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[3] Heptane (5 mL) and **1** (59.6 mg, 0.083 mmol) were added to a 50-mL glass autoclave. The reaction mixture was heated at 170 °C for 154 h, during which time the solution changed from reddish brown to purplish brown. Removal of the solvent under reduced pressure afforded crude product **2c** as a brown solid (ca. 70% purity based on ^{1}H NMR). The solid was dissolved in toluene and the product purified by column chromatography on neutral alumina. Removal of solvent under reduced pressure afforded 45.3 mg of **2c** as a brown solid (68% yield).

[4] **2b**: ^{1}H NMR (400 MHz, C_6D_6, 23 °C, TMS): $\delta = 4.35$ (d, $J = 4.4$ Hz, 1H; C1-H), 4.30 (dd, $J = 4.4$, 1.6 Hz, 1H; C2-H), 3.88 (brs, $w_{1/2} = 3.3$ Hz, 1H; C3-H), 2.23 (s, 15H; C_5Me_5), 1.85 (q, $J = 7.2$ Hz, 2H; C5-H), 1.82 (s, 15H; C_5Me_5), 1.65 (s, 15H; C_5Me_5), 0.71 (t, $J = 7.2$ Hz, 3H; C6-H), -10.50 (s, 1H; Ru-H); ^{13}C NMR (100 MHz, C_6D_6, 23 °C, TMS): $\delta =$ 144.5 (s, C4), 118.0 (d, J(C,H) = 156 Hz; C1), 90.6 (s; C_5Me_5), 83.0 (s; C_5Me_5), 82.7 (s; C_5Me_5), 66.3 (d, J(C,H) = 178 Hz; C2), 62.7 (d, J(C,H) = 174 Hz; C2), 36.9 (t, J(C,H) = 125 Hz; C5), 19.2 (q, J(C,H) = 128 Hz; C6), 13.3 (q, J(C,H) = 125 Hz; C_5Me_5), 12.2 (q, J(C,H) = 125 Hz; C_5Me_5), 11.7 (q, J(C,H) = 126 Hz; C_5Me_5).

[5] X-ray structural determination of **2b:** Data were collected at 23 °C on a Rigaku AFC5R diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation (ω scan $2\theta_{max} = 50.0°$). Laue symmetry revealed a monoclinic crystal system with the dimensions: $a = 38.477(8)$, $b = 8.635(2)$, $c = 20.712(4)$ Å, $\beta = 94.86(2)°$, and $V = 6856(2)$ Å^3. $\rho_{calcd} = 1.53$ g cm^{-3}, $Z = 8$, $M_r = 790.03$; space group $P2_1/n$ (No. 14). Of the 13326 reflections that were collected, 12946 were unique ($R_{int} = 0.048$). $\mu = 13.3$ cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. The structure was solved by the Patterson method (DIRDIF 94 PATTY) and non-hydrogen atoms other than disordered C_5Me_5 groups were refined on F^2 using the SHELXL-97 program systems. The unit cell contains two molecules and one of the C_5Me_5 groups in each molecule is thermally disordered (occupancy: 51.14:48.86 and 51.23:48.77, respectively). Hydrogen atoms H1–3 and H39–41 were located by sequential difference Fourier synthesis and the remaining hydrogen atoms were included in geometric positions. All hydrogen atoms and disordered carbon atoms of C_5Me_5 groups were refined with isotropic thermal parameters. The final structure for **2b** was refined to $R = 0.0545$ for 8447 observed reflections ($F_o > 4\sigma(F_o)$) and $wR_2 = 0.1615$ for 12006 data and 590 parameters. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118781. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[6] Thus far, a large number of *closo*-metallacyclopentadiene complexes have been known. For example, see a) E. Sappa, A. M. M. Landfredi, A. Tiripicchio, *Inorg. Chim. Acta* **1980**, *42*, 255; b) E. Rosenberg, S. Aime, L. Milone, E. Sappa, A. Tiripicchio, A. M. M. Lanfredi, *J. Chem. Soc. Dalton Trans.* **1981**, 2023; c) D. Nuel, F. Dahan, R. Mathieu, *J. Am. Chem. Soc.* **1985**, *107*, 1658; d) E. Cabrera, J. C. Daran, Y. Jeannin, O. Kristiansson, *J. Organomet. Chem.* **1986**, *310*, 367; e) J. C. Daran, E. Gilbert, M. Gouygou, S. Halut, B. Heim, Y. Jeannin, *J. Cluster Sci.* **1994**, *5*, 373; f) D. Lentz, H. Michael-Schultz, M. Reuter, *Organometallics* **1992**, *11*, 2916; g) B. Heim, J. C. Daran, Y. Jeannin, B. Eber, G. Huttner, W. Imhof, *J. Organomet. Chem.* **1992**, *441*, 81; h) G. Gervasio, R. Giordano, E. Sappa, M. Costa, G. Predieri, A. Tiripicchio, *J. Cluster Sci.* **1993**, *4*, 33; i) M. V. Capparelli, Y. D. Sanctis, A. J. Arce, *Acta Crystallogr. Sect. C* **1995**, *51*, 1819; j) K. J. Adams, J. J. Barker, S. A. R. Knox, A. G. Orpen, *J. Chem. Soc. Dalton Trans.* **1996**, 975.

[7] The reaction of **1** with *n*-hexane was monitored as follows: A 50-mL autoclave was charged with **1** (111.5 mg, 0.156 mmol) and *n*-hexane (10 mL) and the reaction mixture heated at 170 °C for 12 h. The reaction mixture was then cooled down to room temperature. After a portion (0.5 mL) of the reaction mixture had been evaporated, C_6D_6 (0.5 mL) was added to the residue and the ^{1}H NMR spectrum recorded. The rest of the reaction mixture was again heated at 170 °C. The ^{1}H NMR spectra of the reaction mixture were measured at intervals of 12 h.

[8] An equilibrium mixture of regioisomers **3**-*in* and **3**-*out* is obtained quantitatively in the reaction of **1** with 1-hexyne. **3**-*in*: ^{1}H NMR (400 MHz, [D$_8$]THF, -80 °C, TMS): $\delta = 10.22$ (s, 1H; Ru-CH), 1.854 (s, 30H; C_5Me_5), 1.845 (s, 15H; C_5Me_5), 1.38 (m, 2H; CH_2), 1.00 (m, 2H; CH_2), 0.74 (t, $J = 8.0$ Hz, 3H; CH_3), 0.40 (m, 2H; CH_2), -6.95 (brs, $w_{1/2} = 11.0$ Hz, 2H; Ru-H), -25.03 (t, $J = 3.2$ Hz, 1H; Ru-H); ^{13}C NMR (100 MHz, [D$_8$]THF, -80 °C, TMS): $\delta = 180.7$ (d, J(C, H) = 177 Hz; Ru-CH), 90.7 (s; C_5Me_5), 85.4 (s; C_5Me_5), 67.2 (s; Ru-C), 37.8 (t, J(C,H) = 125 Hz; CH_2), 34.9 (t, J(C,H) = 125 Hz; CH_2), 25.1 (t, J(C,H) = 124 Hz; CH_2), 16.2 (q, J(C,H) = 128 Hz; CH_3), 13.7 (q, J(C,H) = 125 Hz; C_5Me_5), 13.6 (q, J(C,H) = 125 Hz; C_5Me_5); **3**-*out*: ^{1}H NMR (400 MHz, [D$_8$]THF, -80 °C, TMS): $\delta = 3.84$ (m, 2H; CH_2), 1.89 (s, 15H; C_5Me_5), 1.77 (s, 30H; C_5Me_5), 1.63 (m, 2H; CH_2), 1.62 (m, 2H; CH_2), 1.00 (t, $J = 6.2$ Hz, 3H; CH_3), -0.38 (brs, $w_{1/2} = 7.0$ Hz, 1H; Ru-CH), -11.78 (d, $J = 4.4$ Hz, 2H; Ru-H), -25.96 (dt, $J = 4.4$, 3.6 Hz, 1H; Ru-H); ^{13}C NMR (100 MHz, [D$_8$]THF, -80 °C, TMS): $\delta = 188.7$ (s, Ru-C), 91.9 (s; C_5Me_5), 85.8 (s; C_5Me_5), 64.6 (d, J(C, H) = 156 Hz; Ru-CH), 43.6 (t, J(C,H) = 125 Hz; CH_2), 37.0 (t, J(C,H) = 122 Hz; CH_2), 25.8 (CH_2; confirmed by ^{13}C-^{1}H HSC and ^{1}H-^{1}H COSY spectra), 16.2 (q, J(C,H) = 128 Hz; CH_3), 14.7 (q, J(C,H) = 125 Hz; C_5Me_5), 13.0 (q, J(C,H) = 126 Hz; C_5Me_5).

Two New Carbaalanes: Compounds with an Al_7C_5 and a $[B_{11}H_{11}]^{2-}$ Analogous Al_7C_4 Cluster[**]

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Some polyhedral borane or carbaborane cluster compounds are known from literature, which contain single aluminium atoms located on positions of high connectivity.[1]

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However, the first synthesis of a carbaborane analogous carbaalane [$(AlMe)_8(CCH_2Ph)_5H$] (**1**), which has a cluster exclusively formed by aluminum and carbon atoms, was achieved only recently in our group by the treatment of $Me_2Al\text{-}C{\equiv}C\text{-}Ph$ with Me_2AlH.[2] According to the Wade rules,[3] **1** may be described as an *arachno* compound, but its molecular core comprises more atoms than usually observed for the corresponding boron compounds. At present, we are much interested in synthesizing further derivatives with different cluster sizes and structures by the systematic variation of the steric demand of their substituents, and we wish to report here on the results obtained with ethyl groups.

Similar to the synthesis of **1**, we dissolved diethylaluminum phenylethinide in a slight excess of diethylaluminum hydride without a further solvent and heated the mixture to 50 °C for 12 h. Triethylalane was formed [Eq. (a)], which was distilled

$$9\ Et_2AlH + 5\ Et_2Al{-}C{\equiv}C{-}Ph \longrightarrow \underset{\mathbf{2}}{(AlEt)_7(C{=}CHPh)_2(CCH_2Ph)_3H} + 7\ AlEt_3\ (+\ \mathbf{3}) \qquad \text{(a)}$$

off in vacuo at the same temperature. Although the residue contained compound **2** owing to the NMR spectroscopic characterization in a high concentration, the crystallization succeeded only with difficulty, and bright orange crystals of **2** were isolated only in a moderate yield of 36 %. The crystal structure determination of **2** (Figure 1)[4] verified the formation of a new carbaalane with a cluster comprising seven Al and five C atoms. Its structure may be derived from that of **1**, if one vertex of the Al_8 cube remains unoccupied. The cluster has three Al_4 faces, which are bridged by carbon-benzyl units similar as in **1**, and further three Al_3 triangles with an open edge, which are capped by the hydrogen atom H1 and two alkenylidene groups C=C(H)−Ph (C3, C3′), respectively. Thus, just one hydroalumination step with $EtAlH_2$ is missing to generate an ethyl compound analogous to **1**. Short Al−Al distances of 260.0 (Al1−Al2) and 256.9 pm (Al1−Al3) are observed to Al1, which is part of all three Al_4 faces, while larger separations occur in the C and H bridged Al_3 triangles (268.2 and 270.7 pm, respectively). All values are similar to Al−Al distances published for $(AlMe_3)_2$ (261 pm) showing a 3c-2e bond or for organoelement compounds having Al−Al single bonds ($R_2Al{-}AlR_2$; 265 to 266 pm).[5, 6] The Al−C separations in the cluster (200 to 215 pm) are lengthened compared to those observed to the terminal ethyl groups (196.2 pm). They strongly depend on the coordination sphere of the Al atoms. The C=C double bonds (136.0 pm) have such an orientation, that the π orbitals are perpendicular to the plane Al4-C3-Al5. They overlap partially with the open face of the cluster. Including the π-electrons, a total number of 16 electron pairs was calculated for the cluster, which has 12 vertices and for which a *hypho* configuration may thus be discussed. Indeed, the cluster of **2** can be derived from that of *closo*-$[B_{15}H_{15}]^{2-}$,[7] which owing to quantum chemical calculations adopts a structure with a tricapped hexagonal antiprism. In **2**, three vertices remain unoccupied. However, this hypothesis must be verified by quantum chemical calculations, which are in progress.

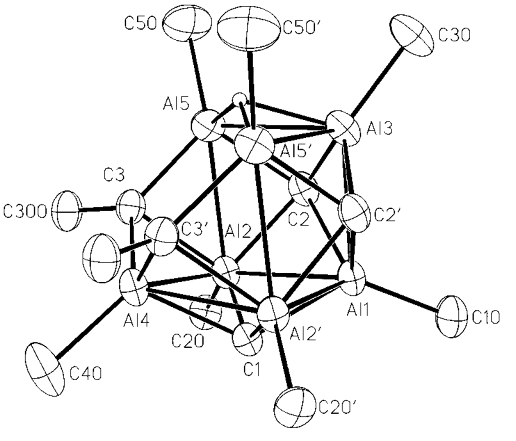

Figure 1. Molecular structure of **2**; the benzyl groups at C1, C2 and C3, the phenyl groups at C300 and the methyl groups of the ethyl substituents are omitted for clarity; bridging hydrogen atom H1 with arbitrary radius. Important bond lengths [pm]: Al1-Al2 260.0(1), Al1-Al3 256.9(2), Al2-Al4 268.5(1), Al2-Al5 267.8(1), Al3-Al5 270.7(1), Al3-H1 185(4), Al5-H1 198(1), Al1-C1 205.7(3), Al1-C2 213.9(3), Al2-C1 203.6(2), Al2-C2 206.1(3), Al2-C3 214.4(3), Al3-C2 202.7(3), Al4-C1 215.0(4), Al4-C3 204.2(3), Al5-C2 205.4(3), Al5-C3 200.3(3), Al1-C10 196.6(4), Al2-C20 195.9(3), Al3-C30 195.6(4), Al4-C40 198.2(5), Al5-C50 194.8(3), C3-C300 136.0(4).

The molecular structure of **2** comprises five chemical different types of ethyl groups, two kinds of nonequivalent benzyl substituents and the ethenylidene groups. Thus, very complicated NMR spectra resulted. Their interpretation showed, that similar as in **1** the C atoms of the cluster have an unusual chemical shift to low field [$\delta = 31.6$ (C1), 25.7 (C2) and 156.9 (alkene C atom C3)], while the α C atoms of the ethyl groups attached to aluminum resonate in the expected range of $\delta = +1$ on average. The hydrogen atoms of the alkenylidene groups are observed at $\delta = 9.33$.

Following the isolation of **2**, evaporation of the mother liquor and recrystallization of the residue from toluene, we obtained a further, yellow compound (**3**) in a low yield. **2** was transformed completely into compound **3**, when a solution in benzene was stored for several days at a temperature of 60 °C (estimated from NMR data: first-order reaction, $k \approx 4 \times 10^{-5}\,\text{sec}^{-1}$, $\Delta G \approx 110\,\text{kJ}\,\text{mol}^{-1}$). A faster rearrangement was achieved, when the rough product out of the synthesis of **2** was heated to 110 °C for one hour without a solvent [Eq. (b)]. **3** is isomeric to **2**, but quite another, remarkable molecular

$$\underset{\mathbf{2}}{(AlEt)_7(C{=}CHPh)_2(CCH_2Ph)_3H} \xrightarrow{\Delta} \underset{\mathbf{3}}{(AlEt)_7(CCH_2Ph)_4(C{\equiv}CPh)H} \qquad \text{(b)}$$

structure was observed possessing a cluster of seven Al and four C atoms (Figure 2).[4] The atoms of the cluster bear terminal ethyl and benzyl groups, respectively. One edge of the cluster (Al3-Al6) is bridged by a hydrogen atom, the opposite one (Al2-Al5) by an ethynide ligand; both bridging atoms are neighbored to Al7 at the top of the cluster, but very long distances (Al7-H1 226, Al7-C5 255.2 pm) indicate only weak interactions. A number of twelve electron pairs was calculated for the Al_7C_4 molecular center, which according to

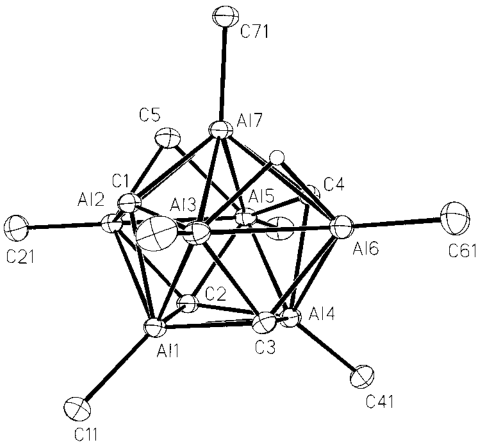

Figure 2. Molecular structure of **3**; the benzyl groups at C1 to C4 and the methyl groups of the ethyl substituents are omitted for clarity; only the first, anionic carbon atom of the ethynide group (C5) above the edge Al2-Al5 was drawn; bridging hydrogen atom H1 with artificial radius. Important bond lengths [pm]: Al1-Al2 259.42(8), Al1-Al3 258.77(8), Al1-Al4 258.65(8), Al2-Al5 267.47(8), Al2-Al7 292.12(9), Al3-Al6 261.23(9), Al3-Al7 281.75(8), Al4-Al5 258.13(8), Al4-Al6 258.91(8), Al5-Al7 290.00(8), Al6-Al7 285.91(8), Al3-H1 178(2), Al6-H1 180(2), Al1-C1 219.6(2), Al1-C2 207.0(2), Al1-C3 209.8(2), Al2-C1 203.5(2), Al2-C2 204.6(2), Al2-C5 211.8(2), Al3-C1 202.5(2), Al3-C3 206.1(2), Al4-C2 208.5(2), Al4-C3 207.2(2), Al4-C4 221.2(2), Al5-C2 206.8(2), Al5-C4 202.3(2), Al5-C5 210.3(2), Al6-C3 204.8(2), Al6-C4 202.6(2), Al7-C1 209.5(2), Al7-C4 209.0(2), Al1-C11 197.7(2), Al2-C21 196.5(2), Al3-C31 195.8(2), Al4-C41 197.5(2), Al5-C51 195.6(2), Al6-C61 195.5(2), Al7-C71 197.1(2).

the Wade rules give a *closo* configuration. Indeed, the arrangement of the atoms in the cluster corresponds to that of *closo*-$[B_{11}H_{11}]^{2-}$[8] with the very characteristic structural element of a six-membered ring in a boat conformation bridged by a high-connectivity atom (Al7 in **3**). Also, a nice similarity exists concerning the inner cluster atomic separations. With the exception of Al7, short distances (258.1 to 259.4 pm, 261.2 and 267.5 pm) are observed between the Al atoms similar to those of the other carbaalanes, of which the larger ones are detected for the bridged edges. Longer Al–Al distances of 281.8 to 292.1 pm result to the atom Al7 above the boat-shaped six-membered heterocycle, which in contrast to the remaining metal atoms has contact to four Al atoms. The Al–C distances are similar to those observed for the other cluster compounds **1** and **2**. In comparison with $[B_{11}H_{11}]^{2-}$, **3** has, however, a deviating connectivity of the C and Al atoms at the bottom of the cluster, which may be caused by the strongly differing atomic radii of carbon and aluminum. The chemical shifts of the cluster atoms in the very complicated NMR spectra are similar to those of compound **2**.

As reported here, two novel members (**2** and **3**) of the new class of carbaalanes have been synthesized and characterized. Owing to their structures and number of cluster electrons, the derivatives **1** and **3** can be attributed to the *arachno* and *closo* type compounds, respectively, and may thus be described as analogues of polyhedral boranes or carbaboranes. Only the classification of the structure of **2** remains doubtful, because of the questionable contribution of the π electrons to the bonding in the cluster. Thus, in a short time the carbaalanes have set up as a new class of compounds with a remarkable variety of structures.[9]

Experimental Section

n-Pentane and cyclopentane were dried over $LiAlH_4$. $Et_2Al{-}C{\equiv}C{-}Ph$ was synthesized according to the corresponding dimethyl compound;[2] it was isolated as highly viscous fluid, which could not be obtained in a crystalline form and decomposed upon an attempt of distillation. Therefore, it was used without further purification [^1H NMR (C_6D_6): $\delta = 1.46$ (t, CH_3), 0.59 (q, $AlCH_2$); ^{13}C (C_6D_6): $\delta = 120.1$ and 93.0 (C°C), 9.7 (CH_3), 3.2 ($AlCH_2$)].

2 and ***3***: A mixture of 4.04 g (5 mL, 46.9 mmol) Et_2AlH[10] and 2.90 g (15.6 mmol) $Et_2Al{-}C{\equiv}C{-}Ph$ without a further solvent was heated to 50 °C under argon for 12 h. All volatile components were distilled off at this temperature in vacuo. A higher temperature led to the complete rearrangement to compound **3**. The residue was dissolved in *n*-pentane. Orange-red, air-sensitive crystals of **2** precipitated upon cooling of the solution to −70 °C (1.02 g, 36 %). The mother liquor was evaporated. The residue was dissolved in toluene. Yellow, air-sensitive crystals of compound **3** were obtained after storing the solution at −30 °C for several weeks (0.255 g, 9 %). **3** was completely formed, if after the separation of the volatile components the rough product of the reaction was heated to 110 °C for 1 h. The product was recrystallized several times from *n*-pentane (yield 42 %). The NMR data were assigned on the basis of ^1H, ^{13}C, H,H-COSY, HMQC and HMBC NMR spectra. Only essential resonances are given here; the complete data are available as electronic background information. Characterization of **2**: Decomposition (argon, sealed capillary): 146 °C. ^1H NMR (500 MHz, $[D_8]$toluene, 275 K): $\delta = 9.33$ (s, 2H, C = CH300), 4.77 (s, 1H, AlH), 3.67 (s, 2H, CH_2 at C1), 3.58 and 3.45 (each 2H, d, $^2J_{HH} = -13.8$ Hz, CH_2 at C2, diastereotopic). ^{13}C NMR (125.8 MHz, $[D_8]$-toluene, 275 K): $\delta = 34.91$(CH_2 at C1), 31.55 (C1), 33.85 (CH_2 at C2), 25.71 (C2), 183.51 (CH at C3), 156.87 (C3), ethyl groups: 1.05 (Al1-C), 9.75 (C11), 2.44 (Al2-C), 8.86 (C21), Al3-Et and Al4-Et: −0.38 (Al-C), 10.36 (Me), −1.00 (Al-C), 9.82 (Me), 3.44 (Al5-C), 9.98 (C51). IR (paraffin, CsBr plates): $\tilde{\nu}$ [cm^{-1}] = 1945 vw, 1802 vw (Ph); 1647 (br) $\tilde{\nu}$AlH; 1598 w (Ph); 1578 w $\tilde{\nu}$C=C; 1506 m δCH; 1462 vs (paraffin); 1406 w δCH_3; 1377 vs (paraffin); 1343 m, 1294 w, 1226 vw, 1198 vw, 1154 w δCH, $\tilde{\nu}$CC; 1073 w, 1030 vw $\tilde{\nu}$CC; 985 m, 957 m, 921 m, 906 m, 832 m (Ph); 748 vs, 703 vs, 689 s, 655 vs, 616 s δPh, δAlH, $\tilde{\nu}$AlC; 556 m, 456 m, 434 m $\tilde{\nu}$AlC. UV/Vis (cyclopentane): λ_{max} [nm] (log ε): 250 (4.4, sh), 310 (4.7). M_r (in benzene by cryoscopy): found 878; calcd 907.0. Characterization of **3**: Decomposition (argon, sealed capillary): 262 °C. ^1H NMR (500 MHz, $[D_8]$toluene, 275 K): $\delta = 4.89$ (s, 1H, AlH), 3.68 and 3.63 (each 2H, d, $^2J_{HH} = -14.9$ Hz, CH_2 at C1 and C4, diastereotopic), 3.47 (s, 2H, CH_2 at C2), 3.34 (s, 2H, CH_2 at C3). ^{13}C NMR (125.8 MHz, $[D_8]$toluene, 275 K): $\delta = 118.89$ ($PhC{\equiv}CAl_2$), 86.95 ($PhC{\equiv}CAl_2$), 35.26 (CH_2 at C1 and C4), 34.76 (CH_2 at C2), 34.24 (CH_2 at C3), 19.57 (C1 and C4), 28.56 (C2), 20.78 (C3), Al1-Et and Al4-Et: 2.57 (Al-CH_2) and 9.91 (Me), Al2-Et and Al5-Et: 2.18 (Al-CH_2) and 10.08 (Me), Al3-Et and Al6-Et: −2.01 (Al-CH_2) and 10.19 (Me), Al7-Et: 0.76 (Al-CH_2) and 13.06 (Me). IR (paraffin, CsBr plates): $\tilde{\nu}$ [cm^{-1}] = 2044 m $\tilde{\nu}$C≡C, 1937 vw, 1800 vw, 1599 m, 1582 w (Ph); 1509 w, 1491 m δCH_3; 1460 vs (paraffin); 1403 m δCH_3; 1377 vs (paraffin); 1297 m, 1226 m, 1201 m (br), 1177 m $\tilde{\nu}$AlH, δCH, $\tilde{\nu}$CC; 1074 w, 1028 w $\tilde{\nu}$CC; 986 s, 955 m, 927 m, 897 m, 823 m (Ph); 790 m (br.) δAlH; 747 vs, 700 vs, 684 vs, 665 vs (br) δPh, $\tilde{\nu}$AlC; 554 m, 484 w, 455 w, 427 w $\tilde{\nu}$AlC. UV/Vis (cyclopentane): λ_{max} [nm] (log ε): 225 (4.0), 250 (4.1), 290 (4.1). M_r (in benzene by cryoscopy): found 887; calcd 907.0.

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[4] Crystal structure of **2**: Crystals from cyclopentane by slow concentration at room temperature over a period of some days; $C_{54}H_{69}Al_7$, orthorhombic, *P*nma; $a = 2028.45(11)$, $b = 1713.07(6)$, $c = 1490.23(6)$ pm, $V = 5178.4(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.163$ gcm^{-3}, crystal dimensions: $0.75 \times 0.46 \times 0.34$ mm, diffractometer Stoe IPDS, $Mo_{K\alpha}$ radiation, 193 K, measurement range: $4.2 < 2\Theta < 52.0°$, 168 exposures, $\Delta\varphi = 1.1°$, 5221 independent reflections, 3512 reflections $F > 4\sigma(F)$, $\mu = 0.175$ mm^{-1}, programs SHELXTL PLUS REL 4.1 and SHELXL-93, 307 parameters, $R1 = 0.052$ and $wR2$ (all data) = 0.156, max/min residual electron density: $0.77/-0.37 \times 10^{30}$ e m^{-3}. Crystal structure of **3**: Crystals from toluene; $C_{54}H_{69}Al_7$, triclinic, $P\bar{1}$, $a = 1082.39(7)$, $b = 1440.15(12)$, $c = 1648.2(2)$ pm, $\alpha = 80.516(11)$, $\beta = 89.883(11)$, $\gamma = 81.348(9)°$, $V = 2504.6(4)$ Å^3, $Z = 2$, $d_{calc} = 1.203$ gcm^{-3}, crystal dimensions: $0.80 \times 0.39 \times 0.26$ mm, diffractometer Stoe IPDS, $Mo_{K\alpha}$ radiation, 193 K, measurement range $4.2 < 2\Theta < 51.8°$, 282 exposures, $\Delta\varphi = 1.1°$, 9016 independent reflections, 6515 reflections $F > 4\sigma(F)$, $\mu = 0.181$ mm^{-1}, 561 parameters, $R1 = 0.035$ and $wR2$ (all data) = 0.107; max/min residual electron density: $0.30/-0.31 \times 10^{30}$ e m^{-3}. The positions of the hydrogen atoms H1 were obtained from a difference Fourier synthesis, they were refined isotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 127469 (**2**) and CCDC 127470 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Tandem Intermolecular–Intramolecular Carbolithiation: A Versatile Method for Synthesis of Cyclopentanes[**]

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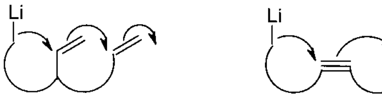
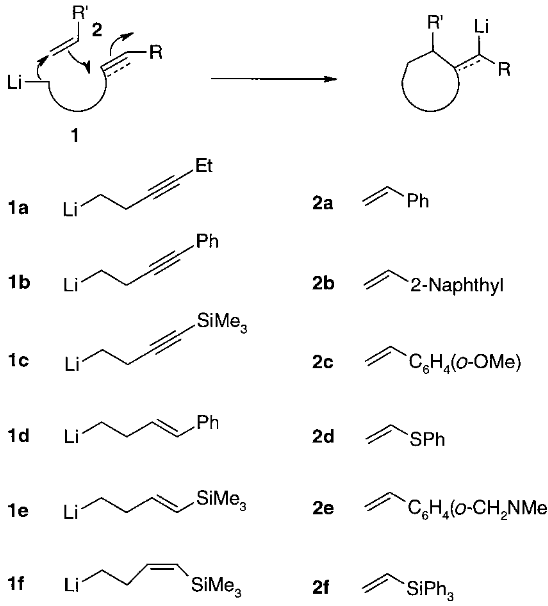
The carbolithiation of alkenes and alkynes is a particularly useful synthetic transformation in that the generation of a new carbon–carbon bond is accompanied by the formation of an organolithium species which can be elaborated directly or after transmetalation.[1–4] To date, this chemistry has been largely confined to alkenes and alkynes activated by conjugation to carbonyl and related electron-withdrawing groups, but within this sub-group a rich diversity of examples have been described. However, in recent years, the development of improved procedures for the generation of organolithium reagents[5] has meant that major advances have been made in the carbolithiation of unactivated alkenes and alkynes.[2–4] Intramolecular variants have attracted particular attention and a range of synthetically useful 4-, 5-, and 6-*exo* carbolithiation procedures have been reported.[2f–2n] In addition, the groups of Bailey and Krief have extended this research to develop tandem intramolecular carbolithiation procedures (Scheme 1).[3]



Scheme 1. The principle of tandem intramolecular carbolithiations.

Encouraged by our research in the intermolecular carbolithiation area[4] we designed a tandem intermolecular–intramolecular carbolithiation sequence (Scheme 2). This procedure employs organolithium reagents as difunctional, conjunctive reagents and represents a versatile anionic [3+2] approach to substituted cyclopentanes.[6] This convergent sequence is especially attractive as, in contrast to many tandem processes, the precursors are readily available. After the completion of our studies, we discovered that one isolated example of this procedure had been described: Krief and Barbeaux trapped a homoallylic lithium reagent with ethene, with the resulting organolithium intermediate undergoing cyclization followed by protonation to give a methylcyclopentane.[3b] Our plan was to establish a general and versatile method for the preparation of complex cyclopentanes with a high level of functionality in a stereocontrolled mannner from functionalized organolithium reagents and alkenes. Herein we report the successful realization of this plan.



Scheme 2. Tandem intermolecular–intramolecular carbolithiation.

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