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Unexpected Ti-catalyzed formal intramolecular [4+4] cycloaddition of 1,1′-bi[(S^*,S^*)-6-(trimethylsilyl)-cyclohepta-2,4-dien-1-yl]

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Abstract—Reductive disilylation (Li+Me_3SiCl–THF) of 1,3,5-cycloheptatriene led to 1,1′-bi[(S^*,S^*)-6-(trimethylsilyl)cyclohepta-2,4-dien-1-yl] (**2**). In the presence of $TiCl_4$ in dichloromethane, **2** gave rise to a spherical molecule **5** resulting from an intramolecular formal [4+4] supra–supra cycloaddition.

The bis-silylation of dienic or trienic hydrocarbons is a particularly interesting transformation, which allows the simultaneous creation of two new Si–C bonds. This reaction constitutes a convenient route to obtain bis-(silyl) unsaturated compounds that can represent useful intermediates in organic chemistry or can be used as building blocks for the organic synthesis. A very simple procedure is the reductive disilylation of 1,3-dienes by lithium in the presence of chlorotrimethylsilane giving rise to a mixture of 1,4-bis(trimethylsilyl)-2-butene derivatives and 1,8-bis(trimethylsilyl)-2,6-octadiene derivatives.[1]

In order to obtain unsaturated silanes with a cycloheptadiene rings, we carried out the reductive silylation of 1,3,5-cycloheptatriene. In the presence of lithium and chlorotrimethylsilane in THF, cycloheptatriene led to a mixture of 1,6-bis(trimethylsilyl)cyclohepta-2,4-diene (**1**) and 1,1′-bi[(S^*,S^*)-6-(trimethylsilyl)cyclohepta-2,4-dien-1-yl] (**2**).[2] After separation by distillation and chromatography on silica gel, **2** appeared as one isomer with a *C*2 axis[3] (Scheme 1).

The stereoselectivity of the reductive dimerization is an interesting result.[4] Anion-radical **3** resulting from the addition of one electron was neutralized by silylation to form dienic radical **4**, which dimerized into **2** (in the HOMO of the dienic radical **4**, the atomic coefficient at C(6) is of major importance).[5] For each cycle, the cis relationship between the two substituents implies a transition state where the two trimethylsilyl groups are on the opposite faces because of steric hindrance (Scheme 2).

With the aim to reveal the reactivity of **2** toward electrophilic reagents, this disilyldiene was added in the presence of $TiCl_4$ to various compounds such as 4-(trifluoromethyl)benzaldehyde, 1-naphthaldehyde, 2-naphthaldehyde, benzoyl chloride, 1-naphthoyl chloride, 4-nitrobenzoyl chloride, oxalyl chloride, and acetic anhydride. In each case, no addition product is isolated but the presence of some silylated hydrocarbon derivatives has been detected. Consequently, **2**—in dichloromethane—was treated with $TiCl_4$ at low temperature. After usual work-up, a crystalized silane **5** was isolated in 36% yield (Scheme 3). The NMR data show that **5** was a symmetrical molecule,[6] but the determination of the structure has been achieved by an X-ray diffraction analysis (Fig. 1).[7] Clearly, **5** is a result of an intramolecular formal [4+4] supra–supra cycloaddition of **2**. Interestingly, the new bonds are the longest C–C bonds of adduct **5** (1.577 and 1.583 Å).

Keywords: Reductive silylation; 1,3,5-Cycloheptatriene; [4+4] Cycloadditions; Titanium tetrachloride.

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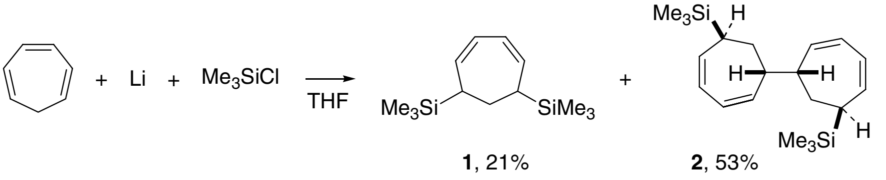
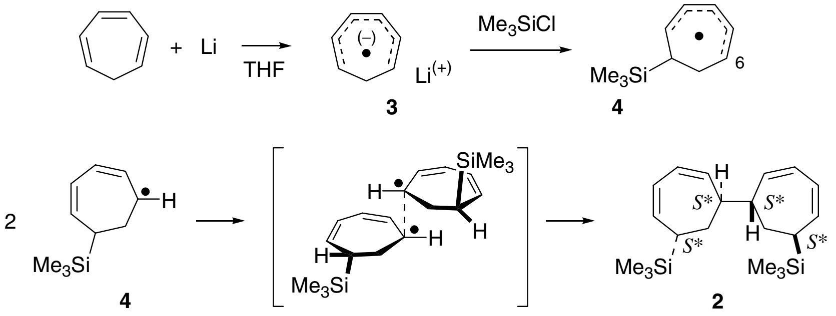
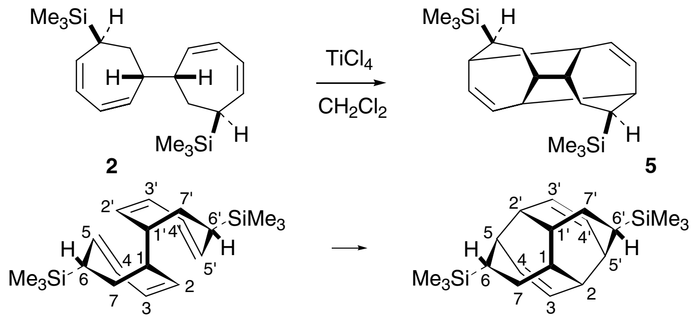


Scheme 1. Synthesis of 1,6-bis(trimethylsilyl)cyclohepta-2,4-diene (**1**) and 1,1′-bi[(*S**,*S**)6-(trimethylsilyl)cyclohepta-2,4-dien-1-yl] (**2**).



Scheme 2. Stereochemistry of the reductive dimerization of 1,3,5-cycloheptatriene.



Scheme 3. Intramolecular formal [4+4] cycloaddition of **2**.

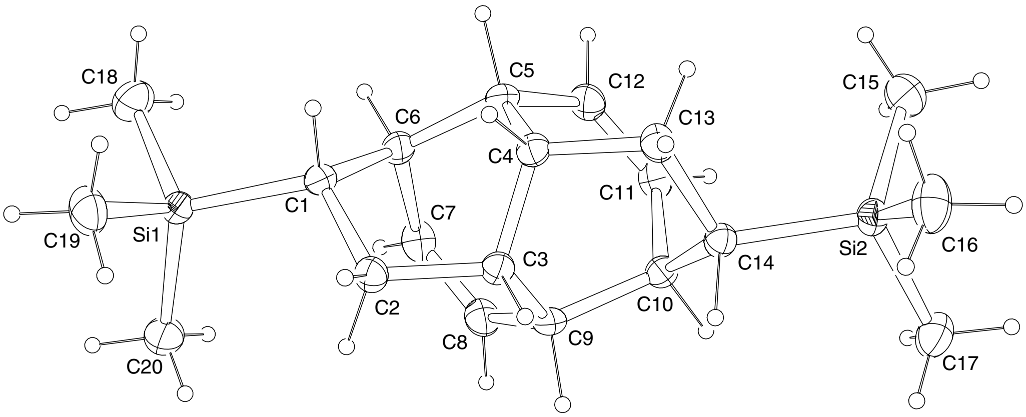


Figure 1. ORTEP drawing for **5**. Non-hydrogen atoms are drawn with 25% probability thermal ellipsoids, while the hydrogen atoms are portrayed with an artificial small radius.

The [4+4] cycloaddition reaction giving rise to a 1,5-cyclooctadiene generally occurs under photoirradiation or in the presence of transition-metal catalysts, while the genuine thermal [4+4] cycloadditions are predicted to be difficult by the Woodward–Hoffmann rules.[8] On the basis of the precursor works of Wilke and other German chemists,[9] the syntheses of many 1,5-cyclooctadienes[10] and natural products containing a cyclooctane ring have been achieved by a Ni(0)-catalyzed intramolecular cycloaddition of 1,3-dienes.[11,12] The overall process, while formally a cycloaddition reaction, proceeds mechanistically through a series of intermediates.[13]