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Synthesis and Reactions of Tricyclo[9.3.0.0^{4,8}]tetradeca-4,7,11,14-tetraene

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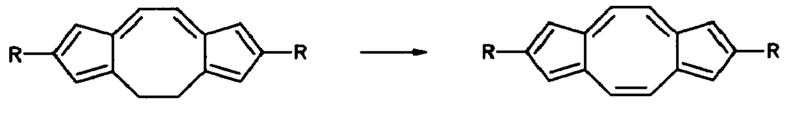
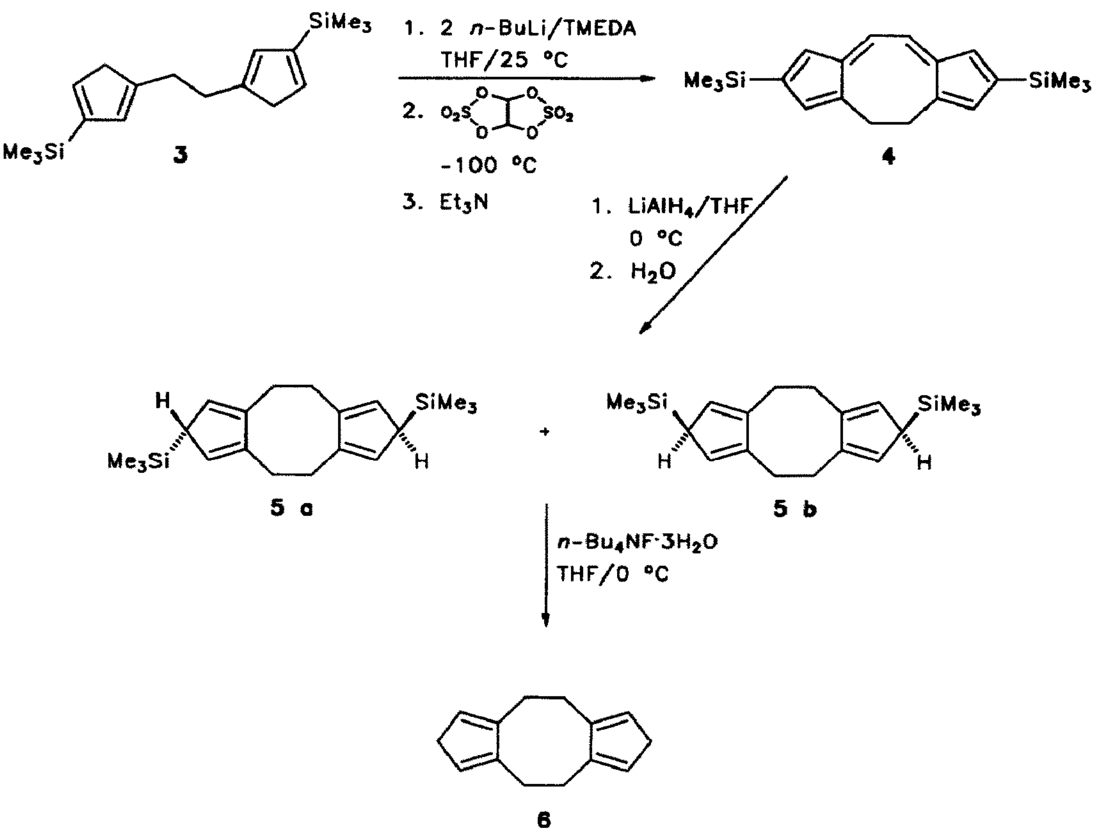
Abstract: The title compound **6** has been synthesized by condensation of 1,2-bis(trimethylsilylcyclopentadienyl)-ethane (**3**) with glyoxal sulfate to the tricyclic system **4** and following reduction as well as desilylation. Twofold deprotonation of **6** yields the dilithium compound **7**, which was transformed into the pentafulvenophanes **8** and **9**.

Derivatives of the title compound like **1** proved to be useful intermediates for the synthesis of the dicyclopenta[a,e]cyclooctene system **2** with a delocalized 14π-electron system, which exhibits interesting physical and chemical properties.[1] Furthermore, they should open an access to so far unknown pentafulvenes with two ethano-bridges as well as [2][2]metallocenophanes; these are bent metallocenes containing two cyclopentadienyl ligands in a non-parallel geometry and therefore deserve increasing interest as precursors for efficient catalysts for the stereoselective polymerization of alkenes.[2]

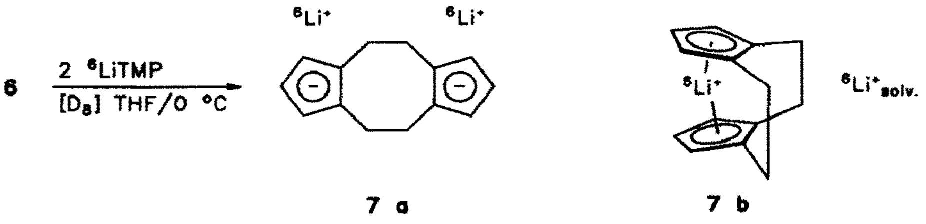


1 2

We report herein a first synthesis of tricyclo[9.3.0.0^{4,8}]tetradeca-4,7,11,14-tetraene (**6**)[3] from 1,2-bis(trimethylsilylcyclopentadienyl)-ethane (**3**),[4,5] which is obtained in 67% yield as a mixture of tautomers by reaction of the dilithium salt of the easily available 1,2-bis(cyclopentadienyl)-ethane[6] and trimethylsilyl chloride.[7] Deprotonation of **3** with 2 equiv. n-BuLi and cyclizing condensation with glyoxal sulfate yields the 2,7-bis(trimethylsilyl)-4,5-dihydrodicyclopenta[a,e]cyclooctene (**4**)[8] (dark red violet crystals, mp 130°C; yield 4%). **4** is reduced with LiAlH$_4$ to a mixture of anti- and syn-6,13-bis(trimethylsilyl)-tricyclo[9.3.0.0^{4,8}]tetradeca-4,7,11,14-tetraene (**5a,b**), which can be separated by chromatography on Al$_2$O$_3$ with n-pentane (**5a**[9]: colorless crystals, mp 87°C, 65%; **5b**[10]: colorless crystals, mp 81°C, 22%). Desilylation of **5** with tetra-n-butylammonium fluoride leads with 65% yield to the hydrocarbon **6**, isolated as colorless, below room temperature melting and even at -50°C rather unstable crystals. ^{1}H, ^{13}C NMR and UV spectra[11] are in accordance with the proposed structure of **6**. The 2-fold deprotonation of **6** with ^{6}Li-enriched LiTMP in [D$_8$]THF furnishes the dilithium salt **7**, which was studied by

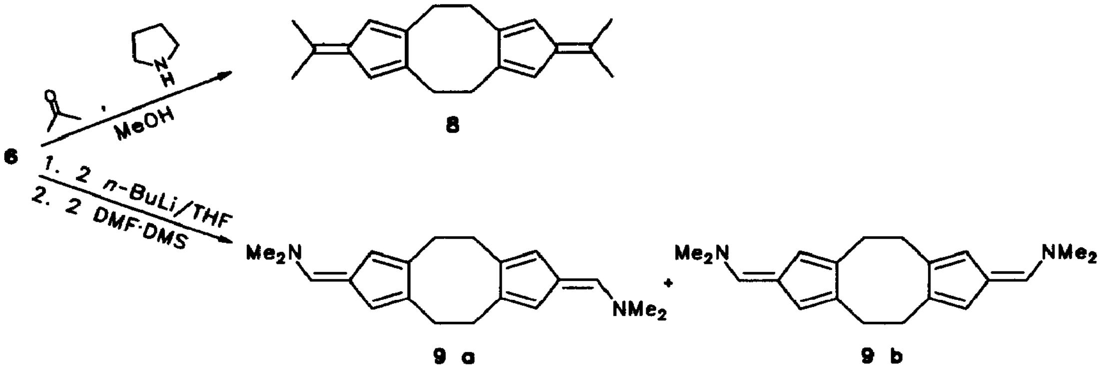


^{1}H,^{13}C and ^{6}Li NMR spectroscopy. While the ^{1}H and ^{13}C NMR spectra[12] prove a symmetric structure of the dianion of **7**, additional information about the interaction with the metal cations was expected from its ^{6}Li NMR spectra. The spectrum taken at -60°C exhibits only one signal at $\delta_{Li} = -7.70$, while at r.t. two signals at $\delta_{Li} = -7.42$ and $\delta_{Li} = -10.15$ are observed. With regard to recent studies on the structure of organolithium compounds[13] these findings let assume that at -60°C **7** exists as a contact ion pair **7a**, while the second signal observed at r.t. probably is due to an ate-complex-type structure **7b**, wherein



one lithium ion is coordinated to solvent molecules, whereas the other is located in between the two anionic five-membered rings, causing a significant high field shift in the ^{6}Li NMR spectrum.

Reaction of **6** with acetone in the presence of pyrrolidine yields 44% of the 6,13-diisopropylidene-tricyclo[9.3.0.0^{4,8}]tetradeca-4,7,11,14-tetraene (**8**) as deep yellow crystals (mp 201°C)^{14}; this forms even at -50°C under N$_2$ within a few days a yellow unsoluable solid. Similar to this 2-fold ethano-bridged



pentafulvenophane also the dark yellow crystalline 6,13-bis(N,N-dimethylaminomethylidene)-tricyclo-[9.3.0.0^{4,8}]tetradeca-4,7,11,14-tetraene could be synthesized as E/Z-mixture (1:1) (**9a,b**) (decomp. >250°C; yield 23%)^{15} by deprotonation of **6** with 2 equiv. n-BuLi in THF and following reaction with two moles of the DMF/DMS-complex in dichloromethane.

The first synthesis of so far unknown [2][2]metallocenophanes from **5** and **6** will be reported elsewhere.

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3. Dâvila, A.; McLaughlin, M.L., mentioned in two identical abstracts of the 206th and 207th ACS National Meeting (*ORGN* **1993**, 446; *ibid.* **1994**, 472) a synthesis of **6** by bis(cyclopentadienylannu-

lation) of 1,5-dibromo-1,5-cyclooctadiene, but so far no details were reported.

4. Colorless oil, bp 137°C/10^{-2} mbar; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.0-0.39(m, 18H, Me$_3$Si), 2.70-3.30(m, 8H, CH$_2$), 6.08-6.77(m, 4H, olefinic H); UV(n-hexane): λ_{max}(lgϵ): 249nm(3.80).
5. All the described compounds gave correct elemental analyses.
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7. Reaction of the dilithium salt of 1,2-bis(cyclopentadienyl)-ethane with *t*-BuSiMe$_2$Cl in 1,2-dimethoxyethane at 90°C yields as a mixture of tautomers of 1,2-bis(*t*-butyldimethylsilylcyclopentadienyl)-ethane as colorless oil (bp 215°C/10^{-2} mbar) with 51% yield; ^{1}H NMR (300 MHz, CDCl$_3$): δ = -0.20-0.13(m, 12H, Me$_2$Si), 0.87-0.97(m, 18H, *t*-Bu-Si), 2.64-3.34(m, 6.5H, CH$_2$), 5.98-6.73(m, 5.5H, CH).
8. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.19(s, 18H, Me$_3$Si), 2.44(br.s, 2H, CH$_2$), 2.95(br.s, 2H, CH$_2$), 6.23(s, 4H, 1,3,6,8-H), 6.66(s, 2H, 9,10-H); ^{13}C NMR(75.47MHz, CDCl$_3$): δ = -1.48(Me$_3$Si), 28.81(CH$_2$), 129.65(C-1, C-3 or C-10), 135.05(C-1, C-3 or C-10), 136.67(C-2, C-3a or C-10a), 137.56(C-1, C-3 or C-10), 146.04(C-2, C-3a or C-10a), 150.27(C-2, C-3a or C-10a); UV(n-hexane): λ_{max}(lgϵ) = 331 nm(4.16)(sh), 349(4.44)(sh), 365(4.59), 385(3.52), 470(2.65)(sh).
9. ^{1}H NMR (300MHz, CDCl$_3$): δ = 0.00(s, 18H, Me$_3$Si), 2.48(d, J=11.0Hz, 4H, CH$_2$), 2.86(d, J=11.0Hz, 4H, CH$_2$), 3.01(s, 2H, 6,13-H), 6.05(s, 4H, 5,7,12,14-H); ^{13}C NMR (75.47MHz, CDCl$_3$): δ = -1.98(Me$_3$Si), 29.96(CH$_2$), 47.92(C-6,13), 129.59(C-5,7,12,14), 147.07(C-1,4,8,11); UV(n-hexane): λ_{max}(lgϵ) = 240(3.72)(sh), 248(3.69)(sh).
10. ^{1}H NMR (300MHz, CDCl$_3$): δ = -0.03(s, 18H, Me$_3$Si), 2.65(br.s, 8H, CH$_2$), 3.05(s, 2H, 6,13-H), 6.07(s, 4H, 5,7,12,14-H); ^{13}C NMR (75.47MHz, CDCl$_3$): δ = -1.77(Me$_3$Si), 30.37(CH$_2$), 47.78 (C-6,13), 129.46(C-5,7,12,14); 147.72(C-1,4,8,11); UV(n-hexane): λ_{max}(lgϵ) = 239nm(3.78)(sh), 246(3.74)(sh).
11. ^{1}H NMR (300MHz, CDCl$_3$): δ = 2.64(s, 8H, 2,3,9,10-CH$_2$), 2.81(s, 4H, 6,13-CH$_2$), 6.01(t,J=1.5Hz, 4H, 5,7,12,14-H); ^{13}C NMR (75.47MHz, CDCl$_3$): δ = 28.86(C-2,3,9,10), 38.79(C-6,13), 128.49 (C-5,7,12,14), 148.60(C-1,4,8,11); UV(n-hexane): λ_{max} = 255.
12. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.15(br.s, 8H, 2,3,9,10-CH$_2$), 5.44(d,J= 2.9Hz, 4H, 5,7,12,14-H), 5.53(br.s, 2H, 6,13-H); ^{13}C NMR (75.47MHz, CDCl$_3$): δ = 42.26(CH$_2$), 101.13(C-6,13), 104.79 (C-5, 7,12,14), 118.09(C-1,4,8,11).
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14. ^{1}H NMR (300MHz, CDCl$_3$): δ = 2.09(s, 12H, Me), 2.68(s, 8H, CH$_2$), 6.17(s, 4H, CH); ^{13}C NMR (75.47MHz, CDCl$_3$): δ = 22.54(CH$_2$), 29.60(Me), 117.68(CH), 140.11(C$_{quat.}$), 144.83(C$_{quat.}$), 147.83(C$_{quat.}$); UV(n-hexane): λ_{max}(lgϵ) = 274nm(4.62)(sh), 281(4.67), 290(4.58)(sh), 329(2.93), 340(2.94), 357(2.92)(sh).
15. ^{1}H NMR (300MHz, CDCl$_3$); δ = 2.81(m, 8H, 2,3,9,10-CH$_2$), 3.15(s, 12H, Me); 6.04(d, J= 2.0Hz, 2H, 5,14-H or 7,12-H), 6.26(d, J= 2.0Hz, 2H, 5,14-H or 7,12-H), 6.82(s, 2H, CH$_{exocycl.}$); ^{13}C NMR (75.47MHz, CDCl$_3$): δ = 30.92(CH$_2$), 31.13(CH$_2$), 31.79(CH$_2$), 31.99(CH$_2$), 43.14(Me), 112.65(C-5, 7,12 or C-14), 112.68(C-5,7,12 or C-14), 115.04(C$_{quat.}$), 122.53(C-5,7,12 or C-14), 122.57(C-5,7,12 or C-14), 128.40(C$_{quat.}$), 138.40(C$_{quat.}$), 138.50(C$_{quat.}$), 144.44(C$_{quat.}$), 144.52(C$_{quat.}$), 145.39(C$_{exocycl.}$); UV(n-hexane): λ_{max} = 331nm(sh), 339.

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