Organometallic Chemistry

Synthesis and transformations of metallacycles
24.* Zr-Catalyzed cycloalumination of asymmetrical disubstituted acetylenes

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Cp_2ZrCl_2-Catalyzed cycloalumination of asymmetrical alkyl-, phenyl-, and allyl-substituted acetylenes under the action of Et_3Al was studied. The reactions afforded regioisomeric 2,3-disubstituted aluminacyclopent-2-enes whose yields and ratio depend on the nature of the substituents in the starting acetylenes.

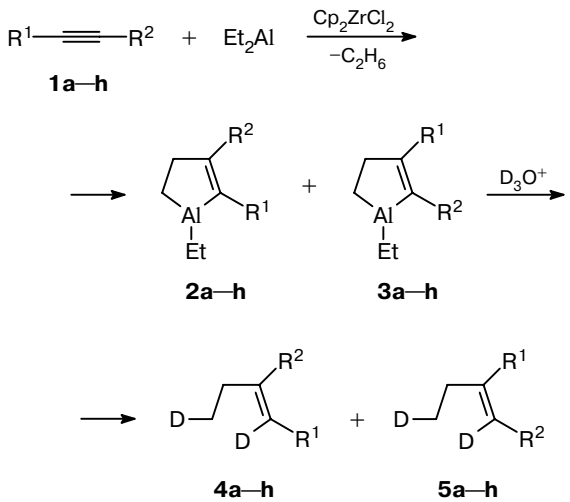
Key words: organoaluminum compounds, aluminacyclopentenes, cycloalumination, cyclic carboalumination.

Previously,[2] we have reported the first example of the synthesis of 2,3-dialkyl(phenyl)-1-ethylaluminacyclopent-2-ene from symmetrical disubstituted acetylenes. More recently,[3] we have studied the mechanism of this reaction.

With the aim of extending the fields of application of this reaction, in the present work we studied cycloalumination of asymmetrical disubstituted acetylenes containing alkyl, phenyl, or allyl substituents at the triple bond under the action of Et_3Al in the presence of catalytic amounts of Cp_2ZrCl_2 and examined the effect of the structures of the starting acetylenes and the influence of the electronic and steric factors on the direction of the reaction and its regularities (Scheme 1).

The reactions of asymmetrical disubstituted acetylenes **1a**—**h** with Et_3Al in the presence of Cp_2ZrCl_2 (acetylene : Et_3Al : Cp_2ZrCl_2 = 1 : 2.5 : 0.05, 20—25 °C) in aliphatic (hexane) or aromatic (benzene) solvents afforded regioisomeric mixtures of 2,3-disubstituted

Scheme 1



R^1 = *n*-C_5H_{11} (**a**—**d**); Ph (**e**—**h**)
R^2 = Me (**a**, **e**); Pr (**b**, **f**); All (**c**, **g**); $CH_2CH{=}CHMe$ (**d**, **h**)

* For Part 23, see Ref. 1.

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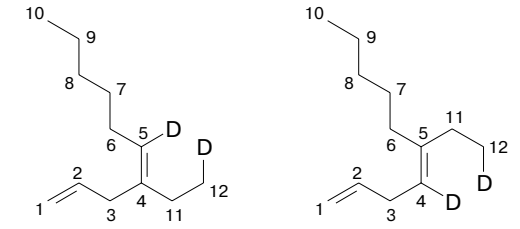
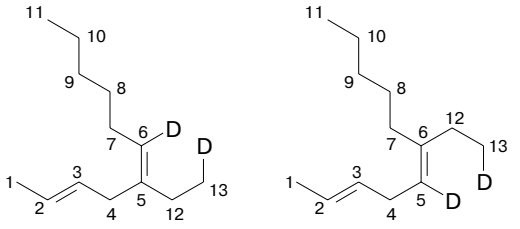
aluminacyclopent-2-enes **2a—h** and **3a—h**, respectively. The yields and the ratios of regioisomers **2** and **3** were determined by GLC of their deuterolysis products **4a—h** and **5a—h**, respectively. The atomic numbering schemes for the deuterolysis products are given in Scheme 2. The results are summarized in Table 1.

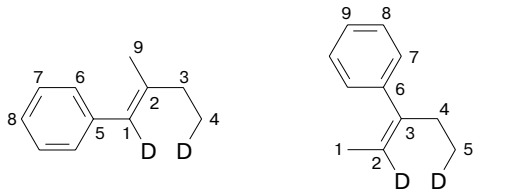
Scheme 2



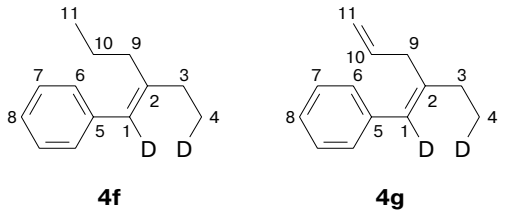
4c **5c**



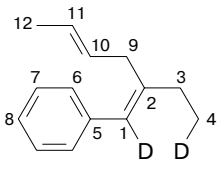
4d **5d**



4e **5e**



4f **4g**



4h

From Table 1 it follows that phenyl-substituted acetylenes **1e—h** are less reactive in the reaction under study than their alkyl analogs. At the same time, the presence of the phenyl substituent at the triple bond enhances the regioselectivity of the reaction yielding predominantly regioisomer **2**. In the case of alkyl-substituted acetylenes **1a—d**, the reactions proceeded nonregioselectively. The alkyl and allyl substituents have similar effects on the behavior of acetylenes in catalytic cycloalumination, the double bond of the allyl fragment remaining intact.

Table 1. Catalytic cycloalumination of asymmetrical disubstituted acetylenes

Compound	τ/h*	Total yield **2** + **3** (%)	Regioisomer ratio, **2**/**3**
1a	8	85	1/1
1b	8	85	1/1
1c	14	80	1/1
1d	14	80	1/1
1e	8	75	3/2
1f	14	65	>9/1**
1g	24	60	>9/1**
1h	24	60	>9/1**

* Reaction time.

** According to the GLC data for deuterolysis products, the regioselectivities of formation of compounds **2f—h** were 94—98%.

We attempted to attribute these results to the influence of the electronic and steric factors on the preferential orientation of acetylene upon its introduction into the zirconacene complex[2,3] as well as on the reaction rate.

It is known that carboalumination of acetylenes proceeds through a four-center transition state[4] in which the metal atom is coordinated by the triple bond through the carbon atom possessing the highest π-electron density. Apparently, carbozirconation proceeds according to the same scheme.[5] Therefore, a correlation between the regioselectivity of cycloalumination and the electron density at the carbon atoms involved in the multiple bond of acetylenes can be roughly derived.

According to the results of calculations (Table 2), the triple bond in phenyl-substituted acetylenes **1e—h** is more polarized than those in alkyl- and allyl-substituted acetylenes **1a—d**, the highest electron density being localized at the carbon atom to which the phenyl substituent is bound. A comparison of the data in Tables 1 and 2 and analysis of steric factors, which are of importance for the formation of the four-center transition state, disclose that the regioselectivity of the reaction under consideration is determined primarily by the electronic factors. The regioisomer ratio in the case of methylphenylacetylene is somewhat unexpected. Apparently, the steric factors in the latter compound play a larger role due to a substantial difference in the effective size of the phenyl and methyl substituents and, as a consequence, the fraction of regioisomer **3** increases. From Table 2 it follows that the degree of polarization of the triple bond in acetylene, taken alone, does not

Table 2. Calculated[a] charges q(C) and q(C*) (a.u.) on the carbon atoms of the triple bond in $R^1—C≡C^*—R^2$ acetylenes **1a—h**

Compound	q(C)	q(C*)
1a	−0.036	−0.033
1b	−0.032	−0.034
1c	−0.025	−0.037
1d	−0.029	−0.033
1e	−0.052	+0.012
1f	−0.049	+0.012
1g	−0.048	+0.010
1h	−0.048	+0.011

[a] RHF/6-31G//3-21G. The populations of the molecular orbitals were analyzed by the NBO method.

govern the reactivity of the compound in the reaction under study. Probably, the steric factors are responsible for a decrease in the reaction rate of catalytic cycloalumination of phenyl-substituted acetylenes **1e—h**.

Since the chemical shifts in the ^{13}C NMR spectra depend, in a way, on the electron occupancies of the π orbitals of the multiple bond,[6] we attempted to use the experimental spectral parameters of the acetylenes for estimating the regioselectivity of cycloalumination and the reactivities of the acetylenes. However, these correlations are unreliable due to a substantial difference in anisotropy of the substituents at the triple bond in the series **1a—h**.

To summarize, Cp_2ZrCl_2-catalyzed cycloalumination of asymmetrical alkyl-, phenyl-, and allyl-substituted acetylenes under the action of Et_3Al gives rise to regioisomeric 2,3-disubstituted aluminacyclopent-2-enes whose yields and ratio depend on the nature of the substituents in the starting acetylenes.

Experimental

Ab initio quantum-chemical calculations were carried out with full optimization of geometry by the restricted Hartree—Fock method with the 3-21G basis set. Subsequent analysis of the populations of the molecular orbitals was performed by the NBO method with the 6-31G basis set. All calculations were carried out with the use of the GAMESS program.[7]

The starting disubstituted acetylenes were synthesized by cross-coupling of alkyl halides with Iocich reagents,[8] which were prepared from terminal acetylenes and the Grignard reagent (EtMgBr); Cp_2ZrCl_2 was prepared according to a known procedure.[9] Commercial 95% Et_3Al (the Redkinskii pilot-production plant) was used.

The reactions with organoaluminum compounds were carried out under an atmosphere of dry argon. The solvents were distilled over $LiAlH_4$ immediately before use. The reaction products were analyzed on a Khrom-5 chromatograph (a flame ionization detector; PEG-6000 or SE-30 as the stationary phase; a 2000×3-mm column; the operating temperature was 50—170 °C). The mass spectra were measured on a Finnigan 4021 instrument; the energy of ionizing electrons was 70 eV; the temperature of the ionization chamber was 200 °C. The ^1H and ^{13}C NMR spectra were recorded on Jeol FX-90Q (22.5 MHz for ^{13}C and 90 MHz for ^1H) and Bruker AM-300 (75.46 MHz for ^{13}C and 300 MHz for ^1H) spectrometers with the use of $SiMe_4$ and $CDCl_3$, respectively, as the internal standard.

The structures of compounds **2a**,**b—5a**,**b** have been established in our previous studies.[10,11] Regioisomeric aluminacyclopent-2-enes **2c—h** and **3c—h** were identified[12] based on the results of analysis of their deuterolysis products **4c—h** and **5c—h**, respectively.

According to the data from GLC of deuterolysis products **4f—h** and **5f—h**, the observed regioselectivity of cycloalumination of acetylenes was 94—98% (**4f—h**). Therefore, the structures of minor products **5f—h** were not established.

Compounds **4c** and **5c** and compounds **4d** and **5d** were studied by NMR spectroscopy as mixtures of regioisomers. The assignment of the overlapping signals was made based on the known analogies[12] and using the Lindeman—Adams additive scheme.[13] The mass spectra of the individual compounds were obtained on a GLC-mass spectrometer equipped with an efficient capillary column (Ultra-1, Hewlett Packard; 50 m × 0.2 mm). Compounds **4e—h** and **5e** were isolated in the individual state.

Synthesis of 2,3-disubstituted 1-aluminacyclopent-2-enes. Disubstituted acetylene (2 mmol), Cp_2ZrCl_2 (0.1 mmol, 0.029 g), hexane (5 mL), and Et_3Al (5 mmol) were successively charged under an atmosphere of argon into a 50-mL glass reactor, which was placed in an ice bath and put on a magnetic stirrer. The reaction mixtures were stirred at 20 °C (the reaction times are given in Table 1).

Deuterolysis of 2,3-disubstituted 1-aluminacyclopent-2-enes. Hexane (5 mL) was added to aluminacyclopentene prepared according to the above-described procedure and the mixture was hydrolyzed with a 10% solution of DCl in D_2O upon cooling of the reactor in an ice bath. The organic layer was extracted with diethyl ether and kept over anhydrous $CaCl_2$.

The yields of the products were determined by GLC with the use of dodecane as the internal standard.

5-Deutero-4-(2-deuteroethyl)deca-1,4*Z*-diene (4c), b.p. 87 °C (10 Torr). Found (%): C, 85.91; H, 13.78. $C_{12}H_{20}D_2$. Calculated (%): C, 85.63; H, 11.99. ^{13}C NMR ($CDCl_3$), δ: 114.2 (C(1)); 138.0 (C(2)); 35.1 (C(3)); 138.3 (C(4)); 124.5 (t, C(5), $^1J_{CD}$ = 23.4 Hz); 28.3 (C(6)); 29.9 (C(7)); 32.2 (C(8)); 22.8 (C(9)); 14.2 (C(10)); 29.6 (C(11)); 12.5 (t, C(12), $^1J_{CD}$ = 19.1 Hz). ^1H NMR ($CDCl_3$), δ: 0.68—2.36 (m, 15 H, $C(10)H_3$, $C(6,7,8,9,11)H_2$, $C(12)H_2D$); 2.80 (d, 2 H, $C(3)H_2$, $^3J_{CH}$ = 6.4 Hz); 4.88—5.20 (m, 2 H, $C(1)H_2$=); 5.56—6.07 (m, 1 H, =C(2)H). MS, m/z: 168 [M^+].

4-Deutero-5-(2-deuteroethyl)deca-1,4*Z*-diene (5c), b.p. 69 °C (5 Torr). Found (%): C, 84.94; H, 13.42. $C_{12}H_{20}D_2$. Calculated (%): C, 85.63; H, 11.99. ^{13}C NMR ($CDCl_3$), δ: 114.8 (C(1)); 136.7 (C(2)); 30.3 (C(3)); 120.0 (t, C(4), $^1J_{CD}$ = 23.4 Hz); 142.6 (C(5)); 32.2 (C(6)); 29.6 (C(7)); 31.8 (C(8)); 22.8 (C(9)); 14.2 (C(10)); 27.8 (C(11)); 12.7 (t, C(12), $^1J_{CD}$ = 19.1 Hz). ^1H NMR ($CDCl_3$), δ: 0.60—2.29 (m, 15 H, $C(10)H_3$, $C(6,7,8,9,11)H_2$, $C(12)H_2D$); 2.62 (d, 2 H, $C(3)H_2$, $^3J_{CH}$ = 6.4 Hz); 4.75—5.25 (m, 2 H, $C(1)H_2$=); 5.60—6.00 (m, 1 H, =C(2)H). MS, m/z: 168 [M^+].

6-Deutero-5-(2-deuteroethyl)undeca-2*E*,5*Z*-diene (4d), b.p. 103 °C (12 Torr). Found (%): C, 86.02; H, 13.76. $C_{13}H_{22}D_2$. Calculated (%): C, 85.63; H, 12.16. ^{13}C NMR ($CDCl_3$), δ: 17.9 (C(1)); 125.4 (C(2)); 130.6 (C(3)); 33.8 (C(4)); 139.2 (C(5)); 123.9 (t, C(6), $^1J_{CD}$ = 23.5 Hz); 27.7 (C(7)); 30.0 (C(8)); 30.3 (C(9)); 22.8 (C(10)); 14.2 (C(11)); 29.6 (C(12)); 12.5 (t, C(13), $^1J_{CD}$ = 19.1 Hz). ^1H NMR ($CDCl_3$), δ: 0.57—1.10 (m, 5 H, $C(11)H_3$, $C(13)H_2D$); 1.13—1.44 (m, 6 H, $C(8,9,10)H_2$); 1.59—1.67 (m, 3 H, $C(1)H_3$); 1.87—2.16

(m, 4 H, C(7,12)H_2); 2.50—2.79 (m, 2 H, C(4)H_2); 5.30—5.47 (m, 2 H, C(2)H=C(3)H). MS, *m/z*: 182 [M^+].

5-Deutero-6-(2-deuteroethyl)undeca-2*E*,5*Z*-diene (5d), b.p. 110 °C (15 Torr). Found (%): C, 85.83; H, 13.87. $C_{13}H_{22}D_2$. Calculated (%): C, 85.63; H, 12.16. ^{13}C NMR ($CDCl_3$), δ: 17.9 (C(1)); 124.6 (C(2)); 129.3 (C(3)); 31.1 (C(4)); 121.0 (t, C(5), $^1J_{CD}$ = 23.4 Hz); 141.7 (C(6)); 32.2 (C(7)); 28.4 (C(8)); 31.8 (C(9)); 22.8 (C(10)); 14.2 (C(11)); 29.6 (C(12)); 12.7 (t, C(13), $^1J_{CD}$ = 19.1 Hz). ^{1}H NMR ($CDCl_3$), δ: 0.68—1.19 (m, 5 H, C(11)H_3, C(13)H_2D); 1.23—1.48 (m, 6 H, C(8,9,10)H_2); 1.61—1.73 (m, 3 H, C(1)H_3); 1.90—2.20 (m, 4 H, C(7,12)H_2); 2.50—2.77 (m, 2 H, C(4)H_2); 5.30—5.51 (m, 2 H, C(2)H=C(3)H). MS, *m/z*: 182 [M^+].

(1,4-Dideutero-2-methylbyt-1*E*-en-1-yl)benzene (4e), b.p. 80 °C (12 Torr). Found (%): C, 88.56; H, 10.13. $C_{11}H_{12}D_2$. Calculated (%): C, 89.13; H, 8.16. ^{13}C NMR ($CDCl_3$), δ: 123.5 (t, C(1), $^1J_{CD}$ = 23.5 Hz); 140.5 (C(2)); 33.3 (C(3)); 12.5 (t, C(4), $^1J_{CD}$ = 19.1 Hz); 138.8 (C(5)); 125.8 (C(6)); 128.0 (C(7)); 128.9 (C(8)); 17.7 (C(9)). ^{1}H NMR ($CDCl_3$), δ: 1.09 (t, 2 H, C(4)H_2D, $^3J_{CH}$ = 7.3 Hz); 1.83 (s, 3 H, C(9)H_3); 2.14 (t, 2 H, C(3)H_2, $^3J_{CH}$ = 7.3 Hz); 7.08—7.36 (m, 5 H, Ph). MS, *m/z*: 148 [M^+].

2-Deutero-1-(2-deuteroethylprop-1*Z*-en-1-yl)benzene (5e), b.p. 90 °C (20 Torr). Found (%): C, 89.54; H, 9.79. $C_{11}H_{12}D_2$. Calculated (%): C, 89.13; H, 8.16. ^{13}C NMR ($CDCl_3$), δ: 14.5 (C(1)); 119.5 (t, C(2), $^1J_{CD}$ = 23.5 Hz); 143.4 (C(3)); 32.0 (C(4)); 12.9 (t, C(5), $^1J_{CD}$ = 19.1 Hz); 141.5 (C(6)); 126.3 (C(7)); 128.1 (C(8)); 128.6 (C(9)). ^{1}H NMR ($CDCl_3$), δ: 0.95 (t, 2 H, C(5)H_2D, $^3J_{CH}$ = 7.3 Hz); 1.54 (s, 3 H, C(1)H_3); 2.23 (t, 2 H, C(4)H_2, $^3J_{CH}$ = 7.5 Hz); 7.07—7.40 (m, 5 H, Ph). MS, *m/z*: 148 [M^+].

[1-Deutero-2-(2-deuteroethyl)pent-1*Z*-en-1-yl]benzene (4f), b.p. 109 °C (10 Torr). Found (%): C, 89.13; H, 10.88. $C_{13}H_{16}D_2$. Calculated (%): C, 88.57; H, 9.15. ^{13}C NMR ($CDCl_3$), δ: 123.6 (t, C(1), $^1J_{CD}$ = 23.4 Hz); 145.0 (C(2)); 29.9 (C(3)); 12.6 (t, C(4), $^1J_{CD}$ = 19.1 Hz); 138.7 (C(5)); 125.8 (C(6)); 128.0 (C(7)); 128.6 (C(8)); 32.9 (C(9)); 21.6 (C(10)); 14.2 (C(11)). ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, 3 H, C(11)H_3, $^3J_{CH}$ = 7.3); 1.08 (t, 2 H, C(4)H_2D, $^3J_{CH}$ = 7.3 Hz); 1.28—1.69 (m, 2 H, C(10)H_2); 2.17 (t, 2 H, C(9)H_2, $^3J_{CH}$ = 7.6 Hz); 2.22 (t, 2 H, C(3)H_2, $^3J_{CH}$ = 7.6 Hz); 7.12—7.45 (m, 5 H, Ph). MS, *m/z*: 176 [M^+].

[1-Deutero-2-(2-deuteroethyl)penta-1*Z*,4-dien-1-yl]benzene (4g), b.p. 124 °C (15 Torr). Found (%): C, 90.48; H, 9.51. $C_{13}H_{14}D_2$. Calculated (%): C, 89.60; H, 8.10. ^{13}C NMR ($CDCl_3$), δ: 125.2 (t, C(1), $^1J_{CD}$ = 23.5 Hz); 141.9 (C(2)); 35.6 (C(3)); 12.4 (t, C(4), $^1J_{CD}$ = 19.1 Hz); 138.3 (C(5)); 126.1 (C(6)); 128.1 (C(7)); 128.5 (C(8)); 29.9 (C(9)); 136.3 (C(10)); 115.9 (C(11)). ^{1}H NMR ($CDCl_3$), δ: 1.08 (t, 2 H, C(4)H_2D, $^3J_{CH}$ = 7.3 Hz); 2.15 (t, 2 H, C(3)H_2, $^3J_{CH}$ = 7.3 Hz); 2.96 (d, 2 H, C(9)H_2, $^3J_{CH}$ = 6.1 Hz); 4.97—5.17 (m, 2 H, C(11)H_2=); 5.64—6.07 (m, 1 H, =C(10)H); 7.21 (s, 5 H, Ph). MS, *m/z*: 174 [M^+].

[1-Deutero-2-(2-deuteroethyl)hexa-1*Z*,4*E*-dien-1-yl]benzene (4h), b.p. 130 °C (8 Torr). Found (%): C, 90.37; H, 9.07. $C_{14}H_{16}D_2$. Calculated (%): C, 89.30; H, 8.56. ^{13}C NMR ($CDCl_3$), δ: 124.9 (t, C(1), $^1J_{CD}$ = 23.5 Hz); 142.9 (C(2)); 29.8 (C(3)); 12.3 (t, C(4), $^1J_{CD}$ = 19.1 Hz); 138.3 (C(5)); 126.3 (C(6)); 128.2 (C(7)); 128.5 (C(8)); 34.4 (C(9)); 126.0 (C(10)); 123.1 (C(11)); 18.0 (C(12)). ^{1}H NMR ($CDCl_3$), δ: 0.92—1.21 (m, 2 H, C(4)H_2D); 1.53—1.67 (m, 3 H, C(12)H_3); 2.08 (t, 2 H, C(3)H_2, $^3J_{CH}$ = 6.6 Hz); 2.78—3.17 (m, 2 H, C(9)H_2); 5.30—5.98 (m, 2 H, —C(10)H=C(11)H—); 6.76—7.41 (m, 5 H, Ph). MS, *m/z*: 188 [M^+].

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