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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+Me₃SiCl–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 TiCl₄ in dichloromethane, 2 gave rise to a spherical molecule 5 resulting from an intramolecular formal [4+4] supra–supra cycloaddition.
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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 cyclohepta-diene 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 C2 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 electro-philic reagents, this disilyldiene was added in the presence of TiCl₄ to various compounds such as 4-(tri-fluoromethyl)benzaldehyde, 1-naphthaldehyde, 2-naph-thaldehyde, benzoyl chloride, 1-naphthoyl chloride, 4-nitrobenzoyl chloride, oxalyl chloride, and acetic anhy-dride. In each case, no addition product is isolated but the presence of some silylated hydrocarbon derivatives has been detected. Consequently, 2—in dichlorometh-ane—was treated with TiCl₄ 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 intramole-cular 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).
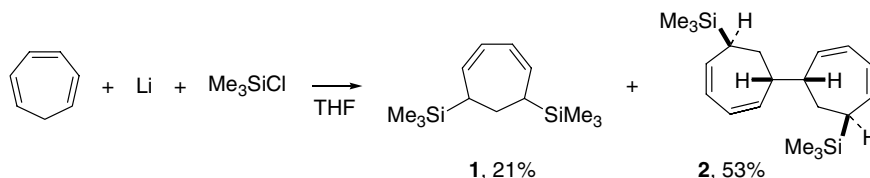
Scheme 1. Synthesis of 1,6-bis(trimethylsilyl)cyclohepta-2,4-diene (**1**) and 1,1′-bi[(S*,S*)6-(trimethylsilyl)cyclohepta-2,4-dien-1-yl] (**2**).
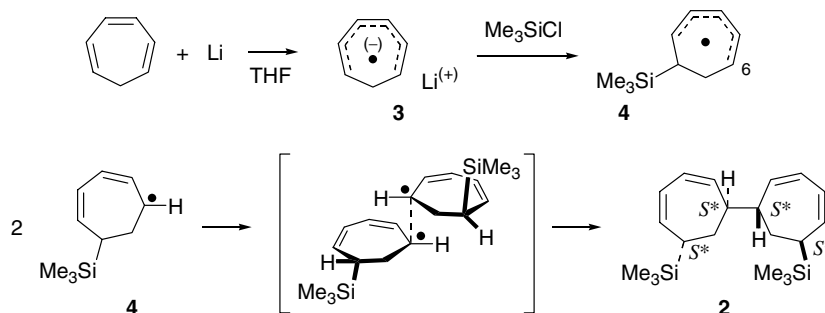
Scheme 2. Stereochemistry of the reductive dimerization of 1,3,5-cycloheptatriene.
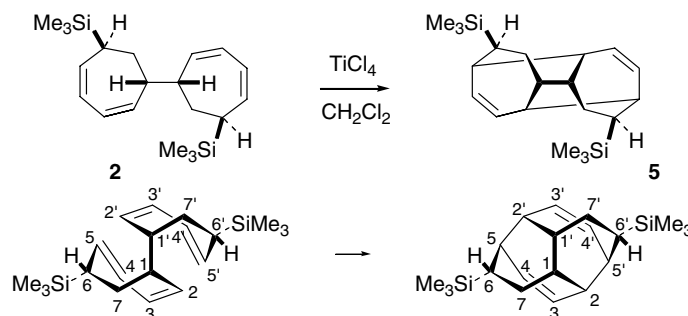
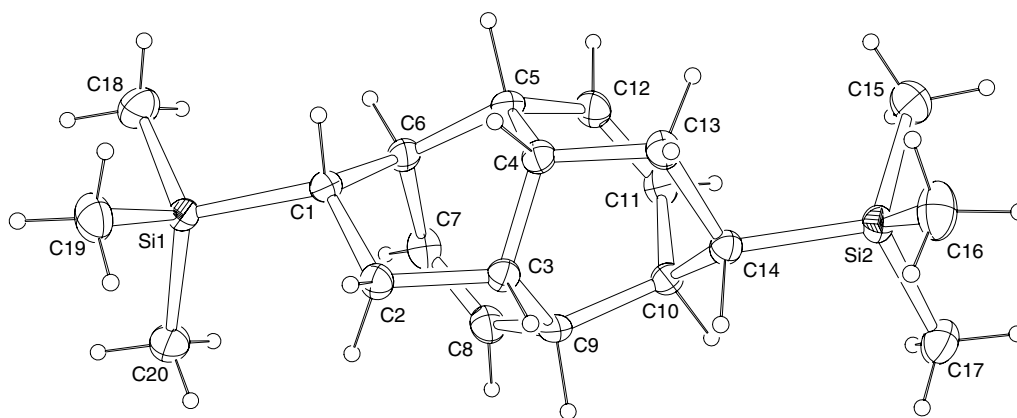**Scheme 3.** Intramolecular formal [4+4] cycloaddition of **2**.

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 Ger-

man 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 mechanically through a series of intermediates.[13]

Three other transition metals, Pd(0),[14] Ru,[15] and Fe(0)[16] have been successfully used. Moreover, some thermal [4+4] dimerizations have been described, but it was shown that these cyclizations proceeded via a stepwise mechanism involving a diradical intermediate.[17]

As a thermal cycloaddition can be ruled out, we conclude that the formal [4+4] cycloaddition of **2** has been catalyzed by a titanium species. The pioneer observations of Wilke concerning the efficiency of the first-row transition metals in the formation of cycloaddition product lead us to envisage the intervention of a low-valent titanium species. Thus, titanium tetrachloride should be reduced in Ti(II) and able to coordinate with a carbon–carbon double bond[18] (as the Kulinkovich reagent).[19] However, it is difficult to consider that titanium tetrachloride in dichloromethane solution has been reduced by **2**. Another hypothesis was the intervention of a cation radical derivative containing titanium. From the work of Bauld, it is well known that Diels–Alder reaction and [2+2] cycloadditions concerning electron-rich substrates could be initiated via catalytic amounts of a stable cation radical salt, tris(bromophenyl)aminium hexachloroantimonate.[20] Moreover, previous, works of Ledwith have shown that *N*-vinyl-carbazole led to a thermal forbidden [2+2] cycloaddition under the catalytic influence of suitable inorganic one-electron oxidants such as Fe(III), Ce(IV), and Cu(II).[21]

In conclusion, we have described a particular intramolecular thermal formal [4+4] supra–supra cycloaddition catalyzed by titanium tetrachloride and occurring at low temperatures. The obtained disilane **5** was a spectacular spherical molecule more stable than the bicyclic precursor **2**. The most accurate hypothesis concerning this process is the intervention of titanium tetrachloride as one-electron oxidant.

Acknowledgements

References and notes

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2. A 500 mL three-necked flask equipped with a thermometer, a dropping funnel, a reflux condenser connected with a stopcock to a rubber balloon filled with argon and a magnetic stirring bar was charged with anhydrous THF (100 mL). The solution was cooled to 0 °C in an ice bath. Lithium metal (3 mm wires cut as pieces of 1.5 cm length, 1.9 g, 0.27 g-atom) was added. From the dropping funnel, trimethylchlorosilane (34.5 mL, 0.27 mol) was added in 15 min and then 1,3,5-cycloheptatriene (25 g, 0.27 mol) in 45 min. The solution was stirred for 6 h at 0 °C and then at

room temperature for 20 h. After usual work-up, crude products was distilled to give **1** (55–60 °C, 0.2 mmHg) and **2** (120–122 °C, 0.2 mm Hg). Compound **2** was purified by chromatography on silica gel (petroleum ether). Compound **1**, ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.74–5.64 (m, 2H), 5.57–5.51 (m, 1H), 5.29 (dd, *J* = 11.9, 4.3 Hz, 1H), 2.65–2.50 (m, 1H), 2.25 (t, *J* = 6.1 Hz, 1H), 2.19–2.10 (m, 2H), 0.05 (s, 9H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 131.8 (d), 129.6 (d), 127.3 (d), 124.1 (d), 39.1 (t), 31.6 (d), 29.9 (d), −1.66 (q), −1.91 (q). Compound **2**, ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.69–5.64 (m, 4H), 5.43 (br s, 4H), 2.53 (m, 2H), 2.27 (m, 4H), 0.05 (s, 18H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 132.6 (t), 131.7 (t), 128.1 (t), 44.8 (t), 39.0 (t), 31.0 (d), −1.5 (q); MS *m/z* (%) = 330 [M]$^+$ (12), 91 (52), 91 (52), 73 (100), 45 (25).

3. Direct silylation of guaiazulene gave tetrasilylated derivative (91%) and product of reductive dimerization (6%), see: Félix, G.; Dunogues, J.; Petraud, M.; Barbe, B. *J. Organomet. Chem.* **1983**, *258*, C49–C51.

4. The reduction (Mg—2 HMPA—THF) of cycloheptatriene in the presence of dimethyldichlorosilane led to the 8,8-dimethyl-8-silabicyclo[3.2.1]octa-2,5-diene (12% yield), see: Laguerre, M.; Dunoguès, J.; Calas, R. *Tetrahedron* **1978**, *34*, 1823–1827.

5. At the unrestricted B3LYP/6-311G(d, p) level and for radical **4**, sums of the absolute values of 2p atomic coefficients of the HOMO showed that the greater values were borne by the C(1), C(3), and C(5) of the unsaturated system. The Mulliken atomic spin densities show a similar pattern.

Σ of HOMO 2p atomic coeff.   Mulliken atomic spin densities
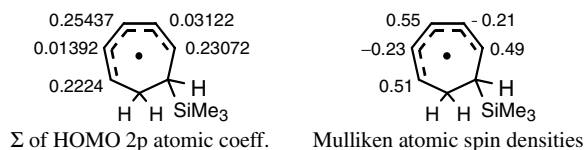
6. A 50 mL two-necked flask equipped with a thermometer, a stopcock to a rubber balloon filled with argon and a magnetic stirring bar was charged with anhydrous CH$_2$Cl$_2$ (15 mL). The solution was cooled to −90 °C and TiCl$_4$ was introduced (0.7 mL, 6 mmol). Then a solution of **2** (1 g, 3 mmol) in CH$_2$Cl$_2$ (2 mL) was slowly added. After 1 h of stirring, the solution was allowed to warm to −60 °C for 24 h. The reaction mixture was poured onto ice and NH$_4$Cl. After the common work-up procedure, the crude product was flash chromatographed on silica gel eluting with petroleum ether/ether (90:10) to give **5** (363 mg, 1.1 mmol). Compound **5**, mp 110 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.47 (dd, *J* = 6.3, 3.4 Hz, 4H), 1.60 (m, 2H), 1.54 (s, 2H), 1.23 (s, 2H), 0.85 (m, 4H), 0.05 (s, 2H), −0.06 (s, 18H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 131.2 (d), 130.2 (d), 48.4 (d), 38.9 (d), 24.7 (t), 21.6 (d), −0.2 (q).

7. Crystal data and structure refinement. CCDC-643991 contains the supplementary crystallographic data. These data can be obtained free of charge at www.ccdc.cam. ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk]. Formula: C$_{20}$H$_{34}$Si$_2$; M_w: 330.65; Crystal color: colorless; Crystal size/mm^3: 0.2 × 0.2 × 0.2; Crystal system: triclinic; space group: $P-1$; *a*/Å: 9.3050(2); *b*/Å: 9.8696(2); *c*/Å: 12.4022(3); α/°: 106.9271(9); β/°: 109.3093(9); γ/°: 95.652(1); *V*/Å^3: 1004.12(4); *Z*: 2; D_c/g^{-3}: 1.094; μ (Mo–Kα)/cm^{-1}: 1.74; No of unique data: 3458; No. parameters refined: 199; No. refl. in refinement: (3458; $F^2 > 4\sigma F^2$: 3187); *R*: 0.0525 [$F^2 > 4\sigma F^2$]; *wR*: 0.1325 [$F^2 > 4\sigma F^2$] ($w = 1/[\sigma^2(F_o^2) +$

$(0.0738P)^2 + 0.266P]$) where $P = (F_o^2 + 2F_c^2)/3$; Goodness of fit: 1.154; Residual Fourier/e. Å^{-3}: −0.219; 0.198.

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