

Facile Synthesis of an Unsaturated Spiro Germane by Hydroalumination and Intramolecular 1,1-Carbalumination[†]

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Treatment of the tetraethynylgermanium compound $Ge(C \equiv CC_6H_5)_4 4$ with 2 equiv of H-Al-[CH(SiMe_3)_2]_2 yielded the addition product $Ge(C \equiv CC_6H_5)_2[C\{AIR_2\} = C(H)C_6H_5]_2$ (5, R = CH-(SiMe_3)_2) by reduction of two of its C = C triple bonds. Heating of 5 to 260 °C for 10 min gave a unique rearrangement reaction which via intramolecular 1,1-carbalumination afforded the spiro germane 6 (a 3,7-bis[1-phenylmeth-(Z)-ylidene]-4-germaspiro[3,3]hepta-1,5-diene derivative). The molecular structure of 6 comprises two unsaturated 1-germacyclobut-2-ene heterocycles with a joint germanium atom and two exocyclic C=C double bonds.

Introduction

Hydroalumination¹ and hydrogallation reactions are powerful methods for the reduction of unsaturated organic compounds. Furthermore, they are suitable to generate a broad variety of unusual oligoaluminum or -gallium compounds when oligoalkynes were employed as starting materials.² Different reaction courses occurred, depending on the substituents attached to the C=C triple bonds. Alkynylaluminum or -gallium compounds gave carbaalane clusters or heteroadamantane cages by the release of the corresponding trialkylelement derivatives.³ Similar condensation reactions yielded cyclophane-type molecules by the dialkylaluminum or -gallium hydrides.⁴ Relatively stable addition products have been obtained by the corresponding reactions of ((trimethylsilyl)ethynyl)benzenes.⁵ In only a few of the latter reactions release of trialkylelement compounds took place, which as a particularly important class of compounds yielded molecular capsules.^{5,6} Di-*tert*-butylbutadiyne afforded unique carbocationic species by C–H bond activation and chelating coordination of hydride anions.⁷ Recently we started investigations into the hydroalumination of phosphorus-, silicon-, or germanium-centered oligoalkynes.^{8,9} The partially reduced compounds show a remarkable activation of the P–C, Si–C, or Ge–C bonds by intramolecular interactions of the coordinatively unsaturated aluminum atoms with the α -carbon atoms of remaining ethynyl

treatment of bis- or tris(tert-butylethynyl)benzenes with

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Figure 1. Molecular structure of 5. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms (with the exception of the vinylic hydrogen atoms) and methyl groups of SiMe₃ substituents are omitted. Important bond lengths (A) and angles (deg) [values of the second molecule in brackets]: Ge(1)-C(11) = 1.949(2) [1.958(2)], Ge(1) - C(21) = 1.952(2) [1.952(2)],Ge(1)-C(31) = 1.929(2) [1.919(2)], Ge(1)-C(41) = 1.921(2)[1.919(2)], C(11)-C(12) = 1.351(2) [1.348(3)], C(21)-C(22) =1.347(3) [1.351(3)], C(31)-C(32) = 1.203(3) [1.207(3)], C(41)-C(42) = 1.203(3) [1.205(3)], Al(11) - C(11) = 1.966(2) [1.976(2)],Al(12)-C(21) = 1.978(2) [1.973(2)]; C(11)-Ge(1)-C(21) =127.31(8) [127.77(8)], C(31)-Ge(1)-C(41) = 106.31(8) [104.15-(9)], Ge(1)-C(11)-Al(11) = 122.67(9) [125.1(1)], Ge(1)-C(21)-Al(12) = 126.1(1) [123.4(1)], Ge(1)-C(31)-C(32) = 170.4(2)[172.6(2)], C(31)-C(32)-C(33) = 176.7(2) [176.8(2)], Ge(1)-C(41)-C(42)=164.3(2)[173.4(2)], C(41)-C(42)-C(43)=176.5(2)[177.1(2)].



moieties (1; Scheme 1). In the case of the phosphorus compounds these interactions resulted in the spontaneous elimination of dialkylethynylaluminum and the formation of novel mono- or bicyclic AlP_2C_2 (2) or AlP_2C_4 ring systems (3).⁸ As reported in this article, we observed another type of secondary reaction when we treated a tetraethynyl-germanium compound with 2 equiv of a sterically shielded

dialkylaluminum hydride. Similar results have been obtained with boron compounds.¹⁰

Results and Discussion

Reaction of Tetra(phenylethynyl)germane with H-Al[CH-(SiMe₃)₂]₂. Treatment of 2 equiv of the sterically encumbered dialkylaluminum hydride H-Al[CH(SiMe₃)₂]₂ with a solution of tetrakis(phenylethynyl)germane (4) at room temperature led to the complete consumption of the starting compounds in less than 4 h (eq 1). Colorless crystals of compound 5 were isolated from these reaction mixtures after crystallization from cyclopentane in 86% yield. A crystal structure determination (Figure 1) revealed the expected product of the addition of Al−H bonds to two of the C=C triple bonds of 4. Despite the bulkiness of the bis(trimethylsilyl)methyl groups the aluminum atoms attacked selectively the α -carbon atoms of the ethynyl groups which are attached to the germanium atoms and bear a partial negative charge. Aluminum and hydrogen atoms occupy cis positions at the resulting C=C double bonds, which reflect the initial step of these addition processes. Cis/trans isomerization to afford the thermodynamically favored trans product is prevented in this case by steric shielding.⁵ The lengths of the C=C double bonds (1.349 Å on average) correspond to standard values.¹¹ The germanium atom has a distorted-tetrahedral environment with a relatively large angle between the alkenyl carbon atoms (127.5°) which may be caused by a strong steric repulsion between the bulky dialkylaluminum substituents. The different Ge-C bond lengths correlate to the different hybridization of the carbon atoms (Ge–C(sp²) = 1.953 Å; Ge–C(sp) = 1.920 Å). Two C-C triple bonds remained intact and possess the expected lengths of 1.205 Å on average.



The NMR data are in accordance with the molecular structure in the solid state. We observed the expected resonances for the carbon atoms of the C=C double bonds

 $(\delta 160.7 \text{ and } 151.8 \text{ (A1C)})$ and C=C triple bonds $(\delta 109.3 \text{ and }$ 96.9 (GeC)) in the ¹³C NMR spectrum. In the ¹H NMR spectrum the vinylic hydrogen atoms gave a singlet at δ 7.89 in the normal range.⁵ A further two singlets were observed for the trimethylsilyl groups and the AlCH protons. The latter exhibit an unusual chemical shift of δ 0.53 compared to the expected value of about $\delta - 0.3^{12}$ (see for comparison compound 6 below). In the solid-state structure these hydrogen atoms are almost ideally in the nodal plane of the C=C double bonds and their chemical shift may be influenced by this particular position. The dihedral angles C-Al-C=C are 14.5° on average and indicate an almost coplanar arrangement of the C=C bonds and the AlC₃ planes and hence a parallel orientation of the C=C π orbitals and the empty p orbitals of the aluminum atoms. The dihedral angles C-Al-C-H, including the C-H groups of the CH(SiMe₃)₂ substituents and the α -carbon atoms of the C=C double bonds, are close to the ideal value of 0° (4.8° on average). A similar correlation between molecular conformation and chemical shift of Al-C-H hydrogen atoms has previously been observed in a few bis(trimethylsilyl)methylaluminum compounds.¹³ These NMR data may indicate that the molecular conformation of 5 in the solid state predominates also in solution.

Thermal Rearrangement of 5 and Formation of the Spiro Compound 6. Compound 5 decomposed at 215 °C to give a red, highly viscous liquid. We conducted this experiment on a preparative scale and heated compound 5 without a solvent to 260 °C for 10 min (eq 1). Dissolution of the product in cyclopentane and slow evaporation of the solvent at room temperature yielded colorless crystals of 6 in 81% yield. Crystal structure determination (Figure 2) showed that a remarkable rearrangement reaction had taken place. A spiro compound was formed in which a joint germanium atom is part of two electronically unsaturated germacyclobutene heterocycles. These planar four-membered rings (maximum deviation of an atom 0.036 Å for C31) have an almost ideally perpendicular arrangement with an angle between the normals of their planes of 87°. One carbon atom of the endocyclic C=C double bonds is bonded to a phenyl group; the second one bears the dialkylaluminum group with a coordinatively unsaturated aluminum atom. The third carbon atom of the GeC₃ rings is part of an exocyclic C=C double bond. The germanium atom has a strongly distorted tetrahedral environment with acute endocyclic C-Ge-C angles of 70.4° on average. The exocyclic C=C double bonds have normal lengths of 1.341 Å on average, while the endocyclic ones are slightly lengthened to 1.369 Å. The Al-C distances to the alkenyl carbon atoms (1.995 Å) are slightly lengthened compared to the corresponding bond lengths in the starting compound 5. This lengthening may indicate some steric stress in the molecule. The formation of 6 may be described by the insertion of the α -carbon atoms of the C=C triple bonds of 5 into the Al-C bonds of the aluminum-alkenyl units (1,1-carbalumination). Hence, a Ge-C bond has to be



Figure 2. Molecular structure of **6**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms (with the exception of the vinylic hydrogen atoms) and methyl groups of SiMe₃ substituents are omitted. Important bond lengths (Å) and angles (deg) [values of the second molecule in brackets]: Ge(1)–C(11) = 1.975(4) [1.977(4)], Ge(1)–C(21) = 1.981(4) [1.976(4)], Ge(1)–C(22) = 1.974(4) [1.966(4)], Ge(1)–C(42) = 1.971(4) [1.972(4)], C(11)–C(12) = 1.348(6) [1.335(6)], C(11)–C(31) = 1.488(6) [1.492(6)], C(31)–C(32) = 1.368(6) [1.374(6)], C(21)–C(22) = 1.343(6) [1.338(6)], C(21)–C(41) = 1.484(6) [1.491(6)], C(41)–C(42) = 1.365(6) [1.367(6)], Al(11)–C(31) = 2.001(4) [1.985(4)], Al(12)–C(41) = 1.994(4) [1.998(4)]; C(11)–Ge(1)–C(32) = 70.2(2) [70.7(2)], C(21)–Ge(1)–C(42) = 70.5(2) [70.2(2)], C(11)–C(31)–C(32) = 105.1(4) [105.4(4)], C(21)–C(41)–C(42) = 106.4(4) [105.2(4)].

broken, and a new bond has been formed between germanium and the original β -carbon atom of the alkynyl group. This transformation may be considered as a special case of the well-known carbalumination reactions¹⁴ which, however, usually proceed via an 1,2-addition of the Al–C bond to the unsaturated organic system. In contrast, the corresponding 1,1-carbaboration is quite common¹⁰ and leads to the formation of unsaturated heterocyclic compounds, including spiro silanes similar to **6**.¹⁵ The reaction mechanism based on quantum chemical calculations is discussed in detail below. Some spiro germanes with a germanium atom in the bridging position are reported in the literature, but they do not contain four-membered unsaturated heterocycles.^{16,17}

Resonances of two different C=C double bonds were observed in the ¹³C NMR spectrum (δ 158.4 and 132.4;

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 δ 181.5 and 177.0). The signals at lower field belong to the endocyclic C=C bond. The vinylic hydrogen atoms resonate at δ 7.43 in the ¹H NMR spectrum. The hydrogen atoms of the AlCH groups have a chemical shift of δ -0.24, which in contrast to the corresponding resonance of compound 5 is in the range normally observed for bis(trimethylsilyl)methylaluminum compounds with tricoordinated aluminum atoms.11 Probably due to steric interactions, the endocyclic C=C bond and the AlC_3 plane are not coplanar as in 5 but are almost perpendicularly arranged with dihedral angles C-Al-C=C (including the central carbon atom of the CH-(SiMe₃)₂ substituents) of about 68°. Hence, in contrast to 5 the C-H bonds of the AlCH groups are not in the nodal planes of the π orbital of the C=C bond. Molecular symmetry gives rise to chemically different trimethylsilyl groups, and a temperature-independent splitting of the correspond-ing resonances into two singlets in the ¹H, ¹³C, and ²⁹Si NMR spectra is observed.

Quantum Chemical Calculations and Rearrangement Mechanism. Quantum chemical calculations using the Gaussian 09 suite of programs¹⁸ have been performed on the simplified model system 7, in which the germanium atom is bonded to two methyl groups and alkynyl and alkenyl substituents. The rearrangement reaction of 7 to give 8 proceeds synchronously via the transition structure $TS7 \rightarrow 8$ shown in Figure 3. The calculations for the sterically relatively poorly shielded model compound result in a significant direct interaction between the carbon atom C(2) and Al(5) (Al(5)-C(2) = 2.60 Å) in the ground state of the molecule. This interaction is favored by the relatively high negative charge at C(2) (NBO: -0.49; Al, +1.96). In the transition state the Al(5)-C(2) distance is shortened to 1.93 Å and corresponds to a normal Al-C bond. Simultaneously the Ge(3)-C(2) distance increases from 1.98 to 2.58 Å, and a new bond is formed between Ge(3) and the carbon atom C(1) (2.00 Å), which represents the β -carbon atom of the intact ethynyl moiety of the starting compound 7. A transannular approach of the carbon atoms C(2) and C(4) (2.19 Å) may reflect the first step of the C-C bond formation to give the GeC₃ heterocycle $(1.48 \operatorname{A in} 8)$. The Al-C bond to the vinylic carbon atom C(4)



Figure 3. Calculated structures and relative energies (kcal/mol) for the conversion of the model compound 7 to 8.

is weakened (2.00 to 2.21 Å). It is completely opened in the final product 8. The C–C bond length C(1)-C(2) increases continuously from 1.22 Å for the triple bond in 7 to 1.31 Å (transition state) and 1.38 Å in 8, which is slightly lengthened compared to the standard value of a C=C double bond. The bond lengths calculated for the germacyclobutene heterocycle of 8 are in excellent agreement with the experimental data of the spiro compound 6 (Figure 2). The NBO charges calculated for 8 are -0.36 (C(1)), -0.62 (C(2)), -0.34 (C(4)), +1.41 (Ge(3)), and +1.97 (Al(5)). The activation barrier is calculated to be 34.9 kcal/mol, which is in accordance with the relatively drastic reaction conditions (260 °C) required for the formation of 6. The complete reaction is slightly exothermic (-2.8 kcal/mol). The bond forming process mainly proceeds in the HOMO-1 and HOMO-2 (see Supporting Information). A dissociation of the starting compound 7 into dimethyl(2-phenylethenylidene)germane and di-tert-butylphenylethynylaluminum and subsequent cycloaddition seems to be unlikely, as this system is 57.4 kcal/mol higher in energy compared to 7.

Experimental Section

All procedures were carried out under purified argon. *n*-Pentane, *n*-hexane, and cyclopentane were dried over LiAlH₄, toluene, and diethyl ether over Na/benzophenone. The dialkyl-aluminum hydride R_2Al-H ($R = CH(SiMe_3)_2$) was obtained according to a literature procedure.¹⁹ Tetrakis(phenylethynyl)-germane was synthesized in high yield by a slight modification of a method described by Wrackmeyer.¹⁷ Germanium tetrachloride and phenylethyne were employed as purchased. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data. Only the most intensive masses of the mass spectra are given; the complete isotopic patterns are in accordance with the calculated ones.

Synthesis of Tetrakis(phenylethynyl)germane (4).¹⁷ A solution of *n*-butyllithium in *n*-hexane (1.6 M, 58.2 mL, 93.2 mmol) was added dropwise to a solution of phenylethyne (9.51 g, 10.2 mL, 93.2 mmol) in 100 mL of diethyl ether at -78 °C. After 2 h a solution of germanium tetrachloride (5.00 g, 2.7 mL, 23.3 mmol) in 50 mL of diethyl ether was added dropwise at the

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same temperature. Stirring was continued at -78 °C for 2 h. The solution was warmed to room temperature and stirred for a further 14 h. The mixture was treated with dilute HCl (10%, 100 mL) and additional diethyl ether (50 mL). The organic layer was separated, and the aqueous phase was extracted three times with 20 mL of diethyl ether. The combined organic layers were dried over MgSO4 and filtered. The solvent was removed under vacuum, and compound 4 was obtained as a colorless solid after crystallization from *n*-pentane at -30 °C. Yield: 7.65 g (69%). Mp (argon, sealed capillary): 186 °C. Anal. Calcd for C₃₂H₂₀Ge (477.2): C, 80.5; H, 4.2. Found: C, 80.1; H, 4.1. ¹H NMR (C₆D₆, 400 MHz): § 7.35 (8 H, m, o-H), 6.89 (4 H, m, p-H), 6.83 (8 H, m, *m*-H). ¹³C NMR (C₆D₆, 100 MHz): δ 132.7 (*o*-C), 129.4 (*p*-C), 128.4 (*m*-C), 122.3 (ipso-C), 105.8 (C≡CPh), 85.2 (C≡CPh). IR (KBr plates, paraffin, cm⁻¹): 2164 m (ν (C=C)); 2031 vw, 1954 vw, 1906 vw, 1884 vw, 1807 vw, 1701 vw, 1686 vw, 1595 vw (phenyl); 1456 vs, 1377 vs (paraffin); 1300 w, 1277 vw, 1240 vw, 1215 w, 1155 w, 1067 vw, 1051 vw, 1024 w, 966 vw, 916 w, 843 vw, 814 m, 754 s (ν (CC), δ (CH), δ (CC)); 723 s (paraffin); 687 m, 590 m, 532 s, 463 w (v(GeC)). MS (EI, 20 eV, 120 °C): m/z (%) 478 (92) [M]⁺, 404 (100), 276 (18) [Ge(CCPh)₂]⁺.

Synthesis of 5. A solution of 4 (0.203 g, 0.425 mmol) in 10 mL of toluene was added dropwise to a solution of bis[bis-(trimethylsilyl)methyl]aluminum hydride (0.296 g, 0.855 mmol) in 15 mL of toluene at room temperature. The colorless solution was stirred for 4 h. The solvent was removed under vacuum, and the residue was recrystallized from cyclopentane (+20 to -15 °C) to yield colorless crystals of 5. Yield: 0.421 g (86%). Mp (argon, sealed capillary): 215 °C dec (formation of 6). Anal. Calcd for C₆₀H₉₈Al₂Si₈Ge (1170.7): C, 61.6; H, 8.4. Found: C, 61.8; H 8.2. ¹H NMR (C₆D₆, 400 MHz): δ 7.89 (2 H, s, C=CHPh), 7.63 (4 H, m, o-H of alkynyl-Ph), 7.26 (4 H, m, o-H of alkenyl-Ph), 7.19 (4 H, m, m-H of alkenyl-Ph), 7.10 (2 H, m, p-H of alkenyl-Ph), 7.07 (4 H, m, m-H of alkynyl-Ph), 7.00 (2 H, m, p-H of alkynyl-Ph), 0.53 (4 H, s, CHSi₂), 0.31 (72 H, s, SiMe₃). ¹³C NMR (C₆D₆, 100 MHz): δ 160.7 (C=CHPh), 151.8 (C=CHPh), 140.6 (ipso-C of alkenyl-Ph), 132.6 (o-C of alkynyl-Ph), 129.1 (o-C of alkenyl-Ph), 128.9 (p-C of alkynyl-Ph), 128.5 (m-C of alkynyl-Ph), 128.2 (m-C of alkenyl-Ph), 128.1 (p-C of alkenyl-Ph), 124.3 (ipso-C of alkynyl-Ph), 109.3 (C=CPh), 96.9 (C=CPh), 10.1 (AlCHSi₂), 5.0 (SiMe₃). ²⁹Si NMR (C₆D₆, 79.5 MHz): δ -3.1. IR (KBr plates, paraffin, cm⁻¹): 2164 m, 2151 m (ν (C=C)); 1944 vw, 1802 vw, 1699 vw, 1597 w, 1576 vw, 1543 m (v(C=C), phenyl); 1466 vs, 1377 vs (paraffin); 1300 w, 1248 s (δ(CH₃)); 1215 m, $1155 \text{ w}, 1072 \text{ w} (\nu(\text{CC}), \delta(\text{CH}), \delta(\text{CC})); 1015 \text{ m} (\delta(\text{CHSi}_2)); 947 \text{ m},$ 927 m, 845 vs, 777 w, 754 m (ρ(CH₃(Si))); 723 m (paraffin); $689 \text{ m}, 671 \text{ m} (v_{as}(SiC)); 633 \text{ vw}, 614 \text{ vw}, 601 \text{ vw} (v_{s}(SiC)); 575 \text{ w},$ 532 m, 498 w, 470 w, 428 w (v(GeC), v(AlC)). MS (EI, 20 eV, 180 °C: $m/z 1170 (1) [M]^+$, $1155 (1) [M - CH_3]^+$, $1011 (3) [M - CH_3]^+$ $CH(SiMe_3)_2^{+}, 622 (43) [Ge(C = CPh)(CAlR_2 = CHPh)]^{+}$

Synthesis of 6. Neat compound 5 (0.305 g, 0.261 mmol) was melted and heated to 260 °C for 10 min. The product was cooled to room temperature and dissolved in cyclopentane. Slow evaporation of the solvent at room temperature afforded compound 6 as colorless crystals. Yield: 0.246 g (81%). Mp (argon, sealed capillary): color change to red occurred > 210 °C; sublimation of a colorless substance started > 260 °C before melting. Anal. Calcd for $C_{60}H_{98}GeAl_2Si_8$ (1170.7): C, 61.6; H, 8.4. Found: C, 62.0; H, 8.4. ¹H NMR (C_6D_6 , 400 MHz): δ 7.72 (4 H, m, *o*-H of C=C(H)-Ph), 7.47 (4 H, m, *o*-H of GeC-Ph), 7.43 (2 H, s, C=CHPh), 7.21 (4 H, m, *m*-H of C=C(H)-Ph), 7.14 (4 H, m, *m*-H of GeC-Ph), 6.97 (2 H, m, *p*-H of C=CHPh), 6.94 (2 H, m, *p*-H of GeC-Ph), 0.33 and 0.31 (each 36 H, s, SiMe₃), -0.24

(4 H, s, AlCHSi₂). ¹³C NMR (C₆D₆, 100 MHz): δ 181.5 (GeC₃ ring, C-Al), 177.0 (GeC₃ ring, C-Ph), 158.4 (GeC₃ ring, exceyclic C=C), 140.9 (ipso-C of GeC-Ph), 139.0 (ipso-C of C=C(H)Ph), 132.4 (C=CHPh), 129.4 (*m*-C of C=C(H)Ph), 129.2 (*m*-C of GeC-Ph), 128.3 (*p*-C of GeC-Ph), 127.7 (*m*-C of C=C(H)Ph), 127.4 (*o*-C of GeC-Ph), 126.3 (*o*-C of C=C(H)Ph), 11.8 (AlCSi₂), 4.7 and 4.6 (SiMe₃). ²⁹Si NMR (C₆D₆, 79.5 MHz): δ –2.44 and –2.39. IR (KBr plates, Nujol, cm⁻¹): 1951 vw, 1934 vw, 1595 m, 1574 w, 1526 vw, 1493 m (ν (C=C), phenyl); 1458 vs, 1377 vs (paraffin); 1248 vs (δ (CH₃)); 1175 vw, 1153 w, 1051 s (ν (CC), δ (CH), δ (CC)); 1012 s (δ (CHSi₂)); 930 m, 914 w, 843 vs, 779 m, 750 s (ρ (CH₃(Si))); 723 w (paraffin); 689 s, 673 m (ν_{as} (SiC)); 633 w, 613 w (ν_{s} (SiC)); 565 m, 550 w, 505 w, 465 w (ν (GeC), ν (AlC)).

Crystal Structure Determinations of Compounds 5 and 6. Single crystals were obtained by crystallization from *n*-hexane (5, +20 to -15 °C) or by slow evaporation of a solution in *n*hexane at room temperature (6). The crystallographic data were collected with a Bruker APEX diffractometer. The structures were solved by direct methods and refined with the program SHELXL- 97^{20} by a full-matrix least-squares method based on F^2 . Both compounds crystallize in the centrosymmetric triclinic space group $P\overline{1}$ with two independent molecules in the asymmetric unit. A trimethylsilyl group (Si71) of compound 5 showed disorder; the atoms of the methyl groups were refined on split positions (0.61: 0.39). The crystals of 6 enclosed one *n*-hexane molecule in the unit cell; it is located on a center of symmetry. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-774576 (5) and CCDC-774577 (6.0.25C₆H₁₄).

Quantum Chemical Calculations.¹⁸ The B3LYP functional with the 6-311G(d,p) basis set was used to compute the geometries and the normal mode vibration frequencies of the structures. For single-point energy calculations on DFT-optimized geometries the SCS-MP2 method was applied.²¹ All energies discussed are 0 K energies including zero-point corrections. The character of the stationary points was verified on the basis of frequency analyses. The vibration related to the imaginary frequency of the transition structure corresponds to the nuclear motion along the reaction coordinate under study. An intrinsic reaction coordinate (IRC) calculation was performed in order to unambiguously connect the transition structure with the reactant and the product. NBO charges were determined using the Gaussian 09 program.²²

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Supporting Information Available: CIF files giving the crystal data for compounds 5 and $6 \cdot 0.25C_6H_{14}$, a table of crystal data and structure refinement details, and tables and figures giving optimized geometries and MO plots of the calculated structures. This material is available free of charge via the Internet at http:// pubs.acs.org.

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