ti, Zr, Hf) with a terminally disubstituted α,ὠ-diyne, according to equation (1).



(1)

These zirconabicyclic compounds may be acidified to release the organic ligand, leading exclusively to the (E,E)-1,2-bis(alkylidene)-cycloalkanes.[1-4] These exocyclic dienes can serve as starting materials in Diels-Alder reactions leading to polycyclic compounds.[5] In addition, the zirconabicylic compounds may be used directly with appropriate main group compounds to transfer the organic ligand to the main group element, forming heterocyclic compounds such as borole Diels-Alder dimers, siloles, phospholes, and thiophenes.[6]

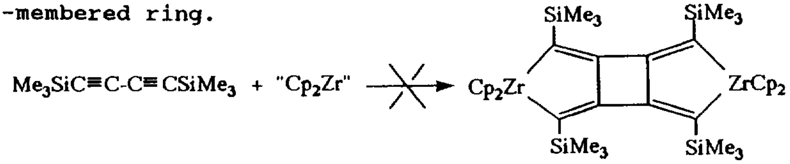
Zirconabicycles are known for compounds where n = 2, 3, 4, 5, and 6. Table 1 shows examples of the bicyclic zirconacyclopentadienes that have been reported.

Table 1. Some Bicyclic Zirconacyclopentadienes.

$R_1CC(CH_2)_nCCR_2$

R_1	R_2	n	Yield, %	Reference
Me	Me	2	89	1
Me	n-Bu	2	67	2
Me	Me	3	70	1
Et	Et	3	80	2
Me_3Si	Me_3Si	3	86	3
Me	Me	4	71	1,2,4
Et	Et	4	77	1
i-Pr	i-Pr	4	67	1
t-Bu	t-Bu	4	65	1
Me	i-Pr	4	69	1
Me	t-Bu	4	49	1
Me_3Si	Me_3Si	4	89	3,4
n-Pr	Me_3Si	4	89	4
n-Pr	Ph	4	90	4
Me	Me	5	45	1,2
Me	Me	6	< 2	1

Noticeably absent from the list of compounds in Table 1 are those diynes where n = 0 or 1. During the course of our investigation of reactions of "Cp_2Zr" with those diynes where n = 0 and 1, a paper by Buchwald's group appeared, which reported the results of the reaction of "Cp_2Zr" with 1,4-bis(trimethylsilyl)buta-1,3-diyne.[7] The expected product, by analogy to the formation of the bicyclic compounds listed in Table 1, would be a bis(zirconacyclopentadiene) attached by a fused four-membered ring.



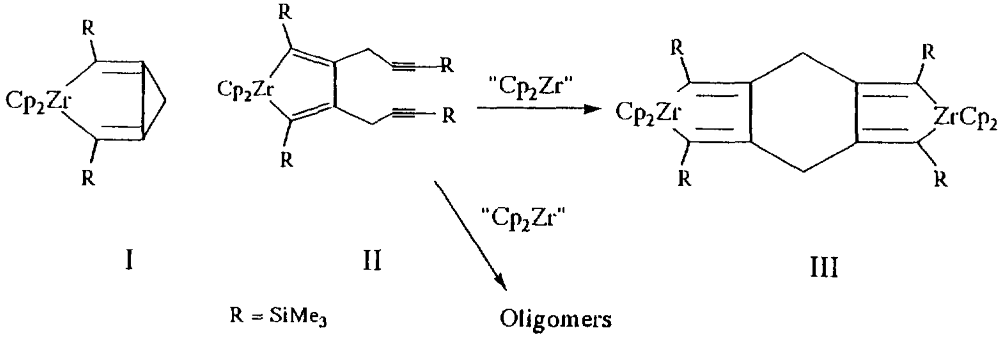
However, this compound was not formed; instead three products were isolated. The principal product was a seven-membered cyclic cumulene, while a second compound resulted from scission of the carbon-carbon single bond in the 1,3-diyne. The third product, a zirconacyclopentadiene with two free trimethylsilylacetylenic groups, could reasonably be invoked as an intermediate to the principal product. Those authors used butyllithium as the reducing agent to produce "Cp_2Zr". With the thought that a different reducing agent might give the expected bis(zirconacyclopentadiene), we used $Mg/HgCl_2$ in the reaction with the 1,3-diyne. The products we isolated were identical to those reported by Buchwald, et al., as confirmed by x-ray crystallographic studies.

This work presents the results of the reaction of "Cp_2Zr" with 1,5-bis(trimethylsilyl)-1,4-pentadiyne, i.e., that diyne where $n = 1$.

Results and Discussion

Whereas bis(trimethylsilyl)-1,3-butadiyne is available commercially, the homologous 1,4-pentadiyne is not. The compound 1-trimethylsilyl-1,4-pentadiyne is available, but attempts to trimethylsilylate the acetylenic carbon with Grignard reagent and chlorotrimethylsilane generally failed. Where a slight excess of Grignard reagent was used, the 1,3 isomer was obtained, and when a slight deficiency of Grignard reagent was employed, polymerization occurred. Therefore, the 1,5-diyne was synthesized from trimethylsilylacetylide and 1-trimethylsilyl-3-bromo-1-propyne. From this reaction, both the 1,3- and 1,4-isomers are obtained. These isomers were separated by fractional vacuum distillation, giving the desired 1,4-isomer in 67% yield.

The reaction of "Cp_2Zr" with the 1,4-diyne, assuming that metallacycles are formed in the expected manner, can lead to three possible structures, shown below. Compound I is analogous to those bicyclic structures shown in equation (1).

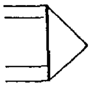


I II III

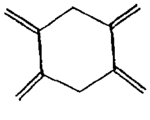
R = SiMe$_3$

However, if the strain of the three-membered ring is too great, an intermediate, II, can be formed, leading to a tricyclic derivative of two zirconacyclopentadienes fused to a cyclohexane ring (III). Alternatively, oligomers of zirconacyclopentadienes can also be formed from II.

Negishi's method[4] was used to generate "Cp$_2$Zr" from Cp$_2$ZrCl$_2$ and butyllithium, and then allowed to react with 1,4-bis(trimethylsilyl)penta-1,4-diyne. After isolation of the crude product, a portion of it was treated with HCl, and the organic ligands, which could be of structures IV, V, and/or VI, were subjected to GC/MS analysis.



IV



V

VI

In fact, evidence for all three organic compounds was found. According to GC/MS analysis, about 2% of the organic compounds is IV, m/e = 210 ($C_5H_4(SiMe_3)_2$). Other fragments in the MS spectrum were at m/e 195 (P - CH_3), 122 (P - $SiMe_4$), 73 ($SiMe_3$). V was found in about 30% abundance, m/e = 420. Comprising about 68% of the remainder of the crude product are several compounds of mass greater than 420. These GC peaks represent various oligomeric derivatives of compound VI.

Single crystals of III were obtained and subjected to x-ray diffraction analysis. The structure and numbering scheme are shown in Figure 1.

Description of the structure. Each zirconium atom of the complex exists in a distorted tetrahedral environment, formed by the centroid of the Cp rings and the terminal carbon atoms of the diene. Tetrahedral angles are shown in Tables 2 and 3. Each diene forms sigma bonds between the terminal carbons and zirconium producing two five-membered rings. The average distance between the terminal diene carbon atoms and zirconium is 2.248(3) Å. The metallacycles are planar with the greatest deviations from the least-squares planes being -0.0682 for C_2 and 0.0759 for C_4. Table 4 displays the least-squares plane equations and the deviations.

The metallacycles are joined together by methylene carbons C_3 and C_8, thus forming a central cyclohexane ring. The ring exists in a twist boat conformation as evidenced by torsion angles $\angle\ C_3$-C_4-C_7C_8 = 19.9^0, and $\angle\ C_3$-C_2-C_7-C_8 = 16.4^0; a view of the cyclohexane ring is exhibited in Figure 2. The distance between the two flagpole hydrogen atoms, H_{3A} and H_{8A} is 2.329 Å, or slightly less than the sum of the Van der Waals radii. A similar compound made from "Cp_2Zr" and 1,8-bis(t-butyl)-1,7-octadiyne shows that the cyclohexane ring of the bicyclic structure is in the twist-chair conformation.[1,8]

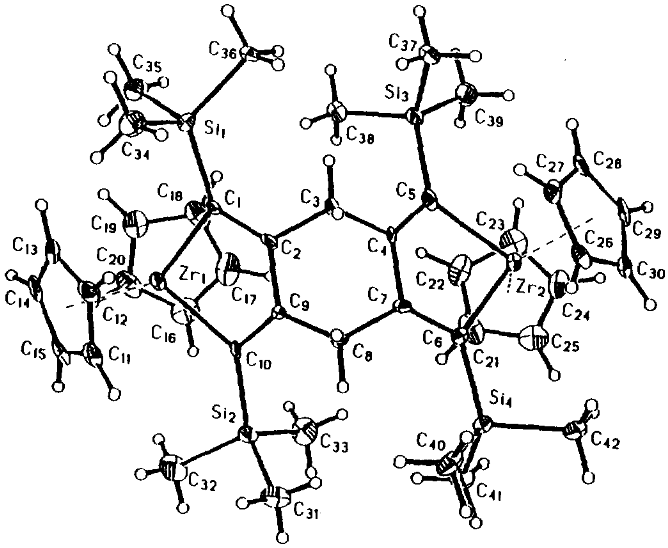


Figure 1. ORTEP Labeling Diagram for $Cp_4Zr_2C_{10}H_4[Si(CH_3)_3]_4$

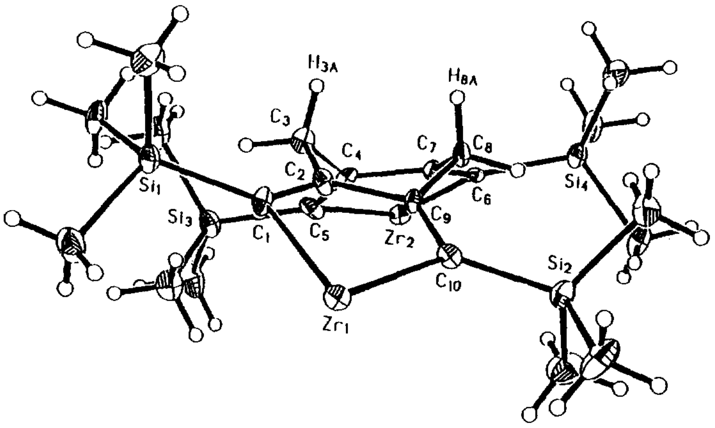


Figure 2. ORTEP Diagram Showing the Cyclohexane Ring. Cp rings have been eliminated for clarity.

Table 2. Angles $(^{0})$ About Zr_1

$\angle\ C_1-Zr_1-C_{10}$	85.1(2)	$\angle\ C_1-Zr_1-Cp_1$	108.8
$\angle\ C_1-Zr_1-Cp_2$	107.2	$\angle\ C_{10}-Zr_1-Cp_1$	107.4
$\angle\ C_{10}-Zr_1-Cp_2$	107.0	$\angle\ Cp_1-Zr_1-Cp_2$	131.5

Cp_1 and Cp_2 are the centroids of the cyclopentadienyl rings formed by $C_{11}-C_{12}-C_{13}-C_{14}-C_{15}$ and $C_{16}-C_{17}-C_{18}-C_{19}-C_{20}$, respectively.

Table 3. Angles $(^{0})$ About Zr_2

$\angle\ C_5-Zr_2-C_6$	84.1(2)	$\angle\ C_5-Zr_2-Cp_3$	108.3
$\angle\ C_5-Zr_2-Cp_4$	103.1	$\angle\ C_6-Zr_2-Cp_3$	105.7
$\angle\ C_6-Zr_2-Cp_4$	109.0	$\angle\ Cp_3-Zr_2-Cp_4$	134.8

Cp_3 and Cp_4 are the centroids of the cyclopentadienyl rings.

Table 4. Least-Squares Plane

Atom	Deviation (Å)	Atom	Deviation (Å)
Zr_1	-0.0321	Zr_2	0.0083
C_1	-0.0616	C_4	0.0759
C_2	-0.0682	C_5	-0.0451
C_9	0.0192	C_6	0.0241
C_{10}	0.0195	C_7	-0.0632

The least-squares plane formed by Zr_1-C_1-C_2-C_9-C_{10} is given by the equation: $1.954x - 2.303y + 13.695z = 4.5302$. The average deviation is 0.0401 Å. The least-squares plane formed by Zr_2-C_4-C_5-C_6 is given by the equation: $-9.933x - 2.196y + 11.876z = 6.6832$. The mean deviation is 0.0433 Å.

The ^1H NMR spectrum of compound III exhibits one sharp singlet at 6.08 ppm arising from the 20 equivalent Cp protons. Another sharp singlet appears at 0.14 ppm, attributable to the 36 equivalent protons of the four $Si(CH_3)_3$ groups. The remaining singlet resonance at 2.90 ppm is thus assigned to the methylene protons of the cyclohexane ring.

The proton decoupled ^{13}C NMR spectrum shows a total of five signals. The sharp signal at 110.2 ppm is assigned to the carbons of the Cp rings. The carbons of the trimethylsilyl groups resonate at 2.88 ppm. The signal at 47.9 ppm arises from the methylene carbons in the cyclohexane ring, i.e., C_3 and C_8. The signals at 138.9 and 195.2 ppm are attributable to the carbons of the double bonds. The signal at 138.9 ppm is assigned to the cyclohexane ring carbon atoms, namely, C_2, C_4, C_7, and C_9, while carbon atoms C_1, C_5, C_6, and C_{10} resonate at 195.2 ppm. These assignments are consistent with those made for analogous metallacycles.[3,9]

Table 5. Selected Interatomic Distances (Å) With Standard Deviations

Zr_1-Cp_1	2.230	Zr_2-Cp_3	2.235
Zr_1-Cp_2	2.230	Zr_2-Cp_4	2.235
Zr_1-C(Cp) avg.	2.529(2)	Zr_2-C(Cp) avg.	2.531
Zr_1-C_1	2.263(6)	Zr_2-C_5	2.239(6)
Zr_1-C_{10}	2.241(6)	Zr_2-C_6	2.247(5)
Si_1-C_1	1.852(6)	Si_3-C_5	1.850(6)
Si_1-C_{34}	1.874(7)	Si_3-C_{37}	1.893(7)
Si_1-C_{35}	1.876(7)	Si_3-C_{38}	1.874(7)
Si_1-C_{36}	1.893(6)	Si_3-C_{39}	1.879(7)
Si_2-C_{10}	1.855(6)	Si_4-C_6	1.868(6)
Si_2-C_{31}	1.870(7)	Si_4-C_{40}	1.889(6)
Si_2-C_{32}	1.876(7)	Si_4-C_{41}	1.886(7)
Si_2-C_{33}	1.871(7)	Si_4-C_{42}	1.870(7)
C_1-C_2	1.369(9)	C_2-C_3	1.536(9)
C_2-C_9	1.494(9)	C_3-C_4	1.532(8)
C_4-C_5	1.361(7)	C_7-C_8	1.532(8)
C_8-C_9	1.529	C_9-C_{10}	1.369(9)

Table 6. Bond Angles (°) With Standard Deviations

Zr_1-C_1-C_2	101.3(4)	Zr_1C_{10}-C_9	103.6(4)
Zr_1-C_1-Si_1	128.3(3)	Zr_1-C_{10}-Si_2	130.5(3)
Zr_2-C_5-C_4	103.5(4)	Zr_2-C_6-C_7	104.3(4)
Zr_2-C_5-Si_3	131.1(3)	Zr_2-C_6-Si_4	129.3(3)
Si_1-C_1-C_2	130.3(5)	Si_2-C_{10}-C_9	125.7(5)
Si_3-C_5-C_4	124.8(5)	Si_4-C_6-C_7	126.4(4)
C_1-C_2-C_9	126.2(6)	C_2-C_9-C_{10}	122.8(6)
C_5-C_4-C_7	123.8(5)	C_6-C_7-C_4	122.5(5)
C_2-C_3-C_4	112.6(5)	C_7-C_8-C_9	113.4(5)
C_1-C_2-C_3	122.5(5)	C_3-C_4-C_5	124.3(5)
C_6-C_7-C_8	122.6(5)	C_8-C_9-C_{10}	123.8(5)

Experimental

Materials and Solvents. Zirconocene dichloride (98+%), butyllithium (1.6 M in hexanes), 3-bromo-1-trimethylsilyl-1-propyne (98%), and trimethylsilylacetylene (98%), were purchased from Aldrich and used as received. Ether and THF were obtained from Fisher, and distilled from sodium/benzophenone immediately before used. Other reagents and materials were purified by standard methods or used as received.

General experimental conditions. The glassware used for the reactions was washed thoroughly in a KOH/MeOH bath, rinsed with dilute HCl, water, and acetone, then dried overnight in an oven at 120^{0}C. For each reaction set-up, the glassware was flamed under vacuum and allowed to cool under argon prior to use. All air and moisture sensitive compounds were handled by standard syringe/serum cap techniques. Manipulations of air and moisture sensitive compounds were performed in an argon filled glove box.

Synthesis of 1,5-bis(trimethylsilyl)penta-1,4-diyne. A 125 mL, three-necked flask containing a magnetic stir bar, was fitted with a dropping funnel, a reflux condenser with a drying tube, and an adaptor connected to an argon cylinder. THF (20 mL) was added, followed by 5.5 mL (16.5 mmol) of CH_3MgBr. Trimethylsilylacetylene (2.83 mL, 20 mmol) was added dropwise over a period of 15 min, just fast enough to keep the solution at reflux. The catalyst CuCl (50 mg in 0.25 mL THF) was added and the mixture was refluxed for 1 hr. Propargyl bromide (2.72 g, 14.25 mmol in 2.5 mL THF) was added to the refluxing solution and the mixture was heated one additional hour. The reaction mixture was poured into 25 mL ice water and acidified with 1.25 mL of concentrated H_2SO_4, extracted with 3 x 15 mL of ether, and the organic phase was neutralized with saturated $NaHCO_3$ solution, washed with water, and dried over anhydrous $MgSO_4$. Vacuum fractional distillation, under nitrogen, gave two colorless liquids. The first was obtained at 40-41^{0}C/2 mm Hg, weighed 2.0 g (67% yield, based on propargyl bromide) and was identified as the desired 1,4-bis(trimethylsilyl)-1,4-pentadiyne. Anal. Found: C, 62.04; H, 9.75%. $C_{11}H_{20}Si_2$ calc: C, 63.38; H, 9.67%. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.14 (s, 18 H, $Si(CH_3)_3$), 3.17 9s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$), δ (ppm): 99.5 (C_2, C_4), 85.2 (C_1, C_5), 11.9 (C_3), -0.09 ($Si(CH_3)_3$. The second product, obtained at 43-45^{0}C/2 mm Hg, was identified as the isomeric 1,3-diyne, by NMR spectroscopy.

Synthesis of compound III. A 200 mL flask containing a magnetic stir bar was charged with a solution of Cp_2ZrCl_2 (2.92 g, 10 mmol) in 40 mL of THF, and the contents were cooled to -78^{0}C in a dry ice-acetone bath. n-Butyllithium in hexanes (1.6 M, 12.5 mL, 20 mmol) was added, and the reaction mixture was stirred for 1 hr, allowed to warm to room temperature, and stirred for an additional hour. The reaction mixture was cooled to -78^{0}C, and 1,5-bis(trimethylsilyl)-1,4-pentadiyne (2.08 g, 10 mmol) was added dropwise. The solution was allowed to warm to room temperature, and stirred for 3 hr. During this period, the mixture changed from yellow to deep red, and a white precipitate formed. The mixture was placed under vacuum to reduce the volume to about one-third of the original, and 80 mL ether was added. The solution was filtered in the glove box, and the solvent was evaporated under vacuum to give 3.8 g (88%) of a deep-red solid. The crude product was dissolved in a minimum amount of benzene and filtered to remove any residue. To this solution was added pentane (about one-fourth the amount of benzene) slowly and carefully in order to form two layers. As the pentane slowly diffused into the benzene layer, crystals were formed. The solvent was decanted, and the crystals were washed with pentane and dried under vacuum. Anal. Found: C, 57.67; H, 7.11%. $C_{42}H_{60}Si_4Zr_2$ calc: C, 58.68; H, 7.03%. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.14 (s, 36H, $Si(CH_3)_3$), 2.90 (s, 4H, CH_2), 6.08 (s, 20H, Cp). ^{13}C NMR ($CDCl_3$), δ (ppm): 195.2 (C_1, C_5, C_6, C_{10}), 138.9 (C_2, C_4, C_7, C_9), 110.2 (Cp), 47.9 (C_3, C_8 [methylene]), 2.88 ($Si(CH_3)_3$).

The crude compound III was treated with HCl in a manner described previously,[10] in order to release the organic ligand(s), which were isolated from the organic fraction after vacuum evaporation of the solvent. The remaining liquid was subjected to GC-MS analysis.

Physical methods. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX90Q FT spectrometer. $CDCl_3$ was used as the solvent, and the residual proton peak or solvent triplet were used as the internal references for the proton and carbon spectra, respectively.

Gas chromatography-mass spectrometry were carried out on a Hewlett-Packard 5890 GC 5971 MSD instrument.

Collection of X-ray diffraction data. Crystallographic data were collected using a Syntex $P2_1$ diffractometer with MoK_α radiation (λ = 0.71073 Å). The SHELXTL PLUS program set was employed for direct methods structure solution and full matrix least-squares refinement (Siemens Analytical X-ray Instruments, Inc., Madison WI, 1990). Experimental data are shown in Table 7.

Table 7. Experimental Data for the X-ray Diffraction Study.

Formula	$C_{42}H_{60}Si_4Zr_2$
Formula weight	859.7
Crystal class	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 13.225(3)
	b = 21.965(4)
	c = 14.788(3)
	ß = 102.83(3)^{0}
Volume	4188.5(15)
F(000)	1792
Density (calc)	1.363 g/cc
Crystal dimensions (mm)	0.50 x 0.26 x 0.12
Diffractometer	Syntex $P2_1$
Monochromator	Highly oriented graphite crystal
Absorption coefficient	0.629 mm^{-1}
Min/Max transmission	0/7968/0.9051
Temperature	130^{0}K
Scan type	ω
Scan speed	Constant; 8.37^{0}/min in ω
Scan range (ω)	2.00^{0}
Standard reflections	3 per 97 reflections
Reflections collected	7714
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
No. of Parameters refined	434
R_F $\|F_o\| > 4.0\,\sigma\,\|F_o\|$	5.27%
R_W	4.48%
Goodness of fit	1.25
Ind. reflections	7376
R indices (all)	R_F = 9.99%; R_W = 5.15%

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