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Synthesis, Structure, and Absorption Spectra of the Well-Defined 1,1'-Bicyclopentadiene Derivatives

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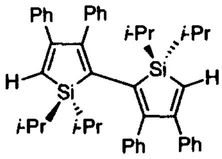
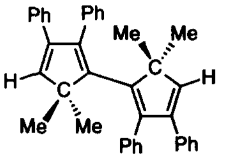
Abstract: The well-defined 1,1'-bicyclopentadiene derivatives have been prepared by an *endo-endo* mode intramolecular reductive cyclization of a 1,4-diyne using lithium naphthalenide followed by oxidative coupling via a higher order cyanocuprate. The crystal structure and UV spectra of the bicyclopentadienes have also been determined. Copyright © 1996 Elsevier Science Ltd

Silacyclopentadiene (silole) represents a new entry among the building units of novel π-conjugated polymers.[1-3] In the course of our research aiming at the synthesis of silole homo-polymers, polysiloles, we have recently succeeded in preparation of the 3,3',4,4'-tetraphenyl-2,2'-bisilole **1** as their model compound.[1b] The bisilole **1** has been found to have an unusually long absorption maximum (398 nm) among π-conjugated two-ring systems,[4] implying its unique π-electronic structure. Comparison of the bisilole with its carbon analogue, 1,1'-bicyclopentadiene, is deemed essential for elucidation of the electronic structure of the bisilole. While absorption maxima for a few 1,1'-bicyclopentadiene derivatives have been reported so far,[5] these data were not pertinent to our purpose, prompting us to prepare a structurally well-defined 1,1'-bicyclopentadiene having almost the same substituents as the bisilole **1** has. Herein we describe the synthesis, structure, and absorption spectra of 2,2',3,3'-tetraphenyl-1,1'-bicyclopentadiene **2**.



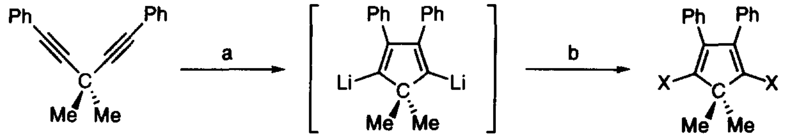
1



2

1,4-Difunctionalized cyclopentadienes were prepared by the *endo-endo* mode[1b] intramolecular reductive cyclization of a 1,4-diyne using lithium naphthalenide as a reducing agent, as shown in Scheme 1. Thus, diyne **3** was added dropwise into an excess amount of the reductant at -78 °C to form 1,4-dilithiocyclopentadiene **4**, which was immediately quenched with some electrophiles such as H_2O, Me_3SiCl, and diiodoethane to give the desired products, cyclopentadiene **5**, 1,4-disilylcyclopentadiene **6**, and 1,4-diiodocyclopentadiene **7**, respectively, in 13 - 20 % yields. Although the yields are rather low, this is the first general method for the synthesis of 1,4-difunctionalized cyclopentadiene derivatives.

Scheme 1

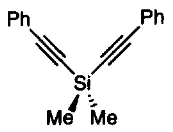


3

4

5 (X = H) 20 %
6 (X = Me_3Si) 13 %
7 (X = I) 18 %

Reagents and Conditions: (a) lithium naphthalenide (4 equiv), THF, -78 °C, 1 min. (b) H_2O, Me_3SiCl (4 equiv), or 1,2-diiodoethane (4 equiv), -78 ~ 0 °C.



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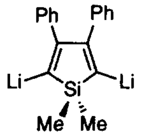

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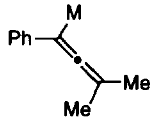
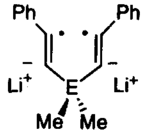


10 (M = Li)
11 (M = H)



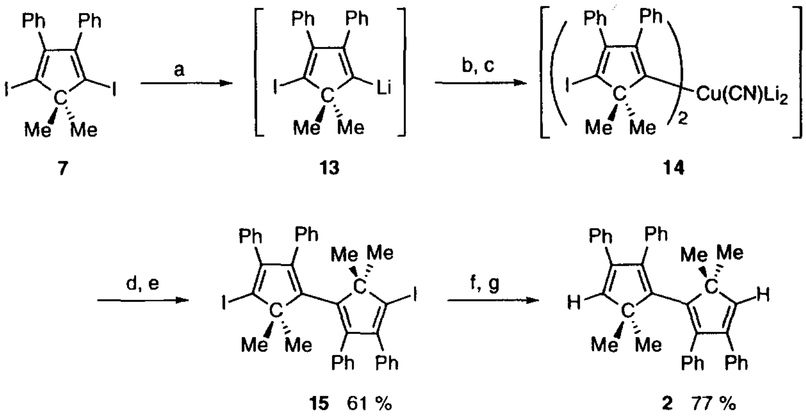
12
(E = C or Si)

This cyclization is a carbon version of the silole synthesis, which we developed recently.[1b] While, in the silicon case, the reductive cyclization of **8** afforded 2,5-dilithiosilole **9** exclusively, in the present carbon case the main reaction course was the formation of 1-lithioallene **10**, which was trapped as **11**. Presumably, the formation of the allene is due to the cleavage of the central carbon-acetylene bond in **3** prior to the formation of the bis(anion radical) species **12** (E = C), crucial for ring closure.[1b] The different reactivities may emphasize the stabilization of the bis(anion radical) intermediate **12** (E = Si) by the silicon atom and the unfavored formation of the silicon-carbon double bond in the silicon case.

1,1'-Bicyclopentadiene **2** was prepared in two steps from diiodocyclopentadiene **7**, oxidative coupling via a higher order cyanocuprate[6] and reduction of the terminal halogens, as shown in Scheme 2. Thus, lithiation of **7** with *n*-BuLi in a mixture of ether and hexane afforded the (lithio)(iodo)cyclopentadiene **13**. After removal of the solvents in vacuo, the residue was dissolved in THF and treated with 0.5 equiv of CuCN to form a higher order cyanocuprate **14**. Oxidation of **14** with an excess amount (5 equiv) of *p*-dinitrobenzene gave 4,4'-diiodo-1,1'-bicyclopentadiene **15**.[7] The whole transformation from **7** to **15** was performed in one-pot in 61 % overall yield. The compound **15** was transformed to 1,1'-bicyclopentadiene **2**[8] in 77 % yield by successive treatment with *t*-BuLi and H_2O. The bicyclopentadienes **2** and **15** are air-stable pale-yellow crystals.

Crystal structure of diiodobicyclopentadiene **15** has been determined by X-ray crystallography,[9] which is composed of a 1:1 mixture of two conformers, *anti* form and *syn* form with respect to the orientation of two cyclopentadiene rings, as shown in Figure 1. Both conformers have highly twisted structures. The torsion angles between the least square planes of the two cyclopentadiene rings are 70° and 62° for *anti* and *syn* conformers, respectively.

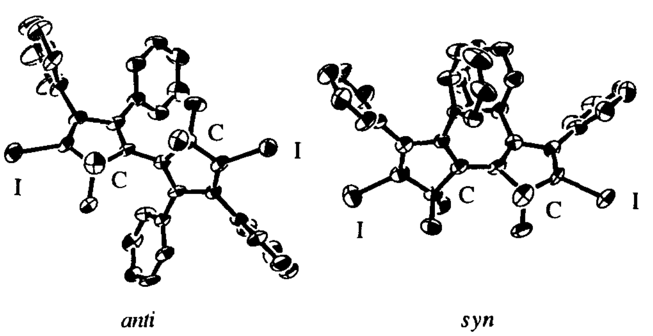
Scheme 2



***Reagents and Conditions*:** (a) *n*-BuLi (1.05 equiv), Et$_2$O, -78 ~ 0 °C, 4 h. (b) *in vacuo*, 0 °C, 1 h. (c) CuCN (0.5 equiv), THF, -40 ~ -30 °C, 1 h. (d) TMEDA (1.5 equiv), -78 °C. (e), *p*-dinitrobenzene (5 equiv), THF, -78 °C, 1 h. (f) *t*-BuLi (4 equiv), THF, -78 °C, 1 h. (g) H$_2$O.

The diiodobicyclopentadiene **15** has a twisted conformation also in solution. Thus, the ^{1}H NMR spectrum of **15** in CDCl$_3$ showed two singlets for the two diastereotopic methyl groups on the respective 5-position at δ 0.92 and 1.41 ppm at room temperature, which did not coalesce even at 100 °C in toluene-d_8. This means that the racemization of the axial chirality due to atropisomerism does not occur on the NMR time scale. The rotation barrier ($\Delta G^{\neq}$) in **15** was thus estimated to be more than 18 kcal mol^{-1}. This is in sharp contrast to the fact that the bisilole **1** also has a twisted structure in solution, but racemization occurs at room temperature.[1b]

UV absorption data for bicyclopentadienes **2** and **15** are as follows: λ_{max} nm (log ε) in CHCl$_3$: **2**, 249 (4.53), 340 (3.43); **15**, 242 (4.55), 342 (3.85). The absorptions around 250 nm are assigned to the π–π* transition of phenyl moieties. The other absorption maximum (340 nm) of **2**, assigned to the bicyclopentadiene moiety, is 58 nm shorter than that of **1** (398 nm). From this observation it is inferred that the silicon atoms in the silole rings contribute largely to the π-electronic structures of bis(butadiene) moiety in



anti *syn*

Figure 1. *ORTEP* drawings of diiodobicyclopentadiene **15**.

the bisilole. Theoretical analysis of the silicon effect has now become the main subject of our study in this series. The results will be reported elsewhere in detail.

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4. For comparison, several UV absorption data for non-substituted conjugated dimers of five-membered cyclic dienes are listed as follows; compound, λ_{max} (nm): 2,2'-bipyrrole, 276;[a] 2,2'-bifuran, 278;[b] 2,2'-bithiophene, 302;[b] 2,2'-biselenophene, 321;[b] 1,1'-bicyclopentadiene (isomeric mixtures), 352(sh), 340.[5a] (a) Zotti, G.; Martina, S.; Wegner, G.; Schülter, A. -D. *Adv. Mater.* **1992**, *4*, 798. (b) Shabana, R.; Galal, A.; Mark, Jr. H. B.; Zimmer, H.; Gronowitz, S.; Hörnfeldt, A. -B. *Phosphorus, Sulfur, and Silicon* **1990**, *48*, 239.
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7. **15**: mp 216-218 °C (decomp.). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.92 (s, 6H), 1.41 (s, 6H), 6.62-6.74 (m, 4H), 6.86-7.04 (m, 10H), 7.14-7.25 (m, 6H). ^{13}C NMR δ 23.70, 27.01, 58.46, 116.93, 126.42, 127.03, 127.26, 127.53, 129.43, 129.54, 136.15, 136.95, 145.39, 147.64, 148.73. MS *m/e* (relative intensity) 742 (M^+, 100), 616 (20). UV-vis ($CHCl_3$) λ_{max} nm (log ε): 242 (4.55), 342 (3.85). Anal. Calcd for $C_{38}H_{32}I_2$: C, 61.47; H, 4.34. Found: C, 61.65; H, 4.33.
8. **2**: mp 198-199 °C (decomp.). ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.04 (s, 6H), 1.46 (s, 6H), 6.26 (s, 2H), 6.72-6.80 (m, 4H), 6.88-7.04 (m, 10H), 7.08-7.17 (m, 6H). ^{13}C NMR δ 22.61, 25.72, 54.75, 125.86, 126.27, 127.21, 127.49, 128.14, 129.51, 136.82, 142.21, 143.13, 146.29, 148.21. MS *m/e* (relative intensity) 490 (M^+, 100), 245 (89). UV-vis ($CHCl_3$) λ_{max} nm (log ε): 249 (4.53), 340 (3.43). Anal. Calcd for $C_{38}H_{34}$: C, 93.02; H, 6.98. Found: C, 93.05; H, 7.12.
9. Crystal data of **15** (instrument; Rigaku AFC7R): $P2_1/c$ (#14); a = 11.211(3) Å, b = 30.845(4) Å, c = 18.350(3) Å, β = 94.75(1)°, V = 6323(1) Å^3, Z = 8, D_c = 1.560 g cm^{-3}, μ (Cu Kα) = 157.90 cm^{-1}, temperature 20 °C, R = 0.075, R_w = 0.087, and S = 2.52; number of unique reflections=9614. All hydrogen atoms were included but a part of them (No. 7, 9, 10, 19, 20, 37, 38, 52) were not refined.

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